

INFLUENCE OF THE GAS RESIDENCE TIME ON THE FORMATION OF SOOT FROM C₂H₄ PYROLYSIS

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Abstract

The influence of the gas residence time on the formation of soot from C₂H₄ pyrolysis is studied. Pyrolysis experiments are carried out in a quartz reactor in the 1000-1200 °C temperature range, for an inlet C₂H₄ concentration of 15000 ppmv, and for two different gas residence times, 1706/T(K) and 4552/T(K) seconds. In all experiments, gases are analyzed by gas chromatography and the amount of soot produced measured. The reactivity of the soot samples formed towards O₂ and NO is also studied. Additionally, the soot samples are further characterized by means of different techniques: elemental analysis, determination of BET area, transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Under the conditions studied, results show that the gas residence time is a parameter of great influence on both the yields to soot and to gases, and also on the reactivity of the resultant soot samples.

Introduction

Soot is a harmful pollutant generated in combustion systems. The knowledge of its reactivity in different environments is of great significance for pollution control in combustion processes. The soot reactivity is directly related to its structure and composition, and the soot nanostructure depends as well upon its formation conditions, like fuel identity, residence time and temperature (Du et al., 1998; Hays and Vander Wal, 2007; Vander Wal and Tomasek, 2003). Therefore, a knowledge of these dependences is fundamental to control the physical properties of the soot and therefore, its chemical reactivity (Grieco et al., 2000; Murr and Soto, 2005; Vander Wal and Tomasek, 2004).

In previous works (Ruiz et al., 2007a, 2007b, 2007c), the influence of the pyrolysis temperature, inlet hydrocarbon concentration and gas residence time in soot formation from acetylene pyrolysis has been studied. In this context, the aim of the present work is the study of the influence of the gas residence time on the formation, properties and reactivity of the soot formed from C₂H₄ pyrolysis, compound that is considered as an important soot precursor, since its thermal decomposition mainly produces acetylene, which is a key compound in soot formation process via acetylene addition-hydrogen abstraction (HACA) mechanism (Frenklach, 2002; Frenklach and Wang, 1994).

Experimental

Soot Formation

Experiments of C₂H₄ pyrolysis have been carried out in a facility described in detail in previous works (Ruiz et al., 2007a, 2007b). Reaction takes place in a quartz tube reactor of 45 mm internal diameter and 800 mm in length. The reactor inlet and outlet can be cooled by an air flow, which allows controlling the temperature profile inside the reactor. Additionally, the reactor outlet is mobile and can be adjusted at different positions in order to vary the reaction zone volume and thus, the gas residence time inside this reaction zone.

The C₂H₄ pyrolysis experiments have been performed for an inlet ethylene concentration of 15000 ppmv, in the temperature range of 1000-1200 °C. The total flow rate (C₂H₄ and N₂) in all experiments is 1000 ml/min (STP). As has been mentioned, the gas residence time into the reactor, defined as the reaction zone volume divided by the total gas flow rate introduced, can be varied changing the position of the reactor cooled outlet. In this study, the reactor outlet is

held on two different positions, resulting gas residence times of $1706/T(K)$ and $4552/T(K)$ seconds. In each experiment, the outlet gas composition has been analyzed by gas chromatography and the soot obtained has been measured. For further soot reactivity study and characterization analyses, and in order to eliminate the adsorbed compounds on the formed soot samples, the raw samples are annealed during one hour in a N_2 atmosphere at $1100\text{ }^\circ\text{C}$, except the soot samples produced at lower temperatures, which are annealed at their formation temperature to avoid possible structural changes.

Soot Reactivity

In order to study the reactivity of the soot samples formed, soot/ O_2 and soot/ NO interaction experiments have been carried out at a temperature of $1000\text{ }^\circ\text{C}$, with a total flow rate of 1000 ml/min (STP). In soot/ O_2 tests, an inlet O_2 concentration of 500 ppmv is employed, while in soot/ NO experiments, an inlet NO concentration of 2000 ppmv is used.

