PII: S0016-2361(96)00120-2

Assessment of PAH emissions as a function of coal combustion variables

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(Received 31 March 1996; revised 30 May 1996)

The influence of fluidized bed combustion (FBC) temperature and coal rank on polycyclic aromatic hydrocarbon (PAH) emissions was assessed. A low-rank coal and a high-rank coal were burnt in a fluidized bed reactor (FBR) on a laboratory scale. An outlet gas sample was passed through a capture system provided with three traps: nylon filter, Teflon filter and XAD-2 resin. The PAH captured were analysed by fluorescence spectroscopy (FS) after sonic extraction with dimethylformamide (DMF). The results show that the total PAH emission depends mainly on the pyrolytic process and to a lesser degree on the combustion efficiency. Although the total amount of PAH emitted follows a specific trend as a function of the combustion temperature, the amount of each PAH emitted seems to be consequence of a random distribution due to PAH interconversion and association. Under all conditions of combustion, the amount of PAH emitted in the gas phase is higher than that collected in two cyclones preceding the gas sampling location. Copyright © 1996 Elsevier Science Ltd.

Many organic materials, such as fossil fuels, have a chemical structure able to form polycyclic aromatic compounds (PAC) under pyrolysis[1] and combustion[2] conditions. In coal structure, the dominant component is considered to be a macromolecular three-dimensional network composed of aromatic and hydroaromatic units connected by alkylic, ether and thioether bridges[3].

Upon heating, coal structure undergoes important physical and chemical changes and a fraction is released to the atmosphere. As consequence of the thermal process, both the released and the remaining fractions undergo cyclization reactions[4] leading to polycyclic compounds which can exist in the gas and in the solid phase, depending on their molecular volume and on the environmental temperature[5].

In coal combustion there are two possible sources of PAC formation:

(1) incomplete combustion, in which fragments of the mainly aromatic structure of the coal are emitted;

(2) as consequence of the chemical changes during combustion, reactions such as cyclization of alkyl chains and radical condensations[6] can lead to polycyclic compounds through polymerization reactions, which are favoured over oxidation in fuel-rich regions of the flame[7].

The mechanisms producing polycyclic aromatic hydrocarbons (PAH) in the combustion process are complex, but it seems that the chemical reactions in flames proceed via the radicals released during the pyrolysis which precedes combustion. Some authors[8,9] have suggested synthesis mechanisms of PAH from C_2 species to benzo[a]pyrene, but similar pathways could lead to most of the known PAH produced in coal combustion and prioritized by the US EPA[10] as important pollutants because of their carcinogenic and mutagenic effects.

The simplest and earliest PAH formed can, depending on the flue gas conditions, undergo further pyrolytic reactions to form larger, highly condensed PAH by intermolecular reactions, such as condensation and cyclization[11]. Therefore the PAH can exist in the gas emitted or be supported on particulate matter, or even give rise to particulate matter, depending on their association[12].

These small particles can travel long distances in the atmosphere, depending on the meteorological conditions. Some PAH photodecompose very rapidly in the atmosphere because of their high reactivity to ozone, while more stable PAH can exist for long periods[13].

There is a lack of information on PAH formation and distribution in their emissions (between gas and particulate matter) and on the influence of coal combustion process variables. In this paper, the PAH emissions from fluidized bed combustion (FBC) of coal on a laboratory scale are assessed as a function of the combustion temperature and coal rank, as continuation of previous work[2] in which the analytical protocol for PAH analysis from FBC was established.

EXPERIMENTAL

Two Spanish coals, a low-rank coal from Teruel and a high-rank coal from Asturias, were used. The coal characteristics are shown in *Table 1*.

Table 1 Proximate and ultimate analyses of the coals

	Low-rank coal	High-rank coal
Ultimate (wt%)		
C (daf)	69.4	87.4
H (daf)	5.80	6.05
N (daf)	1.11	1.90
S (db)	6.12	0.26
Proximate (wt% ar)		
Moisture	7.2	1.1
Ash	22.5	50.5
Volatile matter	39.7	19.6
Fixed carbon	30.6	28.8

Table 2 Fluidized bed combustion efficiencies of the coals

Temperature (°C)	650	700	750	800	850	900	950
Low-rank coal	99.03	98.75	98.83	98.96	99.06	99.29	99.40
High-rank coal	–	–	88.57	–	96.40	–	97.10

The combustion experiments were carried out at temperatures ranging from 650 to 950°C, in a laboratory fluidized sand bed combustor with a continuous feed (up to 200 g h^{-1}), which has been described elsewhere[2,14].

As the combustion temperature increased and the rest of combustion variables were kept constant, the combustion efficiency changed. *Table 2* shows the efficiencies for the two coals at each temperature, calculated by the formula:

$$\text{Efficiency (\%)} = 100 \times \frac{\begin{array}{c}\text{Initial organic matter in coal}\\ -\text{ final organic matter in ash}\end{array}}{\text{Initial organic matter in coal}}$$

The amount of the outlet flue gas was estimated by making a mass balance taking into account the complete combustion of coal elements (carbon, hydrogen and sulfur) and the moisture in the coal.

