ADDITION OF ETHANOL IN RICH PREMIXED FLAMES OF ETHYLENE: THE EFFECT OF THE EQUIVALENCE RATIO

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Abstract

Biofuels have been arisen in the last decades as a new source of energy both because of the possible production all over the world and for their intrinsic capability to be a renewable source of carbon.

The most used biofuels are biodiesel and bioethanol. Ethanol has been studied under several combustion conditions. It has been found that its use reduces or promotes the amount of the formed particulate depending on the combustion configuration. In diffusion flames, for example, the addition of a small amount of ethanol to the fuel increases particle formation. Vice versa, in premixed flames with different equivalent ratios a decrease in the particulate matter is obtained. This latter configuration has been investigated just for very fuel-rich conditions, whereas there is a lack of experimental data for flames near the soot threshold.

The aim of this work is to study the effect of the equivalent ratio near the soot threshold when different amount of ethanol are added to the fuel.

Ethylene laminar premixed flames with equivalent ratios ranging from 2.01 to 2.31 have been studied varying the ethanol amount from 0 to 30%. The flames were stabilized with a stainless steel plate on a capillary burner with a cold gas velocity of 10 cm/s. To avoid condensation and keeping constant the temperature in all the investigated conditions, recirculating water in the burner was fixed at 75°C. Premixed gases were preheated at 150°C and sent to the burner. The ethanol was supplied by a New Era syringe pump that allows having high repeatability of the measurements with stable and constant flow rate. The measure of nanoparticle and soot was made by laser induced fluorescence (LIF) and laser induce incandescence (LII), respectively. The laser light source was the fourth harmonic of a Nd:YAG pulsed laser, i.e. at 266 nm. The LIE signal was measured with an ICCD camera 90 deg to the incident excitation light.

In the investigated conditions, the lower is the equivalent ratio the higher is the reduction of total particulate matter. Moreover wavelength peaks of emission signal did not change when ethanol was added. This means that particles produced with and without ethanol are quite similar. Hence, the effect of ethanol in the flame is probably related to the effect on the flame front through its decomposition, rather than to a change in the growth process of the particles in flame.

Introduction

The use of biofuels has increased rapidly over the last decades aimed to the possibility of reducing both the worldwide petroleum dependence and the greenhouse gases production. The impact of biofuels on pollutants is interesting because they can promote the formation or reduction of these according to the operative conditions. Among the different bioalcohols, ethanol is one of the most studied and used oxygenated additives because it can be obtained from biomass at reasonable cost. On this purpose several processes for cost reduction and efficiency improving are being developed [1].

Most of the previous studies on ethanol effect were focused on the total amount of particulate matter produced in combustion whereas less attention has been put on sizes of particles and their composition [1-4]. Recent studies have shown that size distribution function of the combustion formed carbonaceous particles is important because of particle toxicity typically increases when decreasing particle sizes and strongly depends on particle number more than mass concentration [5-6]. Some combustion conditions such as temperature and equivalent ratio can change particle size and distribution. In a laminar flat premixed flame, and for a specific residence time, a higher maximum particle diameter is observed when increasing the equivalent ratio for the same fuel [7].

The aim of this work is to understand the effect of the amount of ethanol added to the fuel on the particle size distribution and the reduction of fluorescent and incandescent species. They were used ethylene premixed flames with 10, 20 and 30% of ethanol added and with three different equivalent ratio (ϕ = 2.01, 2.16, 2.31) by Differential Mobility Analysis (DMA), Laser Induced Fluorescence and Laser Induced Incandescence.

Experimental

Three different equivalent ratio where studied in atmospheric pressure laminar premixed ethylene/ethanol/air flames. These flames have a mass flow rate such that the velocity of the cold gas at room conditions was fixed at 10 cm/s. The flames were stabilized on a capillary burner like the one used by Sgro et al. [7]. High purity air and ethylene (>99.96%) were supplied by using mass flow controllers. Premixed gases were preheated at 150°C and sent to the burner. The ethanol was supplied by a syringe. The ethanol added was varied from 0 to 30% of total carbon fed. The conditions for the flames are show on Table 1.