The experimental set-up used for the soot reactivity experiments has been described in detail in previous works (Ruiz et al., 2007a, 2007b). A quartz reactor of 575 mm in length and 15 mm internal diameter has been used. For each experiment, the amount of soot introduced into the reactor is approximately 10 mg and it is always previously mixed with 350 mg of silica sand ($150\text{ }\mu\text{m}$ particle diameter). The mixture is located on a quartz wool plug placed in a bottleneck in the middle of the reactor, resulting in a thin layer. An inert flow of N_2 is fed while the sample is heated up to the reaction temperature ($1000\text{ }^\circ\text{C}$). Once this set point is reached, the reactant gas mixture is fed. The reaction temperature is measured by a thermocouple placed 0.5 cm just below the quartz wool plug where the reaction takes place. The reaction products are continuously measured by Uras14/IR NO and CO/CO_2 analyzers.

During soot reactivity experiments, carbon is mainly lost from the particles in the form of CO and CO_2 . The carbon weight in the reactor at any time can be calculated from the measured time variation of CO and CO_2 concentrations in ppmv (C_{CO} and C_{CO_2} respectively) of the exhaust gas. In this way, the total initial amount of carbon (in moles) in the reactor, N_{C_o} , is calculated as:

$$N_{C_o} = F_T \cdot 10^{-6} \int_0^{\infty} (C_{CO} + C_{CO_2}) dt \quad (1)$$

where F_T is the outing flow expressed in mol per unit time and is expressed by Equation (2):

$$F_T = \frac{Q \cdot P}{R_g \cdot T} \quad (2)$$

where Q is the feeding flow rate, P is the reactor pressure, R_g is the universal gas constant in appropriate units and T is the reactor temperature.

The amount of carbon (in moles) in the reactor at any time is calculated as:

$$N_C = N_{C_o} - F_T \cdot 10^{-6} \int_0^t (C_{CO} + C_{CO_2}) dt \quad (3)$$

Therefore, the carbon weight in the reactor at any time, W_C , is determined as:

$$W_C = N_C \cdot M_C \quad (4)$$

where M_C is the atomic weight of carbon.

In this way, the evolution of carbon conversion (X_c) as a function of time can be calculated for every experiment. The carbon conversion is defined as the amount of carbon reacted in the experiment at any time, related to the amount of carbon fed into the reactor. The X_c values have been considered as representative values of the soot reactivities.

Soot Characterization

As has been mentioned, the soot samples formed have been characterized using different techniques: elemental analysis, determination of BET area, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The elemental analyses have been carried out in a Carlo Erba CHNS-O EA1108 analyzer. A Quantachrome AUTOSORB-6 gas adsorption analyzer is used for the surface area analyses with N₂ at 77 K. TEM images have been obtained using a JEOL JEM-2010 microscopy. XPS analyses are made in a VG-Microtech Mutilab 3000 analyzer and XRD analyses, in a Seifert JSO-DEBYEFLEX 2002 model.

Results

Soot Formation

The results of soot and gas yields, as well the outlet gas composition obtained in the ethylene pyrolysis experiments carried out at two different gas residence times, are shown in Table 1. The yields are defined as the percentage of the amount of carbon (in moles) in the soot and gases, respectively, related to the amount of carbon (C₂H₄, in moles) fed into the reactor. As can be observed, an increase in gas residence time leads to an increase in soot yield and a subsequent decrease in gas yield. For both residence times, no soot formation is yet observed at 1000 °C, and the soot yield values reached at 1200 °C are similar. Respect to the outlet gases analyzed in the experiments, it can be noted that H₂ is the main final gas product from ethylene decomposition and its formation is favored with gas residence time. The ethylene conversion is high in all experiments (> 80 %) and increases with increasing residence time. Acetylene is an intermediate product in the ethylene pyrolysis and a key factor in soot formation. Its decomposition produces soot and thus, the outlet acetylene concentration decreases with increasing residence time. Methane and benzene are other compounds produced in ethylene pyrolysis at lower concentrations. Their trends with gas residence time are not very clear.

Table 1. Values soot and gas yields and outlet gas composition in the ethylene pyrolysis experiments carried out at different gas residence times (t_r).

