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Effects of Limestone on Polycyclic Aromatic Hydrocarbon Emissions during Coal Atmospheric Fluidized Bed Combustion

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The aim of this paper is to investigate the effects that the incorporation of limestone to the feed may have on polycyclic aromatic hydrocarbon (PAH) emissions during coal atmospheric fluidized bed combustion (AFBC). The study was performed at a combustion temperature of 850 °C, an oxygen excess percentage of 10%, and a total air velocity of 0.24 m/s (around twice the minimum fluidization velocity of the heaviest solid) in a laboratory scale pilot plant with a fluidized bed reactor (7 cm i.d., 76 cm height). The emissions of 16 PAH's (listed by the US Environmental Protection Agency as priority pollutants) were analyzed considering their feeding and their fluidized bed nature. The samples analyzed were taken from a cyclone, a condenser, a Teflon filter (1-micron pore size), and XAD-2 resin. After sonication extraction with dimethylformamide (DMF) as the solvent, the 16 PAH's were analyzed by fluorescence spectroscopy (FS) in the synchronous mode. The results obtained show that not all the PAH's could be detected and that the highest PAH content was emitted when a limestone bed was used. With regard to the PAH gas/solid partitioning emissions, most of them were concentrated on the solid phase when limestone coal blend was added to the reactor, while most of the emissions were produced in the gas phase when only coal was fed. To assess a possible Ca catalytic role, additional combustion experiments were performed through feeding coal (without limestone) to the bed obtained from coal-limestone blend feed. Finally, the influence of the calcite porosity and the Ca presence on PAH formation, emission, and distribution are also reported and discussed.

Introduction

Fixed beds, as a traditional method for coal combustion, were successfully replaced in the 1920s by pulverized coal combustion.¹ In the 1960s, fluidized bed combustion² (FBC) started to replace pulverized combustion. Since then, a better FBC technology has been developed,³ with fluidized bed combustors becoming more and more complex. Nowadays, they can be classified—according to their working pressure—into atmospheric⁴ (AFBR) and pressurized⁵ (PFBR) and—according to their air flow—as bubbling⁶ or circulating.⁷ These technological changes were promoted by the search for cheaper and cleaner energy generation, together with pressing legislation on environmental aspects. The aim of all these technological changes has

been to decrease combustion temperature, to avoid thermal NO_x and to improve limestone performance, without losing efficiency during the combustion process.

The main advantage of the FBC is related to the control of inorganic emissions.² Thus, in FBC, the bed behaves like a fluid, which facilitates that solid particles (coal, ash and other materials that could be added to the bed and move freely), can interact minimizing heat and mass transfer problems. This property allows the control of unwanted emissions if a proper material is fed into the combustor. Limestone and dolomite are the classical materials added to meet emission limits.

The temperature at FBC power stations rises up to 825–850 °C—lower than that of a pulverized combustion—in order to avoid thermal NO_x formation and to improve the limestone yield in relation to SO_x capture, which is better at these temperatures, reaching the maximum SO_x and NO_x abatement. However, the effect of pollution abatement and control technologies used for the abatement of inorganic pollutants—such as SO_x, NO_x, and CO_x—has not been contrasted with the variations on organic emissions.

Organic emissions (ppbv range) are emitted in smaller amounts than inorganic emissions. However, the hazardous nature of the former entails a greater negative environmental impact. The mechanisms involved in the emission of organic compounds during coal combustion are very complex and deserve further investigation.

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Previous works⁸ have shown that it is not necessary for the emission of organic compounds to be part of the original fuel and emitted as unburned material, but the devolatilization and the pyrolytic processes characteristic of any fuel combustion imply the release of radicals, which are the cause of new organic and particulate matter emissions by pyrosynthetic retrogressive reactions. Therefore, the combustion process variables—temperature, excess oxygen, flow, pressure, etc.—will be determinant concerning the emission of volatile organic compounds.

