Final Report

COST ACTION CM1404- STSM
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Introduction

Soot is one of the main airborne contaminant in the atmosphere. The anthropogenic sources of this contaminant are the emissions produced in the combustion of different fuels in transport, especially diesel engines and powerplants.

Soot class includes particles of different sizes that can be classified according to their aerodynamic diameter: PM_{10} (diameters smaller than 10 μm), fine particles (diameters below 2.5 μm), ultrafine particles (diameters below 100 nm) and nanoparticles (diameters smaller than 50 nm) [1].These ultrafine particles can contain polycyclic aromatic hydrocarbons (PAHs), compounds known for being extremely harmful for human health. So that, it is important to characterize soot emissions in order to understand the effects of this harmful pollutant on human health. In fact, nanoparticles can enter easily human respiratory system and cause serious health problems [2].

The composition of emitted soot depends strongly on the fuel used, as well as on the combustion conditions. Acetylene (C_2H_2) is one of the recognized main precursors of soot, and thus, it is easy to find in early steps of most of the soot formation processes. The characterization of soot produced during the combustion processes can be made by different techniques such as elemental analysis, specific surface analysis, electronic microscopy observation (SEM, TEM, HRTEM).About the impact of soot on human health, toxicological analyses are carried out to investigate the behavior of human cells when these are in contact with carbonaceous nanoparticles. One of these analyses is the study of cytotoxicity consisting of a cell culture exposed to pollutants. The effect is observed via fluorescence, cell count or nuclear area among other techniques. Two common results are the end of the cell division process and the activation of the cell death process carried out by necrosis (the cell membrane is broken and the cell dies rapidly) or apoptosis (the cell activates a programmed death).

The scientific community has addressed its efforts toward the research of fuels coming from non-fossil source in order to reduce soot emissions. Recent studies have shown that the use of oxygenated compounds blended with regular fuels can reduce the amount of particles in the exhaust emissions [3-6]. Among oxygenated fuels, furanic compounds have received great attention in last years as possible substitutes of fossil fuels. Furan is the simplest among furanic compounds containing an aromatic ring closed with an oxygen atom. It can be obtained in biotechnological processes and it has interesting characteristics that made it good fuel alternative such as an energy density similar to gasoline [7-9].

In this context, the purpose of the present Short Term Scientific Mission (STSM) in collaboration with the University Federico II in Naples is the characterization of soot samples produced by acetylene's pyrolysis under well controlled conditions, in order to

understand the influence of different operation conditions such as temperature, reactant concentration or residence time; the experimental study of the effect of furan addition on soot formation in lab-scale flame; and the toxicological study on human cells in contact with acetylene soot.

Experimental methods

1) Flames doped with furan

Premixed ethylene/air atmospheric flames were performed in a capillary burner with a recirculation water system that allows to keep the burner temperature at 70°C. A steel plate was located at a minimum distance of 3 cm from the burner in order to stabilize the flame.

A steel pipe with a 0.8 mm hole was positioned between the burner and the steel plate with the hole focused in the center of the burner base in order to collect nanoparticles from the flame. 1 Nl/min Nitrogen was used as carrier gas in order and 44 Nl/min of air was used in order to dilute and cool the particles sample before enter the analyzer. The global dilution ratio achieved with these two dilutions is 680.

The furan additive, liquid at room conditions, was added by a syringe pump to the fuel stream and vaporized passing through a pre-heating pipe (80°C). This system besides allowing the vaporization of the additive, also guaranties a good mixing with the fuel stream before reaching the burner.

Particle size distributions (PSDs) was obtained by using a nano-differential mobility analyzer (TapCon 3/150 DMA) in high voltage mode, corresponding to a nominal size range 2-100 nm and equipped with a Faraday Cup electrometer. At DMA entrance, there is a radioactive (Am-241) bipolar diffusion charger where the particles reach Fuchs' steady-state charger distribution. Particles are separated according to their electrical mobility in DMA and counted in the electrometer.

Ethylene/Air flames were performed at four different equivalence ratios (ϕ): 2.01, 2.16, 2.31 and 2.46. The velocity of cold gas entering the burner was kept constant at 10 cm/s for all measurements. Furan was added as carbon substituting the 20% of the total carbon flow rate and keeping constant the equivalence ratio when the additive was added. In order to keep constant also the total gas flow rate a small amount of nitrogen was added besides furan in the fuel stream.

