Toxic organic emissions from coal combustion

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Abstract

Atmospheric fluidized bed combustion (AFBC) is considered to be an environmentally favorable combustion technology where the control of emissions can be integrated into the combustion system. FBC operates at low temperatures, 800–900°C, to prevent thermal NO formation and to favor the sulfur removal by the sorbent, but it has not been taken into account that when coal is burnt, not only NO_x, SO_x and CO_x are emitted. In addition, volatile organic pollutants (VOCs) are emitted. From these VOCs, the polycyclic aromatic hydrocarbons (PAHs) constitute one of the most dangerous compounds because of the possibility of interacting with biological nucleophiles. It is expected that new legislation about the regulation on PAH emissions will be very restrictive. In this work, PAH emissions from coal AFBC as a function of the coal combustion variables (combustion temperature, gas flow and percentage of excess oxygen) are reported. In addition, the effect of bed nature on PAH emissions is also assessed.

Polyaromatic hydrocarbon emissions at the standard conditions used at the AFBC power stations are assessed by the study carried out in an AFBC laboratory pilot plant. The PAHs listed by the US EPA as priority pollutants are analyzed by fluorescence spectroscopy (FS) at the synchronous mode. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Coal constitutes the main fuel source in power stations to produce electrical energy. For many years, the only law limitation has been to control the NO_x, SO_x [1], CO_x and particulate matter emissions in energy generation.

Atmospheric fluidized bed combustion (AFBC) is generally considered to be an environmentally favorable combustion technology where the control of emissions can be

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integrated into the combustion system. AFBC systems burning coal usually operate with a combustion zone temperature around 800–900°C. These low temperatures not only prevent thermal NO formation, but promote NO-reducing reactions during the combustion process. The temperature range in AFBC is also suitable for the addition of sorbent into the bed to reduce SO_2 emissions. In any case, optimum process conditions have to be identified whenever opposing effects are observed. For instance, there is a strong effect of temperature on sorbent demand if the combustion temperature in the FBC is outside the optimum range of 800–850°C. On the other hand, NO emissions increase as temperature increases, whereas N_2O emissions show exactly the opposite trend. Due to the range of temperatures used in FBC, the emissions of CO are in general higher than those from conventional boilers. Another important factor is the excess oxygen, which mainly affects the emissions of NO, N_2O and CO, together with the economics of the process. The NO_x decreases with decreasing amount of excess oxygen. A decrease in excess oxygen will, however, increase the CO emission and result in decreased combustion efficiency. Both operational factors, bed temperature and excess oxygen, and others as primary air ratio or sorbent feed rate, have been extensively studied and reported [2], but only for the above-cited pollutants.

In current research, the efforts are aimed toward technical and economic improvements seeking new ways to get cheaper and cleaner coal-conversion processes. In this way, the work conditions and the possible modifications carried out have been focused to the use of different mechanisms as washed and desulfurization of coal, addition of $CaSO_4$ [3] to retain and to avoid high emissions of sulfur compounds, all of them to abate atmospheric pollution.

In reported work, volatile organic compounds (VOCs) [4] have not been taken into account. From these VOCs, the PAC, and within these, the polycyclic aromatic hydrocarbons (PAHs) [5–8], constitute some of the most dangerous compounds due to the possibility of their interacting with biological nucleophiles, inhibiting their regular functions. Nowadays, PAH emissions are reaching a growing interest in the concern about the emissions of VOCs [9–11] because it is expected that new legislation about the regulation on emissions of these compounds will begin to be very restrictive. Concerning the PAH nature, one of the ways to abate their emissions would be to control the different variables that affect combustion. Therefore, it would be necessary to study the PAH formation in relation to combustion process conditions [12–14] with the aim of minimizing their formation. While such variables, as the nature of coal [15], are difficult to modify, others such as temperature of combustion and percentage of excess oxygen, can be controlled to avoid higher emissions.

In this work, AFBC of coal is carried out at different temperatures, different air flows and different excess oxygen percentages, while studying the corresponding PAH emissions.