In this context, the addition of limestone to abate inorganic emissions seems to have some influence on the interactions between the released organic radicals that cause those organic emissions. For this reason, this paper is focused on the emissions of polyaromatic hydrocarbons from coal AFBC when limestone is added to the feeding blend, in comparison to the ones taking place in a coal AFBC when only coal is burnt. Our aim, then, is to obtain information on the effects of limestone on volatile organic compounds (VOC) and, specifically, on polycyclic aromatic hydrocarbons (PAH). The reported bibliography dealing with this topic is scarce and mainly restricted to PAH in fly ash from FBC,¹² PAH from polystyrene pyrolysis with calcium oxide addition,¹³ PAH from polystyrene pyrolysis in the presence of manganese sulfate,¹⁴ and coal–plastic cocombustion with limestone addition.¹⁵ Unclear and often contradictory results (promoting or reducing PAH during pyrolysis) are sometimes reported in these papers. Therefore, considering both the increasing importance of these novel energy systems and the fact that pyrolysis is the first step of the combustion process, further investigations are needed in order to determine whether the addition of limestone to control inorganic emissions in the energy power station has an influence on the corresponding organic emissions.

Experimental Section

A low-rank coal, 0.5–1 mm particle size [Ultimate analysis: % C, 73.8 (daf); % N 0.9 (daf); % S, 6.3 (db); % H, 6.4 (daf). Immediate analysis: % moisture, 15.7 (ar); % ashes, 23.9 (ar); % volatiles, 15.0 (ar); % fixed carbon, 45.4 (ar); and calorific power, 17.3 MJ/kg.], and a limestone, (0.3–0.8 mm particle size), were burned in an atmospheric fluidized bed combustion plant, AFBC (see Figure 1).

The limestone used in the AFBC was characterized. The limestone SEM-EDX analysis shows Ca as the unique identified element, and its XRD analysis shows calcite as the only crystalline chemical species. After calcination at 100 °C, calcite showed¹⁶ an apparent surface area of 19 m²/g, 48.5% porosity with unimodal small pores of 5.5 nm.

The combustion experiments were performed in a fluidized bed pilot plant, laboratory scale, consisting of a 2800W furnace,

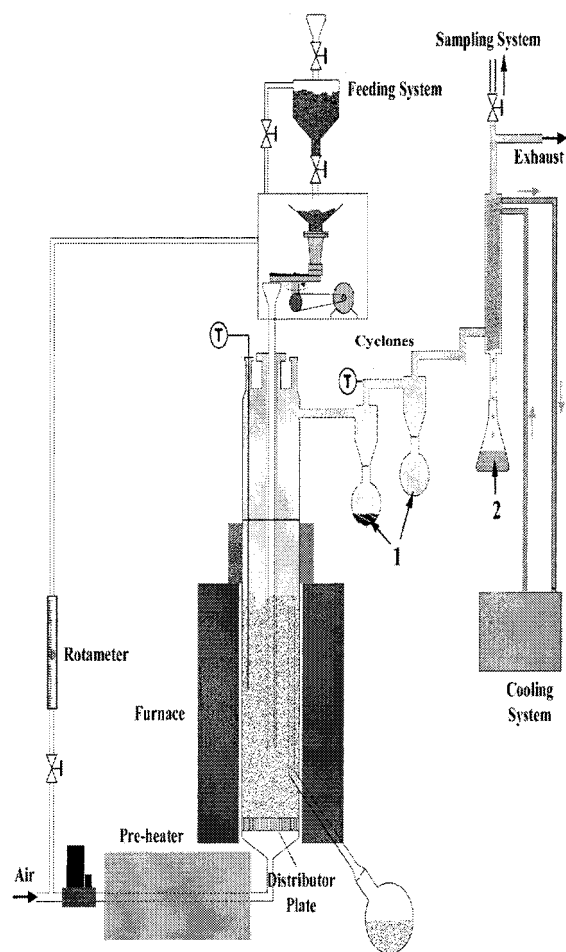


Figure 1. Scheme of the fluidized combustion plant: 1, cyclones; 2, condenser.

