CHEMICAL ENGINEERING TRANSACTIONS

VOL. 48, 2016

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eddy de Rademaeker, Peter Schmelzer

ISBN 978-88-95608-39-6; **ISSN** 2283-9216

DOI: 10.3303/CET1648064

Explosions of Gas/Carbon Black Nanoparticles Mixtures: an Approach to Assess the Role of Soot Formation

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The influence of carbon blacks nanoparticles addition to methane/air mixture explosions has been studied. Low concentrations of carbon black nanoparticles ranging from 20 to 300 nm average diameter have been mixed with methane. Explosion tests have been performed in the 20 L sphere and in a flame propagation tube at different initial degrees of turbulence. The burnt gases have been analysed by micro gas-chromatography. The influence of carbon black nanoparticles on the explosion severity and on the velocity of the front flame has been appreciated by comparing the results obtained for pure methane explosions.

It appears that the maximum explosion overpressure can slightly increase when a few percent of carbon blacks are introduced for lean mixtures but decrease for rich mixtures. This trend can be explained by using an analogy and assuming that carbon nanoparticles are soot nuclei, which enhance the physical and/or chemical condensation of combustion products. Furthermore, the explosion severity seems to decrease due to the increase of the radiation heat exchange with the introduction of low concentrations of nanoparticles.

Finally, the front flame was modified from a semi-parabolic profile to a non-uniform profile, which was formed of multiple perturbations generated by the burnt particles (flamelets). These perturbations makes the flame front surface wrinkled, resulting in noticeable changes on the heat transfer, flame velocity and explosion properties.

1. Introduction

Flammable gas/solid mixtures are frequently present in diverse industrial applications and their explosions are not well understood because of their complex thermal transfers, combustion kinetics mechanisms and turbulence/combustion interactions (Khalili et al., 2011). Recent efforts have been made in order to understand the influence of these phenomena on the explosion parameters; however there remains a need for continued research (Amyotte, 2014). In parallel, nanoparticles offer new opportunities for the study of flame propagation and more generally, dust explosion. When dispersed in air, they follow the fluid streamlines, neglecting particle-fluid interactions and considering that the turbulence intensity is not very sensitive to nanoparticles insertion. Due to their high stability in dispersion, they can thus be introduced as solid fuel together with low turbulence levels in the dust cloud, which is not possible with microparticles. It notably allows to isolate turbulence/combustion interactions by decoupling efficiently the flame stretch due to the initial turbulence from the effect of the particle presence ahead of the flame front.

This work aims to study the influence of low concentrations of carbon black nano-sized particles in gas mixtures on the severity of the explosion. Nanoparticles of carbon black can be regarded as initial soot or soot-nuclei in the system, which also allows studying the influence of such particles on gas explosions. This case is specifically encountered during gases combustion with high fuel equivalent ratio. At first, tests were performed on 20 litres explosion sphere and on a flame propagation tube to determine both the explosion indexes and the turbulent flame velocity. The composition of the burnt gases was also studied to better understand the impact of nanoparticles insertion on the combustion process. Finally, at medium term, a model representing the flame propagation in presence of soots will be developed based on the previous experimental results.

Please cite this article as: Torrado D., Cuervo N., Pacault S., Dufour A., Glaude P., Murillo C., Dufaud O., 2016, Explosion of gas/carbon blacks nanoparticles mixtures: an approach to assess the role of soot formation, Chemical Engineering Transactions, 48, 379-384
DOI:10.3303/CET1648064

2. Materials and methods

In this study, Printex XE2 and Corax N550 (Evonik) have been chosen as carbon black nanoparticles. The characteristic diameter of the powder d_{50}, the BET specific surface (using Brunauer-Emmett-Teller method) and the equivalent BET diameter are reported in Table 1. It appears that the primary nanoparticles are arranged in agglomerates of micrometric size. Moreover, Printex XE2 presents a much larger specific surface area than Corax N550, which can have an impact on their respective reactivity and physical properties.

The explosion severity of nanopowders/methane hybrid mixtures has been studied by measuring the maximum overpressure P_{max}, the maximum rate of pressure rise $(dP/dt)_{max}$, the front flame profile and propagation velocity. The measurements of the explosion severity were performed in a 20-liter spherical vessel. In order to study the influence of an initial concentration of soot in a methane/air mixture, low concentrations of carbon blacks were chosen. With regard to the scale precision, the lowest concentration of carbon black was set at 0.5 $g.m^{-3}$. Tests were also performed at 2.5 $g.m^{-3}$, which is still far below 60 $g.m^{-3}$, the minimum explosive concentration of such powders (Bouillard et al., 2010). Samples of burnt gases were taken without dilution and analyzed by micro gas-chromatography (Varian 490 MGC).

