Determination of Polycyclic Aromatic Hydrocarbons (PAH) Adsorbed on Soot Formed in Pyrolysis of Acetylene at Different Temperatures

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The quantification of 16 polycyclic aromatic hydrocarbons (PAH) adsorbed on the soot produced in the pyrolysis of acetylene at different temperatures has been carried out. Pyrolysis experiments took place in a quartz reactor between 1073 and 1473 K, for an inlet C₂H₂ concentration of 30,000 ppmv and residence times between 3.1 and 4.2 s. The soot samples were collected in the outlet gases stream using glass fiber thimbles. The different kinds of soot have undergone soxhlet extraction and the obtained extracts were finally analyzed by means of a gas chromatograph coupled to a mass spectrophotometer. Using the toxic equivalent factors proposed by Nisbet and LaGoy (1992) and PAH concentration adsorbed on soot, the KE (carcinogenic equivalence) values were calculated in order to specify the carcinogenic potential of soot samples formed under different temperature conditions. The results of this research work indicate that temperature of soot formation has significant influence on the PAH concentration adsorbed. Comparatively, it can be observed that the concentrations of heavier PAH together with acenaphthylene and phenanthrene show a maximum value at 1173 K. On the other hand, for some lighter PAH, their concentrations decrease with increasing temperatures.

1. Introduction

It is well known that thermochemical processes are one of major sources of airborne species associated with health problems. Atmospheric aerosols, such as soot emitted in pyrolysis and combustion processes, are known to be among the main environmental pollutants, especially those defined by smaller diameter. A possible explanation for those hazardous health effects of soot may be their association with polycyclic aromatic hydrocarbons (PAH) (Richter and Howard, 2000). PAH are semivolatile compounds considered highly toxic for human beings, some of which have been found to be carcinogenic, mutagenic or tumorigenic compounds (16 PAH priority) (ATSDR, 2005). Because of this, the study of these adsorbed organic compounds should be promoted. Besides, those PAH are key intermediates in soot formation. Bigger PAH congregate resulting on primary condensed particles in gas phase (Ruiz et al., 2007a), whereas...
others attach soot particles depending on vapor pressure. Chemical and physical processes keeping soot and PAH intimately linked and the different kinds of semivolatile adsorbed on soot have been scarcely studied and consequently remain poorly understood.

Characterization of adsorbed species on soot gives information about the nature of compounds responsible for their surface growth and the gaseous phase composition (Mathieu et al., 2007). Also, knowledge of speciation and concentration of PAH is of interest for evaluating the harmful potential of soot particles. In this context, this work focuses on the determination of PAH adsorbed on soot particles formed in the pyrolysis of acetylene as a function of temperature. Acetylene is known to be one of the most important soot precursors; therefore, it has been selected to run the pyrolysis experiments and to obtain the soot samples. Concerning to PAH detection, a gas chromatograph coupled to a mass spectrometer has been used. This technique is commonly used for determination and quantification of semivolatile compounds (Ballesteros et al., 2010).

2. Experimental Equipment and Procedures

Soot analyzed was formed under pyrolysis conditions in a reaction system that consists on a gas feeding system, a quartz reactor and soot collection system. More details about the installation and operation procedure used in this work can be found in a previous work (Ruiz et al., 2007b).

In order to obtain the different soot samples, several pyrolysis experiments were run for 1.5 h, using an acetylene-nitrogen mixture with a total flow rate of 1,000 mL(STP)/min and keeping the acetylene concentration constant at 30,000 ppmv. The soot samples formed in these conditions at different temperatures, between 1073 and 1473 K, were carefully collected and quantified. 0.4 g of each soot sample produced at any temperature were selected for further analysis.

The soot samples have undergone soxhlet extraction using internal standards, with an extraction time of 24 h using 200 mL of dichloromethane for a cycle time of approximately 15 min. Following the EP3540C EPA method (EPA, 1996), after soxhlet extraction, the samples were reduced to 5 mL by rota-evaporation followed by concentration under nitrogen stream to 1.5 mL. In order to determine the PAH concentrations, the following compounds were used as standards: naphthalene (NAPH), acenaphthylene (ACNY), acenaphthene (ACN), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FANTH), pyrene (PYR), benzo(a)anthracene (B(a)A), chrysene (CHR), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene (DB(a,h)A), indeno(1,2,3-cd)pyrene (I(123-cd)P) and benzo(g,h,i)perylene (B(ghi)P). Six deuterated standards: 1,4- dcluirorobenzene-d4, acenaphthene-d10, chrysene-d12, naphthalene-d8, perylene-d12, and phenanthrene-d10 were added to the solvent at the beginning of the extracting process. In order to determinate the concentration levels of each PAH, the response factors were calculated according to the EP8270C method (EPA, 2007).

Finally, the sample was immediately analyzed by GC/MS, using an Hewlett-Packard Model 6890A GC/MS equipped with a 60 m long DB-17Ms fused silica capillary
column (0.25 mm ID, 25 μm film thickness). Samples were injected (1 μL) in splitless mode, the oven temperature was ramped from 353 to 563 K at 278 K/min, remaining at 563 K for 35 min, followed for a 274.5 K/min ramp rate to 593 K and held at this temperature for 5 min. Helium was used as the carrier gas. PAH in the total chromatograms were identified by means of the retention times of each one and by the NIST 2.0 mass spectral library.

