

EFFECT OF 2,5-DIMETHYLFURAN ON PARTICLES FORMATION IN PREMIXED FLAMES: AN EXPERIMENTAL STUDY

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Abstract

Particulate matter pollution is one of the most common problems of the big town and industrial areas. Epidemiological studies carried out in last years have demonstrated a correlation between particulate presence in atmosphere and an increased mortality rate. To cope with this problem, research efforts address the pollution reduction and the search of alternative sources of the transportation fuels like biodiesel, methanol, bioethanol, buthanol, dimethylether. Furanic biofuels have been investigated in last months because considered possible fossil fuel substitutes thanks to their high energy density close to gasoline one, the renewable source from they come and low green-house gas emissions. Not a rich literature is present about the behaviour of these compounds in laboratory flame reactor, thus after their study in counter-flow diffusion flames, we have expanded the knowledge about their particulate formation propensity during the combustion employing them in premixed atmospheric flames of ethylene at four different equivalence ratios: 2.01, 2.16, 2.31 and 2.46. Liquid 2,5-dimethylfuran has been added at the inlet stream as 10% and 20% of total carbon fed. In-situ spectroscopy, namely laser UV-induced emission, has been used as diagnostic tool to detect different types of nanoparticles by changing the detection wavelength from the UV to the visible. Laser induced incandescence has instead been used to detect soot particles. Results show that 2,5-dimethylfuran addition in high percentage causes a reduction of particulate formation: the highest reduction is for the incandescence emission at high equivalence ratio.

Introduction

Biofuel consumption has increased through years, however, the opportunity of using different biofuels is essential for their environment friendly usage. Several oxygenated biofuels such as alcohols, ethers, ethyl tertiary butyl ether and methyl esters are already available as potential additives for conventional gasoline and

diesel. In last years a new class of furanic compounds has been selected as platform for biofuels, in particular, furan, 2-methylfuran and 2,5-dimethylfuran (DMF). Previous experimental studies regarding furanic fuels have been mainly focused on their thermal decomposition [1-5] at very low pressure or at high pressure, on their sooting propensity through studies in shock-tubes and engines [6-10] showing in the last case that furanic fuels, in particular DMF, exhibit very similar combustion and emissions characteristics to gasoline. Different results have been obtained from studies performed in low-pressure lab-scale reactors, such as jet-stirred reactor and premixed flames. In these conditions in particular DMF, produce a larger amount of soot precursors [11, 8, 12, 2, 3, 13]. Only recently, Gogoi et al. [14] have studied the effect of DMF addition in a diesel atmospheric diffusion flame founding soot emission reduction and soot reactivity toward oxygen enhancement. The lack of information on sooting tendency of furans at atmospheric pressure has aimed our research group to study them by modelling and experimentally first in counter-flow diffusion flames at atmospheric pressure [15], and now in premixed flames.

Experimental methods

Ethylene/air premixed flames with equivalence ratios of 2.01, 2.16, 2.31, and 2.46 and cold gas velocity of 10 cm/s have been investigated at atmospheric pressure in a capillary burner cooled with a 1 l/min of water at 70°C. DMF has been added to these flames by substituting 10% and 20% of the total carbon fed. DMF has been fed by a syringe pump into the preheated fuel stream in order to pre-vaporize it. When the DMF has been introduced, equivalence ratio and the cold gas velocity have been kept constant. Nitrogen has been used as further diluent to take into account the reduced number of moles of fuel due to the different molecular weight of DMF with respect to ethylene, maintaining practically unchanged the maximum temperature value and its location for each equivalence ratio investigated. Combustion conditions are reported in table 1.

Table 1. Flow rates (StdLPM) for equivalence ratios: 2.01, 2.16, 2.31, 2.46.