Soot formation experimental conditions			Soot yield (%)	Gas yield (%)	Outlet gases (ppmv)				
[C ₂ H ₄] (ppmv)	T (°C)	t _r (s)			H ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₆ H ₆
15000	1000	1706/T(K)	0.0	83.0	2851	796	8262	2839	157
		4552/T(K)	0.0	67.9	3720	900	7550	1373	154
	1050	1706/T(K)	13.3	68.4	6688	664	8419	667	128
		4552/T(K)	23.5	50.6	9709	729	6086	546	130
	1100	1706/T(K)	21.8	56.1	9943	513	7032	380	86
		4552/T(K)	28.7	40.3	10727	525	4939	270	93
	1150	1706/T(K)	30.2	43.2	12575	413	5316	140	57
		4552/T(K)	37.3	31.6	12946	412	3996	150	45
	1200	1706/T(K)	39.8	36.2	14027	355	4266	93	31
		4552/T(K)	39.7	26.4	14315	296	3413	60	34

Soot Reactivity

The results of evolution of carbon conversion as a function of time, obtained in soot/O₂ experiments, are shown in Figure 1. As can be observed, in all the temperature range studied, the soot samples produced with a higher gas residence time exhibit a higher reactivity towards oxygen. The differences between the results obtained for both pyrolysis gas residence times are greater with the soot samples produced at lower temperatures.

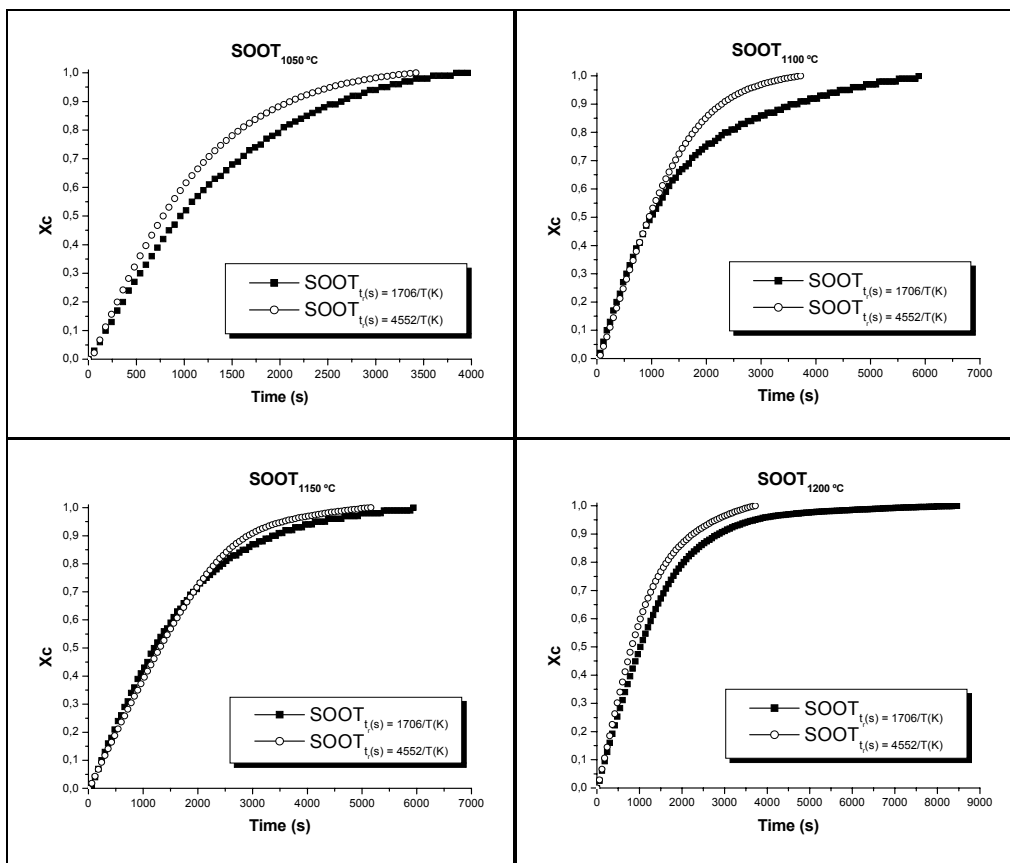


Figure 1. Evolution of carbon conversion with time in soot/ O_2 experiments.