a continuous feeder (40–300 g/h), which allows to modify the amount of burnt coal, a fluidized bed reactor made of Khantal steel (6.7 cm id, 76 cm height), a furnace (maximum temperature 1000 °C), and an air preheater (up to 800 °C). The pilot plant worked at atmospheric pressure. The entry air was divided into two gas streams, one enough to fluidize the bed and blown from the base of the reactor and the other/blown at the top of the continuous feeder, making the entry of the fuel fed into the reactor easier. Both air flows were controlled by a mass flow controller and a rotameter, respectively.

Calibration curves with each feeding were experimentally determined in order to establish the combustion conditions at which experiments had to be carried out. The combustion experiments were performed, keeping constant the total air flow (0.24 m/s air velocity high enough to ensure a proper fluidization, avoiding the slugging regime), the percentage of excess oxygen (10%), and the combustion temperature (850 °C) and modifying the feed and the nature bed (coal/sand, Rf = CS; limestone-coal blend/limestone, Rf = LCL; and coal/limestone, Rf = CL). The variables were fixed according to a previous work¹⁷ in order to obtain high-efficiency values (Table 1). These values were calculated in each combustion experiment according to the following equation:

$$\% \text{ efficiency} = 100 \times \frac{\text{OM}_{\text{initial flow}} - \text{OM}_{\text{final flow}}}{\text{OM}_{\text{initial flow}}} \quad (1)$$

where OM is the organic matter in fuel fed and in the particulate matter collected in cyclones and ashes of the ash-

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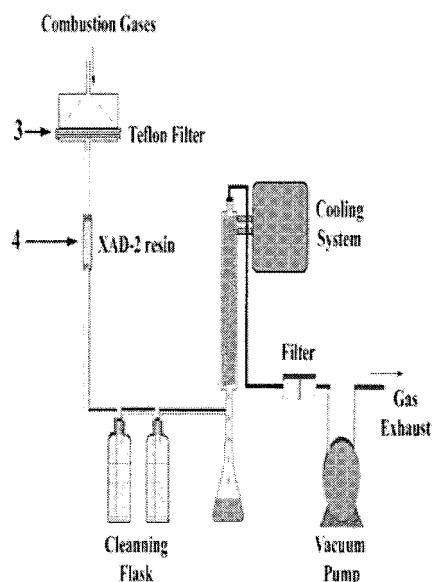
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Table 2. Total PAH Amount Emitted ($\mu\text{g/kg}$ Burned Coal) from Each Run in Terms of Bed Nature (850 °C, 0.24 m/s, 10% Excess Oxygen)

bed	feed	ref	N° run					mean	s
			1	2	3	4	5		
sand	coal	CS	0.7	1.2	2.0	2.5	1.7	1.6	0.7
limestone	coal–limestone	LCL	14	31	20	11	17	19	8
	coal	CL	3.0	2.1	—	—	—	2.5	0.6

**Figure 2.** Scheme of the trapping system: 3, Teflon filter; 4, XAD-2 resin.**Table 1. Coal AFBC Efficiencies as a Function of Bed Nature (850 °C, 0.24 m/s, 10% Excess Oxygen)**

bed	feed	ref	N° run				
			1	2	3	4	5
sand	coal	CS	99.2	99.2	99.1	99.3	99.2
limestone	coal–limestone	LCL	99.0	98.6	98.5	98.5	98.5
	Ca/S = 3						
	coal	CL	99.4	99.4	—	—	—

hopper. The organic matter content initial and final in fuel was calculated following the equations:

$$\text{OM initial fuel} = g/h \text{ fuel fed} \times t(1 - (h + \text{Ce})) \quad (2)$$

$$\text{OM final} = (\text{PM}_{\text{cyclones}} \times \text{OM}_{\text{ash}}) + (\text{ash}_{\text{ash-hopper}}(g) \times \text{OM}_{\text{ash-hopper}}) \quad (3)$$

where t is the sampling time (in hours), h the moisture of elemental analysis, % per unit, Ce the ash of immediate analysis, % per unit, and $\text{PM}_{\text{cyclones}}$ the particulate matter collected in cyclones (grams).