The burner was translated along the vertical axis in order to make particles collection at different positions of the flame. Measurements were performed with the probe positioned at seven different distances from the burner base: 6 mm, 7 mm, 8 mm, 9 mm, 10 mm, 12 mm and 15 mm. The experimental flow rates are compiled in Table 1.

| Experiment number	Φ	Q$_{C2H4}$ [l/min]	Q$_{air}$ [l/min]	Q$_{furan}$ [ml/min]	Q$_{N2}$ [l/min]
1	2.01	1,82	12,95	0	0
2		1,46	12,30	0,18	0,83
3	2.16	1,94	12,83	0	0
4		1,55	12,19	0,19	0,83
5	2.31	2,06	12,71	0	0
6		1,64	12,08	0,21	0,84
7	2.46	2,17	12,6	0	0
8		1,74	11,97	0,22	0,85

Table 1: Inlet stream flow rates.

PSDs obtained were corrected for the sample dilution and the particles losses along the pipeline and around the probe orifice.

2) Toxicological analysis

Murine macrophage cell line was selected in order to evaluate in-vitro secretion of Interleukin-1α and Interleukin-1β when the cells are in contact with soot.

Soot used for this purpose was produced in a three hours pyrolysis reaction of acetylene (5%vol. in inlet gas stream) at 1000 °C.

Soot samples has to be prepared with water as solvent in order to avoid interactions between solvent and cells. However, soot used for the samples is extremely hydrophobic and the use of a surfactant to enhance its solubility in water was necessary. The surfactants used were sodium dodecyl sulfate (SDS) and dimethyl sulfoxide (DMSO). Their chemical structures are shown in Figure 1.
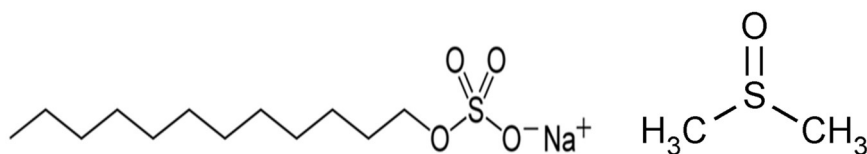
Figure 1: Chemical structures of SDS (left) and DMSO (right).

Two samples were prepared for each surfactant, one control sample without soot and another with soot. Several samples at different soot and surfactant concentrations were realized in order to get the best ratio between them. Finally, the following samples were prepared:

- 20 µg/ml of SDS and 5 µg/ml of soot in water;
- 10% vol. of DMSO in water and 5 µg/ml of soot.

The preparation of the two samples consisted of the following steps:

1) Soot powder was added in water+surfactant sample
2) Sample sonication for 3 days
3) Filtration of the samples with a paper filter (2.5 μm)
4) Sample sonication for 1 day
5) Filtration of the samples with a paper filter (2.5 μm)
6) Sample sonication for 3 hours

Absorbance measurements were carried out in order to understand if soot was dispersed correctly in liquid samples.

Samples were delivered to researchers of the Dipartimento di Farmacia of Università degli Studi di Salerno for the toxicological analysis.

