DIOXIN CATALYTIC FORMATION IN FIREPLACES AND COAL HEATING STOVES IN POLAND

Grochowalski A.[1]*, Węgiel M.[1], Maslanka A.[1], Chrząszcz R.[1], Chyc M.[2]

[1]Department of Chemical Engineering and Technology, Kraków University of Technology, Kraków, Poland
agrochow@chemia.pk.edu.pl, www.dioksyny.pl
[2]Grupa Azoty S.A. Azoty Tarnów (Chemical Factory), Tarnów, Poland

Introduction

The paper describes a result of the experiments of the catalytic effects of copper in promoting formation of polychlorinated dibenzodioxins and dibenzofurans (dioxin) during wood burning in fireplaces and coal burning in boilers for power generation.

Certain metals act as catalysts for halogenated aromatic compounds formation in thermal processes, providing a surface upon which dioxins can readily form during and post-combustion processes on the fly ash and bottom ash obtained from wood or coal combustion[1].

Copper is one of the most potent catalyst for dioxin-like compounds formation in thermal processes and have been found in multiple studies to be correlated with increased dioxin/furan formation[2-5].

The catalyst used in this experiment is commercially available on the market in Poland and widely used for chimney cleaning as a soot removal agent in house heating stoves, fireplaces as well in power generation boilers. It contains mainly copper sulphate and ammonium chloride. In numerous of industrial scale boilers the catalyst is continuously feed with the average load of 1 kg/ton of hard coal.

Produced during combustion of volatile copper compounds catalyze the oxidation of carbon monoxide and unburned soot particles. At temperatures above 400º C, copper salts are an efficient catalyst for the formation of dioxins. This process is uncontrollable.

It has been shown in this experiment that even if dioxin concentration is relatively low from burning a clean wood in fireplace only, copper salt if present, significantly rise up in dioxin concentration in bottom ash, fly ash as well in stack gas.

Materials and methods

The experiment was carried out using a typical, a closed fireplace where it was burned seasoned beech, oak and birch wood. In addition, tests were performed for the combustion of coal from local Coal Mine Company SA KWK "Piast", Bieruń, Poland. The average calorific value of 26 MJ / kg. Ash content of ca. 10%. Sulfur content of 0.9%. The fraction of 8 - 25 mm.

Wood and coal is burnt in the range of 2 - 3 kg / h using manual feeding. The exhaust gases are discharged into the chimney with glazed ceramic surface. Natural draft. The present study was the bottom ash resulting from the combustion of wood and coal, as well as an identical process with the addition of a catalyst, for removing soot from the chimney. In this case, a small bag containing 100g of the catalyst is directly placed on burning coal or wood chips. The ash collected for analysis at the end of the combustion cycle, which lasted 5 hours. The ash collected in its entirety, ground to a powdery form, and homogenized.

Stored for analysis in sealed glass jars in the dark at room temperature.

The exhaust gases were collected in accordance with EN-1948 p.1 using filter/condenser method.

Dioxins in ash and stack gas samples were determined in accredited Laboratory for Trace Organic Analyses of Krakow University of Technology in Poland. The methodology has been described elswhere[6].

Results and discussion

For clean beech, oak and birch wood burning in closed fireplace in this work, the bottom ash and fly ash obtained from ca 15 kg of burned wood, contained dioxin on the level of 10.6 ± 0.85 ng-I-TEQ/kg and 2.8 ± 0.4 ng-I-TEQ/kg respectively. The use of the catalyst caused dioxin concentration of about 15,600 ng I-TEQ/kg in bottom ash and even 30,000 ng I-TEQ/kg in fly ash with the uncertainty of 25 - 50%. In stack gas the concentrations were 0.05 ± 0.01 ng I-TEQ/m^3 and 350 ± 50 ng I-TEQ/m^3 respectively. HCB and PeCB catalyzed formation also can be observed, however in much less scale.

For hard coal firing in this work, the bottom ash and fly ash obtained from ca 10 kg of burned coal in closed stove feeded manually, contained dioxin on the level of 1.60 ± 0.12 ng-I-TEQ/kg and 1.45 ± 0.10 ng-I-TEQ/kg respectively. The use of the catalyst caused dioxin concentration of about 550 ng I-TEQ/kg in bottom ash and 1200 ng I-TEQ/kg in fly ash with the uncertainty of 20 - 30%. In stack gas the concentrations were 0.010 ± 0.005 ng I-TEQ/m^3 and 28 ± 5 ng I-TEQ/m^3 respectively. HCB and PeCB catalyzed formation was observed in this case, however - like for wood burning - in much less scale.

It has been shown that the use of this catalyst causes a few hundred fold increase in the content of dioxins in the bottom ash and more than one hundred fold increase in the emission of dioxins in the exhaust gas as compared to the clean combustion of the fuel be added catalyst.

A higher content of dioxins in bottom ash as compared to the stack gas comes from the fact that at the time of the introduction of catalyst bag to the fuel burned on the grid dioxin forms at maximum amount. During the combustion activity of the catalyst decreases which reduces the weight of the formed dioxins.

In the bottom ash, these compounds remain as the majority component of the package along with the ash falls to the bottom of the combustion chamber and stays there. Probably even then there is a synthesis of dioxins, but this phenomenon has not been studied.

It is important, however, that not only the ash, but also the ceramic body of the furnace and fireplace contains considerable mass of dioxins. This was demonstrated by analysis of the solid scraped from the surface of ceramics - the refractory bricks after the combustion process.

The accumulation of dioxins and HCB in the ceramic that may result in the accumulation of dioxins and HCB in the oven, which uses catalysts containing copper salts.

