

Characterization and reactivity of soots obtained under different combustion conditions

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The knowledge of the properties of soot obtained from different sources may allow understanding in what extent its origin and the formation atmosphere are key parameters on its structure and its capability to interact with other compounds, such as NO, leading to its reduction. Three different kinds of soots have been subject of this study, one of them is commercial soot (Printex-U) as a diesel soot surrogate, and two of them were obtained from lab scale experiments, from the pyrolysis of acetylene-ethanol mixtures and the pyrolysis of ethylene in a CO₂ atmosphere. Different characterization techniques have been applied and reactivity studies towards O₂ and NO have been carried out in order to identify the differences and similarities among the selected soot samples.

The outcome from the reactivity experiments shows that commercial soot, Printex-U, presents higher reactivity towards O₂ and NO than soots obtained in laboratory, reaching NO reductions around 25%. This soot presents the lowest degree of organization, the highest surface area and the highest content in hydrogen, being the least reactive, the soot produced in the pyrolysis of C₂H₄ in CO₂ atmosphere.

1. Introduction

Soot and NO_x are unwelcome products in many combustion systems, which emissions are mainly conditioned by the competition of the reactions that participate in their formation and elimination (Xi and Zhong, 2006). Soot may be formed under oxygen-lean conditions (Stanmore et al., 2008) and NO_x may be reduced in this environment. Taking advantage of this situation, it can be considered that the reaction between soot and NO within the combustion chamber could be used as a technique for minimization of the emissions of these pollutants since they both, soot and NO, may react *in situ* with each other (Aarna and Suuberg, 1997, Illán-Gómez et al., 1993, Mendiara et al., 2008). Also, the oxygen present in the combustion systems may interact with carbonaceous particles contributing to the diminution of the emissions of soot.

In this context, it has been considered interesting to perform a study on the reactivity of different soots obtained from very different conditions: one commercial surrogate for soot was found in literature (Neeft et al., 1997) as a representative model compound for diesel soot, and two soots obtained from laboratory facilities, from the pyrolysis of acetylene-ethanol mixtures in N₂ atmosphere and the pyrolysis of ethylene in CO₂ atmosphere. The present study has the general aim of contributing to reach a better knowledge of the reactivity of different kind of soots in the oxidation processes, as well

as their interaction with NO. A series of experiments has been performed for each soot sample under similar operating conditions for the different soots in order to be able to analyze the results in relation to their reactivity, structure and origin. To that end, a characterization, including morphology and composition analyses, of these soots has been also performed.

2. Experimental Set-up and Methodology

Three different soot samples have been the object of this study. First of all, a commercial surrogate soot, Printex-U, as a model material of diesel soot, coming from thermal-oxidative decomposition of mineral oil. Furthermore, two different kinds of soots were obtained under well-controlled lab scale conditions in the installation described in previous works (e.g. Esarte et al., 2009). In this facility, soot samples were obtained from the pyrolysis of 30000 ppm of acetylene and 20000 ppm of ethanol in nitrogen atmosphere, and also from the pyrolysis of 30000 ppm of ethylene in CO₂ atmosphere.

The reactivity experiments towards O₂ and NO of the different soot samples have been performed in an experimental installation described in detail elsewhere (Ruiz et al., 2007a), and therefore only a brief description is given here.

The reaction takes place at atmospheric pressure in a quartz reactor of 15 mm inside diameter, placed in an electrically heated oven. A mixture of around 10 mg of soot and silica sand, using a soot/sand weight ratio of 1/30 to prevent soot particle agglomeration, is placed forming a thin layer on a plug inside the reactor.

The study of the reactivity of the soot samples towards O₂ and NO has been performed at 1275 K, for an initial O₂ concentration of 500 ppm in the oxidation experiments, and for 2000 ppm inlet NO concentration in the soot-NO interaction experiments. The total gas flow rate in all the experiments was 1000 mL(STP)/min. Continuous Infra Red (IR) gas analyzers were used to measure and register the outlet concentration values of CO, CO₂ and NO, when it was necessary.

Additionally to the reactivity study, soot samples have been characterized by means of different techniques: scanning electron microscopy (SEM), transmission electron microscopy (TEM), elemental analysis, determination of Brunauer-Elmett-Teller (BET) surface area by N₂ adsorption at 77 K and Raman spectroscopy (Illán-Gómez et al., 1993, Van Poppel et al., 2005, Hays and Vander Wal, 2007).