The PAH sampling procedure, previously described[2], consisted in passing an aliquot of the outlet gas from the FBR through five traps: first cyclone, second cyclone, nylon filter (20 nm pore size), Teflon filter (0.5 nm pore size) and XAD-2 resin. After sonicated extraction with dimethylformamide (DMF), the samples were analysed by fluorescence spectroscopy (FS) in synchronous mode and by capillary gas chromatography (DB-1, 60 m) with flame ionization detector. The analytical conditions have been published previously[15].

RESULTS AND DISCUSSION

In spite of some interesting work reported lately[16], there is a lack of reported data about atmospheric emissions of volatile organic compounds (VOC) from coal combustion in power generation. In this work, different combustion temperatures and two coals of different rank were studied in an attempt to show their influence on PAH emissions. The combustion temperatures for the low-rank coal ranged from 650 to 950°C at 50 K intervals, while for the bituminous coal they were 750, 850 and 950°C. The 650°C combustion temperature was avoided with this high-rank coal due to the low efficiency already reached at 750°C.

The PAH analysed were those prioritized by the US EPA and showing fluorescence properties: fluorene,

Table 3 Amount (ng kg^{-1}) of the PAH studied collected in each trap and emitted from FBC with the low-rank coal[a]

Temperature (°C)	950	900	850	800	750	700	650
Cyclone 1	153.2	240.6	165.1	180.0	695.9	330.8	154.1
Cyclone 2	246.3	269.6	103.1	153.1	84.0	248.8	115.2
Nylon F	150.4	113.8	158.1	196.4	140.2	308.0	224.2
Teflon F	166.4	408.1	524.9	381.7	264.4	138.5	182.3
XAD-2	149.6	92.2	256.7	379.8	286.2	272.7	125.7

[a] Note that the amounts collected on the nylon and Teflon filters and XAD-2 are only aliquots

Table 4 Amount (ng kg^{-1}) of the PAH studied collected in each trap and emitted from FBC with the high-rank coal[a]

Temperature (°C)	950	850	750
Cyclone 1	162.0	315.0	98.8
Cyclone 2	218.0	178.4	180.6
Nylon F	180.9	159.3	175.0
Teflon F	118.2	175.3	141.1
XAD-2	122.6	125.6	109.0

[a] As in *Table 3*

benzo[a]pyrene, pyrene, chrysene, anthracene, acenaphthene, benz[a]anthracene, dibenz[a, h]anthracene, coronene, perylene and benzo[k]fluoranthene. The total amounts of these PAH emitted and trapped are shown in *Tables 3* and *4* for the low- and high-rank coals respectively.

Influence of incomplete combustion

The results obtained show that the total emissions of the PAH studied depend on both the combustion efficiency and the combustion conditions (temperature, flow, etc.) at the outlet from the reactor. The combustion efficiencies calculated for the low-rank coal do not show a significant influence of combustion temperature; the very small differences (0.7% maximum) could be due to experimental error. For the high-rank coal, the efficiency varies notably with the combustion temperature and is 88% at the lowest temperature studied for this coal, 750°C, where combustion problems were encountered.

However, at this lowest temperature, the total emission of the PAH studied is 4284 ng kg^{-1} (see *Table 6* below), the lowest amount emitted with this coal. These data seem to show that incomplete combustion is not the main factor responsible for PAH emission, taking into account the difference in coal structure aromaticity. While the high-rank coal shows a higher aromaticity, the low-rank coal has a greater abundance of alkyl chains and ether bridges (ethers and thioethers)[17], due to the shorter coalification process, and hence a lower aromaticity. In spite of these reasons, the amount of PAH emitted from the high-rank coal combustion is not much higher than that emitted by the low-rank coal, so the PAH emitted from incomplete combustion do not seem to be the main contribution to the total PAH emitted. This conclusion is corroborated at 850°C. At this temperature, the combustion efficiencies are closer but the low-rank coal shows higher emissions, confirming that the contribution of the coal structure due to bad combustion to the total PAH emitted has a lower influence.

Influence of the pyrolytic process

The other possible factor influencing the PAH emission is the secondary pyrolytic process. At the reactor top

Table 5 Amount of each PAH studied (ng kg^{-1}) and total amounts emitted from the low-rank coal combustion in the FBR

Temperature (°C)	650	700	750	800	850	900	950
Fluorene	1192	838	1274	1442	716	806	1182
Anthracene	759	609	920	801	822	542	577
Pyrene	45	27	141	162	93	119	87
Benz[a]anthracene	70	260	175	167	174	92	110
Chrysene	362	315	427	226	855	304	92
Benzo[a]pyrene	31	58	41	46	157	138	33
Perylene	5	40	44	97	180	42	7
Dibenz[a, h]anthracene	100	56	76	34	168	33	26
Coronene	755	318	463	3384	1621	307	639
Total	3319	2521	3559	6358	4787	2383	2753

Table 6 Amount of each PAH studied (ng kg^{-1}) and total amounts emitted from the high-rank coal combustion in the FBR

Temperature (°C)	750	850	950
Acenaphthene	421	994	391
Fluorene	722	1273	1045
Anthracene	852	778	657
Pyrene	170	44	16
Benz[a]anthracene	238	196	185
Chrysene	471	186	579
Benzo[a]pyrene	13	64	115
Benzo[k]fluoranthene	162	105	173
Perylene	76	27	7
Dibenz[a, h]anthracene	31	70	125
Coronene	1125	612	1113
Total	4284	4351	4408

Figure 1 Total amount (ng kg^{-1}) of the PAH studied collected in the five traps, as a function of combustion temperature

and in the stream from the reactor, there will be radicals whose abundance will be a function of the combustion temperature and of the flow velocity of the outlet gas, together with the amount of coal fed.