Table 1: Main characteristics of the nanopowders (Bouillard et al, 2010)

Nanopowders	BET specific surface area ($m^2.g^{-1}$)	d_{BET} (nm)	d_{50} (µm)
Printex XE2	950	3	10
Corax N550	40	75	15

The influence of the initial turbulence was characterized by varying the ignition delay tv, i.e. time between the beginning of the air pulse and the ignition (at 100 J with chemical igniters). The severity of the explosion depends on the turbulence level which is necessary for the dust dispersion and especially for microparticles. The explosions test were carried out at three ignition delays which are related to an intensity of velocity fluctuations u', as is presented in Table 2. Due to the low settling velocity of nanoparticles, a quiescent case was also considered. It corresponds to the insertion of dust without a pulse of air. The correspondence between u' and tv was obtained by performing a Particle Image Velocimetry (PIV) analysis with a continuous laser sheet and wheat starch as tracer. The results are in good agreement with those presented by Dahoe (2000), i.e. root-mean-square (RMS) velocity fluctuations of approximately 3 and 0.9 at 60 and 120 ms respectively.

Table 2: Relation between ignition delay and turbulence level in the 20 L sphere

Ignition delay tv (ms)	Intensity of velocity fluctuations u' ($m.s^{-1}$)
0	0
60	3.40
120	1.05

The flame velocity was measured in a vertical 1 m long tube with a square cross-section of 0.07 m connected to a gas mixing system (Di Benedetto et al., 2011). Dust clouds are generated by a pulse of methane/air mixture at 5.2 barg from the bottom of the tube. A high speed video camera (Phantom V9.1) is used for recording videos of the flame propagation at 1000 to 4000 fps.

3. Experimental results and discussion

3.1 Influence of carbon black insertion on gas explosion severity

At first, tests were performed on pure methane at different concentrations and turbulence levels. In addition, CEA software was also used to determine the maximum explosion pressure at equilibrium in adiabatic conditions (Figure 1 - left). The same experiments were notably carried out with 0.5 $g.m^{-3}$ Printex XE2 (Figure 2). By comparing figures 1 and 2, it appears that the insertion of carbon blacks at low concentrations does not modify significantly the maximum explosion pressure, whatever the gas concentration and turbulence level. Such behaviour is consistent with thermodynamic equilibrium calculated by CEA because the ratio carbon black/methane is very low and the global fuel equivalent ratio is nearly unmodified by the addition. However, slight but noticeable shifts in the maximum rate of pressure rise are observable: $(dP/dt)_{max}$ slightly decreases down to 15% when carbon black is added, especially for high turbulence levels and fuel-rich mixtures. For quiescent mixtures, no significant modifications are noticeable.

Similar tests were carried out with 0.5 g.m^{-3} Corax N550 dispersed in methane/air mixture (Figure 3 - left). Trends observed for Printex XE2 are rather similar for Corax N550. Nevertheless, slight differences can be seen for higher turbulence levels: for an ignition delay of 60 ms, the negative effect of carbon black insertion on the explosion severity is less perceptible for Corax than for Printex. It is the contrary when the ignition delay increases. This behaviour can be explained by considering previous studies highlighting the impact of the fragmentation phenomenon during the dust dispersion (Murillo et al., 2013). As seen on Table 2, the agglomerates of Printex are composed of elementary particles having a diameter lower than those of Corax N550. As a consequence, their effect, for instance on heat transfer and radiation, could be greater than the impact of the same weight of Corax. At lower turbulence, shear forces are less efficient and fragmentation is less perceptible. The difference which are observed between the two kinds of carbon blacks are probably related to the characteristics of their agglomerates more than to those of the nanoparticles.