Results

1) PSDs functions

Particle size distribution profiles have been obtained for each position of the flame (6 mm, 7 mm, 8 mm, 9 mm, 10 mm, 12 mm and 15 mm) in all the experiments shown in Table 1. PSD profiles of different Ethylene/Air flames are reported in Figure 2.
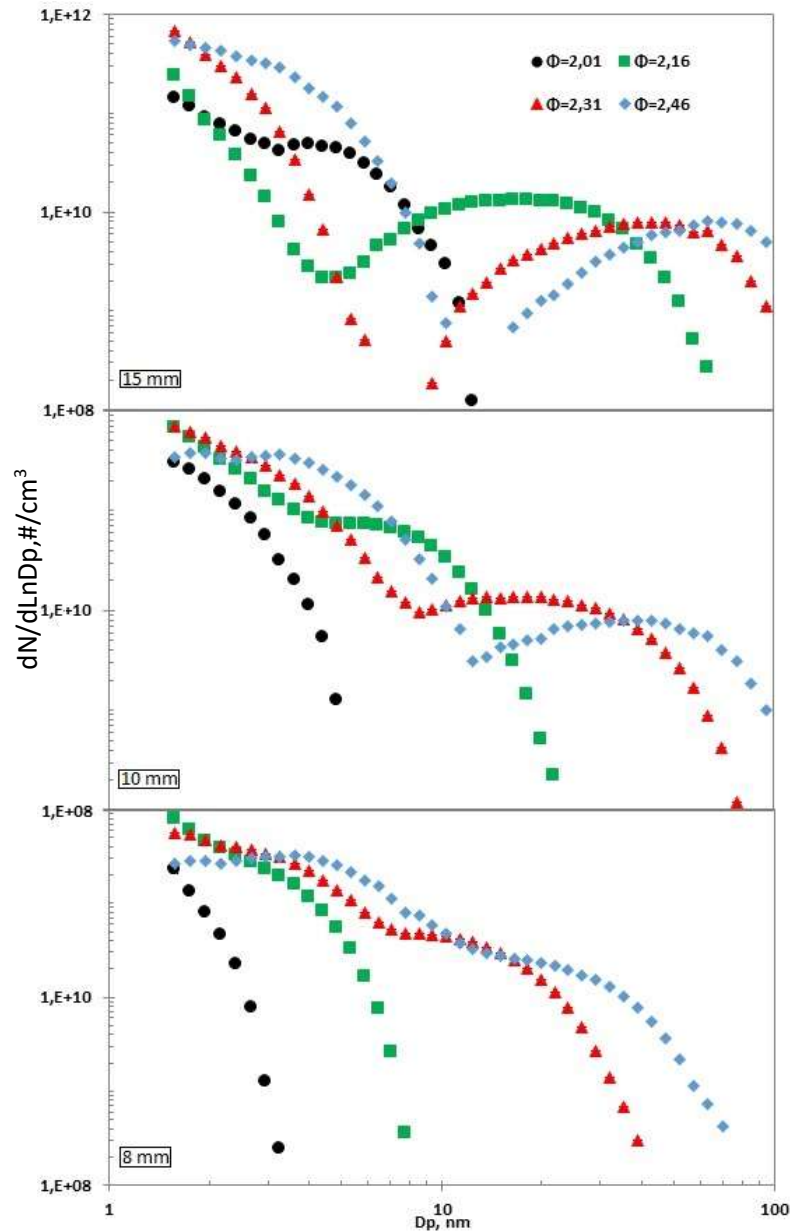

Figure 2: PSD of Ethylene/Air flames with different equivalence ratio (ϕ) obtained in low (8 mm), medium (10 mm) and high (15 mm) positions of the flame.

PSDs measured at ϕ=2.01 do not show the presence of particle larger than 10 nm except for the 15 mm position. Small nanoparticles are present in fairly large number concentrations. Moving at larger equivalence ratio (ϕ=2.16), the presence of a bimodality in the measured PSDs appears at 10 mm position (also at 15 mm position of

ϕ=2.16 flame) to be fully clear at 15 mm position. This flame condition can be considered the threshold for soot formation. The flame with ϕ=2.31 is clearly a sooting flame since the PSD bimodality is marked already for 8 mm position and, at 15 mm position, the second mode of the PSD is located at 45 nm. In the fully sooting flame (ϕ=2.46), particles larger than 10 nm are largely produced also for 8 mm position and, at the end of the flame, the second mode of the PSD is located at 70 nm. Small nanoparticles are present for all equivalence ratios and for all positions. It is possible to note that for ϕ=2.01 nanoparticle number concentration remains high all along the flame. A slight increase can be observed as the equivalence ratio increases. Nanoparticles number concentration increases at increasing flame heights as well, reaching a maximum and finally slightly decreasing at the end of the flame (ϕ=2.16-2.46). However, also for the richest equivalence ratio (ϕ=2.46), the nanoparticles at the end of the flame are present in significant number concentration. The presence of nanoparticles in the end of the flame can be attributed to their low coagulation efficiency together with the possibility to have a continuous nucleation in flame. Also it is worth to recall that the presence of large amount of soot particles can increase the losses of small nanoparticles due to coagulation in the sampling lines.

