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Determination of Soot Refractive Index as a Function of Height in an Inverse Diffusion Flame

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With the scope of combustion diagnostics increasing, it is becoming ever more important for some of the more basic physical properties of soot to be addressed. Soot refractive index values were obtained as a function of height in a benzene inverse diffusion flame (IDF). The IDF was chosen for ease in extraction of soot particles, with minimal flame interference. Refractive index measurements were obtained in the infrared with a Kramers-Kronig transformation of diffuse reflectance from a Fourier Transform Infrared Spectrometer (FTIR), and ellipsometry measurements extended the range of index values into the visible. A comparison of results from previous investigators indicates refractive index varies as a function of fuel type, residence time (height), wavelength and temperature.

1. Introduction

The field of combustion diagnostics relies on knowing the physical properties of soot aggregates for the determination of soot volume fractions, number densities, and particle sizes. Efforts have focused on quantifying the refractive index of soot and decreasing the amount of error associated with its determination [1-3]. Experimental determinations for the value of soot refractive index can be broken into two categories; in situ [4-11] and ex situ [12-14] type measurements. In-situ measurements of soot refractive index are typically accomplished using laser light scattering techniques, wherein assumptions regarding the soot size distribution must be known or measured a priori. Traditional light scattering techniques can be used to determine soot particle sizes, by assuming spherical soot particles, and a normalized particle size distribution. An additional assumption is that all particles are in the Rayleigh scattering regime.

Previous investigators [4,5,11] have presented independent measurements of soot refractive index and soot particle size by employing the methods described above. Methods such as these involve many assumptions about the nature of soot particles that are sometimes called into question; namely, that they are spherical in nature, that particle size is normally distributed, and that particles are in the Rayleigh regime. While it is true that Rayleigh scattering theory may be assumed true for the primary particles forming soot aggregates, the aggregates themselves generally do not fall under the conditions necessary to apply Rayleigh scattering theory. Recently, studies have shown that a more physically accurate description of light scattering properties of these aggregates is provided by the Rayleigh-Debye-Gans (RDG) scattering theory [15].

Ex situ type measurements were the method of choice for soot refractive index determinations in the widely cited work of Dalzell and Sarofim [12], due to the need for comparability with gravimetric soot sample tests. In this experiment, soot was collected and then pressed together with high pressure pistons, and reflectance coefficients were measured to determine the index of refraction.

Despite studies claiming refractive indices are independent of fuel type [9], a study by Tregrossi [16] tested a variety of fuels and found that refractive index was a function of flame position and C/O ratio. These studies were conducted in the UV-VIS range, and though the authors present a significant amount of data for their calculations, no direct formula was listed to aid others in applying their findings to other flames. These authors point out that the soot volume fraction measured in their study changes significantly from that obtained by a gravimetric procedure when the variation in optical properties of soot is not accounted for. In addition, in one of the first efforts to show that soot refractive index properties are indeed a function of position, Charalampopoulos [4] cautions that using a single value of refractive index over the entire flame region can cause errors on the order of 25% for number densities and 15% in soot particle size determinations. A variation in refractive index to account for the soot maturity is suggested to aid in the accuracy of scattering and extinction diagnostics.

The aim of this paper is to aid diagnostics technicians in applying a more representative value for refractive index in light extinction measurements, in the hopes that the values obtained for dependent determinations of variables such as extinction coefficients, absorption coefficients, and soot volume fraction will be more representative of the actual values of these variables.

2. Experimental Procedure

Collection

Benzene soot samples were collected in an inverse diffusion flame (IDF) burner shown in Figure 1. The IDF burner consists of three concentric circular sections with inner diameters of 12.02, 37.06, and 73.34 mm. Air is introduced through the innermost section while the fuel and nitrogen are introduced through the middle and outer sections, respectively. A fuel flow rate of 3.19 mol/hr was achieved by heating 100 ml of benzene on a hot plate. The temperature of the hot plate was controlled by a Variac, which maintained the fuel just below its boiling point to achieve vaporization. Air and nitrogen flow rates were maintained at 3.5 and 29 mol/hr by flow meters. Gaseous nitrogen bubbled through the fuel aided in the transport of the vapor phase fuel to a tube with an inner diameter of 1.8 mm, which fed to the IDF.