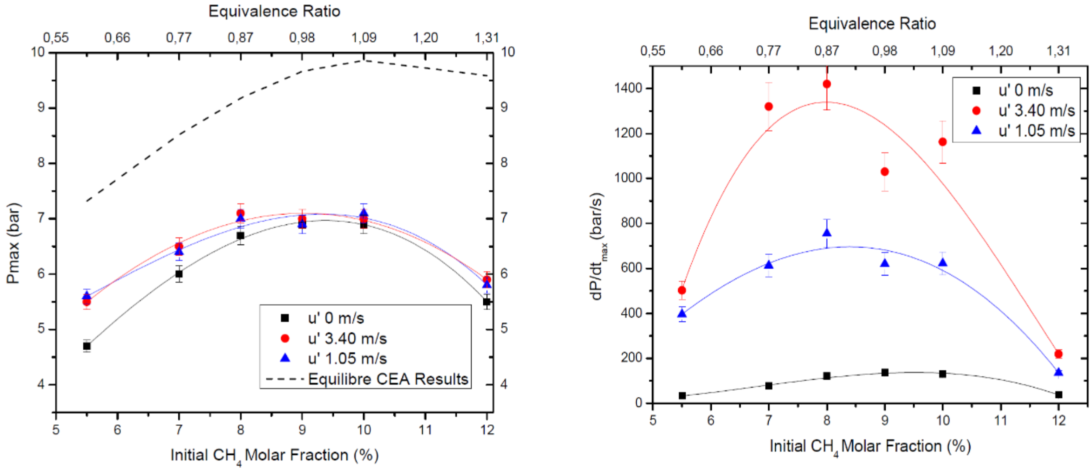

Figure 1: Influence of turbulence level on the maximum overpressure – P_{max} (left) and on the maximum rate of pressure rise – dP/dt_{max} (right) for Methane/Air mixtures.

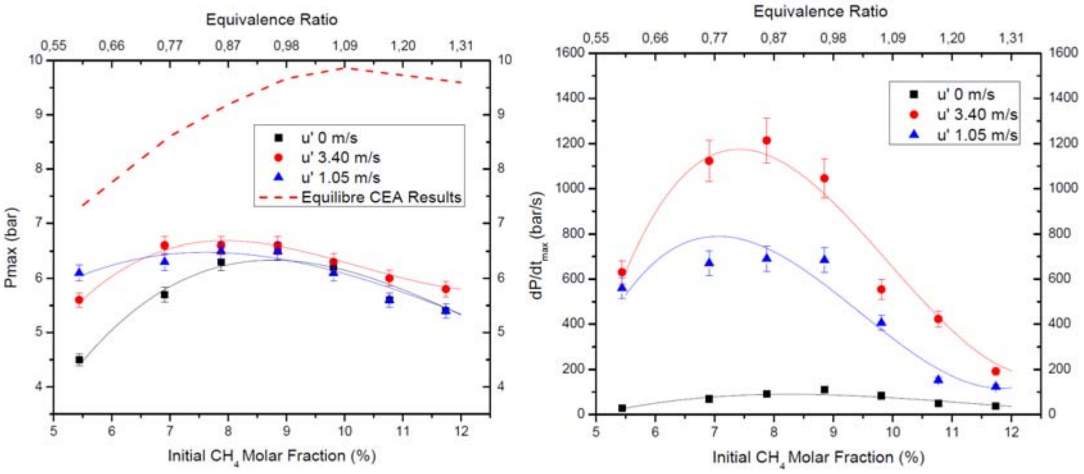

Figure 2: Influence of turbulence level on the maximum overpressure – P_{max} (left) and on the maximum rate of pressure rise – dP/dt_{max} (right) for a 0.5 g.m^{-3} Printex XE2/Methane/Air mixture.

3.2 Influence of the initial carbon black concentration on the explosion severity

The maximum explosion pressure and the maximum rate of pressure rise are also affected when the initial amount of carbon nanoparticles is increased in the system. As the latter parameter is always more sensitive to the variation of the initial conditions, we will focus on it. In Figure 3, the maximum rate of pressure rise decreases when the carbon black content is increased from 0.5 g.m^{-3} to 2.5 g.m^{-3}. It is especially the case when the turbulence level is great. For instance, for lean fuel-air mixtures at 5.4 %v. of CH_4, such increase of carbon black contents induces a decrease of 45 to 50 % of the maximum rate of pressure rise, i.e. from 750 bar.s^{-1} to nearly 400 bar.s^{-1} at 3.4 m.s^{-1}.