Experiments with flames blended with furan at 20% have been made in order to study the effect of this additive on the number concentration of small and large nanoparticles formed during the combustion process. Figures 3 and 4 show the comparison between PSDs profiles of pure and doped flames.
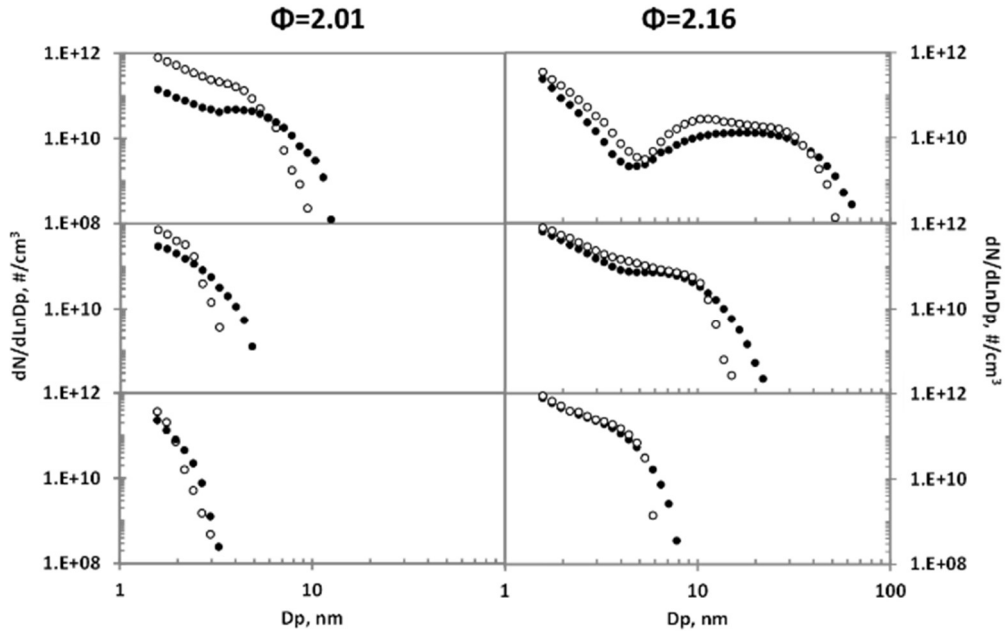
Figure 3. PSDs measured in the pure ethylene (●) and ethylene/DMF (○) flames for equivalence ratio of 2.01 (left column) and 2.16 (right column) at selected H. From bottom to top: 8 mm, 10 mm, 15 mm.
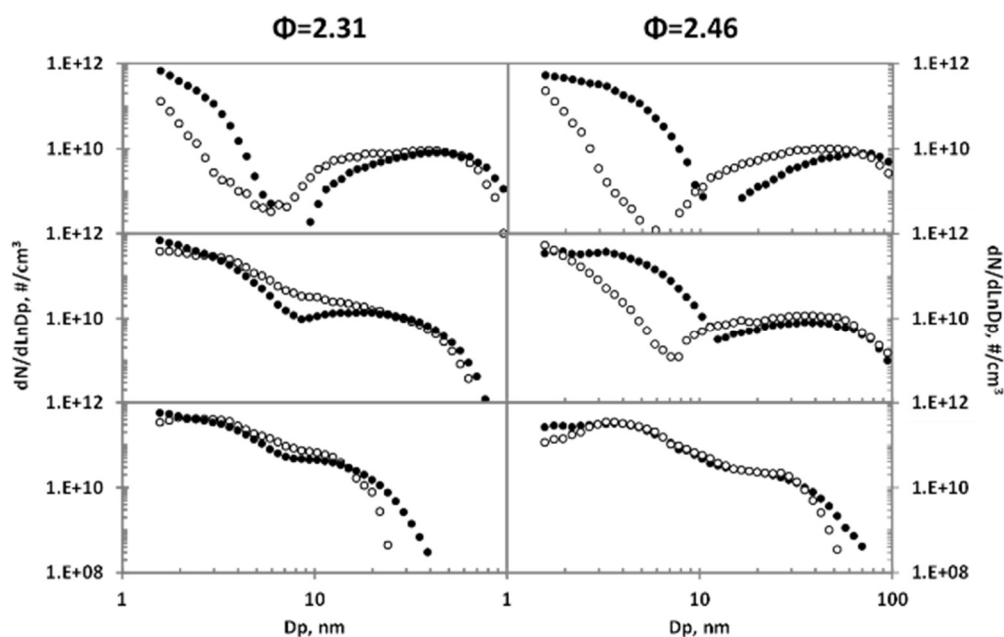
Figure 4. PSDs measured in the pure ethylene (●) and ethylene/DMF (○) flames for equivalence ratio of 2.31 (left column) and 2.46 (right column) at selected H. From bottom to top: 8 mm, 10 mm, 15 mm.

The presence of furan in flames for the lower equivalence ratios results in a strong reduction of large particles number concentration, but an increase of the concentration of very small nanoparticles is found at the end of the flame, especially for ϕ=2.01.