In power generation plants for no catalyst used in coal fired CFB boiler dioxin in stack gas was below 0.06 ± 0.01 ng I-TEQ/m^3 [6] but the use of the catalyst resulted in dioxin stack gas concentration of 4 ± 2 ng I-TEQ/m^3.

Conclusion is that the result supports a theory of catalytic effect of copper for dioxin formation during wood and coal burning. The use of any additives containing copper as catalyst for soot removal and so on in burning processes should be prohibited.

Table 1: Dioxin concentration in bottom ash from 15 kg of mixed (beech, oak, birch) wood firing
where 100g bag of „Sadpal" catalyst was used. Firing time was 5 hours.
As a result of this experiment were obtained 0.350 kg of bottom ash.

Congener PCDD/F	I-TEF	Congener mass conc. ng/kg	Partial TEQ ng I-TEQ/kg
Wood fired with 100g SADPAL bag			
2,3,7,8-TCDD	1	67	67
1,2,3,7,8-PeCDD	0.5	319	159.5
1,2,3,4,7,8-HxCDD	0.1	915	91.5
1,2,3,6,7,8-HxCDD	0.1	1 450	145
1,2,3,7,8,9-HxCDD	0.1	1 930	193
1,2,3,4,6,7,8-HpCDD	0.01	125 000	1 250
OCDD	0.001	1 370 000	1 370
2,3,7,8-TCDF	0.1	596	59.6
1,2,3,7,8-PeCDF	0.05	1 290	64.5
2,3,4,7,8-PeCDF	0.5	5 370	2 685
1,2,3,4,7,8-HxCDF	0.1	6 550	655
1,2,3,6,7,8-HxCDF	0.1	12 100	1 210
1,2,3,7,8,9-HxCDF	0.1	2 010	201
2,3,4,6,7,8-HxCDF	0.1	48 400	4 840
1,2,3,4,6,7,8-HpCDF	0.01	119 000	1 190
1,2,3,4,7,8,9-HpCDF	0.01	31 200	312
OCDF	0.001	1 110 000	1 110
Summarized result in ng I-TEQ/kg			**15 600 ± 3 600**
Summarized result in ng I-TEQ/kg	**If no catalyst is used (only wood)**		**10.6 ± 0.85**

Table 2: Dioxin concentration in bottom ash from 10 kg of hard coal firing where 100g bag of „Sadpal" catalyst was used. Firing time was 5 hours.
As a result of this experiment were obtained 850 g of bottom ash.

Congener PCDD/F	**I-TEF**	**Congener mass conc. ng/kg**	**Partial TEQ ng I-TEQ/kg**
Hard coal fired with 100g SADPAL bag			
2,3,7,8-TCDD	1	2.95	2.95
1,2,3,7,8-PeCDD	0.5	9.11	4.56
1,2,3,4,7,8-HxCDD	0.1	19.8	1.98
1,2,3,6,7,8-HxCDD	0.1	35.9	3.59
1,2,3,7,8,9-HxCDD	0.1	35.8	3.58
1,2,3,4,6,7,8-HpCDD	0.01	784	7.84
OCDD	0.001	90 800	90.8
2,3,7,8-TCDF	0.1	33.6	3.36
1,2,3,7,8-PeCDF	0.05	84.5	4.23
2,3,4,7,8-PeCDF	0.5	185	92.5
1,2,3,4,7,8-HxCDF	0.1	521	52.1
1,2,3,6,7,8-HxCDF	0.1	570	57.0
1,2,3,7,8,9-HxCDF	0.1	49.0	4.90
2,3,4,6,7,8-HxCDF	0.1	918	91.8
1,2,3,4,6,7,8-HpCDF	0.01	9 140	91.4
1,2,3,4,7,8,9-HpCDF	0.01	851	8.51
OCDF	0.001	29 400	29.4
Summarized result in ng I-TEQ/kg			**550 ± 45**
Summarized result in ng I-TEQ/kg	**If no catalyst is used (only hard**		**1.60 ± 0.12**

Due to the inability to calculate stack gas emissions from coal-fired furnaces for heating individual houses and wood-fired fireplaces not calculated emission of dioxin in stack gas. However, it is demonstrated a significant increase in the emission of dioxins and polychlorinated benzenes in stack gas caused by the use of copper catalysts.

Table 3: Calculated values of dioxin emissions as dispersion of bottom ash in the environment from the combustion of the fuel itself and with the addition of copper catalyst "Sadpal".

		Fuel	**µg I-TEQ / J**	**g I-TEQ / year**
A	**No catalyst**	Hard coal	5.4	2.9
B	**With catalyst**	Hard coal	1800	**972**
			µg I-TEQ / ton	**g I-TEQ / year**
C	**No catalyst**	Wood	0.20	0.04
D	**With catalyst**	Wood	367	**73.5**

Data for calculation: COAL
Annually energy production in Poland from hard coal is ca. **150 TW$_{e}$h**
1 Wh = 3.6 KJ. It gives 540 PJ of energy. Experimental coal calorific value = 26 MJ/kg
10 kg of coal generates ca. 0.0014 µg I-TEQ dioxin if no catalyst and 0.47 µg I-TEQ dioxin with "Sadpal" copper catalyst.

Data for calculation: WOOD
Annually wood consumption in Poland for individual heating is ca. 200 000 tons
15 kg of wood generates ca. 0.003 µg I-TEQ dioxin if no catalyst and 5.5 µg I-TEQ dioxin with "Sadpal" copper catalyst.

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