3. Results and Discussion

As previously commented, the soot samples were collected from acetylene pyrolysis experiments, varying temperature between 1073 and 1473 K. In the literature, there are authors reporting no formation of soot for the interval 1073-1173 K (Mansurov, 2005). Nevertheless, for that temperature range, observations in this work show that the glass fiber thimbles used for soot collection change from white to brown-black color, and the material formed (detected through difference of weight of the filter) was considered as soot, since its characteristics are similar to the found ones at higher temperatures. Under that supposition, the quartz filters of soot samples at 1073 K and 1173 K were extracted and analyzed using the same procedure previously described (soxhlet extraction followed by CG/MS).

Figures 1a and 1b show the PAH concentration present on soot samples formed under different temperature conditions. Two behaviours can be observed. In Figure 1a, the concentrations of some light PAH-priority are seen to decrease with temperature. These results are in agreement with previous studies reported in literature (Aracil et al., 2005). On the other hand, the second behavior that can be observed in Figure 1b relates to heavier PAH together with ACNY and PHEN. In this case, the heavier PAH concentrations increase with increasing temperature until a maximum identified at 1173 K. This maximum could be attributed the competition between the formation and destruction reactions of PAH at low and high temperatures, respectively. This tendency was also observed by Font et al. (2003).

Figure 1. PAH Concentrations versus temperature of soot formation in acetylene pyrolysis. a) some lighter PAH b) heavier PAH, together to ACNY and PHEN
It can be observed from Figure 1a that NAPH was the dominant compound in all range of temperatures considered. The results are consistent with data collected in previous researches (Font et al., 2003; Ballesteros et al., 2010). Additionally, it can be observed in Figures 1a and 1b that for higher temperatures, PAH concentration decreases. In order to understand this behaviour, it is necessary to analyze the experimental conditions of soot formation. Mathieu et al. (2007) found a relationship among the amount of PAH adsorbed on soot depending on operation conditions and soot properties. They explained that for higher temperatures, the yield to soot is higher that yield to gases, and thus a considerable percentage of carbon is converted into soot, leaving little carbon available for gaseous species formation and consequently little concentration of compounds such as PAH are adsorbed on soot. This fact coincides with the results of Ishiguro et al. (1997) who showed that the soot particles formed at higher temperatures are less reactives and porous, and thus, little amount of PAH adsorbed would be expected to be found. The lower reactivity and porosity of soot samples found with increasing temperature was also demonstrated by Ruiz et al. (2007c), who made studies on soot characterization by TEM, XRD and Raman spectroscopy, finding that increasing the temperature of formation results in developing a more organized graphitic soot structure as well as higher organization.

3.1 Soot toxicity
PAH have received great attention in air pollution studies because some of these compounds are highly carcinogenic or mutagenic. In particular, B(a)P has been identified as highly carcinogenic. Thus, a parameter called toxic equivalent factor (TEF) was defined with the aim of helping to characterize more precisely the carcinogenic properties of PAH-priority, comparing every compound with the B(a)P, which has the highest value TEF. Nisbet and LaGoy (1992) completed a list of these TEF values which better reflect the carcinogenic potential of PAH. In the present work, the Nisbet and LaGoy approach has been used in order to evaluate the toxicity and health risk of the soot particles formed under different temperature conditions. Using the TEF values, it is possible to determinate a carcinogenic equivalence (KE) for each soot sample, which is a parameter that determine the inhalative carcinogenic potential caused by airborne-PAH. The KE value as the sum of the different products of the TEF value of each PAH-priority times its concentration found on soot (Zorn et al., 2005; Ballesteros et al., 2010).

In order to analyze the soot toxicity, the KE values sum and the total PAH amount for each soot versus its formation temperature are showed in Figure 2. The total sum of PAH concentration adsorbed on soot at 1073 K is as high as the total found one at 1173 K. Nevertheless, at 1073 K, the KE value is lower, which means that a high risk for health of a particulated material, such as soot, is not always related to high PAH concentration. The KE maximum found at 1173 K can be explained taking into account that, as it was mentioned previously, in this temperature, the formation of heavier PAH, which present a higher toxic potential, increases. Likewise, it has been found that, at higher temperatures of soot formation, the PAH total concentrations adsorbed on soot decrease together with KE values. This behaviour was
also found in recent works using biofuels (Ballesteros et al., 2010), who evidenced that even though some blends produce more amounts of PAH, the emitted compounds, and therefore the adsorbed ones on soot, are less dangerous. Therefore, both concentration of PAH and KE potential should be determined, in order to characterize the toxicity from PAH adsorbed.

4. Conclusions

PAH classified by EPA as high priority compounds absorbed in soot samples formed by pyrolysis in a temperature range from 1073 to 1473 K, for an inlet acetylene concentration of 30,000 ppmv, have been analyzed. The PAH quantification was made by means of a combination of soxhlet extraction and CG/MS. In this way, the results obtained together to toxic equivalent factor values have been used in order to analyze the health risk of the different soot samples.

PAH-priority concentrations adsorbed on soot show two behaviors in the temperature range studied: the heavier PAH together with acenaphthylene and phenanthrene present a maximum at 1173 K, which is attributed to the competition between formation reactions and destruction processes of PAH. On the other hand, some lighter PAH decrease with increasing in the temperature of formation, this tendency is observed in all range of temperature studied.

According to results from soot toxicity, the highest total PAH concentrations adsorbed on soot have been found at the lowest temperatures (1073 and 1173 K). However, KE values (carcinogenic equivalence) have showed a maximum at 1173 K. In this way, it is important to emphasize that a high PAH concentration adsorbed on soot has not direct relation with high health risk, therefore both PAH and KE potential should be determinated.
Acknowledgments

The authors express their gratitude to the MICINN (Project CTQ2009-12205), for financial support. Ms. N. E. Sánchez acknowledges the Banco Santander Central Hispano and Zaragoza University for the predoctoral grant awarded.

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