

Destruction of VOCs and dioxin/furan in flue gas by an electrical discharge

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1. Introduction

Many basic investigations in past decade have been made to destroy toxic pollutants in flue gases by electrical discharge. Reports (1)-(3) show that electrical discharge can efficiently reduce NO_x , SO_x . Others present (4)(5) that volatile organic compounds (VOCs) in chemical industries can be strongly reduced by electrical discharge. A study aimed to destroy chlorine bearing toxic volatile dioxin/furan in flue gas by electric discharge in a pilot-near-scale plant has been performed. This paper shows the results achieved recently.

2. Experimental procedure

Since the chlorine bearing volatile dioxin/furan are extremely toxic, for the sake of safety and efficiency, the experimental procedure has been designed: initially tests at laboratory-scale apparatus with Cl-free substance and then with a Cl-bearing substance, which are all structurally similar to dioxin/furan; finally tests at a pilot-near-scale plant with real gas containing dioxin/furan produced by thermal process at a combustion furnace.

2.1. Laboratory-scale experiment

The electrical discharge reactor applied in the investigation is corona discharge reactor which consists of a needle electrode facing a plate electrode. A gas supply system, a gas reaction chamber and an analysis system were set up. By controlling the pressure in the reactor/reaction chamber and adding substances investigated, direct and indirect treatment can be carried out selectively. After treatment, the remaining substances have been analysed by IR absorption spectrometer or GC/MS.

1. With Cl-free substance The goal of the preliminary tests was to know whether the ring structure similar to dioxin/furan can be destroyed by electrical discharge or by low temperature oxidation. A compound diphenylether with such a ring structure was selected. Under a low pressure condition, the diphenylether was heated to 40°C to obtain an adequate partial pressure of 1 torr. The volume of the reactor is 2.2 litre. The synthetic air including diphenylether with a partial pressure of 1 torr was purged into the reactor, where the total pressure in the reactor was controlled at 750 torr and the corona discharge was generated. This was the **direct treatment**. If the synthetic air was first subjected to the discharge and then mixed with diphenylether of 1 torr partial pressure in a reaction chamber, we refer to **indirect treatment**. Because of no chlorine in the test, it was easy to analyse the gas after treatment by a infrared spectrometry (IR).

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2. With chlorine-bearing substance For further investigation, a compound of 1,2 dichlorobenzene was chosen. It consists of a benzene ring attached with two chlorine atoms at the position of 1 and 2. Because of its toxicity and possible corrosion by its decomposition products, it was reasonable to absorb the emerging products by a solvent, which was then analysed by GC/MS. Figure 1 shows the layout of this test.

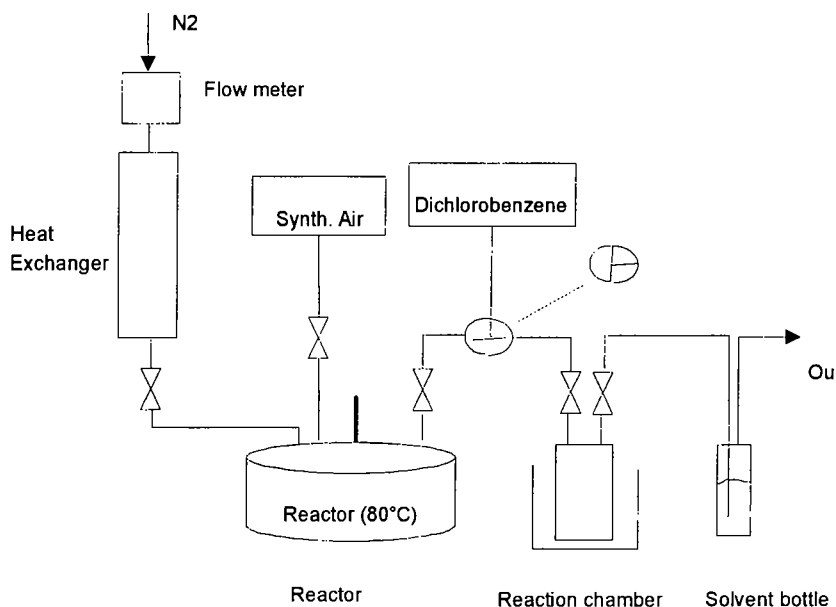


Figure 1 : Layout of the electrical discharge reactor, testing on Cl-bearing substance

For direct treatment, 1 μ l of 1,2 dichlorobenzene was injected into the T-bore of 3 way valve and there heated to 200°C. When the valve barrel was rotated to connect T-bore to the reactor, the vapour of 1,2 dichlorobenzene was flowed into the reactor, which was then filled with synthetic air up to the pressure of 1.23 bar. After 30 minutes exposure to electrical discharge, the barrel was rotated to provide connection to reaction chamber. It allowed further reaction between ring-radical and active radical which took place for 20 minutes. N₂-flow heated to 80°C was used to flush the apparatus with a flow rate of 0.5 l/h for 15 minutes. In the adsorption chamber, hexane as solvent was cooled down by dry ice to prevent vaporisation. The solvents containing the reaction products were analysed by HP 5990 GC and HP 5971A MS.