A small vacuum sampling tube is connected perpendicular to the flame and samples were taken at a flow rate of 0.5 L/min at heights of 6, 10, 12, 15, and 30 mm from the burner surface along the lateral sampling axis shown in Figure 1. Flow straighteners in the outer concentric sections provided uniform velocity profiles for the fuel and nitrogen entering the flame. Soot was collected by the metal vacuum tube and deposited on a Teflon filter. The vacuum pump pressure was kept constant by a flow meter.

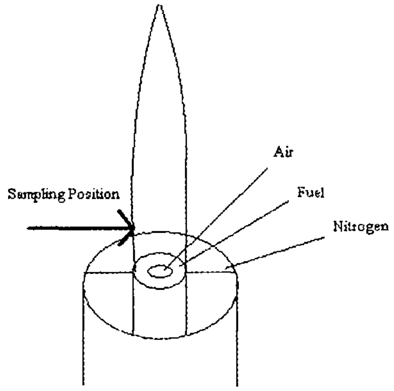

Figure 1: Inverse diffusion flame burner

FTIR

Small agglomerates of the soot collected on the Teflon filters were placed on the sample area of a diffuse reflectance cell in a BioRad FTS 6000 FTIR spectrometer. The samples were then scanned from 400 to 4000 cm^{-1} and plots of reflectance versus wavelength were generated. A background scan of the filter was subtracted from all of the samples in order to obtain a pure sample spectrum. Once the spectra were obtained, a Kramers-Kronig transform was used to determine the real and imaginary indices of the refractive index of the soot for each sample.

Ellipsometry

Soot collected on Teflon filters was scraped off and placed on silicon dioxide wafers. A second wafer was then used to cover the sample, and a 2 ton pressure exerted by a mechanical press served to compress the soot particles into thin reflective sheets. These compressed soot sheets were then mounted to a VASE Ellipsometer (Model VBB-250), and the real and imaginary parts of the refractive indices were measured. The ellipsometer used two angles of incidence, 70 and 75 degrees. A fully automated system was used to calibrate the ellipsometer with a silicon dioxide wafer, and then an alignment process adjusted the pitch and angle of the reflected light, maximizing intensity at the detector. A profilometer measured the thickness of the compressed soot sheet, and this thickness was consistently measured to be under 0.1mm.

3. Results and Discussion

Ellipsometry Results

Refractive index results were determined as a function of height for benzene soot collected from an inverse diffusion flame. Results for the real part of the refractive index, shown in Figure 2, increase with height in the flame from 6 to 15 mm, and then decrease at the exhaust sampling height of 30 mm. There are at least two potential explanations for this behavior: 1) either the sampling point at which the soot is extracted is effected by the inward leaning of the flame at greater heights (Figure 1), or 2) immature soot is traveling to this last sampling point unaffected by further agglomeration. A study by Santamaria [17] indicated that in a benzene-fueled inverse diffusion flame, temperature along the same reaches a peak at around 15 mm, decreasing shortly thereafter. It is also possible that the soot has gone through the highest reaction temperature it will experience in the flame, and is being cooled down at this exhaust sampling point. In Figure 3 we note the same sort of trend, with values of the complex part of the refractive index increasing from 6 to 15 mm, then decreasing at the exhaust sampling point.

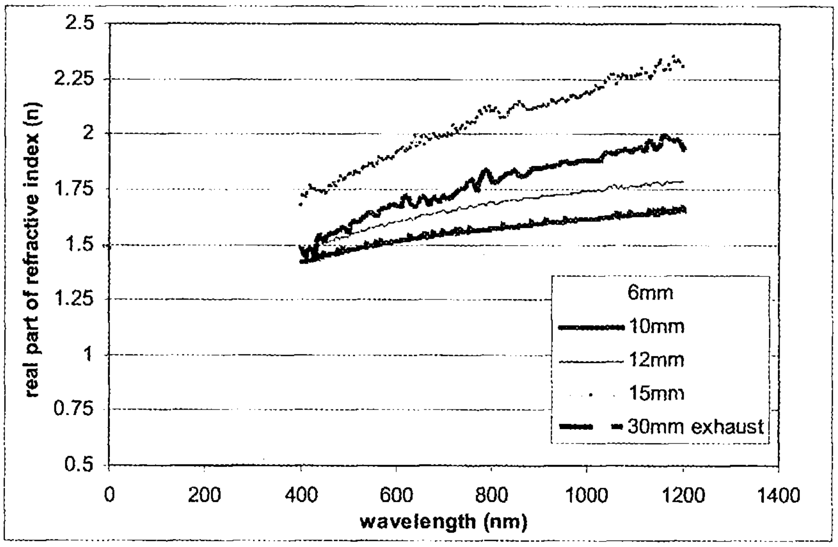

Figure 2: Real part of soot refractive index of benzene soot as a function of height and wavelength in an inverse diffusion flame