	$\Phi=2.01$	$\Phi=2.16$	$\Phi=2.32$	$\Phi=2.46$
	0%/10%/20%	0%/10%/20%	0%/10%/20%	0%/10%/20%
C₂H₄	1.82/1.64/1.46	1.94/1.74/1.55	2.06/1.85/1.64	2.17/1.95/1.74
Air	12.95/12.73/12.52	12.43/12.62/12.4	12.71/12.5/12.3	12.6/12.39/12.18
N₂	0/0.340/0.67	0/0.34/0.69	0/0.35/0.7	0/0.35/0.71
DMF	0/0.06/0.12	0/0.06/0.13	0/0.07/0.14	0/0.07/0.14

Combustion-generated particles have been detected by spectral laser induced emission (LIE) measurements in the 200-550 nm range, performed by using as excitation source the fourth harmonic of a Nd:YAG laser at 266 nm. The experimental setup is the same as that used in previous works [16, 15]. Two broad peaks have been distinguished in the emission spectra associated with Laser Induced Fluorescence (LIF): one in the UV region around 350 nm attributed to

single high-molecular weight aromatic molecules with few condensed aromatic rings connected by σ -bonds and the other in the visible around 400 nm attributed to highly-packed, sandwich-like clusters of aromatic hydrocarbons [17, 16]. For larger wavelength, namely at 550 nm, the signal has been related to Laser Induced Incandescence (LII) attributed to solid soot particles. In order to evaluate and subtract the contribution of the incandescence signal, a black-body radiation curve at 4000 K has been used.

Results and discussion

Profiles of laser induced fluorescence collected at 350 nm (LIF UV), laser induced fluorescence collected at 400 nm (LIF VIS) and incandescence (LII) for ethylene/air flames without additive and for flames doped with 20% of carbon from DMF for all selected equivalence ratios are reported in Figure 1.

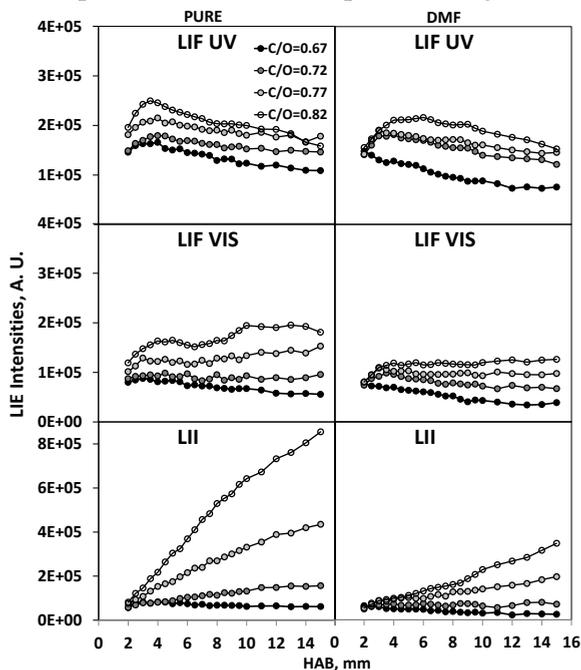


Figure 1. LIE profiles measured along the axis of neat flames (left column), and of flames doped with 20% of DMF (right column) as carbon, performed at equivalence ratios: 2.01, 2.16, 2.31, 2.46.

The LIF UV profiles present a maximum value around 4-5 mm from the burner starting just after the flame front and then slightly decrease approaching the end of the flame. Looking at LIF VIS profiles, a slight increase of the signal starts to be detectable around 10 mm above the burner for richer equivalence ratios ($\phi=2.31$ and 2.46). These trends match with the LII profiles. In fact, LII increases significantly in richer flames ($\phi=2.31$ and 2.46) at high heights above the burner,

whereas it is in the order of the noise in the flames with $\phi=2.01$ and 2.16 . Also, the increase in the LII signal is more evident and marked than the increase in both UV and VIS LIF. Furthermore flame structure does not change when DMF is used, however LIE signals change in intensity. In particular, LII seems to be largely reduced at the highest equivalence ratio ($\phi=2.46$). In fact, whereas for the ethylene flame LII was clearly detectable already at the end of the flame for $\phi=2.31$, it drops down close to the limit of detectability when DMF is added. On the other side, LIF UV and LIF VIS remain almost unchanged when additive is added.

A schematization of the LIE intensity variation, correlated to the two particulate classes of combustion-generated particles, for doped flames with respect to the reference flame (ethylene/air) varying the percentage of DMF addition is reported in Figure 2.