For indirect treatment, synthetic air to a pressure of 1.23 bar was filled into the reactor. 1 μ l of 1,2 dichlorobenzene was injected into the T-bore of the barrel of the 3-way valve and there heated to 200°C. When the barrel was rotated to be open to the reaction chamber, the vapour of 1,2 dichlorobenzene was flowed into the reaction chamber which was evacuated before. After the synthetic air was subjected to corona discharge for 30 minutes, the barrel was rotated to admit the discharge-treated gas to the reaction chamber so that the active radical mixed and reacted with 1,2 dichlorobenzene vapour in the reaction chamber. This process took about 20 minutes. Again, N₂-flow heated to 80°C was used to flush the apparatus with a flow rate of 0.5 l/h for 15 minutes. In the adsorption chamber, hexane as solvent was cooled down by dry ice to prevent vaporisation.

2.2. Pilot plant-near-scale experiment

In order to destroy dioxin/furan in a real flue gas, a burning of propane and transformer oil mixed with 500 ppm Cl and 50 ppm Cu was performed at a combustion plant. When the temperature in the combustion reached 1200°C, transformer oil was fed into the combustion plant with a rate of 5 litre per hour. Thus, a sufficient quantity of dioxin/furan were intentionally produced. The flue gas with an amount of 140 Nm³/h was quenched and washed. A synthetic air stream of 10 m³/h containing with 7g/m³ active radicals was injected into the flue gas stream, which was produced by a industrial scale electrical discharge reactor (CF1) offered by Ozonia Ltd. at Dübendorf. Two comparison tests were carried out: with and without ozone injection.

The measurement of dioxin/furan in the flue gas was in-situ performed by the Department of Environmental and Trace Analysis, CIBA Ltd., Basel, Switzerland. Each measurement took 4 hours continuously. The details of the measurement is described in report (6). Other components in the flue gas, such as NO, NO₂, CO, CO₂, SO_x, O₂, were measured on-line by a set of apparatus TESTO 339 and TESTO 33. Figure 2 shows the corresponding facilities.

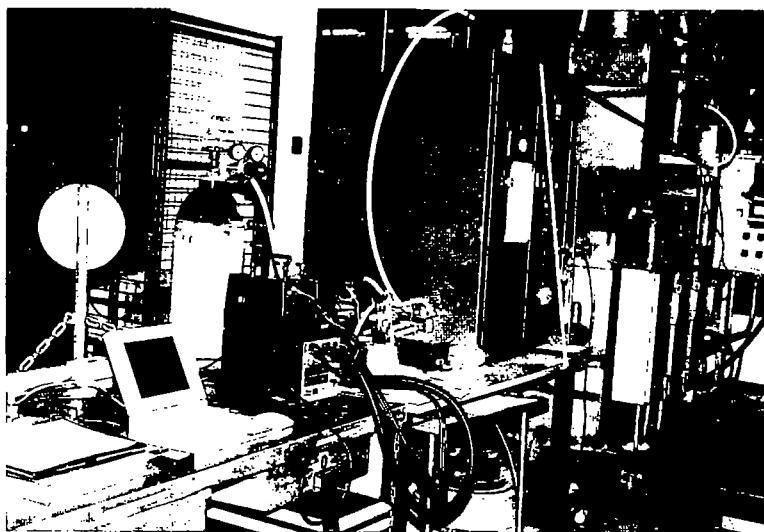


Figure 2 : Testing Facilities: Ozone reactor, flue gas on-line measurement

3. Results

3.1. Test with Cl-free diphenylether in a laboratory-scale reactor

1. Direct treatment Under the corona discharge (negative DC 20kV, 4.18 W) for 30 minutes, the diphenylether with a initial concentration corresponding to partial pressure of 1 torr has almost disappeared, whereas the HNO₃ and O₃ were produced. By the calculation of peak area in the IR spectrum, it can be estimated that the reduction of diphenylether is about 94%.