The combustion experiment was repeated from two to five times in order to obtain the reproducibility and accuracy of the experimental devices. This way, the resulting experimental standard deviations were calculated, and values around 42% were obtained.

The combustion gases were forced to pass through a system formed by two cyclones and a condenser in order to avoid moisture condensation problems in the sampling system. At the exit of the condenser, 1 aliquot of combustion gases was forced to pass through the sampling system formed by a Teflon filter (1 μm) and an adsorbent, XAD-2 resin (see Figure 2). Four samples were taken from each experiment during a period of 3 h. Figures 1 and 2 show the sampling points—1, cyclones (4 g particulate matter); 2, condenser; 3, Teflon filter; and 4, XAD-2 resin. In this study, samples obtained from sampling points 1, 2, and 3 were considered as “solid-phase”

emissions and samples from sampling point 4 as “gas-phase” emissions. All samples were kept in a refrigerator and protected from sunlight until extraction and analysis to eliminate photodegradation reactions. The samples were extracted by sonication three times with 25 mL of dimethylformamide (DMF) for 15 min. Concerning the solution trapped in the condenser, it was extracted after water evaporation. The extracts were filtered and concentrated in a rotary vacuum until a final volume of 10 mL. Percentage recoveries of PAH spiked at appropriate concentrations onto clean particulate matter, filter, and XAD-2 resin, reaching between 88 and 102%.¹⁸

The samples were analyzed by fluorescence spectroscopy at the conditions previously determined for each specific PAH¹⁹ with the model compounds. The PAH's studied were those listed by the U.S. Environmental Protection Agency as priority pollutants²⁰—fluorene, benzo[a]pyrene, pyrene, chrysene, anthracene, acenaphthene, benz[a]anthracene, dibenzo(a,h)anthracene, perylene, and benzo[k]fluoranthene). In addition, coronene emissions were also reported due to their important role on PAH stabilization in extreme conditions.²¹ These 16 PAH's were analyzed from runs in each of the four samples.

Results

The low-rank coal combustion at the AFBC experimental installation was carried out at the described combustion variables. The combustion was optimized at the laboratory plant in order to obtain high efficiencies and to minimize emissions. These emissions would correspond to PM I in Figure 3, one of the two possible forms of particulate matter emissions in combustion process. The combustion efficiencies are shown in Table 1, and the obtained values are very high in all runs regardless of feed and bed nature.

The total PAH's emitted in terms of feed and bed nature are shown in Table 2. Table 2 shows that the total PAH emissions depend on the feed. The total quantity of PAH detected in LCL combustion runs are 1 order of magnitude higher than the ones corresponding to CS and CL runs.

The PAH distribution at each sampling point in CS, LCL, and CL runs are shown in Tables 3, 4, and 5, respectively. In the studied samples, only fluorene, pyrene, acenaphthene, benz[a]anthracene, benzo[a]pyrene, chrysene, anthracene, and coronene could be detected, but only fluorene, pyrene, acenaphthene, benz[a]anthracene, and coronene, were over the quantification limits.

Figure 4 shows the PAH distribution between solid and gas phase in terms of feed and bed nature. It is observed that PAH emissions are mainly found in the gas phase, with PAH adsorbed on the XAD-2 resin,