For the higher equivalence ratios, the peak value of the second mode of the PSDs is shifted towards smaller size. This results in a very strong reduction of particles with dimension ranging from 3 to 9 nm, especially at the end of the flame, while only a slight reduction is found for large soot particles (d>20nm). Furthermore the number concentration of the smallest particles did not undergo variations.

Thus the substitution of part of ethylene with furan provoked a reduction of large soot particles, more marked for low equivalence ratios and for the first zone of the flame for higher ϕ. A strong reduction of smaller particles concentration is seen at the end of the richest flames, but the reduction of the smallest particles concentration is never found. On the contrary, in some cases, concentration increase of very small particles is found.

2) <u>Toxicological study</u>

A preliminary analysis of soot powder from acetylene pyrolysis was made. In order to know the main characteristics of its internal structure, a FT-IR analysis was carried out.

Spectrum in Fig. 5 shows a characteristic broad peak in the range of wavenumber 1100-1600 cm^{-1} ascribable to C=C bond. So, the absence of H and O content makes this soot extremely graphitic.
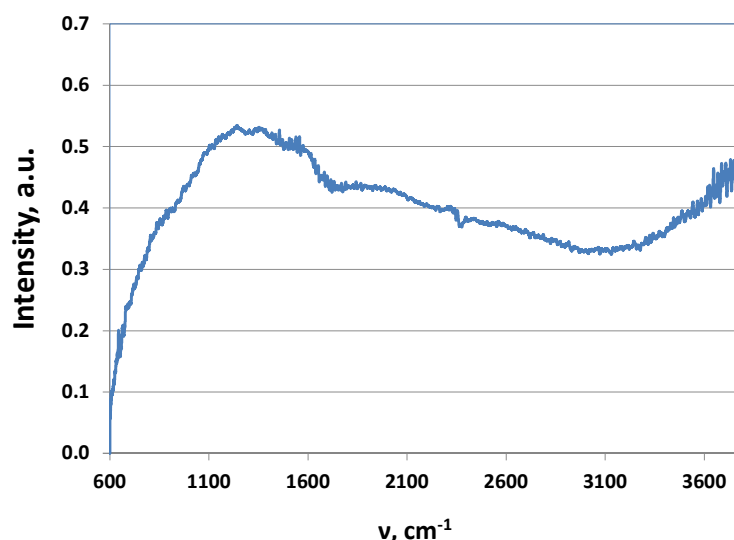
Figure 5. FT-IR spectrum of soot powder from acetylene pyrolysis.

Because of the chemical features of this kind of soot, it was very hard to find a solvent to prepare soot samples. The choice is fallen on the class of surfactants, namely compounds able to enhance the solubility of some species thanks to their hydrophobic and hydrophilic parts. Two surfactants were chosen: Sodium Dodecyl Sulfate (SDS) and Dimethyl sulfoxide (DMSO).

Absorbance measurements of the two samples of soot dispersed in water/SDS solution and in water/DMSO solution were carried out by using a spectrophotometer in order to understand the effect of the two surfactants on soot particles.
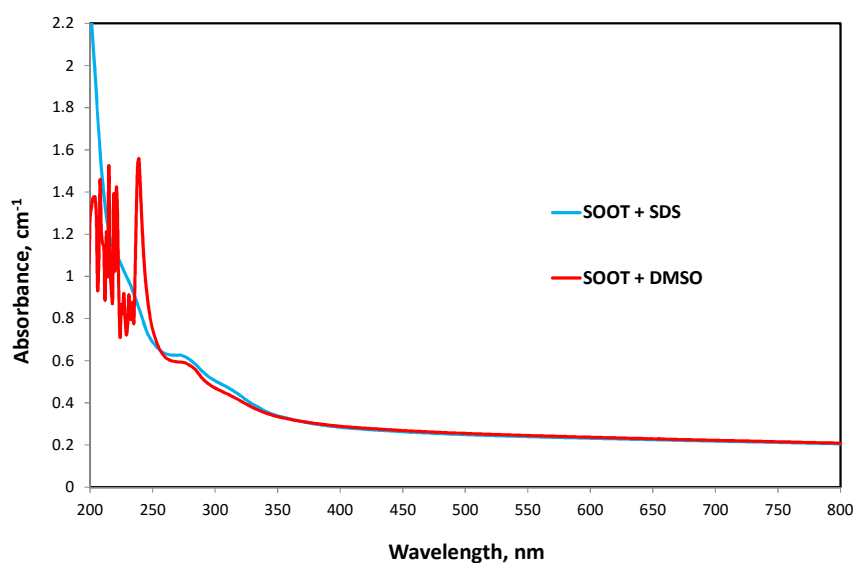
Figure 6. Absorbance spectra for Soot-SDS-water (blue line) and Soot-DMSO-water (red line) samples.