Respect to soot/NO tests, the results of evolution of carbon conversion as a function of time are shown in Figure 2. Besides, in Figure 3, the evolution of NO reduction with carbon weight is shown. In the same way as in oxidation experiments, the soot samples formed with a gas residence time of 4550/T(K) seconds are more reactive towards NO than the samples produced with 1706/T(K) seconds. Moreover, the NO reduction values reached are higher with the soot samples obtained with higher gas residence time. In this case, the influence of gas residence time on soot reactivity is also clearer on the soot samples obtained at lower temperatures.

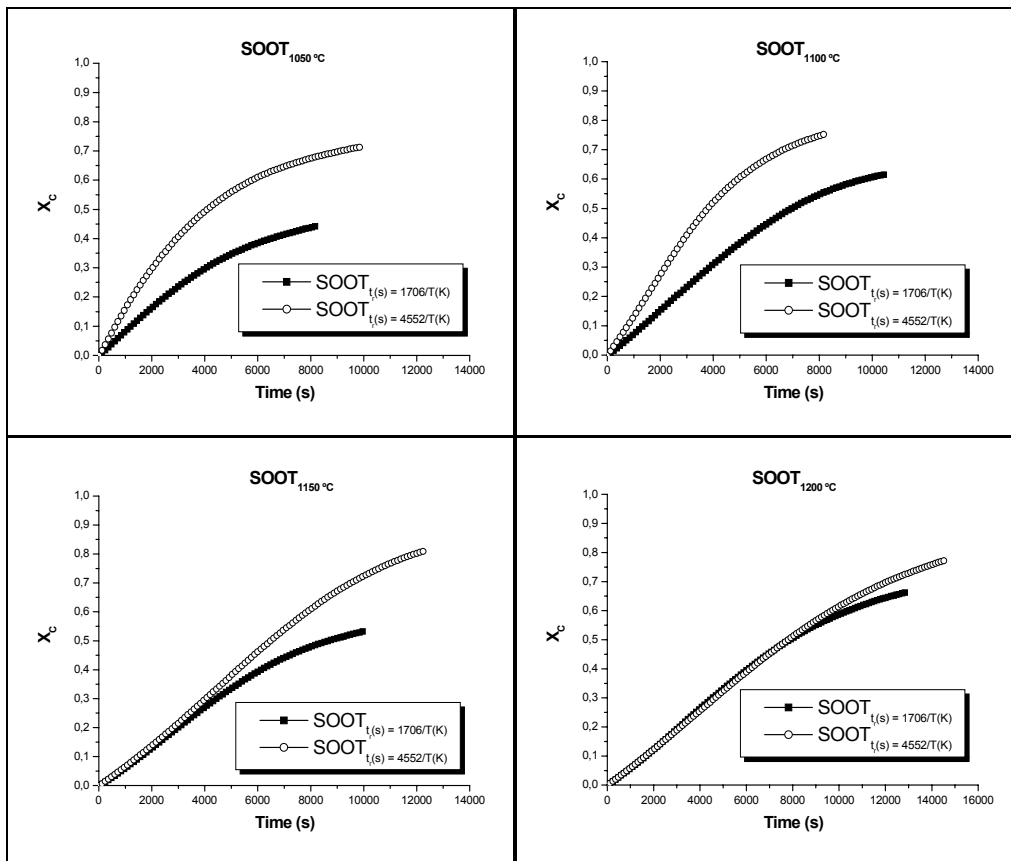


Figure 2. Evolution of carbon conversion with time in soot/NO experiments.