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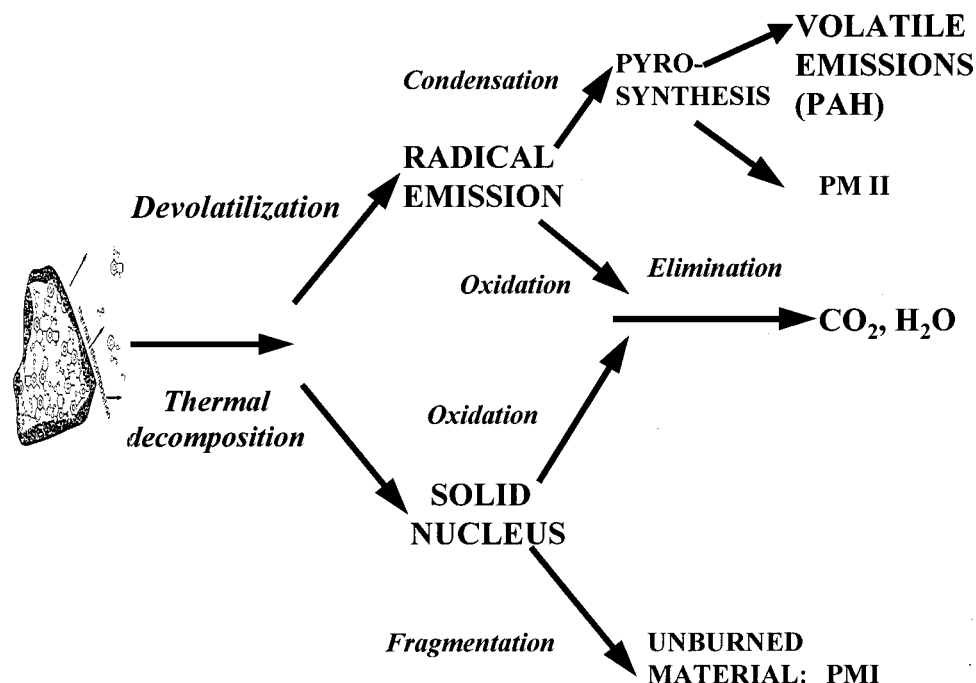


Figure 3. Main mechanisms implied in the combustion process concerning solid and gas emissions.

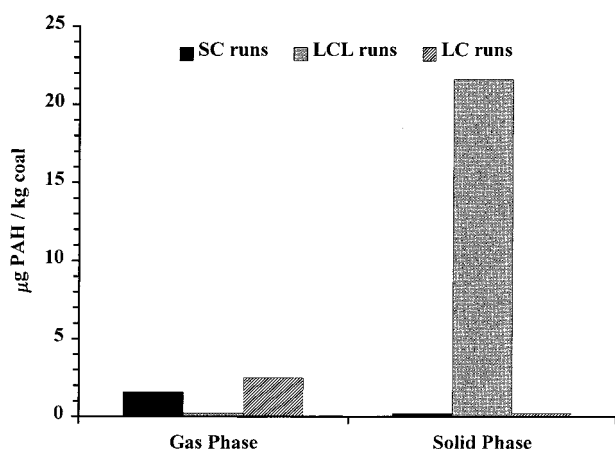


Figure 4. PAH ($\mu\text{g/kg}$) distribution between solid and gas phases in terms of the feeding and bed nature: CS, sand/coal; LCL, limestone/limestone-coal blend; and CL, limestone/coal

when coal is only fed to the reactor, the CS and CL runs. However, when limestone is added to the feed, the LCL runs, the total PAH's are emitted on the solid phase—that is to say, on the particulate matter trapped on the Teflon filter and retained in the condenser and cyclones.

Discussion

It is worth pointing out that this experiment was performed after some modifications had been introduced in the combustion plant aimed to optimize the combustion process. The modifications included the fluidized bed height—in order to increase the residence time—and the down-airflow exhaust by improving its release into the atmosphere. Both mechanical changes were aimed to impede the PAH formation, due to the better radical oxidation caused by increasing the contact time with oxygen and a faster airflow release into the atmosphere. These changes are, without any doubt, the reason why some of the PAH's listed by USEPA are not detected now but were formerly detected and reported.⁷

The combustion at the AFBC experimental installation was carried out at the described combustion variables. The main mechanisms involved in coal combustion are shown in Figure 3. When coal is fed into the reactor a pyrolytic process²¹ takes place because of the heating and as a result of the thermal breaking. The result is a devolatilization process, regardless of the fuel used, with the release of radicals and smaller fragments that can undergo entrainment of unburned material proceeding from the fuel, PMI. PM I could be minimized by combustion optimization and will be mainly composed of the organic and inorganic components of the fuel. The performance of this process is measured using the combustion efficiency, eq 1. Thus, high combustion efficiencies imply low organic PMI emissions.