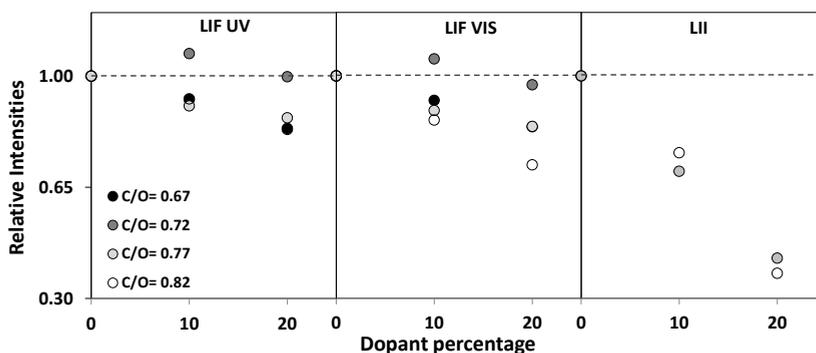


Figure 2. Relative intensities of LIF UV and visible (flame front) and LII (end of flame) emissions of doped flames with respect to ethylene/air flame as a function of the percentage of additive for all equivalence ratios.

The relative fluorescence intensities have been referred to the zone of the flame after the flame front where the signal is definitely clear from interference of incandescence and scattering of large particles. Although this allows to have a better comparison is worth to note that the signal does not exhibit a significant decay after the peak around 4-5mm, minimizing the effect of the choice of the location for the comparison. LII has been evaluated at the end of the flame where the soot has reached the maximum load. It is clearly visible that DMF addition causes a reduction of the LIE signals and that this reduction increases as the dopant percentage increases. LII reduction has been reported just for the two higher equivalence ratios ($\phi=2.31$ and 2.46) since it is close to the limit of detectability in the other flame conditions ($\phi=2.01$ and 2.16).

LII is significantly reduced, more than proportionally with respect to the percentage of the total carbon fed as DMF. However, it is not possible to define a trend of signal reduction with the equivalence ratio, because the differences rely within experimental uncertainty. LIF VIS signal does show a trend with the equivalence ratio and in particular the signal decreases as the equivalence ratio

increases. On the other side LIF UV signal shows overall a slight reduction which however relies within 15% and no significant trend of the signal reduction with the equivalence ratio is possible to be clearly evidenced.

Conclusions

The effect on particle formation of DMF addition in premixed ethylene/air flames has been investigated. DMF has been added as 10% and 20% of the total carbon fed. Laser induced emission techniques has been used. LIF in the UV and in the visible have been used to track nanoparticles whereas LII has been attributed to soot particles. When DMF is added to the flames, LIF in the UV and in the visible does not show a significant reduction of the signal suggesting that the formation of particles smaller than 10nm is not effectively inhibited by this additive, similarly to what found for other oxygenated fuels (ethanol and DME, [18, 19]). LII profiles instead are affected in a strong manner, meaning that DMF acts on soot loading. Regarding the effect of DMF amount, its addition in higher percentages causes a more than linear reduction soot formation. Also the soot reduction is relative more effective as the equivalence ratio increases: in particular the highest reduction was found for the fully sooting flame ($\phi=2.46$) doped with 20% of DMF.

References

- [1] Cullis, C. F., Norris, A.C., “The pyrolysis of organic compounds under conditions of carbon formation”, *Carbon* 10 (5): 525-537 (1972).
- [2] Grela, M. A., Amorebieta, V. T., Colussi, A. J., “Very low pressure pyrolysis of furan, 2-methylfuran and 2,5-dimethylfuran. The stability of the furan ring”, *J. Phys. Chem.* 89 (1): 38-41 (1985).
- [3] Lifshitz, A., Bidani, M., Bidani, S., “Thermal reactions of cyclic ethers at high temperatures. III. Pyrolysis of furan behind reflected shocks”, *J. Phys. Chem.* 90 (21): 5373-5377 (1986).
- [4] Liu, R. F., Zhou, X. F., Zhai, L., “Theoretical investigation of unimolecular decomposition channels of furan^{4*}”, *J. Comput. Chem.* 19 (2): 240-249 (1998).
- [5] Sendt, K., Bacskay, G.B., Mackie, J. C., “Pyrolysis of Furan: Ab Initio Quantum Chemical and Kinetic Modeling Studies”, *J. Phys. Chem. A* 104 (9): 1861–1875 (2000).
- [6] Liu, D., Togbé, C., Tran, L-S, Felsmann, D., Oßwald, P., Nau, P., Koppmann, J., Lackner, A., Glaude, P-A, Sirjean, B., Fournet, R., Battin-Leclerc, F., Kohse-Höinghaus, K., “Combustion chemistry and flame structure of furan group biofuels using molecular-beam mass spectrometry and gas chromatography – Part I: Furan”, *Combust. Flame* 161 (3): 748-765 (2014).
- [7] Tran, L-S, Togbé, C., Liu, D., Felsmann, D., Oßwald, P., Glaude, P-A, Fournet, R., Sirjean, B., Battin-Leclerc, F., Kohse-Höinghaus, K. “Combustion chemistry and flame structure of furan group biofuels using