2. Experimental

A low rank coal from N–E of Spain (SAMCA) has been burned (0.5–1 mm particle size) in a fluidized bed combustion (6.7 cm i.d.) laboratory plant [16] with sand (1 mm)

and limestone as fluidizing agents. The coal ultimate and proximate analysis are: C (%daf), 73.8; N (%daf), 0.9; S (%db), 6.3; H (%daf), 6.4; ash (%ar), 23.9; volatiles (%ar), 15.0; and moisture (%ar), 15.7.

The experiments were performed at temperatures ranging from 750°C to 950°C, airflows ranging from 700 to 1100 L/h and different percentages of excess oxygen ranging from 5% to 40%.

The sampling time was 2 h in all the experiments, once the plant was in the regime of optimum operating conditions. In this way, the starting times, which increase PAH emissions, were avoided.

The samples were analyzed by spectroscopy of fluorescence in synchronous mode (FS) following the analytical procedure reported in previous works [16–18]. The solutions were diluted to avoid the possibility of quenching.

The analytical technique used, FS, is an easy, rapid and non-destructive method, which allows, once the work conditions for each compound have been determined, qualitative and quantitative analyses of every PAH in complex samples. Preliminary work, such as fractionation and cleanup procedures are not necessary with this technique.

3. Results and discussion

The dominant component of coal seems to be composed of a three-dimensional network of condensed aromatic and hydroaromatic units connected by weaker bonds. During coal combustion, some of these units can be emitted as unburned material, and this would be one of the causes of organic emissions. To avoid this kind of emissions, the combustion efficiency should be as close as possible to 100%. For the low-rank coal studied and at the experimental facility used in this work, the efficiencies were, as a function of both combustion temperatures and excess oxygen, always higher than 98.5%.

The second cause of organic emissions can be the pyrolytic process joined to any combustion process. When coal undergoes pyrolysis, important physical and chemical changes [19] occur and radicals are released, which, generally, stabilise between themselves by cyclation reactions. In addition, and as a consequence of the thermal process, further aromatic clusters can be developed [20]. Both the inherent aromatics and those generated during the thermal process are significant atmospheric pollutants, mostly composed of carbon and hydrogen (PAH). Once released to the atmosphere, they can get into the human body, by ingestion and/or by breathing, modifying the regular metabolism of the biological nucleophylics.

Table 1
Combustion efficiencies reached as a function of the combustion temperatures (SAMCA coal, FBC, 20% excess oxygen, 860 L/h)

	T (°C)						
	650	700	750	800	850	900	950
Efficiency	99.1	98.8	99.0	99.0	99.1	99.3	99.4

Table 2
Combustion efficiencies reached as a function of the excess oxygen (SAMCA coal, FBC, 850°C, 860 L/h)

	% Excess oxygen			
	5	10	20	40
Efficiency	98.7	99.3	99.5	99.6

In order to assess the PAH emissions as a function of the combustion variables, the objective of this study was to reach the maximum combustion efficiency. Once achieved (see Tables 1 and 2), it can be assumed that the emissions due to bad combustion have practically been eliminated.

The influence of the combustion temperature was studied between 700°C and 950°C. The PAHs captured in each trap are shown in Table 3, and the total emissions are shown in Fig. 1. As the combustion efficiency is constant and very close to 100%, these data provide information about the importance of the radical interactions released at the pyrolytic process. The radical interactions will depend on the specific temperature at the top of the reactor when the excess oxygen and the air flow are kept constant. The maximum emissions are emitted between 750°C and 850°C, which are the temperatures currently used at the new power stations.

Keeping the temperature and the airflow constant (Table 4 and Fig. 2), it can be observed that the lower the percentage of excess oxygen, the higher the PAH amount emitted, showing a minimum emission when coal is burned with 20% of excess oxygen. Higher excess oxygen generates lower PAH emissions.

From the PAH amounts collected in each trap, it is not be possible to determine any tendency of PAH distribution. This random distribution was also observed when the other combustion variables were studied. However, at the lowest percentages of excess oxygen, most of the total amount of PAHs emitted are supported on the particulate matter trapped in first cyclone. In general, when the percentages of excess oxygen increase, the first cyclone particulate matter amount decreases.