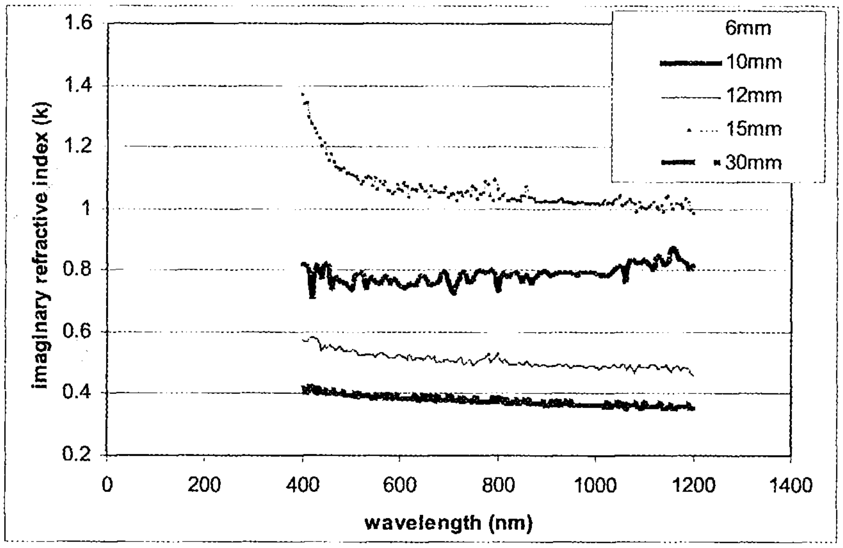

Figure 3: Imaginary part of soot refractive index of benzene soot as a function of height and wavelength in an inverse diffusion flame

FTIR Results

Samples taken at heights of 10, 12 and 15 mm were processed using FTIR spectroscopy and show an increasing trend with increasing wavelength. As shown in Figures 4 and 5, substantial deviation in the high end of the IR spectrum is measured for both the real and imaginary parts of the refractive index for soot sampled at 15 mm. As mentioned earlier, this could be a result of the soot passing through a peak in reacting temperature at around 15mm.

