

PCDDs/PCDFs EMISSION FROM POWER STATION USING COKE-OVEN GAS AS A FUEL

Kim Sam-Cwan, Na Jin-Gyun, Choe Sung-Hun, Lee Jung-Hee, Kim Yeon-Ho, Hwang Seung-Ryul,
You Jae-Cheon¹, Choi Jung-Ho¹, Lee Chang-Jae¹, Choi Kyung Sik¹, Hwang Yong-Youl¹

*NIER (National Institute of Environmental Research), Environmental Research
Complex, Kyungseo-Dong, Seo-Ku, Inchon, 404-170, Republic of Korea*

¹*Analytical Research Center, Environmental Management Co., Boondang-gu Hasanwoon-dong Mt.
26-4, Sungnam City, Kyonggi Do, 463-430, Republic of Korea*

Introduction

Coke is used as a major fuel and a reducing agent in the manufacture of iron and steel. Coke is the carbonized material produced by the pyrolysis of certain coals such as coking or bituminous coals at a high temperature: flue gas temperature is normally 1,150–1,350 °C, indirectly heating the coal up to 1,000–1,100 °C. The coke making process can be subdivided into: 1) coal preparation, 2) battery operation, 3) coke handling and preparation, 4) collection and treatment of coke-oven gas with recovery of by-products¹.

First, coal preparation comprises bed blending, bunker blending and crushing, and recycled substances such as tar can be added at this blending stage. Coke-oven battery operations include coal charging, heating of chambers, coking, coke pushing and quenching. In coal charging, pulverized coal (70–85% is <3mm) is charged into coke ovens, which are approximately 12m long, 4m high and 0.5m wide, equipped with doors on both side. Each oven in the battery can hold up to 30 tons of coal. The single coke ovens are separated by heating walls, in which inside temperatures are usually set between 1,150 and 1,300 °C. Cleaned coke-oven gas is used as a fuel, and other gases like blast furnace gas can be used as well. Charged coal is coked at a temperature of 1,000–1,100 °C for 16–17 hours, producing the coke-oven gas of which composition depends on coking time and coal composition. For each ton of coke produced, approximately 3kg of NH₃ and 2.5kg of H₂S are generated. In some cases, light oil that contains some aromatics such as benzene, toluene and xylene is recovered from the raw coke-oven gas as valuable by-product. Up to 15 kg of light oil can be recovered per ton of coke produced. For gas cooling, the hot pyrolyzed coal gas, coming from the coke ovens, enters the ascension pipes at a temperature of approximately 800 °C, then it is directly cooled in the goose neck by ammonia-liquor spray to a temperature of about 80 °C. After cooling, coke-oven gas is collected to reservoirs as a fuel for power generation because it contains a lot of combustibles such as hydrogen (55.9%), methane (27.4%), carbon monoxide (7.3%) and hydrocarbons (3.1%), thus having a calorific value of approximately 4,450kcal/Nm³. Coke is removed from the ovens by pushing car, and further treated to improve blast furnace productivity.

Blast furnace gas and oxygen converter gas are used as fuels for power generation in the iron and steel foundries as well. Major components of blast furnace gas are carbon monoxide (20.0–23.5%) and hydrogen (1.6–6.0%), having a calorific value of 680–830kcal/Nm³. Unlike the blast gas, oxygen-converter gas contains mainly carbon monoxide at a concentration of above 60%, and its calorific value is approximately 2,000 kcal/Nm³. In comparison to coke-oven gas, since blast furnace gas and oxygen-converter gas have relatively low calorific values, generally these three gases are properly mixed at certain ratios when they are used as fuels. In particular,

these gases from coking, melting and converting processes may contain a small portion of chlorine compounds due to the inherent chlorine contents of coals and iron ores. Thus, it can be thought that chlorine compounds may provide the formation condition of polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/ PCDFs) when they are burned. More recently, some papers reported PCDDs/PCDFs emissions from coke oven² and oxygen converter³.

This study, therefore, was performed to investigate how much PCDDs/PCDFs are produced at the power station, where the coke-oven gas mixed with blast gas and converter is used as a fuel, and to take a proper countermeasure for reducing the emission amounts of pollutants.