Table 1 shows the combustion efficiencies obtained. It could be thought that the small efficiency differences in every set of runs were relevant compared to the total PAH emissions. However, no relationship was found between them. In LCL runs, experiments 3, 4, and 5 had the same combustion efficiency value, but the emitted PAH amount was different. On the other hand, experiments 2 and 4, with very similar combustion efficiencies, had the greatest difference in the total PAH emissions. Therefore, it can be deduced that this influence is negligible and that the small differences between the high efficiencies obtained do not seem to be the determinant effect. These results lead us to infer the importance of the pyrosynthesis step on the PAH emissions.

Pyrosynthesis is another mechanism that could contribute to the PAH formation (Figure 3). As a result of the pyrolytic process, the radicals released, due to their high reactivity and their short average lifetime, undergo different reactions that compete among themselves as a result of the combustion conditions. The reaction of radicals includes two opposite types: on one hand,

Table 3. Total Amount of Each PAH Emitted ($\mu\text{g/kg}$ Burned Coal), Average Value, and PAH Collected on Each Trap at Coal AFBC (Sand Bed, 850 °C, 0.24 m/s, 10% Excess Oxygen)^a

compound	traps			
	XAD-2	Teflon	condenser	cyclons
fluorene	0.8 (± 0.3)	n.d.	n.d.	n.d.
pyrene	0.08 (± 0.03)	n.d.	n.d.	n.d.
acenaphthene	0.7 (± 0.2)	n.d.	n.d.	n.d.

^a n.d.: not detected**Table 4. Total Amount of Each PAH Emitted ($\mu\text{g/kg}$ Burned Coal), Average Value, and PAH Collected on Each Trap at Coal–Calcite AFBC (Limestone Bed, 850 °C, 0.24 m/s, 10% Excess Oxygen)^a**

compound	traps			
	XAD-2	Teflon	condenser	cyclons
fluorene	n.d.	10 (± 3)	0.4 (± 0.3)	7 (± 3)
pyrene	n.d.	1.5 (± 0.5)	0.03 (± 0.02)	1.3 (± 0.9)
BaA	n.d.	bql	bql	0.01 (± 0.01)
coronene	n.d.	2 (± 1)	bql	bql

^a n.d.: not detected. bql: below quantification limit.

condensation reactions, which imply the association between radicals and generate compounds of higher molecular weight; on the other hand, oxidation reactions, which imply the elimination of radicals leading to CO_x and H_2O formation and, therefore, the chance of new PAH formation decrease. The PAH formed can be emitted as a gas or as PM₁₀,²² the small particulate matter. These competitive reactions, between the compounds present in the freeboard, will be the ones that determine the total PAH emissions and will depend on feed and bed nature.

The results obtained in CS and LCL runs shows that there are significant differences between the total PAH emissions (Table 2) and between the PAH distribution by traps (Tables 3 and 4). A possible explanation of these results could be due to species in the reactor and their relationships. In the CS runs, the species involved in the combustion mechanisms will be the released radicals from coal devolatilization and thermolysis, the remaining solid nucleus from coal thermolysis, H_2O and CO_x from radical elimination by the oxidation reaction, and the remaining oxygen. In LCL runs, in addition to the above-mentioned species, a higher amount of CO_2 as well as CaO, from limestone decomposition, will be also involved in the inside reactor mechanisms. These differences allow us to speculate about possible mechanisms implied in the PAH formation and emission due to these new species present in the reactor.