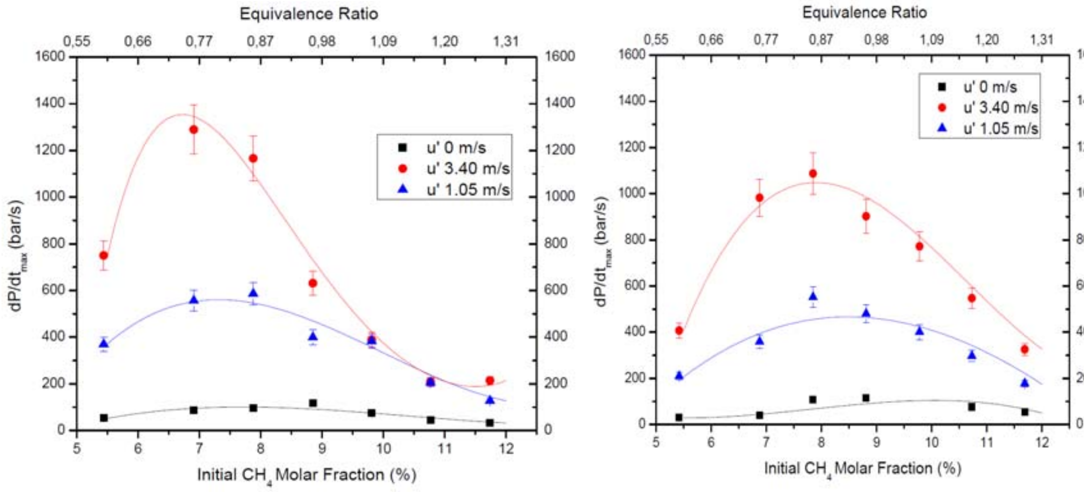

Figure 3: Impact of the turbulence level on the maximum rate of pressure rise – dP/dt$_{max}$ for 0.5 g.m^{-3} (left) and 2.5 g.m^{-3} (right) CoraxN550/Methane/Air mixtures.

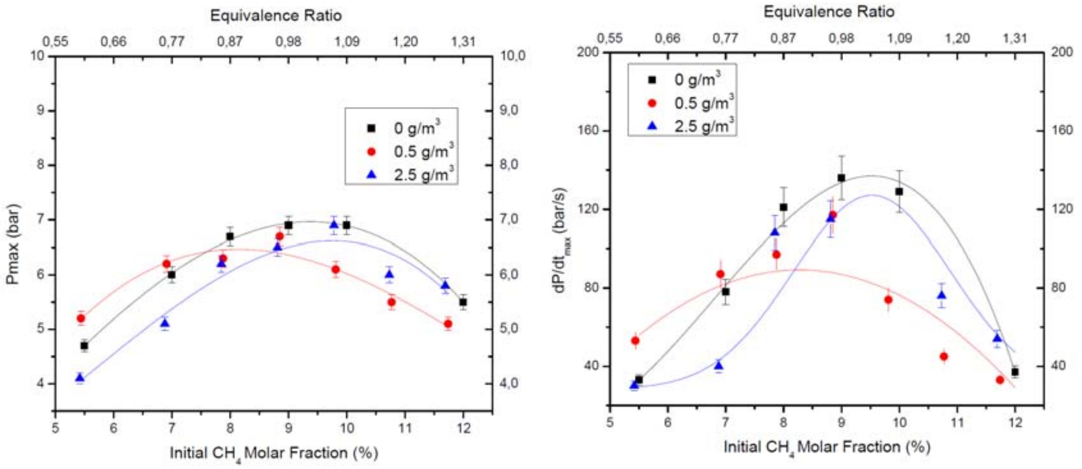

Figure 4: Influence of carbon black concentration on the maximum overpressure - P$_{max}$ (left) and on the maximum rate of pressure rise - dP/dt$_{max}$ (right) for a Corax N550/Methane/Air mixture under quiescent conditions.

Figure 4 represents the influence of the concentration of carbon black nanoparticle on the explosivity of Corax N550/Methane/Air mixtures for an initially quiescent system (u' = 0 m.s^{-1}). The maximum overpressure seems to increase for lean mixtures by the addition of 0.5 g.m^{-3} carbon black nanoparticles but decreases for stoichiometric and rich mixtures. However, when the concentration of Corax N550 rises to 2.5 g.m^{-3}, the severity of the explosion diminishes for all the concentrations studied in this work. The same trends can be observed on Figure 4 (right) for the maximum rate of pressure rise. Once again, it demonstrates that both the concentration, but also the turbulence play an important role on the dust dispersion and, by consequence, on the flame propagation and on the explosion severity. This point will be addressed in the next section.