The spectra in Figure 6 show that the relative concentrations chosen for soot and surfactants allow to have the same degree of soot dispersion in both samples. In fact, both profiles have the characteristic peak at 280 nm and a broad band at 315 nm. Because as reference for the measurements of soot+SDS and soot+DMSO samples, a solution of SDS/water and of DMSO/water have been taken respectively. The peak and broad band are due to the carbonaceous material present in the samples and not to the surfactants.

Furthermore, in order to know the mean size of particles dispersed in the samples, dynamic light scattering (DLS) measurements were performed. Figure 7 reports the size distribution both in volumetric and numerical concentration.
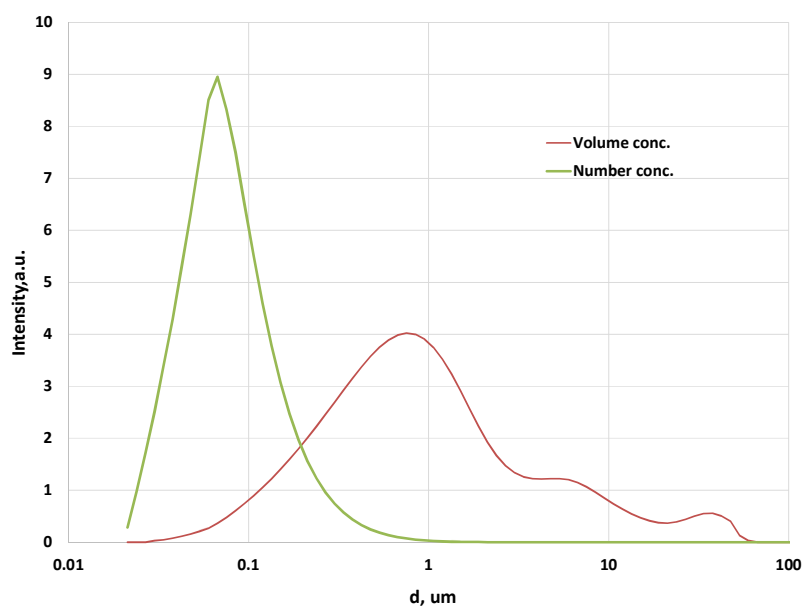
Figure 7. DLS profiles for Soot-SDS-water in volumetric (red line) and number (green line) concentration.

SDS profiles show that the most numerous particles have size of 67 nm, while the highest contribution in term of mass is given by particles of 750 nm.

Soot samples dipersed in water/SDS and in water/DMSO were sent to the researchers of the Dipartimento di Farmacia of Università degli Studi di Salerno for the toxicological analysis on murine macrophage cell line.

Toxicological analysis results will be provided us shortly.

References:

[1] I. Abdul-Khalek, D. Kittelson and F. Brear, SAE Technical Paper no. 1999-01-1142, 1999.

[2] N. Scovronick, P. Wilkinson, Global Environ. Change 24 (2014) 155–164.

[3] S.C.J. Sorenson, Gas Turbines Power Trans. ASME 123 (2001) 652–658.

[4] R. Song, K. Li, Y. Feng, S. Liu, Energy Fuels 23 (2009) 5460–5466.

[5] S.H. Yoon, J.P. Cha, C.S. Lee, Fuel Process. Technol. 91 (2010) 1364–1372.

[6] M.B. Sirman, E.C. Owens, K.A. Whitney, SAE Technical Papers no. 2000-01- 2048, 2000.

[7] D. Liu, C. Togbe´, L.‑S. Tran, D. Felsmann, P. Oswald, P. Nau, J. Koppmann, A. Lackner, P.‑A. Glaude, B. Sirjean, R. Fournet, F. Battin-Leclerc, K. Kohse-Hoinghaus, Combust. Flame 161 (3) (2013) 748‑765.

[8] L.-S. Tran, B. Sirjean, P.A. Glaude, R. Fournet, F. Battin-Leclerc, Energy 43 (1) (2012) 4‑18.

[9] Z. Tian, T. Yuan, R. Fournet, P.‑A. Glaude, B. Sirjean, F. Battin-Leclerc, K. Zhang, F. Qi, Combust. Flame 158 (2011) 756‑773.