The CO_2 concentration at LCL runs is higher than the one at CS runs. Therefore, the interactions between the coal released radicals and the available oxygen will be impeded, and so will the radical elimination by oxidation. On the other hand, the radical interactions among themselves will become more difficult, and so, the pyrosynthetic process leading to a higher PAH formation and emissions will be hindered that is to say, a higher CO_2 concentration does not seem to imply any relevant influence on the total PAH emissions.

Table 5. Total Amount of Each PAH Emitted ($\mu\text{g/kg}$ Burned Coal), Average Value, and PAH Collected on Each Trap at Coal AFBC (Limestone Bed, 850 °C, 0.24 m/s, 10% Excess Oxygen)^a

compound	traps			
	XAD-2	Teflon	condenser	cyclons
fluorene	0.7 (± 0.2)	n.d.	n.d.	n.d.
pyrene	0.8 (± 0.3)	1.0 (± 0.4)	bql	bql
chrysene	0.1 (± 0.1)	n.d.	n.d.	n.d.

^a n.d.: not detected. bql: below quantification limit.

The CaO from CaCO_3 decomposition, the other new species involved in the combustion mechanisms at LCL runs, is a solid porous material. This means that its interactions with radicals from coal are not limited and could be adsorbed²³ into its porous structure, hindering their total oxidation and, in consequence, promoting their interaction. This fact is corroborated by the coronene formation in LCL experiments, the most stable of the PAH studied. Besides, as a result of the fluidization movement and the high temperature, CaO could be fragmented into smaller particles, undergoing entrainment by the airflow. These facts justify that, with the use of limestone, not only are higher PAH emissions detected, but the PAH's emitted are also trapped on the cyclone, the condenser, and the filter (see Table 4), that is to say, on the solid-phase emissions. Moreover, PAH emissions could not be detected in the XAD-2 resin, gas phase, at LCL runs.

The chelating mechanisms reported^{13,14} at polymeric pyrolysis cannot be applied to coal combustion because the inert-reducing atmosphere at pyrolysis process has no relationship to the oxidation conditions at the combustion atmospheres. However, a possible catalytic role of Ca could be an additional effect in the LCL runs influencing the PAH emission and distribution.

To assess a possible Ca catalytic effect, two additional combustion runs (CL runs) were performed, feeding only coal into the reactor with the bed obtained in the LCL runs. In this way, the Ca presence was assured but no additional porous material was fed. The results obtained (see Tables 2 and 5) are closer to the ones obtained with coal as feed (Table 3) than to the ones obtained with coal–limestone feed (Table 4). Moreover, not only are the total PAH emissions similar to the ones in absence of Ca, the PAH solid/gas phase distributions also coincide (see Figure 4). Therefore, all the detectable PAH's were mainly emitted in gas phase, as it happens at CS runs. These results lead us to infer that the Ca catalytic role promoting PAH formation and emissions at coal combustion can be discarded and that the higher PAH emissions seem to be caused by the physical characteristics (porosity) of the limestone. From these results, it can be deduced that although the addition of limestone increases the PAH emissions, its total performance is positive. Limestone helps to control the PAH emission in gas phase by adsorption.

Finally, it can be concluded that, during coal fluidized bed combustion, not only are higher PAH amounts emitted, different PAH distribution between the solid and the gas phase is also observed depending on the feed and, therefore, on the bed nature. With the addition

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of limestone, the PAH's emitted are supported on the particulate matter, whereas in the absence of limestone, the PAH's are emitted only in the gas phase going through a filter with a 1 μm pore size. It can also be concluded that the porous character of the limestone improves the radical interactions by hindering the oxidation process. This conclusion is corroborated by the Coronene emissions detected when a limestone-coal blend is fed into the fluidized bed to control SO_x emissions. In addition, and according to the results obtained, a possible Ca catalytic role promoting PAH

formation can be discarded in the present burning conditions.

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