Particles were sampled with a stainless steel probe place horizontally above the burner for different heights above the burner (HAB) from 6 to 14 mm with a dilution ratio on the order of 10^4. A nano-DMA (Vienna Type Model 3085) was used to separate particles according to their electrical mobility. The classified particles are counted by an Electrometer Faraday Cup. The particles size distribution function obtained by DMA was corrected for losses in the pinhole and in the probe following the procedure of Gormeley and Kennedy [8], and Alonso et

al. [9]. The flames with the equivalent ratio 2.01 were the flames studied with DMA for keeping experiments reproducible.
The laser light source used for Laser Induced Fluorescence (LIF) and Laser Induced Incandescence (LII) was the fourth harmonic of a Nd:YAG pulsed laser (k_0 = 266 nm). The LIF and LII signal were measured with an ICCD camera 90 deg to the incident excitation light. The measurements were made for different heights above the burner (HAB) from 2 to 15 mm. Particle size distribution, fluorescence and incandescence measurements were performed along the central axis of the flames.

Table 1. Flame conditions for ethylene/ethanol air flames.

Experimental conditions		Equivalent ratio		
		2.01	*2.16*	*2.31*
Without ethanol	Air (L/min)	13.89	13.76	13.64
	Ethylene (L/min)	1.96	2.08	2.21
10% Ethanol	Air (L/min)	13.89	13.76	13.64
	Ethylene(L/min)	1.75	1.87	1.98
	Ethanol(mL/min)	0.457	0.486	0.515
20% Ethanol	Air (L/min)	13.89	13.76	13.64
	Ethylene (L/min)	1.57	1.66	1.76
	Ethanol (mL/min)	0.914	0.973	1.031
30% Ethanol	Air (L/min)	13.89	13.76	13.64
	Ethylene (L/min)	1.37	1.45	1.54
	Ethanol (mL/min)	1.37	1.459	1.546

Results and discussion

Previous measurements of temperature were done. It was observed that the addition of ethanol did not show major changes in the temperature profiles and the maximum temperature was at around 1.5 – 2.0 mm HAB.
The Figure 1 shows the particle size distribution function (PSDF) obtained for all flames at different HAB for the same equivalent ratio. For all the flames the PSDFs particle size distribution function appears unimodal at low heights while it becomes bimodal at increased residence time in flame. The first mode was centered at about 2 nm, it is characterized by a high number concentration which slightly decreases when HAB increases and when ethanol is added. The second mode appears at higher height above the burner and the peak value can vary between 5 and 10 nm, whereas the maximum size particle is as large as 20 nm. In the pure ethylene flame, particles strongly increase in size and the appearance of bimodal distribution is already evident at 10 mm above the burner. When 10% of ethanol is added in the flame, a change on PSDF can be clearly seen: in fact bimodality appears only at 12-14 mm above the burner and particles are not larger than 10nm. When 20% of ethanol is added in the flame bimodality of PSDF is not observed and almost all the

particles remain as small as 5 nm. When 30% of ethanol is added in the flame also the first mode is hardly detectable due to strong reduction in number concentration. For the same residence time in the ethanol doped flames the mean size of particles result smaller and also the particle size distribution function is deeply different. However, a comparison has been performed on PSDF measured in two flame conditions with the same total amount of particles. In particular PSDFs of pure ethylene flame taken at 6 and 10 mm have been compared with PSDFs of 10% ethanol flame at 8 and 14 mm, as reported in Figure 2. PSDFs relative to the ethylene flame and those with 10% of ethanol, characterized by the same total amount of particles, present a quite similar behavior and shape, and no evident differences can be observed. This can suggest that the ethanol doped flame can undergo to a slowdown process on the soot and soot precursor's formation. Since in this flame the particles inception process is strongly linked with molecule-radical chemical growth it is possible to individuate the mayor pathways responsible for reduction.