3.3 Importance of the turbulence level

The explosion severity of methane/nanoparticles mixtures is strongly affected by the initial turbulence level of the system, as shown in Figure 2. The maximum explosion overpressure tends to increase as the turbulence level is higher, but for mixtures near the stoichiometric concentration, the influence is minimal. For a lean fuel mixture, a turbulence level u '= 3.40 m.s^{-1} produces a slightly lower P$_{max}$ compared with u' = 1.05 m.s^{-1}. This effect, observed through numerous experiments, may be due to premature extinction of the flame because of the high level of turbulence in the system. In addition, for rich fuel mixture of Printex XE2 and methane, ignition was recorded under quiescent conditions at 12 %v., whereas no ignition were obtained for high turbulence levels. Turbulent quenching may explain this difference observed at shorter ignition delay (Kosinski et al, 2013).

In addition, the maximum rate of pressure rise is considerably enhanced by the transfer properties and thus by the turbulence level of the system, as shown in Figure 2 - right. The effect of turbulence on the maximum rate of pressure rise is significant (almost one order of magnitude) at a high level of turbulence and near stoichiometry (Russo and Di Benedetto, 2007). Eventually, it should been underlined that the reproducibility is also greatly affected by the turbulence.

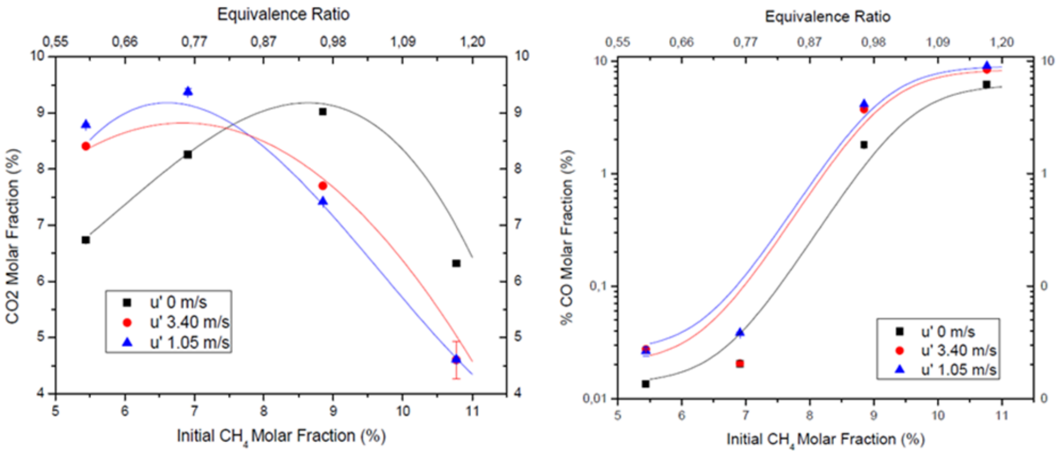

Figure 5: Influence of turbulence level on the final CO_2 molar fraction (left) and on the final CO molar fraction (right) for a 0.5 $g.m^{-3}$ Printex XE2/Methane/Air mixture.

If the effect of the initial turbulence level on the explosion kinetics is clearly visible on Figures 2 and 3 – right, its specific impact on the combustion chemistry is shown on Figure 5 through the evolution of the CO_2 and CO content in the burnt gases. It should be highlighted that, if the carbon dioxide concentration tends to reach a maximum before decreasing, a shift towards the highest concentrations is noticeable for quiescent conditions (with a maximum near stoichiometry). It implies that an increase of the intensity of velocity fluctuations up to 1 $m.s^{-1}$ improves the combustion for lean mixtures having a fuel equivalence ratio (FER, φ) lower than 0.8, but tends to decrease the CO_2/CO ratio for richer mixtures. This reflects a more important heterogeneity of the initial combustible cloud at high turbulence, leading to local φ higher or lower than unity even if the global φ is 1. As a consequence, CO is less oxidized under such conditions (Figure 5 – right). It can be noticed that the oxidation of CO to CO_2 drops off as soon as φ exceeds unity, whatever the turbulence level.

As the carbon black concentration increases, the level of initial turbulence has a negative effect on the gas explosivity for rich mixtures, which is not the case for a quiescent system. As previously discussed, this phenomenon can be explained because higher turbulence levels may create a powder fragmentation and deagglomeration (Murillo et al, 2013), raising the heat transfer surface. Then, a high level of initial turbulence for these mixtures increases the heat loss by radiation, strongly modifies the flame profile and, as a consequence, reduces the severity of the explosion.

