

DIOXIN AND PAH EMISSIONS FROM A SHALE OIL PROCESSING PLANT IN ESTONIA

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Introduction

In March 2003, dioxin emissions were measured from a shale oil producing plant located near the city of Narva in Estonia. The measurement was a part of a project on measuring the dioxin emission from four oil shale fired boilers at two power plants located near the city of Narva in Estonia. These power plants produce more than 90 % of the electricity consumption in Estonia by combusting more than 10 million tons of oil shale per year, which is around 85 % of the total consumption of oil shale in the country. The oil plant is the second largest consumer of oil shale, with an annual consumption of around 800,000 ton. Two other smaller plants producing oil from oil shale is known to exist in Estonia, and one in Australia.

These measurements of dioxin air emission from oil shale pyrolysis are the first performed in Estonia. The aim of the measurements was to get background data for the estimation of the annual dioxin emission from the use of oil shale in pyrolysis processes in Estonia, in order to improve or qualify the estimation based on emissions factors for large coal fired power stations given in the recent DANCEE Project: Survey of anthropogenic sources of dioxins in the Baltic Region /1,2/.

The Danish environmental assistance to Eastern Europe (DANCEE) has sponsored the project, and dk-TEKNIK ENERGY & ENVIRONMENT (now FORCE Technology) was responsible for the measurements, which were conducted in cooperation with EERC in Tallinn.

Oil shale

Oil shale is one of the most important mineral products found in Estonia. Its appearance resembles brownish, flaky stone. Oil shale contains significant amount of non-combustible material, i.e. ash. Oil

Table 1. Crushed oil shale and properties

Parameter	Unit	Range	Mean
Heat value	Kcal/kg	1,800 – 2,400	2,000
Moisture	%	11 – 14	11.4
Organic part	%	28.4 – 39.2	29.4
Carbonate part	%	29.5 – 50	45.0
Ash content	%	–	45
Chloride (dry fuel)	%	0.21 – 0.29	0.22
Sulfur (dry fuel)	%	0.50 – 0.69	0.52

shale has a laminated structure, and is soft enough to be scratched with fingernails. Thin oil shale leaves can be lit with a match. This is the reason why oil shale is referred to as “burning rock” in Estonia. The relatively high content of chlorine (0.22 %) compared to other fuels, could possible lead to an increased formation of dioxins.

Oil processing plant

The oil shale processing plant was built in the late 1970's next to Eesti Power Plant, which is situated 25 km outside Narva. The plant has suffered from many problems, and it took almost 5 years to make the process operate.



Figure 1. The Oil Processing Plant

The organic material in oil shale is kerogen, and the process to change it to an oil-like substance, involves a heating to approximately 500 °C. This process converts the organic material into evaporated liquid, from which different grades of shale oil readily can be produced.

Process

Incoming oil shale is heated with the hot flue gas, separated in cyclones, and mixed with hot ash to attain the reaction temperature of at least 480 °C in the drum reactor. Kerogen is decomposed or pyrolysed into gas, condensable oil, and a solid residue. The decomposition begins at relatively low temperature (300 °C), but proceeds more rapidly and more completely at higher temperature. The rate of kerogen decomposition is the highest at temperature of 480–520 °C.

The vapour phase is cooled and separated in an oil fraction and a gas phase. The gas, which has a calorific power of 10,000 kcal/m³, is burned in the power plant, and the oil fraction is separated in four fractions, heavy oil, light oil, diesel and gasoline. These four fractions are further mixed to produce in total 9 different grades. A substantial part of the oil is used for start-up preheating of the oil shale fired boilers in the power plant.

The solid residue, which contains a high proportion of coke, is subsequently burned with excess air, in a special aerofountain furnace. Combustion temperature on top of the furnace is 750 to 800 °C. Ash and flue gas is separated, and the flue gas is heating the incoming oil shale, treated in an electrostatic precipitator (ESP) and discharged to the air through an 85 meters stack. Two thirds of the hot ash goes back to the reactor to attain required temperature, and the rest is disposed together with the ash from the power plant, in a huge ash landfill.

The O₂ concentration after the boiler is normally 0.2 – 0.3 %, but it is decreased to almost zero at the measuring point just prior to the stack. The oxygen is most likely reacting with oil shale in the heat exchange system. The CO concentration is measured before ESP at least once a week. Data from 2002 is 19 – 30 g/Nm³, with an average of 22 g/Nm³, at the reference condition dry gas and 6 % O₂.