Table 3
Amount (ng/kg) collected from each studied PAH and emitted from a FBC pilot plant with the Samca coal

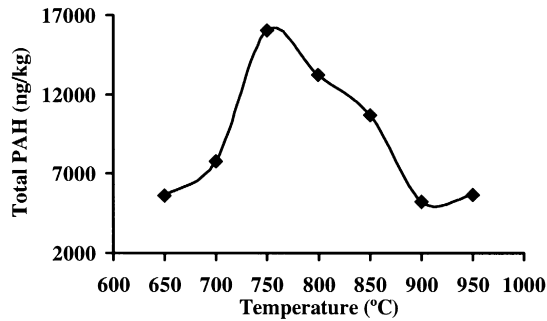|	Temperature						
	650°C	700°C	750°C	800°C	850°C	900°C	950°C
Fluorene	1550.2	1058.6	3632.8	3041.5	1639.9	850.7	1672.2
BaP	39.4	73.2	116.3	111.4	690.7	135.1	47.9
Pyrene	58.5	29.9	402.9	276.1	157.6	123.0	114.4
Chrysene	472.4	396.5	1186.0	826.1	917.6	321.9	127.9
Anthracene	988.0	776.3	1835.0	2449.7	1065.5	558.7	859.7
Acenaphthene	1272.4	4513.4	6800.0	2464.9	2481.2	2693.0	1709.5
BaA	91.2	339.1	461.3	305.0	453.8	96.3	164.0
D(a,h)A	84.4	71.3	260.9	118.0	104.7	32.0	62.1
Coronene	1047.5	388.2	1213.7	3458.6	2850.3	316.4	901.7
Perylene	10.2	49.8	120.4	107.8	138.8	44.2	17.4
BkF	0.0	56.8	0.0	68.6	180.5	40.1	0.0

Fig. 1. Total PAH emitted as a function of the combustion temperature in FBC (860 L/h, 20% oxygen excess, SAMCA coal).

One of the most interesting compounds to study is Coronene. In most of the samples, Coronene is the majority component, especially for those obtained at low excess oxygen. This fact could indicate that the aromatic radicals formed in the first stages of combustion tend to stabilise by forming by pyrosynthesis such species as Coronene. This mechanism seems to be favoured by low velocities in the post-combustion area. In a first approach, the formation of Coronene is an advantage in terms of pollution control. Coronene stability is related to its inertness, so these results seem to indicate that the way of reducing hazardous PAH emissions could be to increase the residence time of radicals, in the presence of large excess oxygen. This promotes the formation of more stable PAHs.

One of the main reasons previously mentioned to study PAH emissions is the carcinogenic effect of some of these compounds. Inside this group, BaP and D(a,h)A, are specially hazardous. The results obtained show low values and a minimum contribu-

Table 4
PAH ($\mu g/kg$) trapped during FBC of coal, 850°C, 860 L/h, with different percentages of excess oxygen

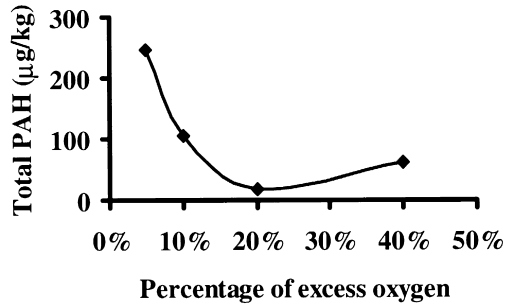|	Oxygen excess			
	5%	10%	20%	40%
Fluorene	43.2	20.9	11.8	2.5
BaP	3.4	0.5	0.0	1.3
Pyrene	23.2	4.7	1.3	9.7
Chrysene	38.1	8.2	0.0	0.6
Anthracene	1.9	0.7	0.0	0.1
Acenaphthene	36.1	14.7	0.0	25.5
BaA	16.2	6.7	0.0	2.7
D(a,h)A	1.5	2.6	0.0	0.0
Coronene	81.8	45.2	5.1	19.3
Perylene	0.5	0.1	0.9	0.0
BkF	0.0	0.0	0.0	0.0

Fig. 2. Variation of the total PAH emitted as a function of the percentages of excess oxygen (850°C, 860 L/h, SAMCA coal).

