

POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN ASH FRACTIONS OF OIL SHALE COMBUSTION: FLUIDIZED BED *vers* PULVERIZED FIRING

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Power generation from fossil fuels is a substantial source of pollution, the extent of which depends on the type of fuel and technology of combustion being used. Currently, more than 90% of electricity produced in Estonia is generated by oil shale-fired power plants (PP), Eesti and Balti PP. The main technology of processing oil shale used in PP was pulverized firing (PF). At present a new technology, fluidized bed combustion (FBC) process, has been introduced. The current study focuses on comparison of solid wastes discharged by both processes, with a special emphasis on hazardous organic compounds, particularly the fraction of polycyclic aromatic hydrocarbons (PAH), present in ash. Ash samples were collected at each unit of electrical precipitators of PF and FBC boilers from the Eesti Power Plant. The organic fraction was separated by Soxhlet extraction. The final determination of 16 priority PAH, according to the US EPA List, was performed by liquid chromatography (HPLC) with fluorescence detection. The total concentration of PAH in different ash fractions was found to be in the range of 82.2–152.1 µg/kg, including benzo[a]pyrene, 7.9–15.1 µg/kg for the PF process, whereas for the new FBC technology the total content of PAH was less, e.g. 30.2–63.7 and 2.6–6.4, respectively. The average content of PAH in all ash fractions studied was 107.8 ± 29.6 µg/kg for PF and 47.0 ± 11.0 µg/kg for FBC system. Thus, the amount of hazardous PAH compounds in ash, generated by combustion of oil shale, was significantly less by using the new FBC process compared to the PF technology.

Introduction

More than 90% of Estonian electricity is produced by oil shale-fired power plants (PP), Eesti and Balti PP; both are situated close to the town of Narva in the northeastern part of Estonia. The main technology applied for processing oil shale at *AS Narva Elektriijaamad* (Narva Power Plants Ltd.) was pulverized firing (PF).

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Table 1. Characterization of Priority PAH Included in US EPA List [15]




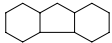

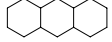
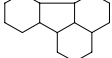

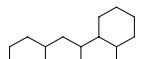
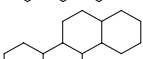
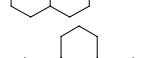
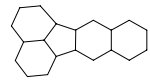
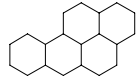
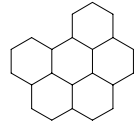
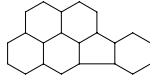
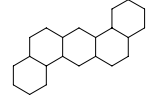
PAH empirical formula	Abbreviation	Formula	MW	Mp, °C	Bp, °C	Vapor pressure, Pa
Naphthalene C ₁₀ H ₈	NA		128	80	218	1.0 × 10 ⁻²
Acenaphthylene C ₁₂ H ₈	ACL		152	93	270	9.0 × 10 ⁻¹
Acenaphthene C ₁₂ H ₁₀	AC		154	95	279	3.0 × 10 ⁻¹
Fluorene C ₁₃ H ₁₀	FL		166	116	295	9.0 × 10 ⁻²
Phenanthrene C ₁₄ H ₁₀	PHE		178	101	340	2.0 × 10 ⁻²
Anthracene C ₁₄ H ₁₀	AN		178	218	342	1.0 × 10 ⁻³
Fluoranthene C ₁₆ H ₁₀	FA		202	111	375	1.2 × 10 ⁻³
Pyrene C ₁₆ H ₁₀	PY		202	156	393	6.0 × 10 ⁻⁴
Benz[a]anthracene C ₁₈ H ₁₂	BaA		228	162	435	2.8 × 10 ⁻⁵
Chrysene C ₁₈ H ₁₂	CHR		228	255	448	5.7 × 10 ⁻⁷
Benzo[b]fluoranthene C ₂₀ H ₁₂	BbF		252	168		—

Table 1. Characterization of Priority PAH Included in US EPA List [15] (end)

PAH empirical formula	Abbreviation	Formula	MW	Mp, °C	Bp, °C	Vapor pressure, Pa
Benzo[k]fluoranthene C ₂₀ H ₁₂	BkF		252	217	480	5.2×10^{-8}
Benzo[a]pyrene C ₂₀ H ₁₂	BaP		252	179	360	7.0×10^{-7}
Benzo[ghi]perylene C ₂₂ H ₁₂	BghiP		276	277	550	1.4×10^{-8}
Indeno[1,2,3-cd]-pyrene C ₂₂ H ₁₂	IP		276	163	530	1.3×10^{-8}
Dibenz[a,h]anthracene C ₂₂ H ₁₄	DBahA		278	266		3.7×10^{-10}

Recently a new, so-called fluidized bed combustion (FBC) technology has been introduced at the Eesti Power Plant, and soon it will be in progress also at the Balti Power Plant. The FBC technology applied for oil shale processing for the first time in the world is a new experience also in environmental issues. It is well known that power generation from fossil fuels is a substantial source of pollution, the extent of which depends on the type of fuel and technology of combustion being used. As for oil shale combustion, its low calorific value (*ca.* 10.3 MJ/kg) and high mineral content (60–70%) results always in a very large total amount of residues, including solid wastes, gaseous and dust products (fly ash) [1–7].