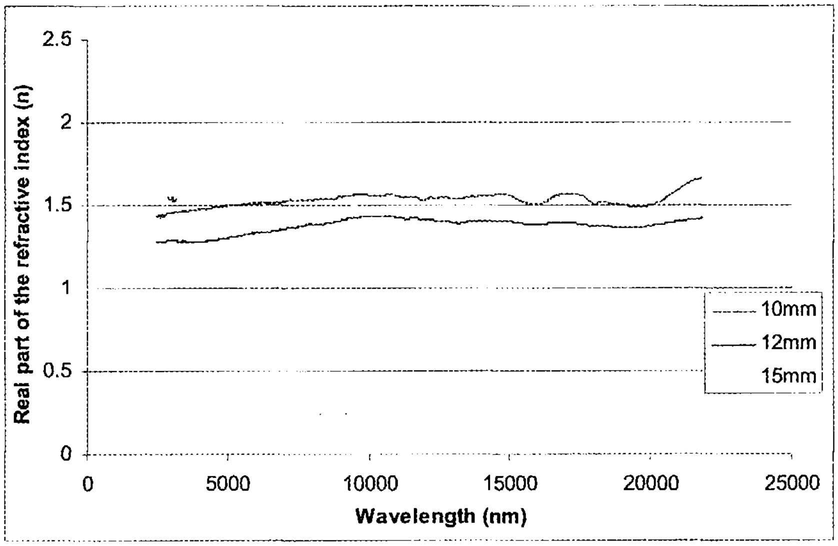

Figure 4: Real part of refractive index of benzene soot in the IR range

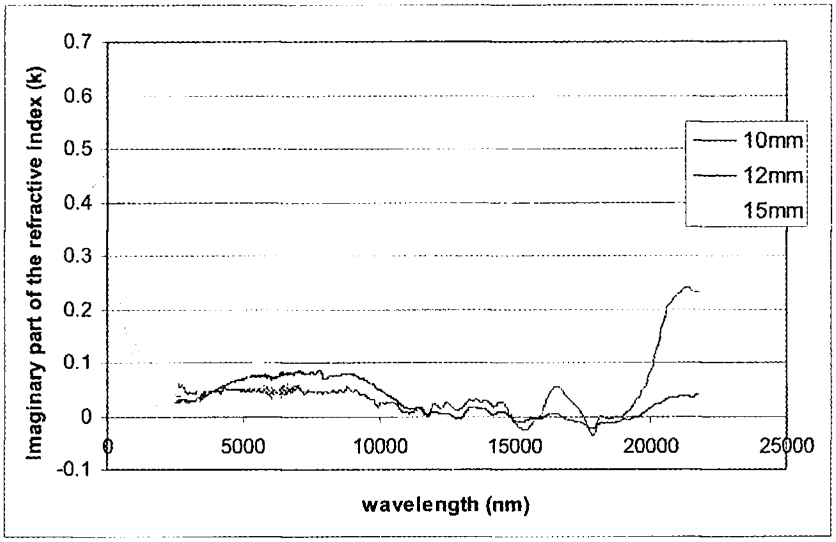

Figure 5: Imaginary part of refractive index of benzene soot in the IR range

Comparison With Results From Other Studies

Results for the refractive index of benzene soot taken as a function of height from the burner surface are plotted for comparison with the results of Charalampopoulos [4, 5] in Figures 6 and 7. These results clearly show an increasing trend in refractive index as a function of height above the burner. The propane index results were inferred from a premixed propane/oxygen flame with an equivalence ratio of 2.4; and the methane results from a methane/oxygen flat flame burner with an equivalence ratio of 2.25. The authors are not suggesting that the conditions of these experiments were at all similar enough to infer comparisons of chemistry or mixing behavior directly; however, it is apparent that multiple studies have illustrated that refractive index values of soot can change with height regardless of whether an in situ or ex situ method is employed.

Charalampopoulos utilized an in situ method, and the values given in these studies were inferred by simultaneously solving expressions relating the extinction coefficients (which assume Rayleigh scattering), the Drude-Lorentz dispersion model, and some approximating ratios between the relation of electrical permittivities of graphite and soot. In conjunction with measuring the particle size distribution, the values of refractive index and particle number density were able to be determined after assuming either monodisperse or polydisperse soot distributions.

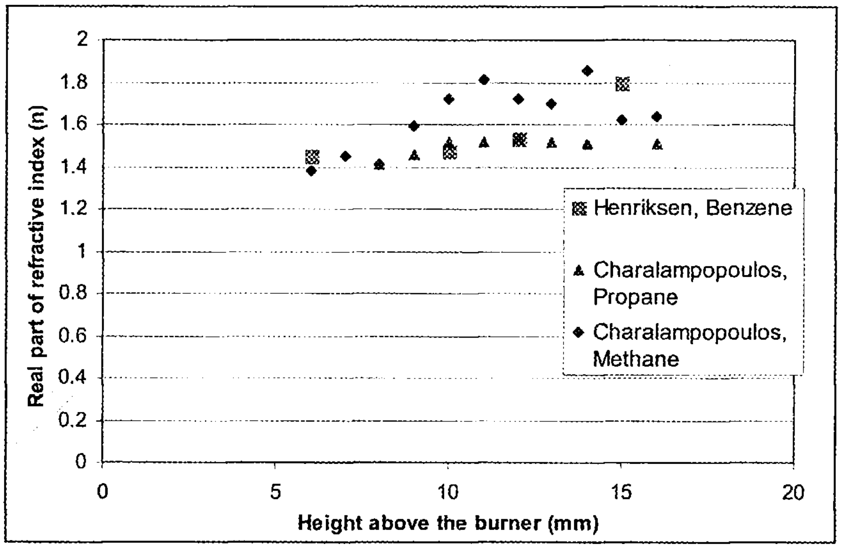

Figure 6: Real part of the refractive index of Benzene soot compared with methane and propane results changing with height