tion of these two compounds to the total PAH emissions from coal combustion. On the other hand, due to their carcinogenic power, it should be interesting to know the PAH distribution once emitted to the atmosphere, see Fig. 3. While those emitted on particulate matter and trapped on cyclones are not released to the atmosphere, the PAHs emitted in the gas phase would be released to the atmosphere affecting large areas. These last compounds could be transported long distances undergoing photochemical
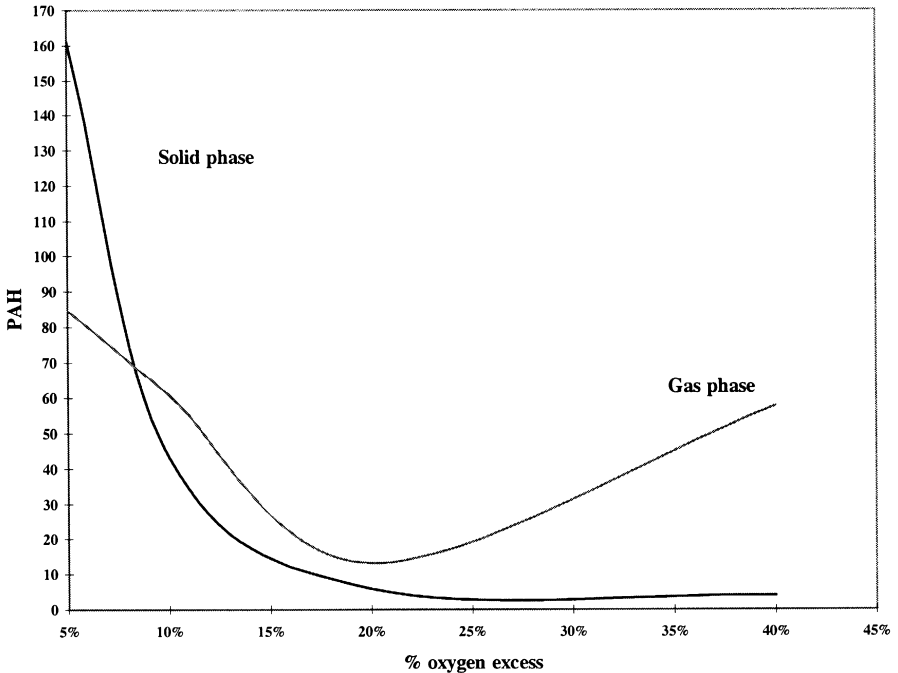

Fig. 3. PAH (μg/kg) distribution between solid and gas phases as a function of the excess oxygen percentages in coal FBC (850°C, 860 L/h, SAMCA coal).

reactions, which could turn them into even more hazardous pollutants. Therefore, the distribution between solid and gas phase has been studied assuming that those PAHs in solid state or supported on the particulate matter were trapped by the first and second cyclone. Those PAHs collected in the bubbling system, nylon filter and adsorbent were included in gas phase. Moreover, the ones trapped in the cyclones of commercial plants are recycled to the bed in order to improve combustion efficiency. In the present work, the results on the distribution of PAHs into solid/gas phase are shown in Fig. 3.

Fig. 3 shows that the higher the excess oxygen percentage, the higher the PAH amount formed in gas phase (% excess oxygen > 20%). That is, the lowest percentages of excess oxygen favour the highest PAH deposition on particulate matter, while the highest percentages of excess air favour the sweep of PAHs to the gas phase.

According to this data distribution, at the real conditions in which a power station works, it could be extrapolated that the PAHs would affect mostly the immediate surroundings of the power plant at the lowest percentages of excess oxygen. At the highest percentages of excess oxygen, the contamination would affect non-specific and larger areas.