Solid residues as well as gaseous and particulate discharge of oil shale combustion by traditional technology, e.g. PF, were studied by numerous authors [1–7]. The investigation of the FBC process for generation of energy from a wide rank of coals as a most common fossil fuel started in the 1960s. The main advantages at utilization of FBC were directly related to abatement of inorganic emissions in such a way that in fluidized beds the inorganic emissions (NO_x , CO_x , SO_x) are under control [8, 9].

Bibliography on FBC is very extensive because many studies have been aimed at reducing inorganic emissions. A complete investigation on the influence of different variables (fuel particle, combustion temperature, percentage of excess oxygen, air flow, residence time, etc.) on FBC emissions relating to NO_x , VOC, CO_x , particulate matter, was recently performed (see the review by Mastral and Callen [8] and references therein).

Reduced operating temperatures characteristic of the FBC process have, however, prompted some concern over possible increased emissions of hazardous organic compounds, e.g. polycyclic aromatic hydrocarbons (PAH). It is well known that the discharge of harmful organic compounds such as various PAH at combustion of fossil fuels is significant [8–14]. The total content of PAH compounds in coal fly ash was found to be in the range of 20–290 $\mu\text{g}/\text{kg}$ [8–12], whereas in oil shale ash (PF process) it was significantly higher, 53–505 $\mu\text{g}/\text{kg}$ [5–7].

As for combustion of any fuel, formation and emission of PAH could occur in two processes [11, 14] – pyrolysis [13] and pyrosynthesis [8]. On heating, organic compounds are partially cracked to smaller and unstable fragments (pyrolysis). These fragments, mainly highly reactive free radicals with a very short average lifetime, lead to the formation of more stable PAH through recombination (pyrosynthesis). The current study focuses on the comparative characterization of solid residues of PF and FBC technology of oil shale combustion, with special emphasis on hazardous organic compounds, particularly 16 priority PAH, present in ash fractions. PAH is a class of structurally similar chemical compounds characterized by the presence of fused aromatic rings (Table 1). It should be noted that, while PAH are often discussed as a group, the individual homologues are evaluated as separate chemicals in the risk characterization [15–18].

There are over a hundred chemicals in the family of PAH compounds, although smaller numbers are routinely reported at disposal sites. The US Environmental Protection Agency (EPA) has fixed 16 PAH as priority pollutants (see Table 1), the latest being effective from 1997 [19–20]. This set is commonly used in the world for hazard identification.

Experimental

Sampling

Ash samples were collected along the gas flow duct, particularly on each unit of electrostatic precipitators, it means after the cyclone and before the stack of boiler No. 5 (PF technology) and boiler No. 8 (FBC technology) of the Eesti PP. The samples were taken during steady-state operation of combustors. Sampling from both boilers was performed approximately at the same time, and characteristics of raw material (oil shale) were established by the specialists of Narva PP. The process characteristics were checked and found to be as representative ones. The samples were transported to the laboratory next day and stored in the cold (4 °C) before their further treatment and chemical analysis.

Chemical Analysis

Extraction, Pre-Treatment and Clean-Up Procedures

The ash samples were Soxhlet extracted for 20 hrs with acetone-hexane (50 : 50 by vol.). The extracts (*ca* 150 ml) were evaporated to *ca* 1 ml in a rotary evaporator at 53 °C and 400–500 mbar. The PAH fraction was separated in a glass column (8 ml), filled with silica gel 60 (0.040–0.063 mm, 230–400 mesh ASTM), equilibrated with *n*-hexane and fractionated by *n*-hexane/dichloromethane (1 : 1). The fraction containing PAH was reduced to 2 ml under N₂, transferred into an autosampler vial and subjected to the HPLC analysis.

Chromatographic Analysis

The HPLC system HP 1100 consisted of a vacuum degasser, a gradient pump, an autosampler, a column thermostat, a diode array detector, a fluorescence detector, and a computer workstation (Agilent Technologies, Germany). The analytical column (MZ-PAH C-18, 5 µm, 250 mm, 3 mm I.D) was from MZ Analysetechnik, Germany. The priority PAH were separated with an acetonitrile gradient at 308 K and 0.5 ml/min.