3. Results and discussion

3.1 Soot reactivity towards oxygen and NO.

In order to compare the reactivities of the three different kinds of soots, the *Shrinking Core Model* for decreasing size particle with chemical reaction control has been used. This model has been applied successfully in similar studies (Mendiara et al., 2007, Ruiz et al., 2007b, Mendiara et al., 2008). The experimental data have been processed according to the selected model for soot oxidation and its interaction with NO (Eq. 1 and 2).

The reaction rate is referred to the external surface of the particle, S_{ext} (Eq. 1) and may be described as function of the carbon weight remaining during the reaction considered, W_C , (Eq. 2). In these equations, N_C represents the moles of carbon, b is the carbon

stoichiometric coefficient according to the global reaction with oxygen and NO, respectively, k_S is the rate constant of each reaction, $C_{gas\ reactant}$ is the gas reactant concentration (O_2 or NO), n is the reaction order with respect to the gas reactant and C is a constant.

$$-\frac{1}{S_{ext}} \cdot \frac{dN_C}{dt} = b k_S C_{gas\ reactant}^n \quad (\text{Eq. 1}) \Rightarrow -\frac{1}{W_C^{2/3}} \cdot \frac{dW_C}{dt} = C b k_S C_{gas\ reactant}^n \quad (\text{Eq. 2})$$

The employment of this model allows the use of the Eq. 3 for relating the time needed for the complete conversion of carbon, i.e. τ , and the carbon conversion at any time (t), i.e. X_C . The τ values obtained are gathered in Figure 1 for soot oxidation and soot interaction with NO.

$$\frac{t}{\tau} = 1 - (1 - X_C)^{1/3} \quad (\text{Eq. 3})$$

The conversion of carbon at any time is determined as the weight of carbon reacted in the experiment, related to the weight of carbon fed into the reactor. Since in the interaction of soot with O_2 and NO, carbon is mainly converted into CO and CO_2 as reaction products, the carbon weight placed at any time within the reactor is calculated from the CO and CO_2 concentrations.

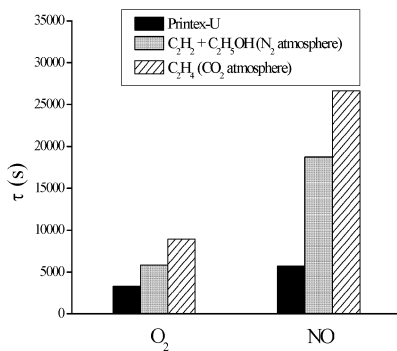


Figure 1. Comparison of the complete conversion times obtained in the reactivity experiments towards O_2 and NO for the different soot samples.

As can be observed in Figure 1, all the soot samples present lower complete conversion times in the interaction with O_2 than in the interaction with NO, indicating the higher reactivity towards O_2 . In the oxidation experiments, the total conversion time for the commercial soot is lower than for the soot sample formed in nitrogen atmosphere and this one is lower than the soot obtained from CO_2 atmosphere. The same trend can be observed for experiments with NO, although in these experiments the difference between τ values is higher. Moreover, NO reduction varies in a significant manner

depending on every soot sample. A reduction of 25% is achieved with Printex-U, while for laboratory obtained soot samples the reduction was lower than 10%. At the sight of the present results, it can be said that the most reactive sample is the commercial soot, followed by the laboratory soot sample formed from acetylene-ethanol mixture in nitrogen atmosphere and, the least reactive is the laboratory soot sample obtained in the pyrolysis of C_2H_4 in CO_2 atmosphere.

3.2 Soot characterization

Characterization analyses of the different soot samples have been carried out in order to relate their structure and characteristics to the observations from the reactivity experiments. The selected characterization techniques are: TEM, SEM, elemental analysis, BET surface area analysis and Raman spectroscopy, which have been chosen due to their demonstrated suitability for carbonaceous materials (Fernandes et al., 2003, Murr and Soto, 2005, Roubin et al., 2005). Table 1 shows the main results obtained from the different characterization tests.

Table 1. Summary of the characterization results for the studied soot samples.

Soot Sample	C wt (%)	H wt (%)	Molar C/H	S_a (m^2/g)	I_G/I_D
Printex-U	95,56	0,92	8,56	92,46	0,63
C_2H_2 -EtOH- N_2	95,98	0,37	21,83	13,64	0,97
C_2H_4 - CO_2	99,71	0,17	48,87	12,49	1,03

The microscopy techniques (SEM and TEM) have been used in this study to address a preliminary analysis of the structure and morphology of the different soot samples. SEM images are useful to observe the macrostructure and morphology of soot, finding that in all the analyzed samples, the particles present a spherical shape and assemble as aggregates (Figure 2a). TEM images help to analyze the microstructure of the samples. The chain-like structure of the soot particles conglomerates is observed (Figure 2b), as well as the onion-like layers in soot particles (Figure 2c).