Due to the relevance of the variable excess oxygen percentage on PAH emissions, the distribution of PAHs by rings number has been also studied (see Fig. 4).
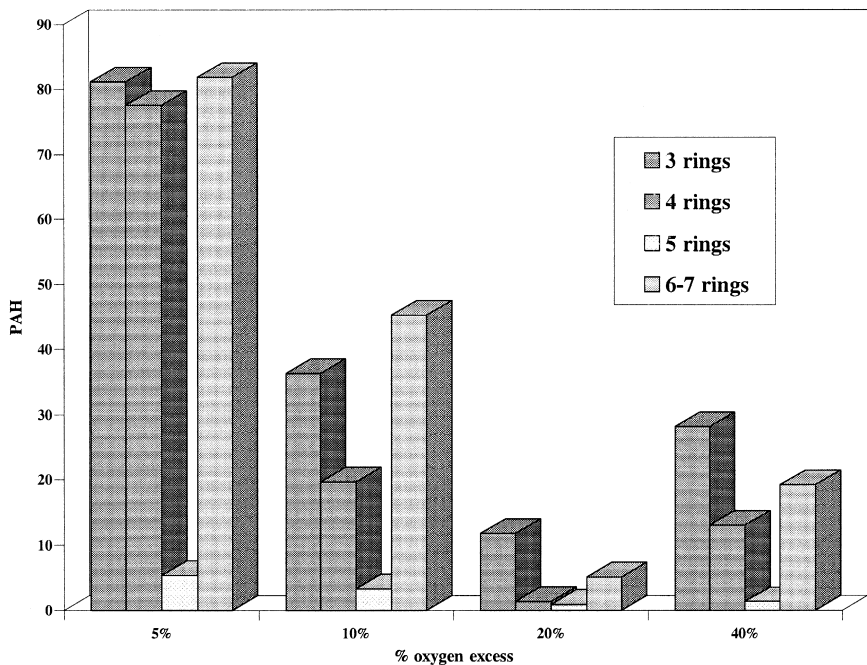

Fig. 4. PAH (mg/kg) distribution by number of rings as a function of the excess oxygen percentage from coal combustion in a FBC at 850°C, 860 L/h, SAMCA coal.

Fig. 4 shows that, in all the cases, independent of the excess oxygen, the PAHs with three and six to seven rings in their molecules are the most abundant. PAHs with five rings are always minor and their relative variation with the excess oxygen is small.

The highest percentages of excess oxygen seem to minimise possible interactions between PAHs (inter-conversion, association and other condensation reactions), giving the lowest hydrocarbons emissions. Perhaps, it is due to the formation of substituted PAHs, PAC and other oxygenated compounds, consequence of the interaction between oxygen atoms and radicals. In this way, at the lowest percentages of excess oxygen, this interaction between oxygen and radicals should be less favoured, and as a result, the PAH amount emitted would be higher.

The influence of the airflow on PAH emissions has been studied keeping constant the combustion temperature and the excess oxygen. Each of the PAH emitted, varying the air flow from 700 to 1100 L/h, are shown in Table 5, and the total PAHs emitted in this range is shown in Fig. 5.

Another variable studied was the fluidising agent. Most of the combustion processes were carried out with sand as inert material, in order to avoid the influence of other materials, like limestone in PAH formation and emissions. But at the power stations, limestone is used to abate sulphur emissions. Therefore, some combustion were performed with limestone, varying the excess oxygen. Fig. 6 shows the PAH emissions with the two agents.

It can be seen that with high excess oxygen, the emissions are quite similar. However, with 10 or 15 excess oxygen percentages, closer to the ones used at the power stations, the PAH emissions with the limestone are higher than those emitted with sand as fluidising agent. The reason behind it is not yet known, but the limestone porous distribution could perform an important role on this fact [21].

It can be concluded that once combustion efficiency is optimised, PAH emissions are a function of the interactions between radicals emitted on the devolatilization of the pyrolytic process and the combustion variables (combustion temperature, airflow, per-

Table 5

Individual PAH (μg/kg) emitted from coal FBC as a function of airflow (850°C, 10% excess oxygen, SAMCA coal)