Methods and Materials

Emission samplings were performed with a sampling train according to the filter/condenser method described in the CEN standard EN 1948 part 1, Sampling. Two simultaneous samples were taken. In addition, the plant staff collected an ash sample, during the emission sampling. The ash sample was a proportional mixture of bottom ash and fly ash.

The obtained emission samples were analysed for PCDD/PCDF according to EN 1948 part 2 and 3, and for PAH according to ISO 11338. As PAH's are sensitive to acid treatment, the samples were first Soxhlet extracted by means of toluene for 6 hours, after addition of both PCDD/PCDF and PAH 13C-UL-labeled internal standards. After a hot aqueous acid treatment of the particle-containing compartment, followed by drying with acetone, extraction of PCDD/PCDF was continued with fresh toluene. The combined extract was reduced in volume, and two aliquots were treated additionally for PCDD/PCDF and PAH analysis respectively.

Cleanup of the PCDD/PCDF aliquote was done on multicolumn systems involving various kind of treated silica gel, aluminium oxide, carbon-on-fibre or carbon-on-celite. The final extract was reduced to dryness and dissolved in syringe standard, and measured by using an HRGC/HRMS combination with HP 5890 series II / VG-AutoSpec on DB 5 and SP2331 capillary columns. For each substance 2 isotope masses were measured.

Clean-up of the PAH aliquote was done by means of silica-gel. The final extract was reduced to dryness and dissolved in syringe standard, and measured by HRGC/LRMS in combination with Agilent 6890 series / 5973 MSD on HP5 capillary columns

The ash samples were extracted by means of toluene after degradation and addition of ^{13}C -UL-labeled internal standards. The cleanup was done on multicolumn systems (compare above). The final extract was reduced to dryness and dissolved in syringe standard.

PAH and naphthalene

The analytical results for PAH is handled and presented according to the regulation in the Danish Air Emission Guidelines /3/. This regulation distinguishes between naphthalene and the rest of the 16 EPA PAH, originally selected by the US EPA and now widely used internationally in connection with characterisation and assessment of PAH mixtures. Denmark has one emission limit value at $300 \text{ mg/m}^3(\text{s,d})$ for naphthalene, and another the sum of the remaining 15 PAH, calculated in toxicity equivalences, in proportion to the toxicity of benzo[*a*]pyrene (unit abbreviation is B[*a*]P-TEQ). The emission limit value is $5.0 \text{ } \mu\text{g B[}a\text{]P-EQ/m}^3(\text{s,d})$, and the toxicity factors used is shown in Table 2.

Table 2. Toxicity factors for the 15 PAH analysed [3].

PAH compound	Equivalence factor	PAH compound	Equivalence factor
Acenaphthene	0.001	Chrysene	0.03
Acenaphthylene	0.001	Dibenz[<i>a,h</i>]anthracene	1.1
Anthracene	0.0005	Fluoranthene	0.05
Benz[<i>a</i>]anthracene	0.005	Fluorene	0.0005
Benzo[<i>b</i>]fluoranthene	0.1	Indeno[<i>1,2,3-cd</i>]pyrene	0.1
Benzo[<i>k</i>]fluoranthene	0.05	Phenanthrene	0.0005
Benzo[<i>ghi</i>]perylene	0.01	Pyrene	0.001
Benzo[<i>a</i>]pyrene	1		

Results and discussion

The main results are shown in Table 2. The range for the dioxin concentration represents the measured values, without the congeners below the detection limits, and the value including the detection limit for these congeners.

LEVELS IN INDUSTRIAL AND OTHER MATRICES

Table 3. Measurement results from the oil plant

Parameter	Unit	Sample A	Sample B	Average
Dioxins	pg I-TEQ/m ³ (s,d)	0.56 – 0.67	0.32 – 0.59	0.44 – 0.63
Dioxins (at 6% O ₂)	pg I-TEQ/m ³ (s,d, 6% O ₂)	0.40 – 4.8	0.23 – 4.2	0.32 – 4.5
Dioxin emission factor	ng I-TEQ/ton oil shale	0.3 – 3.5	0.2 – 3.1	0.2 – 3.3
Dioxins in ash	ng I-TEQ/kg dry ash	1.9 – 2.9		1.9 – 2.9
Naphthalene (at 6% O ₂)	mg/m ³ (n,t, 6% O ₂)	8.6	6.3	7.5
PAH (at 6 % O ₂)	µg B[a]P-TEQ/m ³ (n,t, 6% O ₂)	1.9	1.1	1.5
Particles (at 6% O ₂)	mg/m ³ (s,d, 6% O ₂)	150	350	250
Flue gas temperature	°C	131	134	133
Flue gas flow (actual)	m ³ /h	164,000	167,000	164,000
Flue gas flow (standard)	mg/m ³ (s,d)	74,000	75,000	74,000
H ₂ O content (wet gas)	%	33.3	33.0	33.1
O ₂ content (dry gas)	%	0	0	0
CO ₂ content (dry gas)	%	> 20	> 20	> 20
CO content (dry gas)	mg/m ³ (s,d)	> 1000	> 1000	> 1000

(s,d): s refers to the standard conditions 0°C and 101.3 kPa, and d refers to dry gas.