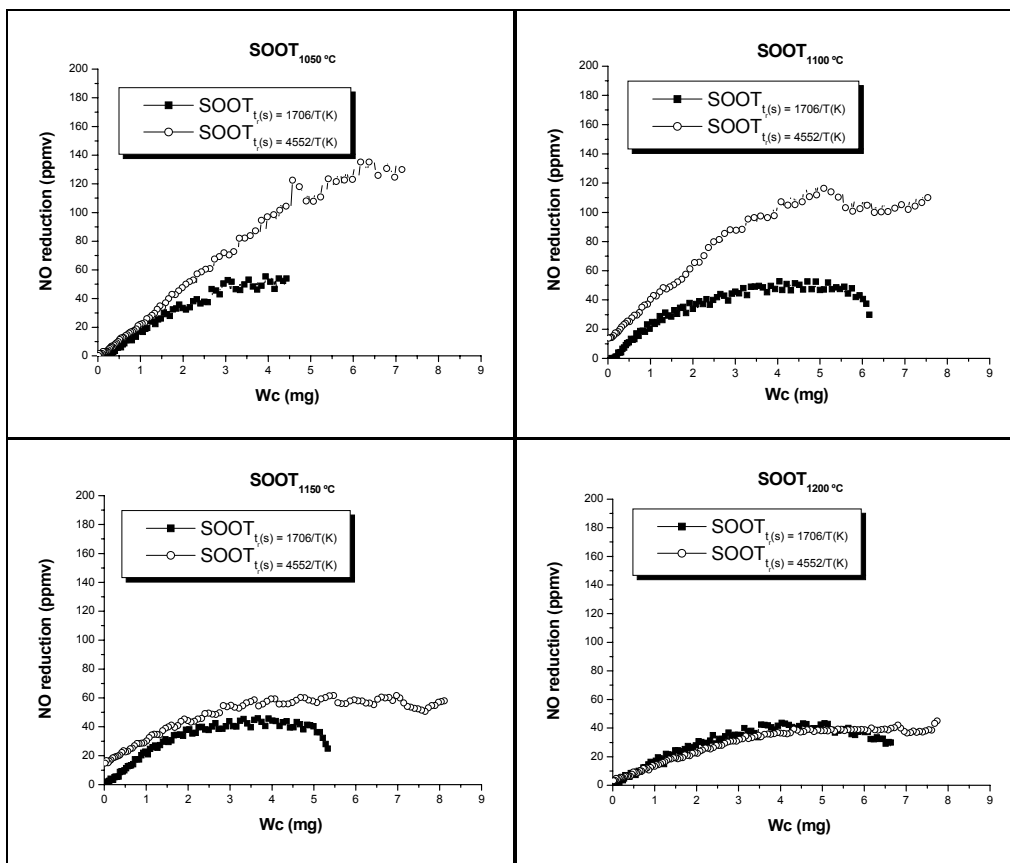


Figure 3. Evolution of NO reduction with carbon weight in soot/NO experiments.

Soot Characterization

As have been previously mentioned, some characterization techniques have been used to study the composition and structure of the soot samples. The results of elemental analysis and BET surface area of some soot samples are summarized in Table 2. It can be observed that the soot samples are mainly composed by carbon (> 90 %), and have a low hydrogen content. On the other hand, the surface area values of the soot samples are significantly low, being of the same order of magnitude as their external surfaces. As can be observed, the differences in soot surface area values between the results corresponding to both pyrolysis gas residence times are more noticeable at lower temperatures.

Table 2. Elemental analysis and BET surface area of the soot samples formed under different conditions.

Soot formation experimental conditions			Elemental analysis (% dry basis)		S_g (m ² /g)
[C ₂ H ₄] (ppmv)	T (°C)	t _r (s)	C	H	
15000	1050	1706/T(K)	95.69	0.34	15.8
		4552/T(K)	97.35	0.14	49.9
	1100	1706/T(K)	96.67	0.16	25.8
		4552/T(K)	99.87	0.12	48.5
	1150	1706/T(K)	96.83	0.17	48.7
		4552/T(K)	98.93	0.12	41.2
	1200	1706/T(K)	92.64	0.14	32.1
		4552/T(K)	99.74	0.13	29.8

Transmission electron microscopy (TEM) has been used to analyze the morphology and structure of the soot samples. All the soot samples present similar TEM micrographs. As an example, the TEM images of one soot selected are shown in Figure 4. It can be observed that soot has the appearance of chain-like aggregates composed of several tens or hundred of sub-units, known as monomers or spherules. The soot particles appear to be encapsulated aggregates of highly defective carbon “onions”, presenting a graphitic structure. These onion-like structures are made from parallel grapheme sheets arranged with their basal planes perpendicular to the radii of the structures.