Data obtained on total emissions of each PAH studied are compiled in *Tables 5* and *6* for the low- and high-rank coals respectively. As the combustion efficiency of the low-rank coal is practically constant, the results obtained with this coal will provide information about the importance of the pyrolytic process. The results obtained show that, in general, each of the studied PAH does not follow any determinate trend as a function of the combustion temperature and that the possible interactions between them will depend on the specific temperature at the top of the reactor and on the flow velocity. For instance, the flue gas temperature inside the first cyclone is ~125°C, while at the entrance of the capture system it is a few degrees above room temperature. These two temperatures show that pyrolytic interactions will take place preferably at the top of the reactor.

On the other hand, the higher the combustion temperature, the higher the outlet flow. As the main interpyrolytic reactions will occur at the top of the reactor and there the temperature will be lower than the bed combustion temperature, this could be the reason why at 950°C (the highest flow speed) and 650°C (the lowest temperature), the total amounts of PAH emitted show minimum values. This occurs with the low-rank coal because the combustion efficiencies are high and almost constant and the influence of incomplete combustion can be discarded. With the high-rank coal, where the influence of poor combustion is significant, this is not so clear.

The consequence of all possible interconversions, which have been supported by other authors[18,19], seems
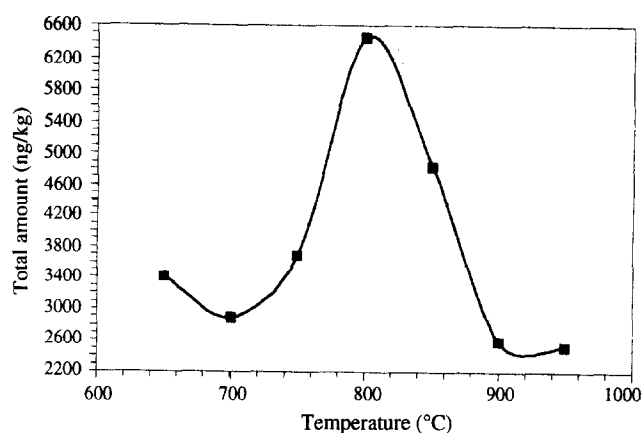
to be a random distribution. The result is that while the total amount of each PAH emitted does not follow any specific trend, the total amount of PAH emitted is a function of the combustion temperature, as *Figure 1* shows.

Gas–solid phase distribution

These pyrolytic processes can lead to different types of radicals, aromatic and alkyl. All the radicals formed can undergo association and as result, through cyclization reactions (aromatic–aromatic interactions and aromatic–alkyl interactions) and successive association, can lead to very large PAH, which can themselves give rise to particulate matter[12,18–20]. In this way, part of the PAH formed could be emitted in the gas phase, leading to atmospheric contamination, while the largest PAH formed will contaminate the soils of the surrounding area of the combustion plant.

The PAH emitted in the solid phase will be those collected in the two cyclones and part of those trapped on the nylon and Teflon filters. The PAH emitted in the gas phase will be those adsorbed on the XAD-2 resin and part of those retained on the two filters, depending on the thickness of the filter cakes. As it is not possible to determine the specific contribution of each phase to the PAH trapped on the two filters, it is not easy to draw conclusions about the PAH distribution on both phases, but the PAH emitted to the atmosphere will be those adsorbed on the XAD-2 resin. According to the data obtained, the greatest amounts of PAH adsorbed on the resin occur at 800 and 850°C for the low-rank coal. With this coal the amounts emitted to the atmosphere are always higher than those collected in the two cyclones. This is also true for the high-rank coal. These data confirm that the contribution of incomplete combustion to the total PAH emitted is lower than the secondary pyrolytic process because particles from incomplete combustion form part of the solid phase.

CONCLUSIONS

According to the results obtained, it can be concluded that the two main factors affecting the PAH emissions from coal FBC are the conditions under which the combustion is carried out and the pyrolytic reactions between the radicals emitted and formed at the top of the combustion reactor. While the former is shown to have a

lower influence, the latter has much greater relevance. Cyclization, interconversion, association and other processes between radicals mean that while the amount of each PAH emitted is variable, the total amount of the PAH emitted follows a specific trend with the combustion temperature. In all the experiments, the amount of PAH emitted in the gas phase was higher than that supported on particulate matter.

ACKNOWLEDGEMENTS

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