Results and Discussion

The results of chemical analysis of ash fractions are presented in Table 2. Different PAH compounds included in Priority List (see Table 1) were identified in the extracts of the ash samples. Acenaphthylene, a relatively light representative of PAH from Priority List, was not found in ash extracts. The total concentration of PAH in the ash fractions was found to be in the range of 82.2–152.1 $\mu\text{g}/\text{kg}$, including BaP, 7.9–15.1 $\mu\text{g}/\text{kg}$ for the PF process, whereas for the new FBC technology (see Table 2), the total content of PAH was less, 30.2–63.7 and 2.6–6.4 $\mu\text{g}/\text{kg}$ for BaP.

Table 2. Content ($\mu\text{g}/\text{kg}$) of Individual PAH in Ash Fractions of Electrical Precipitators, Eesti PP (for abbreviations see Table 1)

Individual PAH	PF technology (boiler No. 5))			FBC technology (boiler No. 8)			
	I unit	II unit	III unit	I unit	II unit	III unit	IV unit
NA	10.11	12.99	7.11	2.93	4.95	2.46	3.03
AC	2.55	3.18	2.02	1.57	1.57	1.31	2.07
FL	2.71	4.12	2.10	1.65	1.93	1.22	2.20
PHE	4.26	7.39	3.95	2.85	3.13	2.05	3.99
AN	3.92	7.54	3.35	2.12	3.14	1.24	2.94
FA	5.30	9.29	5.50	2.54	4.11	2.11	2.45
PY	6.07	10.99	5.93	2.87	4.47	2.02	3.54
BaA	6.82	11.97	6.53	3.20	5.03	2.29	4.11
CHR	8.85	15.12	8.48	3.93	6.76	2.74	4.56
BbF	6.88	12.40	6.62	3.26	5.13	2.34	4.39
BkF	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaP	8.35	15.12	7.89	3.95	6.41	2.75	5.25
DBahA	7.50	13.53	7.33	3.52	5.58	2.49	4.43
BghiP	8.85	16.21	8.69	4.07	6.48	2.90	5.17
IP	6.84	12.24	6.77	3.23	5.03	2.26	4.12
Total PAH	89.00	152.11	82.24	41.69	63.70	30.18	52.24

The average mean content of PAH in all ash fractions studied was $107.8 \pm 29.6 \mu\text{g}/\text{kg}$ for PF and $47.0 \pm 11.0 \mu\text{g}/\text{kg}$ for the FBC system. These results are in good agreement with literature data [14], indicating that the particulate PAH emission for the FBC process tested appears to be lower than those typically reported for conventional coal combustion technology. On the other hand, a relatively higher amount of light PAH derivatives could indicate that during applying of FBC technology the reactions of pyrolysis are more pronounced, whereas for PF technology the pyrosynthesis supposed to be the prevailing process in PAH formation.

It is well known that individual PAH differ substantially in their physical and chemical properties. Vapor pressures of PAH range in five to twelve orders of magnitude (see Table 1). Various conditions of PF and FBC should lead to different behavior of PAH compounds in the process of combustion and realize in distribution of homologues. The most abundant individual

compounds for both technologies applied were DBahA, BaP, and CHR, which all could be characterized as heavy PAH whose vapor pressure is low ($<10^{-7}$ Pa) and boiling points over 448 °C (see Table 1).

The compounds of lower molecular mass were present in much smaller quantities. The relative amount of heavy PAH was found to be more significant in PF process compared to FBC technology. The relationship between the degree of mutagenic activity and the presence of heavier PAH, i.e. masses 252 Dalton and over, has been clearly illustrated by many authors [15–18]. However, the real impact of any pollutant is impressed in terms of its mobility, e.g., bioavailability rather than levels in solid waste itself or soil media. The leaching behavior of fractions of oil shale ash is characterized in our special publication in this issue [21].

Conclusions

1. The full set of 16 US EPA priority PAH, including hazardous heavy representatives, was quantified in ash samples of oil shale combustion.
2. The total concentration of PAH in ash fractions was found to be lower in the case of fluidized bed process completed recently than in the case of the traditional pulverized fuel technology.

Acknowledgement

Financial support from the *Estonian Ministry of Education and Science, Estonian Science Foundation* (Grant No. 5130), and the *project EST-02/003* according to bilateral cooperation in science and technology (WTZ) between Federal Ministry of Education and Research, Germany and Ministry of Education and Research, Estonia, is gratefully acknowledged. The authors would like to thank authorities of Narva PP, especially Mr. *M. Uus* and Mr. *O. Parts* for kind help in providing the representative ash samples and fruitful discussions; Dr. *J. Lintelmann* and MSc *D. Antkowiak* for the advice and support, Mrs. *P. Laas* for technical assistance.

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Received May 17, 2005