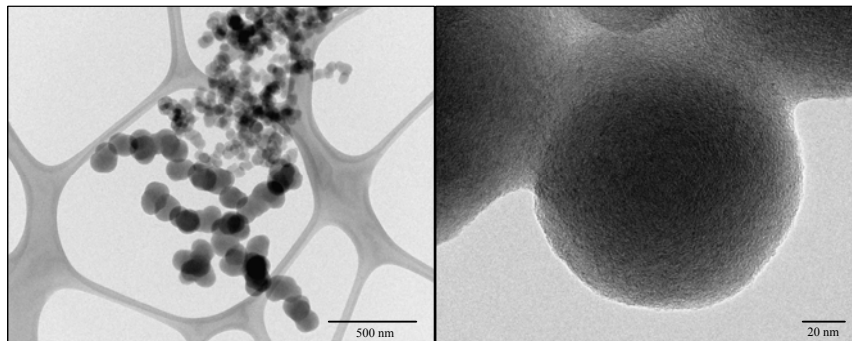


Figure 4. TEM micrographs of the soot produced with [C₂H₄] = 15000 ppmv and t_r(s) = 1706/T(K), at 1100 °C.

X-ray photoelectron spectroscopy (XPS) analyses of the soot samples formed have been also made. XPS is widely used to study the electronic structure and can be applied to the structural characterization of carbon materials. This technique allows quantifying the carbon surface compounds existing in the soot samples. The results show that the main carbon surface compound in the soot samples studied is graphite (more than 90 % in all cases).

X-ray diffraction is a non-destructive and well-established technique with good reproducibility, which has been widely used for the study of size and structure of molecules and clusters. Soot diffractograms have been collected from 5° to 90°. All the soot samples present an overall similar shape of diffractogram. As an example, one of them is shown in Figure 5. The most prominent peak is the (002) Bragg reflex, found at 25° on the 2θ-scale. The (002) peak position reflects the distance between the grapheme sheets. The peak is broad, which is an indicative of the non-graphitic structure of the soot.

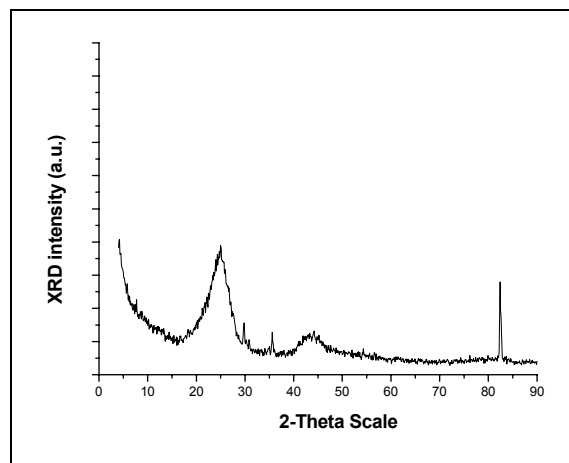


Figure 5. X-ray diffractogram of the soot produced with $[C_2H_4] = 15000$ ppmv and $t_r(s) = 1706/T(K)$, at 1100 °C.

In summary, the results obtained in soot characterization do not show a clear trend with pyrolysis gas residence time, and thus, they can not explain the results obtained in soot reactivity. However, the reason why the soot samples formed with a higher gas residence time are more reactive towards O_2 and NO may be attributed to a higher heterogeneity of these solids, since they are composed by soot particles formed at lower temperatures than the desired one, produced by a wider temperature profile in pyrolysis experiments. This conclusion was addressed in a previous work (Ruiz et al., 2007c), in which the reactivity of soot samples formed from acetylene pyrolysis under different gas residence times was studied. As it was previously noticed (Ruiz et al., 2007b, 2007c), the soot samples formed at lower temperatures are slightly more reactive towards O_2 and NO. Therefore, the ethylene soot samples produced at a higher residence time, due to their higher heterogeneity, present particles formed at lower temperatures than the desired one, which enhance the reactivity of the soot.

Conclusions

The gas residence time in the formation of soot from ethylene pyrolysis has a great influence on the yields to soot and gases, and the composition of the gases formed, as well as on the reactivity towards O_2 and NO of the resultant soot samples. The soot structural properties and composition do not exhibit a clear dependence on pyrolysis gas residence time. Respect to reactivity results, the general trend observed is that the soot samples with higher reactivities towards O_2 and NO are the soot samples formed with a higher gas residence time, due to their higher heterogeneity.

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