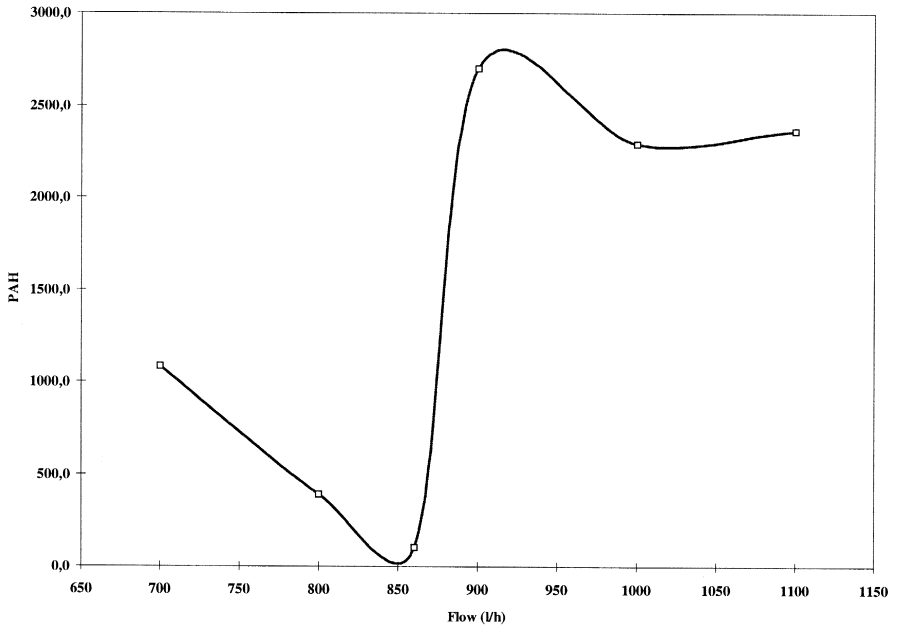|	Flow (L/h)					
	700	800	860	900	1000	1100
Fluorene	316.2	83.3	20.9	256.2	504.3	414.0
BaP	10.3	4.4	0.5	35.4	26.0	29.2
Pyrene	123.5	99.2	4.7	530.8	322.8	328.3
Chrysene	104.8	41.8	8.2	825.0	299.0	901.5
Anthracene	0	2.9	0.7	34.5	0	42.6
Acenaphthene	421.1	117.0	14.7	959.4	1034.1	598.6
BaA	32.6	6.5	6.7	60.1	26.1	44.6
D(a,h)A	5.6	2.1	2.6	0	5.1	5.7
Coronene	69.3	33.0	45.2	0	72.0	0
Perylene	0	0	0.1	0	0	0
BkF	0	0	0	0	0	0

Fig. 5. Total PAH distribution emitted from coal FBC as a function of airflow (850°C, 10% excess oxygen, SAMCA coal).

centage of excess oxygen). The competition between oxidation and condensation reactions will determine the PAH formation, retrogressive reactions, or the radicals conversion in CO_x and H_2O by oxidation reactions.
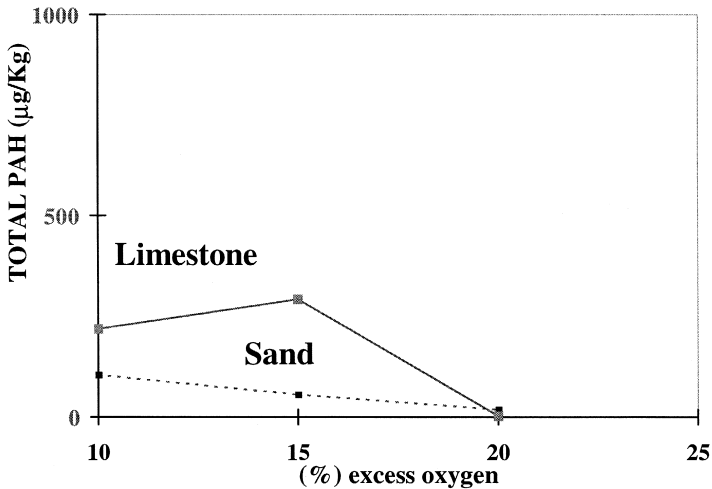

Fig. 6. Total amount of PAH emitted as a function of the percentage of excess oxygen when limestone or sand are the fluidising agents at AFBC of coal (850°C, 860 L/h, SAMCA coal).

Summarising, at the FBC coal power stations, an effort to increase the excess oxygen percentage should be carried out in order to diminish organic emissions, specifically the PAH emissions.

Acknowledgements

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