Material and Methods

Two power stations, which use coke oven gas (COG), blast furnace gas (BFG) and Linz-Donawitz converter gas (LDCG) as fuels, were selected from two iron-and-steel manufacturing factories in Korea. PCDDs/PCDFs samplings were achieved two times at the stacks of each stations by using a sampling train, which consisted, in order, of a probe, a cylindrical filter, two impingers (one was filled with 250 ml of distilled water, and the other was empty), a sorbent (XAD-2) trap, and two impingers (one was filled with 150 ml of ethylene glycol, and the other was empty). After sampling, the collected PCDDs/PCDFs samples were extracted and pretreated, according to the Korean Standard Testing Method for Dioxins and Furans⁴, and were also analyzed by HRGC/HRMS (high resolution gas chromatograph/high resolution mass spectrometer: Micromass Co., Autospec Ultima) above 10,000 resolution with an SP-2331 column of 60m × 0.32mm ID × 0.25µm. HRGC/HRMS analytical condition for PCDDs/PCDFs is listed in table 1. Toxic equivalents, expressed as 2,3,7,8-TCDD (TEQ) values, were all calculated by using the international toxicity equivalency factor (I-TEF) without the correction by oxygen concentration in flue gases.

Results and Discussions

PCDDs/PCDFs emissions were in the range of 0.017 to 0.023ng-TEQ/Nm³, and averaged 0.021ng-TEQ/Nm³ from four measurements. Off-gases contained four times more PCDFs than PCDDs, showing that the ratio of PCDDs to PCDFs was 19:81 on average. The most abundant 2,3,7,8-congener was 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 40.5% and 9.5% of total TEQs, respectively. The most toxic 2,3,7,8-TCDD was detected at the level of 6% of total TEQs. In particular, emission pattern of 2,3,7,8-PCDDs/PCDFs was very similar to that of ferrous metal melting furnaces such as sintering furnace and electric furnace in a fact that three major 2,3,7,8-congeners were 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD and 1,2,3,6,7,8-HxCDF, and their compositional percentile was about 60% to total TEQs.

Emission volumes of off gases averaged about 6,180 Nm³/min, and oxygen concentrations in off gases averaged approximately 4.8%, ranging from 4.1% to 5.6%. But, carbon monoxide concentrations in emission gases showed a considerable difference by power station: one was 2ppm, the other was 876ppm on average. This emission concentration difference of carbon monoxide can be explained by the compositional difference of a fuel used for power generation. That is, in the iron and steel foundries, BFG, COG and LDCG are used as fuels for electric power generation by properly mixing them at certain ratios, but they contains the different concentrations

of carbon monoxide, showing that LDCG (above 60%) has much higher concentration than BFG (5%) and COG (5%). Thus, if the proportion of LDCG in a fuel predominated those of BFG and COG, and the air supply for combusting fuel was insufficient, carbon monoxide could be released into the atmosphere as a high level.

Table 2. PCDDs/PCDFs emissions of power station using COG, BFG and LDCG as fuels in the iron and steel foundries

(Unit: ng TEQ/Nm³)

2,3,7,8-PCDDs/PCDFs	Power Station 1		Power Station 2		Mean (n=4)	
	1 st	2 nd	1 st	2 nd		
2,3,7,8-TCDD	0.001	0.001	0.001	0.002	0.001	5.95
1,2,3,7,8-PeCDD	0.002	0.002	0.002	0.002	0.002	9.52
1,2,3,4,7,8-HxCDD	0.000	0.000	0.000	0.000	0.000	0.00
1,2,3,6,7,8-HxCDD	0.001	0.000	0.001	0.000	0.001	2.38
1,2,3,7,8,9-HxCDD	0.000	0.000	0.001	0.000	0.000	1.19
1,2,3,4,6,7,8-HpCDD	0.000	0.000	0.000	0.000	0.000	0.00
OCDD	0.000	0.000	0.000	0.000	0.000	0.00
PCDDs	0.004	0.003	0.005	0.004	0.004	19.05
2,3,7,8-TCDF	0.001	0.001	0.002	0.002	0.002	7.14
1,2,3,7,8-PeCDF	0.001	0.001	0.001	0.001	0.001	4.76
2,3,4,7,8-PeCDF	0.009	0.008	0.010	0.007	0.009	40.48
1,2,3,4,7,8-HxCDF	0.001	0.001	0.001	0.001	0.001	4.76
1,2,3,6,7,8-HxCDF	0.002	0.002	0.002	0.001	0.002	8.33
2,3,4,6,7,8-HxCDF	0.002	0.001	0.002	0.001	0.002	7.14
1,2,3,7,8,9-HxCDF	0.000	0.000	0.000	0.000	0.000	0.00
1,2,3,4,6,7,8-HpCDF	0.000	0.000	0.000	0.000	0.000	0.00
1,2,3,4,7,8,9-HpCDF	0.000	0.000	0.000	0.000	0.000	0.00
OCDF	0.000	0.000	0.000	0.000	0.000	0.00
PCDFs	0.016	0.014	0.018	0.013	0.017	80.95
PCDDs+PCDFs	0.020	0.017	0.023	0.017	0.021	100.00

Note: The figures in shaded areas represent the compositional percentiles of each 2,3,7,8-congeners to total TEQs.

