

## How EB Radiation could affect the Mechanism of PAH Formation and Emission at Energy Generation

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**Abstract.** At thermal energy generation processes, transport and electricity, organic (polyaromatic compounds) and inorganic emissions ( $\text{CO}_x$ ,  $\text{SO}_x$ ,  $\text{NO}_x$  and trace elements) are released into the atmosphere. Generally it could be said that, while the inorganic pollutants emitted are mostly dependent on the fuels characteristics, the organic pollutants generated and emitted are more depending on the thermal process variables. In addition, inorganic emissions are always released in much more higher amounts but with lower environmental impact than the organic emissions, which are emitted in ppm or ppb but with probed high toxicity. On the other side, while inorganic pollutants are under legislation and a lot of scientific work has been performed to control them, there is a lack of normative on organic pollutants emissions due to the difficulty to provide a non-expensive and on-line procedure to analyse them.

As a post-combustion gas cleaning process, Electron Beam Radiation has been applied for hot gas emissions cleaning at different energy systems when fossil fuels are used. This EB technology has been demonstrated to be adequate for  $\text{SO}_x$  and  $\text{NO}_x$  removal. However, there is a lack of scientific information on how this technology affects the organic emissions. In this paper, an assessment of this technology on the organic emissions mechanisms is analysed, sometimes speculating due to the scarce experimental data available up to now. This information is focussed on Polycyclic Aromatic Hydrocarbons (PAH) formation, not only the those emitted in the gas phase by chimney but also the trapped in the solid phase before and after the irradiation of the flow stream at a coal power station.

### 1. Introduction

Air quality is a worldwide problem affecting mankind exposed to high levels of air pollution that frequently exceed various limit values. Air pollutants are a broad class of chemical and physical substances with very variable nature, formation mechanism and origin, whose composition is variable across the space and time. Health effects associated to air quality are linked to respiratory, cardiovascular troubles and premature mortality.

To obtain information on pollutant sources apportionment, receptor models [1,2,3] have been applied for their sources identification and quantification addressed to develop effective and efficient air quality management plans. These studies have demonstrated that air pollution is mostly due to human activity from energy generation processes, more than to natural sources.

The power generation industry due to air pollution requirements is keenly pursuing strategies to mitigate the emissions of sulphur and nitrogen dioxides ( $\text{SO}_x$ ,  $\text{NO}_x$ ), particulate matter (PM) and other pollutants from power plants. In fact, most countries around the world are now committed to limiting gas emissions from power plants and recent global treaties require all countries to pass and implement laws limiting national  $\text{SO}_2$  and  $\text{NO}_x$  emissions.

The methods to abate these main pollutants originated in power stations are wide and very varied. The most traditional ones consist of solid adsorbent addition (limestone, gypsum) [4], wet flue gas desulphurization scrubber systems [5], flue gas recirculation [6], low NO<sub>x</sub> burners, reburning, selective catalytic reduction (SCR) [7], selective non-catalytic reduction (SNCR) [8], use of activated adsorbents, electrostatic precipitators (ESPs) [9] and fabric filters, etc implying in some cases combustion modifications and others post-combustion treatments.

A technology constituting one of the untraditional methods for flue gas cleaning is the EBT. This technology is recognized as an effective method for removing toxic components from flue gases [10] like NO<sub>x</sub>, SO<sub>x</sub> and VOC<sub>s</sub> [11-16], in particular SO<sub>2</sub> and NO<sub>x</sub>.

The electron beam is generated by an electron accelerator and flows through a titanium foil window into the flue gas interacting with the flue gas and allowing abatement of pollutants. It works by diverting the flue gases through a process, before they escape from the chimney. Gases are cooled with a spray of water to 70-90°C. Ammonia is added to the wet flue gas which is then exposed to low-energy electron radiation from an accelerator. The formation of aerosol droplets upon binary volume condensation of sulphuric and water vapours occurs giving rise to dissolution of other gaseous species in droplets and to liquid phase chain oxidation of SO<sub>2</sub>. As result, the toxic SO<sub>2</sub> and NO<sub>x</sub> are transformed into other chemical forms and the formed aerosols are collected in a filter. Although it is a radiation process, no radioactivity is produced in the operation.

This technology was originally developed in Japan, Germany and USA, some 20 years ago and by the time it became available for applications at industrial scale. Some of the advantages of this technology are related to less costly installation and operation than conventional systems and fulfils the most stringent regulations. Furthermore, because ammonia is added to the wet flue gas, the end product of the scrubbing process is a fertilizer which seems to have agricultural value [17] (Doutskinov, 2004). Because what would have been atmospheric pollutants are turned into useful fertilizer, there is less residue to be disposed than in conventional processes.