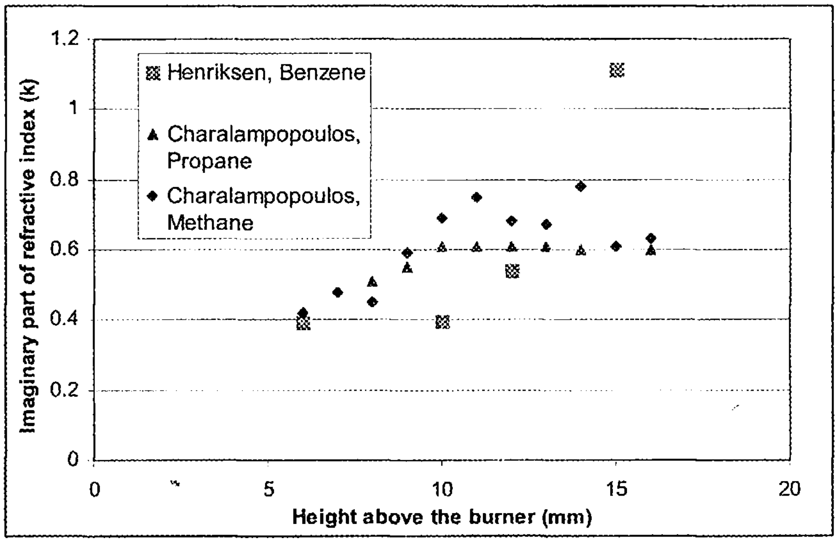

Figure 7: Imaginary part of the refractive index of Benzene soot compared with methane and propane results changing with height

Finally, the results of the refractive index of exhaust benzene soot determined via ellipsometry are plotted against values presented by Dalzell [12], Krishnan [7,8], Stagg [13] and co-workers in Figures 8 and 9. These studies are all widely quoted [3] for their refractive index measurements. The real part of the refractive index (Figure 8) is shown to increase with increasing wavelength, and values in this study extend almost to 2 in the near IR region of the spectrum. Results in the visible range are slightly higher than those reported in other studies; however, results show actual overlap in the widely cited work of Dalzell and Sarofim in this wavelength range. The complex part of the refractive index shown in Figure 9 follows a similar trend to that determined by Dalzell [12] and Stagg [13], with values staying fairly constant throughout the wavelength range. These results however, show the imaginary part of the refractive index of benzene to be much higher than that reported for acetylene and propane soot.

A recent study by Williams [2] points to the deduction that the value of refractive index of soot must be much higher than those previously reported, especially in the imaginary part, to be consistent with values of non-dimensional absorption coefficient and scattering albedo. A suggested value for refractive index at a wavelength of 635 nm was given in that study to be 1.75-1.03*i*.

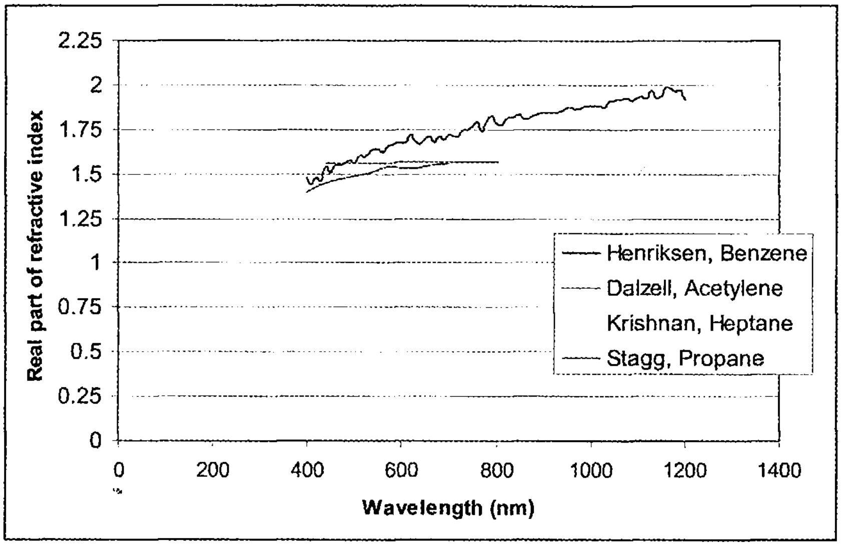

Figure 8: Real part of refractive index values from benzene exhaust, compared to previous exhaust results of acetylene, heptane, and propane