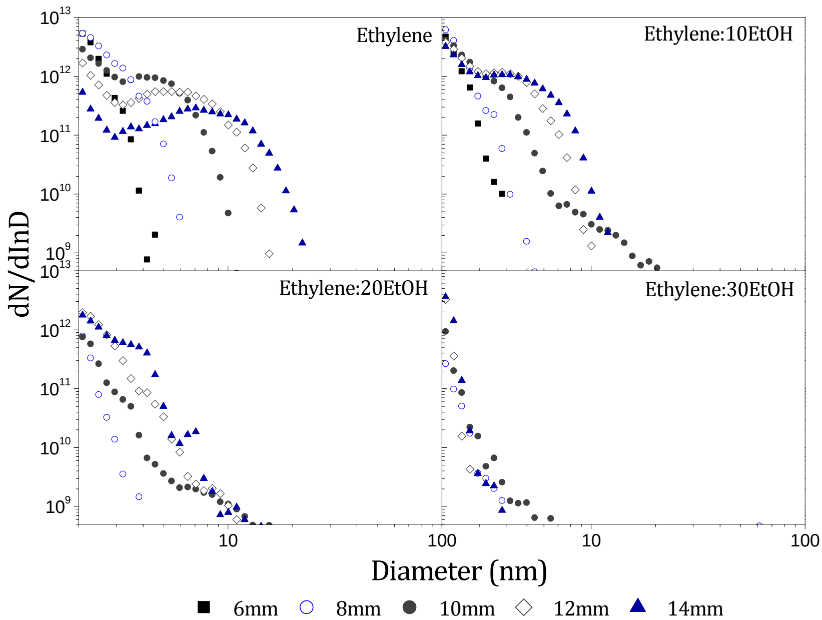

Figure 1. Particle size distribution obtained for all flames at different HAB (Φ = 2.01). HABs reported in the figure refer to the probe position.

Figure 3 shows the reduction of PAH and soot obtained by LIF and LII, respectively. It can be observed that the LII signal has a stronger reduction than the LIF. This indicates that the particulate material is reduced more than PAH. This agrees with the mechanism of formation of soot. This also suggests that ethanol does not slow down the formation of fluorescent species, but it has a specific dependence of the equivalent ratio. For all flames can be seen that the reduction of

PAH and soot is a function of the amount of ethanol added. Moreover the addition of 10% ethanol does not strongly reduce the amount of soot In fact, the LII signal, is already detectable in the flames with 10% and 20% of ethanol and only when 30% is added signals is at background noise level. However, no clear trend among different equivalent ratios was observed.

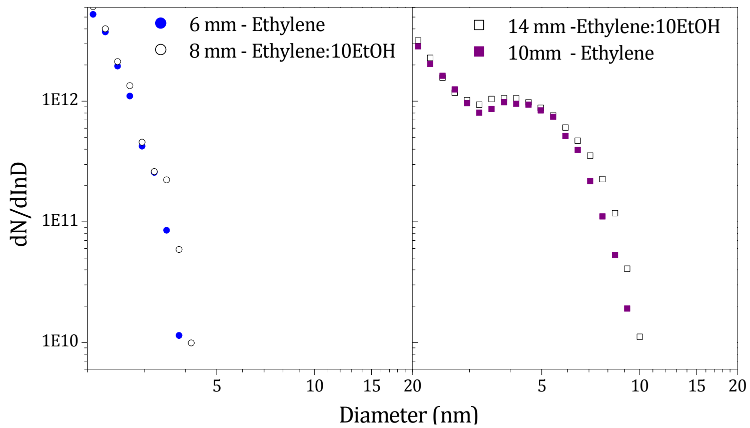

Figure 2. Comparison between similar PSD in ethylene/ethanol/air flames.

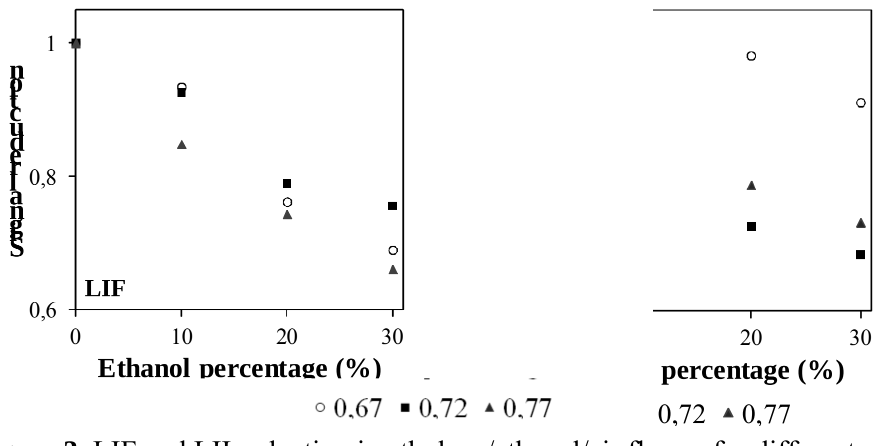

Figure 3. LIF and LII reduction in ethylene/ethanol/air flames for different amount of ethanol.