Although the EB activation technology for desulphurization has already been tested [17] (Doutskinov, 2004), the main aim of this work is related to know the possible advantages that EB technology would imply from an environmental point of view regarding a particular group of organic emissions, the polycyclic aromatic hydrocarbons PAH, abatement without producing other pollutants of high harmful character, not only in the gas phase but also in the solid phase.

Taking into account the PAH formation mechanism [18-20] in combustion processes, it is expected that the introduction of the EB technology at a power station would modify the organic radical concentration in the flue gas under these radiation conditions in such a way that the interaction between radicals would be also favoured. This could modify not only the PAH concentration but also the generated PAH nature, which would be not only emitted in the gas phase but also adsorbed in the originated solids.

In fact, there are publications that during EB treatment of the flue gases, volatile organic compounds (VOC), i.e. polycyclic aromatic compounds (PAC) were influenced as well [21-22]. It has been found [23] that the concentrations of aromatic compounds of small aromatic

rings were reduced while the concentrations of large aromatic rings were increased. However, no published data have been found regarding the PAH contained in the solid products in power generation using EBT with the exception of references [23-24].

In this paper, some theoretical deductions, based on the few data available, are extracted on mechanisms driven to PAH formation and emissions under EB radiation of the flue gas at energy generation systems by using fossil fuels.

## 2. Experimental Procedure

A portion of gas from coal combustion installation was introduced in the EB chamber. The inlet volume of the flue gas irradiated was 5994 m<sup>3</sup>/h. Conditions used at the EB irradiation chamber were: voltage, 800 kV; moisture, 21%; dose, 4kGy; coefficients: ammonium, 1; water, 0.45 and air, 2. By applying these conditions, at the outlet flue gas (8317m<sup>3</sup>/h) the concentration of NO<sub>x</sub> was reduced to 15mg/Nm<sup>3</sup> and the concentration of SO<sub>x</sub> diminished to 510 mg/Nm<sup>3</sup>. To analyse EB effect on organic pollutants, samples from gas phase (flue gas) by using condensers and cartridges and the solid phase (fertilizer and fly ash) were collected.

Solid samples, condensers and cartridges were extracted, dried and after addition of surrogate standards (acenaphthene-d<sub>10</sub>, anthracene-d<sub>10</sub>, benzo(a)anthracene-d<sub>12</sub>, benzo(a)pyrene-d<sub>12</sub>, perylene-d<sub>12</sub> and benzo(g,h,i)perylene-d<sub>12</sub>), samples were cleaned up on a silica-gel column with DCM. The eluted was concentrated by N<sub>2</sub> stream and the solvent exchanged to hexane. Before injection to the GC-MS-MS, p-terphenyl native was added as internal standard to all the samples.

A total of 23 PAH including the 16 PAH established by US-EPA were quantified in flue gas samples with and without the EBT at the inlet and the outlet of an irradiation chamber. In addition, the PAH trapped on solid phase, fly ashes proceeding from the coal combustion without EBT and the by-products obtained in the EBT, ammonium sulphate and ammonium nitrate, were also quantified in order to compare the influence of EBT on these emissions. In this way, it is assessed, on the one hand, the influence of the EBT on PAH emissions in gas phase and on the other hand, the possibility of using these by-products as fertilizers in the agriculture sector.

A total of 23 PAH were quantified: (naphthalene (Np), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), 2,5-/2,7-/4,5-dimethylphenanthrene (Dimephe), 1-methylphenanthrene (1MePhe), 2-methylphenanthrene (2MePhe), 2-/4-methylphenanthrene (2/4MePhe), 9-methylphenanthrene (9MePhe), anthracene (An), fluoranthene (Fth), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP) and coronene (Co) by the internal standard method using deuterated PAH surrogate standards by GC/MS/MS. Blanks were also prepared and subtracted to sample results.

### 3. Results

Average values obtained from the different samples collected at the power station are shown in Tables 1, 2 and 3.

TABLE 1. AVERAGE PAH CONCENTRATION IN THE INLET (BEFORE EB) AND OUTLET (AFTER EB) SAMPLES TAKEN FROM THE GAS PHASE.