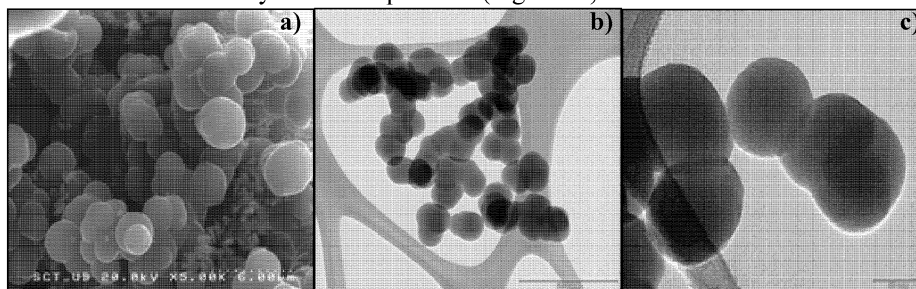


Figure 2. Example of the obtained microscopy images (Laboratory soot sample formed from acetylene-ethanol mixture pyrolysis in N_2 atmosphere): a) SEM, b) TEM, c) TEM.

It can be observed from elemental analysis data (Table 1) that the C/H ratio values obtained agree with values found in the literature for similar soot samples (Hays and Vander Wal, 2007, Ruiz et al., 2007). The content in H, which is directly related to the available active sites and to the reactivity of the material (Chan et al., 1999), is higher for Printex-U, identified as the most reactive of the studied soot samples. Accordingly,

the lowest content in H is found for the least reactive soot sample, obtained from C₂H₄ pyrolysis in CO₂ atmosphere.

Surface area values are calculated by the BET adsorption isotherm model (Table 1). The higher the surface area values the more available active sites. The most reactive soot, Printex-U, shows a noticeable higher value than those soot samples obtained in laboratory facilities.

Two peaks are observed in the Raman spectra, whose changes are related to the microscopic structure of the material. The relation I_g/I_d between the intensity of D peak, corresponding to disordered carbon, and G peak, which corresponds to graphite, is used to compare the soot samples. High values of I_g/I_d are related to high degree of organization of the sample and therefore to low reactivity of the material (Table 1). The highest value of I_g/I_d corresponds to the soot obtained from ethylene pyrolysis in CO₂ atmosphere, while the lowest value is that of the commercial soot, according to the results obtained from the reactivity experiments.

Conclusions

A study on the reactivity of a commercial soot surrogate (Printex-U) and laboratory soots obtained from the pyrolysis of acetylene-ethanol mixtures in N₂ atmosphere and the pyrolysis of ethylene in CO₂ atmosphere has been carried out.

From the reactivity experiments results it can be concluded that all the soot samples are more reactive towards O₂ than to NO. The conversion of soot is faster when interacting with O₂, even though the concentration of such reactant in the corresponding experiments is lower than the concentration of NO used. The most effective soot in reducing NO, among the studied, is the commercial soot (Printex-U) achieving NO reductions of 25% which are significantly high as compared to the reductions achieved by the laboratory soots produced in the pyrolysis of acetylene-ethanol mixtures in N₂ atmosphere and in the pyrolysis of C₂H₄ in CO₂ atmosphere, which were lower than 10% in all cases.

Soot samples characterization by different techniques has been helpful to understand and relate the results obtained in the reactivity experiments to the structural properties of the materials. The highest values in H content and surface area, which are directly related to the reactivity and available active sites, are registered for commercial soot, according with the highest reactivity observed. The lowest degree of organization is observed for commercial soot which presents the lowest I_g/I_d value in opposition to the least reactive material (soot from the pyrolysis of ethylene in CO₂ atmosphere) which presents the highest degree of organization.

From these results it may be concluded that the different origin of soot, which include fuel nature and operating conditions for its formation, has an important influence on its elemental composition, microstructure and degree of organization and thus in its capability of interaction with gaseous compounds, such as O₂ and NO.

Acknowledgements

Authors acknowledge the Spanish Ministry of Science and Innovation (MICINN) (Project CTQ2009-12205) and Aragón Government - La Caixa (Project GA-

LC031/2009) for financial support. C.E. acknowledges to the Spanish Ministry of Science and Education (MEC) and C.A. to Ministry of Education the pre-doctoral grants awarded (BES 2007-15333 and AP2008-03449). Authors acknowledge Evonik Degussa Industries for the supply of Printex-U.

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