Conclusions

The emission pattern of PCDDs/PCDFs from power station using BFG, COG and LDCG in the iron and steel foundries could be summarized as follows:

- 1) PCDDs/PCDFs emission levels were in the range of 0.017 to 0.023ng-TEQ/Nm³, and averaged 0.021ng-TEQ/Nm³
- 2) PCDFs showed an approximately four times higher concentration than PCDDs, showing that the ratio of PCDDs to PCDFs averaged approximately 19:81.
- 3) The main contributor to total TEQs was 2,3,4,7,8-PeCDF followed by 1,2,3,7,8-PeCDD, and their TEQ values constituted 40.5% and 9.5% of total TEQs, respectively.
- 4) Carbon monoxide concentrations in emission gases showed a considerable difference by power station: one was 2ppm, the other was 876ppm on average.

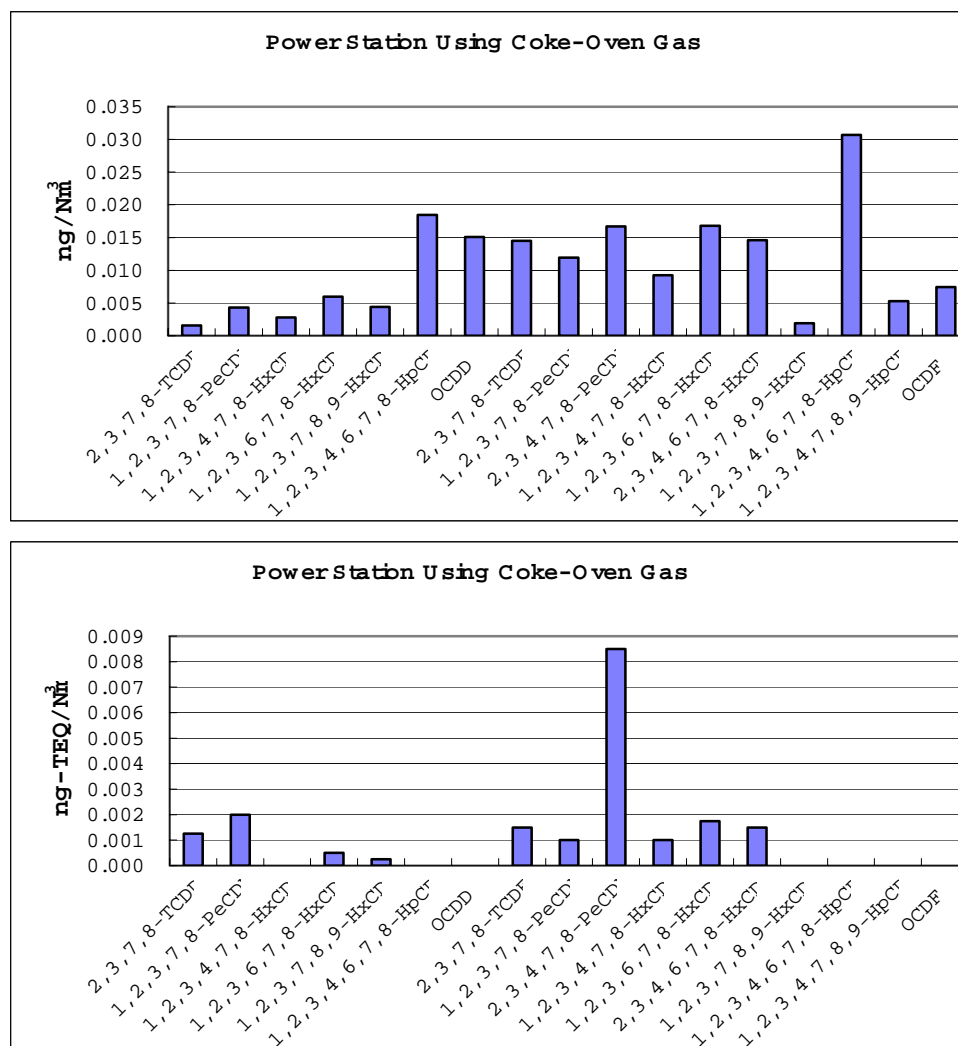


Figure 2. 2,3,7,8-congener profiles in power station using COG, BFG and LDCG as fuels.

References

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