PAH ( $\mu\text{g/g}$ extract)	Inlet	Outlet
<b>Naphthalene</b>	<b>110.06</b>	<b>3.43</b>
<b>Acenaphthylene</b>	<b>2.70</b>	<b>0.74</b>
<b>Acenaphthene</b>	<b>3.29</b>	<b>2.77</b>
<b>Fluorene</b>	<b>25.15</b>	<b>4.91</b>
<b>Phenanthrene</b>	<b>237.10</b>	<b>23.99</b>
<b>Anthracene</b>	<b>0.78</b>	<b>0.39</b>
<b>2MePhe+2/4MePhe</b>	<b>27.86</b>	<b>5.38</b>
<b>9-MePhe</b>	<b>7.00</b>	<b>2.79</b>
<b>1-MePhe</b>	<b>11.93</b>	<b>3.02</b>
<b>DiMePhe</b>	<b>8.97</b>	<b>2.68</b>
<b>Fluoranthene</b>	<b>15.66</b>	<b>1.46</b>
<b>Pyrene</b>	<b>1.22</b>	<b>0.71</b>
<b>Benzo(a)Anthracene</b>	<b>0.00</b>	<b>9.13</b>
<b>Chrysene</b>	<b>2.49</b>	<b>0.74</b>
<b>Benzo(b+j)Fluoranthene</b>	<b>1.26</b>	<b>0.70</b>
<b>Benzo(k)Fluoranthene</b>	<b>0.36</b>	<b>0.31</b>
<b>Benzo(e)Pyrene</b>	<b>0.42</b>	<b>0.30</b>
<b>Benzo(a)Pyrene</b>	<b>1.31</b>	<b>1.83</b>
<b>Indeno(1,2,3-cd)pyrene</b>	<b>0.30</b>	<b>0.48</b>
<b>Dibenzo(a,h)Anthracene</b>	<b>0.15</b>	<b>0.47</b>
<b>Benzo(ghi)perylene</b>	<b>0.00</b>	<b>0.00</b>
<b>Coronene</b>	<b>0.55</b>	<b>2.11</b>
<b>TOTAL PAH</b>	<b>458.54</b>	<b>68.34</b>

TABLE 2. PAH CONCENTRATION IN THE FLY ASHES (REF 1 AND REF 2) COLLECTED IN THE POWER STATION WITHOUT EB.

PAH ( $\mu\text{g/g}$ extract)	Ref 1	Ref 2
Naphthalene	1.05	1.53
Acenaphthylene	1.36	1.90
Acenaphthene	1.25	2.03
Fluorene	12.98	16.37
Phenanthrene	200.50	144.64
Anthracene	3.83	2.47
2MePhe+2/4MePhe	30.00	27.15
9-MePhe	24.09	18.38
1-MePhe	19.89	16.46
DiMePhe	32.33	26.99
Fluoranthene	36.28	25.37
Pyrene	19.81	9.76
Benzo(a)Anthracene	2.49	2.67
Chrysene	5.34	5.45
Benzo(b+j)Fluoranthene	4.82	8.04
Benzo(k)Fluoranthene	0.00	0.00
Benzo(e)Pyrene	2.45	2.85
Benzo(a)Pyrene	1.02	0.00
Indeno(1,2,3-cd)pyrene+DahA	9.76	3.85
Benzo(ghi)perylene	5.23	1.82
Coronene	-	-
<b>TOTAL PAH</b>	<b>414.48</b>	<b>317.72</b>

TABLE 3. PAH CONCENTRATION IN FOUR FERTILIZERS (F1, F2, F3 AND F4) OBTAINED AFTER THE EBT

PAH ( $\mu\text{g}/\text{kg}$ fertilizer)	F 1	F 2	F3	F 4
Naphthalene	0.00	0.00	0.00	0.00
Acenaphthylene	0.22	0.11	0.36	0.33
Acenaphthene	0.04	0.03	0.11	0.12
Fluorene	1.13	1.51	2.59	2.53
Phenanthrene	13.25	15.66	17.62	13.57
Anthracene	1.19	1.80	2.11	2.38
2MePhe+2/4MePhe	4.28	4.97	4.09	4.02
9-MePhe	2.28	1.90	1.58	1.70
1-MePhe	1.42	1.30	0.79	0.83
DiMePhe	3.24	3.05	1.54	1.21
Fluoranthene	13.99	16.98	19.13	18.30
Pyrene	7.27	6.32	6.74	9.83
Benzo(a)Anthracene	0.57	0.53	0.51	0.61
Chrysene	0.77	0.72	0.73	0.99
Benzo(b+j)Fluoranthene	1.00	0.77	0.58	0.75
Benzo(k)Fluoranthene				
Benzo(e)Pyrene	0.35	0.23	0.15	0.25
Benzo(a)Pyrene	0.23	0.27	0.40	0.41
Indeno(1,2,3-cd)pyrene+DahA	0.60	0.35	0.30	0.58
Benzo(ghi)perylene	0.65	0.39	0.48	0.73
Coronene	0.91	0.56	0.45	0.83
<b>TOTAL PAH</b>	<b>53.39</b>	<b>57.46</b>	<b>60.27</b>	<b>59.96</b>