- molecular-beam mass spectrometry and gas chromatography – Part II: 2-Methylfuran”, *Combust. Flame* 161 (3): 766-779 (2014).
- [8] Togbé, C., Tran, L-S, Liu, D., Felsmann, D., Oßwald, P., Glaude, P-A, Sirjean, B., Fournet, R., Battin-Leclerc, F., Kohse-Höinghaus, K. “Combustion chemistry and flame structure of furan group biofuels using molecular-beam mass spectrometry and gas chromatography – Part III: 2,5-Dimethylfuran”, *Combust. Flame* 161 (3): 780-797 (2014).
- [9] Zhong, S., Daniel, R., Xu, H., Zhang, J., Turner, D., Wyszynski, M. L., Richards, P. “Combustion and Emissions of 2,5-Dimethylfuran in a Direct-Injection Spark-Ignition Engine”, *Energy Fuels* 24 (5): 2891-2899 (2010).
- [10] Daniel, R., Tian, G., Xu, H., Wyszynski, M. L., Wu, X., Huang, Z. “Effect of spark timing and load on a DISI engine fuelled with 2,5-dimethylfuran”, *Fuel* 90 (2): 449-458 (2011).
- [11] Tran, L-S, Sirjean, B., Glaude, P-A, Fournet, R., Battin-Leclerc, F. “Progress in detailed kinetic modeling of the combustion of oxygenated components of biofuels”, *Energy* 43 (1): 4-18 (2012).
- [12] Tian, Z., Yuan, T., Fournet, R., Glaude, P-A, Sirjean, B., Battin-Leclerc, F., Zhang, K., Qi, F. “An experimental and kinetic investigation of premixed furan/oxygen/argon flames”, *Combust. Flame* 158 (4): 756-753 (2011).
- [13] Tran, L-S., Sirjean, B., Glaude, P-A., Kohse-Hoinghaus, K., Battin-Leclerc, F. “Influence of substituted furans on the formation of Polycyclic Aromatic Hydrocarbons in flames”, *Proc. Comb. Inst.* 35 (2): 1735-1743 (2015).
- [14] Gogoi, B., Raj, A., Alrefaai, M. M., Stephen, S., Anjana, T., Pillai, V., Bojanampati, S. “Effects of 2,5-dimethylfuran addition to diesel on soot nanostructures and reactivity”, *Fuel* 159: 766-775 (2015).
- [15] Sirignano, M., Conturso, M., D’Anna, A. “Effect of furans on particle formation in diffusion flames: An experimental and modeling study”, *Proc. Comb. Inst.* 35 (1): 525-532 (2015).
- [16] Sirignano, M., Collina, A., Commodo, M., Minutolo, P., D’Anna, A. “Detection of aromatic hydrocarbons and incipient particles in an opposed-flow flame of ethylene by spectral and time-resolved laser induced emission spectroscopy”, *Combust. Flame* 159 (4): 1663-1669 (2012).
- [17] D’Anna, A., Commodo, M., Sirignano, M., Minutolo, P., Pagliara, R. “Particle formation in opposed-flow diffusion flames of ethylene: An experimental and numerical study”, *Proc. Comb. Inst.* 32 (1): 793–801 (2009).
- [18] Salamanca, M., Sirignano, M., Commodo, M., Minutolo, P., D’Anna, A. “The effect of ethanol on size distributions in ethylene premixed flames”, *Exp. Therm. Fluid. Sci.* 43: 71–75 (2012).
- [19] Sirignano, M., Salamanca, M., D’Anna, A. “The role of dimethyl ether as substituent to ethylene on particulate formation in premixed and counter-flow diffusion flames”, *Fuel* 126: 256–262 (2014).