Several studies have been conducted on the gas phase products under similar flame conditions. It has been observed a reduction of the acetylene formed on flames when ethanol is added. This fact decreases the amount of soot precursor formed and slowdown the growth process of the particles [2, 3]. Moreover the water formed by ethanol pyrolysis can modify the mechanism of radical formation. Experimental studies have established that the addition of water to an ethylene

premixed flame decrease the quantity of soot precursors and the total amount of soot [12]. This effect has been linked to the reaction: $H_2O + H \rightarrow OH + H_2$
The removal of H radicals decreases the rate of particle growth because H radicals activate the relatively stable aromatic molecules to radicals and thus propagate the ring growth process.

Conclusions
A reduction of the total quantity of soot as a function of the amount of ethanol added to a laminar premixed ethylene flame was found. The effect on the reduction of particles formed on flame seems to be correlated with the equivalent ratio. For different flame conditions (ethanol percentage and HAB) and equivalent total amount of particulate matter with almost identical PSD were found. Therefore, the most significant effect of ethanol is a slowdown of the mechanism of nanoparticles formation.

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References
[1] Kohse-Höinghaus, K., Oßwald, P., Cool T. A., Kasper, T., Hansen, N., Qi, F., Westbrook, C, K., Westmoreland, P. R. Biofuel Combustion Chemistry: From Ethanol to Biodiesel. *Angew. Chem. In. Ed.* 49: 3572–3597 (2010).
[2] Wu, J., Song, K. H., Litzinger, T.,Lee, S-Y., Santoro, R., Linevsky, M., Colket, M., Liscinsky, D. Reduction of PAH and soot in premixed ethylene–air flames by addition of ethanol. *Combust. Flame*.144: 675–687 (2006).
[3] Inal, I., Senkan, S. M. Effects of oxygenate additives on polycyclic aromatic hydrocarbons (PAHs) and soot formation. *Combust. Sci. Tech*. 174 (9): 1-19 (2002).
[4] Richard, J. Therrien, J.R, Ali Ergut, A. Levendis, Y. A., Richter, H., Howard, J. B., Carlson, J. B. Investigation of critical equivalence ratio and chemical speciation in flames of ethylbenzene–ethanol blends. *Combust. Flame.* 157: 296–312 (2010).
[5] Alföldy, B., Giechaskiel, B., Hofmann, W., Drossinos, Y. Size distribution dependent lung deposition of dieselexhaust particles. *Aerosol. Sci. Tech.* 40: 652–663 (2009).
[6] Franck, U., Herbarth, O., Röder, S., Schlink, U., Borte, M., Diez, U., Krämer, U., Lehmann, I. Respiratory effects of indoor particles in young children are size dependent. *Sci. Total Environ.* 409: 1621–1631 (2011).
[7] Sgro, L.A., Basile, G., Barone, A.C., D'Anna, A., Minutolo, P., Borghese, A., D'Alessio, A. Detection of combustion formed nanoparticles. *Chemosphere.* 51: 1079–1090 (2003).

[8] Gormeley, P.G. Kennedy, M. Difussion from a Stream flowing Through a cylindrical Tube, *P Roy Irish Acad* 52A: 163–169 (1949).
[9] Alonso, M. Kousaka, Y. Hashimoto, T. Hashimoto, N. Penetration of Nanometer – Sized Aerosol Particles Through wire screen and laminar flow tube. *Aerosol. Sci. Tech.* 27: 471-480 (1997)
[10] D'Anna, A. Combustion formed nanoparticles. *P. Combust. Inst*. 32: 593–613(2009) .

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