## 4. Discussion

### 4.1. EB treatment influence on PAH emitted in gas phase

The gas sample corresponding to the “outlet”, after the electron beam treatment, underwent a different PAH distribution with respect to inlet gas. The total PAH concentration decreased considerably from 458  $\mu\text{g}/\text{g}$  to 68  $\mu\text{g}/\text{g}$  (see average data in TABLE 1), implying a reduction of the 85% in the total PAH emissions. It is observed that the EB shows high efficiency to destroy PAH of low molecular weight like Np, Acy, Fl, Phe, 2+2/4MePhe, Fth and Chry. On the contrary, an increase in the PAH concentration of high molecular weight is observed (BaA, DahA, BghiP, Co). Therefore, the application of the irradiation shows a decrease in the 2 aromatic rings with an increase in the 4, 5, 6-7 aromatic rings. Other authors [21] also reported same trends concerning PAH in flue gases after EBT installed in a power plant in Poland.

#### 4.2. EB treatment influence on PAH emitted in solid phase

Fly ash samples from coal combustion without using the EBT (see average data in TABLE 2) were analysed and results were compared to the ones obtained for samples corresponding to fertilizers.

Regarding the total PAH concentration for the two kinds of solid wastes, the obtained values were quite similar with a slight decrease in the fertilizer sample versus the fly ashes (325.6µg/g, 366.1µg/g). The majority PAH trapped in the fly ashes were PAH with 3 aromatic rings. In the case of the fertilizer samples, the majority PAH trapped were PAH of 3 and 4 aromatic rings with an increase in the 4 aromatic rings PAH. Therefore, a high EB efficiency was again observed to destroy low volatile PAH. However, an increase in the concentration of semi-volatile PAH was produced.

When the total PAH trapped in the fertilizers was calculated per kg fertilizer, the total PAH average concentration was 57.8 µg/kg fertilizers (see TABLE 3), much lower than the intervention value for soil sanitation used by the Dutch government that is 40000 µg PAH/kg [25] (Van Brummelen et al., 1996) taking into account a total of only 10 PAH.

#### 4.3. Some inferences from EB treatment influence on total PAH

From the above showed results, same inferences concerning EB treatment influence on PAH formation mechanisms could be extracted. It has been demonstrated [26] that PAH formation is a consequence of carbon-carbon radicals interaction, both at the combustion freeboard and at the chimney when the flue gas stream is cooling down. EB treatment brings energy to the gas stream and therefore increases the C-C radicals concentration by bond breaking of the highest volatile PAH previously generated (PAH with 2 and 3 aromatic rings) and, in this way, promoting a bulkier radicals association and condensation, increasing the PAH with higher molecular weight (4, 5 and 6 aromatic rings) and so, with lower volatility.

This trend has advantages and disadvantages. The main advantage is that it is easier to control the emissions of lower volatility PAH because they are mostly emitted as particulate matter and solid phase can be better handled, from an environmental point of view, than gas phase. However, this trend could increase the emissions toxicity [27] because 5 and 6-aromatic rings PAH are those listed by USEPA as priority pollutants.

### 5. Conclusions

The quantification of PAH generated at energy generation, previous and after EB treatment for air cleaning, has been performed by using a very sensitive analytical technique, gas chromatography with mass spectrometry mass spectrometry detection (GC-MS-MS).

Results showed that PAH are influenced by the EBT showing a reduction of the most volatile PAH in the gas phase and an increase in PAH with higher molecular weight.

PAH concentrations in the fertilizers obtained after irradiation were found to be similar to those in the fly ashes produced when no irradiation is applied. These fertilizers can be

considered like unpolluted soils being adequate for agriculture applications with PAH concentrations below the target value set up by Dutch Government.

It would be necessary a deeper study, including more experimental data, in order to corroborate these preliminary studies addressed to manage a cleaner atmosphere and a better air quality.

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