2. Indirect treatment Under the corona discharge (negative DC 20kV, 5.07 W) for 30 minutes, O₃ was produced from synthetic air. The O₃ containing gases were mixed with diphenylether vapour with a partial pressure of 1 torr. Figure 3 shows that after mixing for 1 minute, the diphenylether peak is strongly reduced, After calculation of the peak area in the IR spectrum, it can be estimated that the reduction of diphenylether by oxidation for 20 minutes is more than 98%.

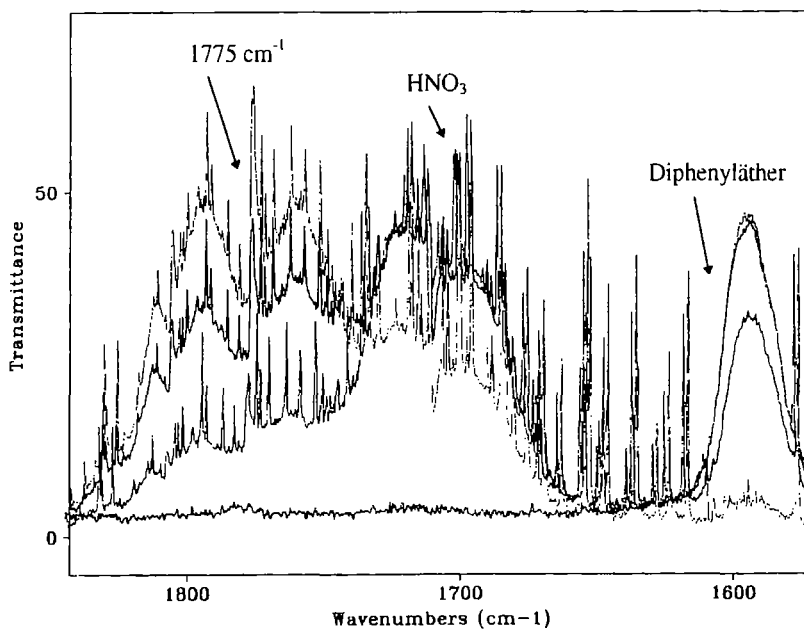
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3. 2. Test with Cl-bearing dichlorobenzene in a labour scale reactor

1. Direct treatment Table 1 shows that under the corona discharge (negative DC 20kV, 4.18 W) for 30 minutes the dichlorobenzene with high initial concentrations is strongly reduced. The reduction rates are between 68% to 88%, respectively.

Table 1 Reduction of dichlorobenzene after direct corona discharge

Test No.	Theoretical conc. in Hexane before discharge (ppm)	Mean measured conc. in Hexane before discharge (ppm)	Measured conc. in Hexane after corona discharge (ppm)	Reduction rate (%)
1	30.46 (65ml)	24.27	3.1	88%
2	30.46 (65ml)	27.40	8.8	68%



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Figure 3: Destruction of diphenylether by mixing with O₃
Green curve: Initial diphenylether concentration
blue curve: concentration after 1 min.
Red curve: concentration after 20 min.

2. Indirect treatment Table 2 shows that under the ozone oxidation (synthetic air corona discharge by negative DC 20kV, 4.18 W for 30 minutes), the dichlorobenzene with high initial concentrations is also reduced. The reduction rates are between 40% to 58%, respectively.

Table 2 Reduction of dichlorobenzene after oxidation by Ozone (indirect treatment)

Test No.	Theoretical conc. in Hexane before O ₃ -oxidation (ppm)	Mean measured conc. in Hexane before O ₃ -oxidation (ppm)	Measured conc. in Hexane after O ₃ -oxidation (ppm)	Reduction rate (%)
3	27.5 (72ml)	20.53	12.3	40
4	29.1 (68ml)	20.45	8.5	58

3.3. Pilot-near-scale test

1. Test with added dichlorobenzene The preliminary test on the Plasmarec plant RIF2 aimed to optimise the characteristic of propane burning behaviour in SCC. The temperature in SCC was fixed at 1200°C. The amount of flue gas was about 140 Nm³/h, the corresponding concentration was approximately: CO₂ 9%, NO 300 ppm, NO₂ 50 ppm, O₂ 8.2%. In the flue gas stream 20 ml dichlorobenzene solution was vaporised in 20 minutes. In order to investigate the destruction behaviour of dichlorobenzene by O₃ in real flue gas, several tests have been carried out without or with 70 g O₃/h injection. Figure 4 shows that after mixing with O₃, there exists no dichlorobenzene peak in the flue gas sample.