Figure 6 shows the differences between a flame propagation for a methane/air mixture (left) and for a hybrid Printex XE2/methane/air at a solid concentration of 6 $g.m^{-3}$ and for the same initial turbulence (same ignition delay of 60ms). The flame profile for the gaseous mixture is initially spherical and becomes parabolic when the flame interacts with the tube walls. The flame front seems well defined, continuous and appears rather smooth, as it is usually reported for a gaseous mixture (Proust, 2006). Only a few “bright points” corresponding to generated soot or to solid impurities (i.e. micrometric paper dusts due to the tube cleaning) can be observed within the flame. In the case of the hybrid mixture, an initial semi-spherical propagation occurs in the first milliseconds, but the flame profile is not uniform and presents many irregularities as the flame kernel encounters the dispersed particles and aggregates. During this step, the kernel can be strongly destabilized by turbulent vortices and even quenched. When the flame propagates upward and interacts with the walls, its surface is increased with respect to methane/air system which causes an increase in flame speed. This turbulent flame propagation and specific flame stretching/wrinkling is also associated with the numerous presence of bright condensation nuclei due to the insertion of carbon blacks (yet only a few milligrams). As a consequence, the thermal exchanges by radiation are considerably increased for hybrid mixtures, which may be the principal reason for the decrement in the explosion severity. Moreover, the burned gases and particles remaining inside the tube burn for a longer time.

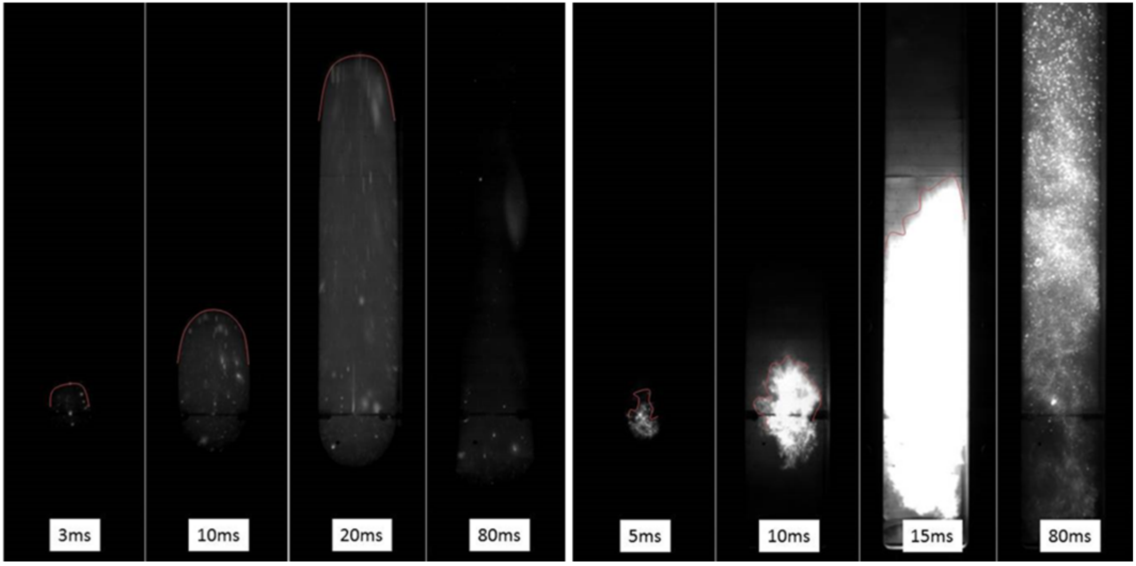

Figure 6: Flame front propagation for a 12%v. CH_4/air explosion at an ignition delay of 60ms (left) and flame front propagation for 30mg of Printex XE2 dispersed in a 12%v. CH_4/air explosion at tv 60ms (right).

4. Conclusions

As carbon black nanoparticles may be associated with soot or soot nuclei, their addition seems to favour the condensation of combustion products. As a consequence, their association with pure combustible gas especially modifies the combustion kinetics and the heat transfer upstream from the flame front, which leads to a decrease in the explosion severity. Nevertheless, this evolution depends on various parameters, notably: i) the carbon black concentration, ii) the particle size distribution and particularly the presence of agglomerates/aggregates, iii) the initial turbulence, the latter two parameters being related. The further quantitative study of the flame speed will shed a new light on this peculiar issue.

Acknowledgments

The authors would like to gratefully thank George Lardier for the provided assistance in the µCPG analyses.

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