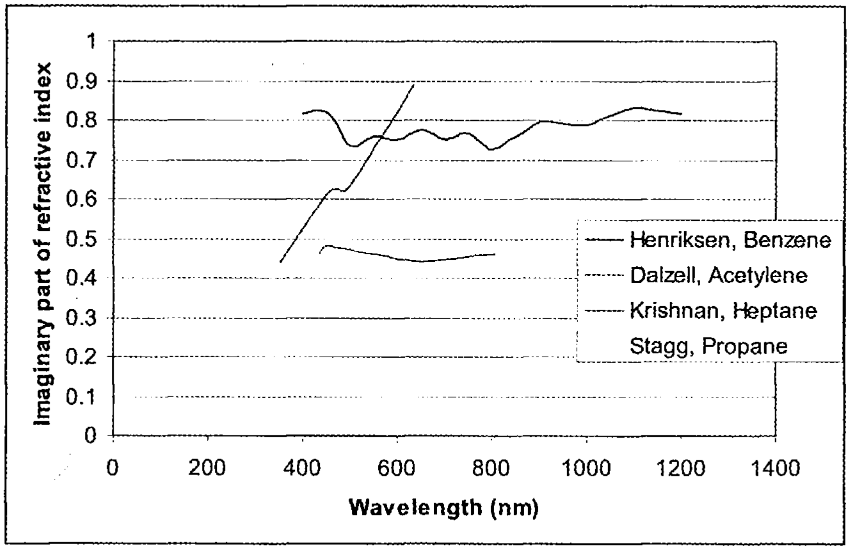

Figure 9: Imaginary part of refractive index values from benzene exhaust, compared to previous exhaust results of acetylene, heptane, and propane

4. Conclusions

Results of refractive index measurements show substantial variation with sampling height in the flame, lending support to the theory that the optical properties of soot are functions of not only temperature, but residence time and chemical composition. Due to the complexity of the soot growth process, this study was not intended to infer relationships between the parameters of size, T, and composition directly. It suffices to say that the optical properties of the sample material commonly referred to as soot does indeed vary with height, or residence time and temperature in a flame. Therefore, it is preferable to avoid use of a universal value of refractive index (m) to describe the entire flame, and to consider soot as a particle undergoing complex transformations throughout the flame that can affect the optical properties of the particle. If the extinction coefficient, which is a function of refractive index, is to be calculated, the variation in refractive index should take into account not only the specific flame parameters, but also the time/temperature history of the soot particles.

Acknowledgements

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References

[1] C.R. Shaddix, A.B. Palotas, C.M. Megaridis, M-Y. Choi, N.Y.C. Yang, *Journal of Heat and Mass Transfer* 48 (2005) 3604-3614
[2] T.C. Williams, C.R. Shaddix, K.A. Jensen, J.M. Suo-Anttila, *Journal of Heat and Mass Transfer* (2006) doi:10.1016/j.ijheatand masstransfer.2006.08.024 *Article in Press*
[3] K.C. Smyth, C.R. Shaddix, *Combustion and Flame* 107 (1996) 314-320
[4] T.T. Charalampopoulos, J.D. Felske, *Combustion and Flame* 68 (1987) 283-294
[5] T.T. Charalampopoulos, H. Chang, B. Stagg, *Fuel* 68 (1989) 1173-1179
[6] J. Zhu, M-Y. Choi, G.W. Mulholland, S.L. Manzello, L.A. Gritzo, J. Suo-Anttila, *Proceedings of the Combustion Institute* 29 (2002) 2367-2374
[7] S.S. Krishnan, K.C. Lin, G.M. Faeth, *ASME Journal of Heat* Transfer 122 (2000) 517-524
[8] S.S. Krishnan, K.C. Lin, G.M. Faeth, *ASME Journal of Heat Transfer* 123 (2001) 331-339
[9] J. Mullins, A. Williams, *Fuel* 66 (1987) 277-280
[10] U.O. Koylu, G.M. Faeth, *Combustion Institute*, Worchester, MA (1995) 211-214
[11] H. Chang, T.T. Charalampopoulos, *Proceedings: Mathematical and Physical* Sciences 430 (1990) 577-591
[12] W. H. Dalzell, A. F. Sarofim, *ASME Journal of Heat Transfer* 91 (1969) 100-104
[13] B.J. Stagg, T.T. Charalampopoulos, *Combustion and Flame* 94 (1993) 381-396
[14] C. E. Batten, *Applied Optics*, 24 (8) (1984) 1193-1199
[15] T.L. Farias, U.O. Koylu, M.G. Carvalho, *Applied Optics* 35 (3) (1996) 6560-6567
[16] A. Tregrossi, M. Alfe, R. Barbella, A. Ciajolo, *4th Mediterranean Combustion Symposium* (2005) 21-27
[17] A. Santamaria, Ph.D. Thesis in Chemical Sciences, University of Antioquia, Columbia (2007).