The dioxin concentrations in emission samples are lower than those from the power plants /6/. Contrary to this, the concentration in the ash is slightly higher, but still very low, with four congeners below the limit of detection.

Dioxin emission has been measured at the Stuart Oil Shale Project in Australia. Their process follows the same principle for producing oil from oil shale, as in the Estonian Oil plant, but the real process is pretty much different, and emissions can only be compared with strong reservations. Four samples from May and August 2000, showed an emission of 0.335 ng I-TEQ/m³, 0.345 ng WHO-TEQ/m³, 0.21 ng I-TEQ/m³ and 0.3 ng WHO-TEQ/m³ respectively [5]. The reference oxygen concentration is not reported.

The Australian and the Estonian emissions are very different. The Australian four samples are 0.3 ng WHO-TEQ/m³ in average, and the Estonian samples are in the range of 0.3 to 0.6 pg I-TEQ/m³, depending of the reference oxygen conditions. The values in I-TEQ and WHO-TEQ units cannot be compared directly, but as the TEF factor is only different for three of the 17 congeners, they normally only differs a few percent from each other. In this way the Estonian samples is about 1000 times lower than the Australian samples.

The very low concentration in the flue gas could be due to very low excess air in the combustion, only leaving 0.2 – 0.3 % in the flue gas O₂ in top of the furnace. Dioxins needs oxygen for the formation, and in absence of oxygen it cannot be formed, and low oxygen concentration is believed to considerable reduce the ability of forming dioxin, but it should also lead to lower concentrations in the ash.

It is considered more likely, that dioxin is formed in the combustion process, and higher concentration is present after the furnace, but the heat exchange system, where the hot flue gas is used for transportation and preheating the incoming oil shale, is functioning as an effective dioxin abatement, by adsorbing the dioxins to the oil shale particles. However, the dioxin concentration is believed to be rather low after the furnace, as indicated by the relatively low concentration in the ash.

Emission of PAH and naphthalene

The naphthalene and PAH concentrations was much lower than the Danish emission limit values, as shown in Table 4.

Table 4. PAH and naphthalene from oil plant

Parameter	Unit	Danish Emission limit value	Measured values
Naphthalene	mg/m ³ (s,d, 6% O ₂)	300	7.5
PAH	µg B[a]P-TEQ/m ³ (n,t, 6% O ₂)	5.0	1.5

Many different organic compounds can be formed by incomplete combustion, which is most likely to occur in the furnace, if the O₂ concentration is as low as the 0.2 – 0.3 % found in the upper part of the furnace. The emission of TOC (Total Organic Carbon) has previously been measured by EERC to 7.8 g/m³(s,d). So there is obviously a high emission of not identified organic compounds.

Total dioxin emission

The total emission of dioxins from the Oil Plant has been estimated to less than 0.2 mg I-TEQ/year, based on the calculated emission factors and a total yearly consumption of oil shale at 0.8 Mt.

The dioxin contents in total ashes from the oil plant were very low compared to other combustion plants. Based on this single sample, the total yearly dioxin emission with the ashes is estimated to approximately 700 mg/year, in approx. 350,000 t/year of ashes

Conclusions

All the measured dioxin emission concentrations from the oil plant are very low, and much lower than the EU emission limit value for MSWI at 0.1 ng I-TEQ/m³(n,d). The total emission of dioxins is estimate to 0.2 mg/year to the air, and 700 mg/year with the ash.

It is likely, that dioxins are formed in the combustion process, and higher concentrations will be present after the furnace, but the heat exchange system, where the hot flue gas is used for transportation and preheating the incoming oil shale, could function as an effective dioxin abatement, by adsorbing the dioxins to the oil shale particles.

The naphthalene and PAH concentrations was much lower than the Danish emission limit values, but there is obviously a high emission of other and not identified organic compounds

Acknowledgements

The authors would like to thank the Danish environmental assistance to Eastern Europe (DANCEE), who has sponsored the project, EERC technicians for assistance in sampling, the Plant Managers and his staff for cooperation and support during the sampling.

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