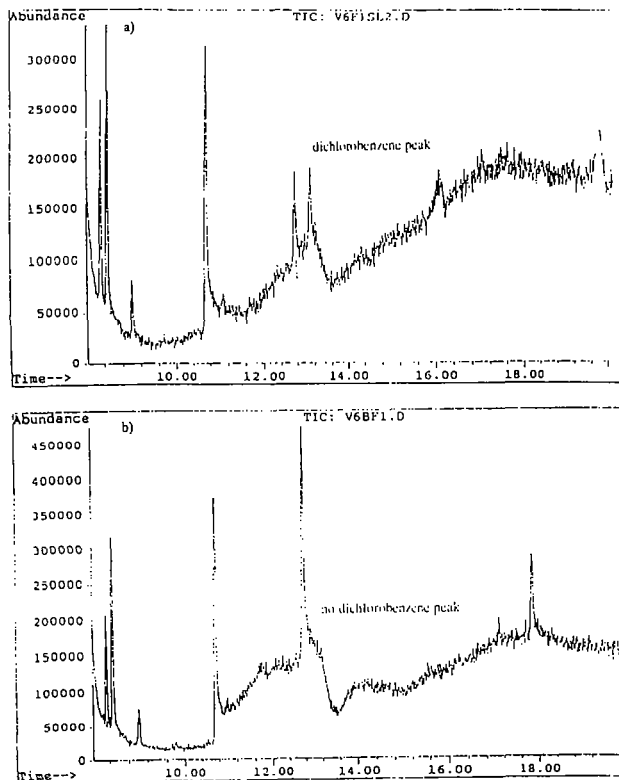


Figure 4 : Dichlorobenzene peak exists (a) and disappears (b) with mixing O₃

2. Test with dioxin/furan The burning of propane and 5 l/h transformer oil mixed with Cl 500 ppm and Cu 50 ppm produced also 140 Nm³/h flue gas. Without ozone injection, the composition of flue gas was: CO₂ 5%, NO 120 ppm, NO₂ 130 ppm, CO 20 - 40 ppm, O₂ 11.2 - 12.6%. After mixing with ozone at 70 g/h, the corresponding composition became: CO₂ - 6.8%, NO 0 - 64 ppm, NO₂

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150 ppm, CO 5 - 0 ppm, O₂ 13 - 16%. Table 3 shows that through the ozone oxidation, the dioxin content in a real flue gas is strongly reduced, the reduction rate is about 90%. The NO content can be fully removed, whereas NO₂ is increased a bit. Since NO₂ is very easily dissolved into water, it is expected that the NO_x-reduction reaches more than 90% as reported in early report(3).

Table 3 Dioxin/furan content before and after ozone oxidation*

		No O ₃ -injection		With O ₃ injection		Reduction
		12. 09. 1995		12. 09. 1995		
		08:15 - 12:17		13:36 - 17:37		
Compound	I-TEQ	O ₂ -cal. ng/m ³	No O ₂ -cal ng/m ³	O ₂ -cal. ng/m ³	No O ₂ -cal ng/m ³	%
2378TCDD	1	3.317	3.019	0.392	0.357	88.2
2378TCDF	0.1	34.698	31.575	5.495	5.000	84.2
Tot. TCDD		46.709	42.505	2.903	2.642	93.8
Tot. TCDF		438.493	399.028	71.267	64.853	83.8
PCDD/F		1333.21	1212.22	117.748	107.151	91.2
Tot. I-TEQ		34.041	37.408	3.076	3.381	91.0

* Ozone injection rate was 70 g/h, Flue gas amount 140 Nm³/h.

4. Conclusions

Based on the primary tests performed at laboratory and at pilot-near-scale plant, the following conclusions can be drawn: 1). Both direct and indirect treatment by electrical discharge can destroy the extremely toxic substances in flue gas, such as dioxin/furan; 2). Indirect treatment destroys about 90% of dioxin in real industrial flue gas; 3). Combination of destroying NO_x, SO_x and dioxin/furan in one step is possible; 4). Convenience in operation and maintenance results in less cost.

Acknowledgement

The authors wish to thank Prof. Dr. W. Zaengl and Dr. T. H. Teich of the High Voltage Laboratory, Swiss Federal Institute of Technology in Zurich, for their co-operation in the project. Many thanks deserves Mr. R. Mueller for his technical assistance. We gratefully acknowledge the financial support of this investigation by the Swiss National Energy Research Fund (NEFF).

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