

REDUCTION OF DIOXIN EMISSION FROM MSW INCINERATOR USING OXYGEN-ENRICHED COMBUSTION TECHNOLOGY: A FULL-SCALE EXPERIMENT OF STOKER-TYPE MSW INCINERATOR

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Abstract

Full-scale experiment was performed to evaluate the effect of oxygen enrichment on the formation and emission of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) from a stoker-type municipal solid waste (MSW) incinerator. Oxygen-enriched air, 23 vol.% (dry basis) oxygen, was used for stable combustion of MSW with a lower heating value of 2500–3000 kJ/kg. Key incinerator operating parameters and composition of flue gas were measured. Oxygen-enriched combustion obviously increased the contents of O₂ and NO_x, significantly decreased CO content, but did not result in significant variations of the contents of SO₂, CO₂, HCl and H₂O in flue gas. With oxygen enrichment, the formation rate of PCDD/Fs was decreased by 9.2% according to TEQ value, and the emission factor of PCDD/Fs was decreased by 19.0%. Moreover, oxygen-enriched combustion did not give rise to a systematical change of the distribution pattern of PCDD/F congeners.

Introduction

Being the largest developing country, China generates annually 170 billion kg of municipal solid waste (MSW), accounting for 26.5% of the total production of the world [1]. The lack of landfill sites for the wastes has forced some big cities to choose the incineration as an alternative technology to treat MSW. The government is planning to construct about 100 commercial-scale MSW incinerators by the year of 2010, including about seventy already existing facilities. However, MSW in China contains a high moisture content of about 50%, with a lower heating value of about 3000 kJ/kg, even below 1000 kJ/kg (e.g., about 1000–2500 kJ/kg in Tianjin during winter), which makes it difficult to be managed by direct incineration for most MSW incineration systems. Co-firing of MSW with agricultural straws and spraying oil are often necessary to improve the combustion chamber temperature to ensure complete combustion with lower emissions of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs).

Oxygen-enriched air combustion of MSW has been proven to be a technique for managing the burning of MSW to obtain both operative and environmental benefits [2–4]. Commercial incinerators with oxygen-enriched air combustion systems have been deployed in Japan and in Germany [5, 6]. It has been found that oxygen-enriched combustion of MSW can reduce PCDD/F emission by 20%–60%. In view of the fact that the lower heating value of MSW results in the insufficient burning and thus possibly increases PCDD/F emission, liquefied oxygen

bomb and a vaporizer for the addition of the oxygen to the combustion air were connected to a stoker-type MSW Incinerator in Tianjin, China. The main purpose of this study is to investigate the effects of using oxygen-enriched combustion technology on the formation and emission of PCDD/Fs from the incineration of MSW with a lower heating value. By the way, the effects of using oxygen-enriched combustion technology on the emission of SO₂, CO, CO₂, NO_x, HCl and H₂O were also investigated.

Materials and methods

Experiment of oxygen-enriched combustion was conducted on a stoker-type MSW incinerator, constructed by Tianjin Teda Environmental Protection Co., Ltd. in Tianjin City in 2004. It has a capacity of about 400 t/d of MSW with the average heating values of 2500–3000 kJ/kg. In order to maintain secondary combustor temperature above 850 °C, about 35 t of cotton straw was mixed into MSW each day. The incinerator and the associated air pollution control devices mainly consisted of a waste feed system, combustor, waste recovery boiler, a semi-dry scrubber (SDS), and a bag filter (BF). The exhaust gas from the combustor is initially cooled by waste heat recovery boiler, and then passes through SDS in which the acid gas is removed by reacting with injected slaked lime slurry. Fly ashes are collected effectively by BF. Liquefied oxygen bomb, a vaporizer and a pressure-controller for the addition of the oxygen were connected with air supply system. A schematic diagram of MSW combustor and injection manner of oxygen is shown in Figure 1. Key incinerator operating parameters, such as refuse feed rate, flue gas temperatures at various positions, primary/secondary air distributions and contents of O₂, CO, CO₂, SO₂, NO_x, and H₂O, are monitored by an extensive computer network system on a “real time” basis. The content of HCl in flue gas was determined using mercuric thiocyanate colorimetric method.

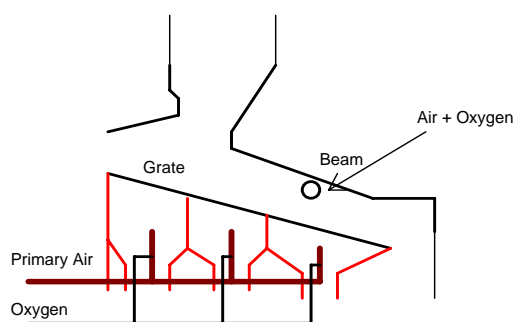


Figure 1 Configuration of MSW combustor and injection manner of oxygen.

Two operating conditions, normal combustion and oxygen-enriched combustion (23 vol.% oxygen content), were established. The train sampling procedure for PCDD/F analysis was conducted at the boiler outlet and BF outlet, respectively. Triplicate samplings were made at each sampling point. At each measurement, more than 1.0 Nm³ of flue gas was collected for about 1.5 h under the condition of isokinetic factor to be with 95–105%. Samples were collected in a multi-component sampling train using filter/condenser method following the Chinese Standard Measurement Procedure HJ/T 77-2001 [7].

As reported in the previous on-line monitoring experiments, Zimmermann et al. (2001) demonstrated that the ‘memory

effects' of PCDD/F formation was significant in real incinerator testing, which may originate from the adsorption-desorption of PCDD/Fs or the deposition of particulate matters on the walls of the boiler and air pollution control devices [8]. In order to prevent or reduce the 'memory effects', 7 hours of steady-state operation was carried out before the start-up of manual train sampling under the condition of oxygen-enriched combustion.

The PCDD/F analysis was performed using isotope dilution technique. The flue gas sample (mixture of XAD resin, dust filter and condensate of rinsing solvent) was initially freeze-dried, and then was spiked with $^{13}\text{C}_{12}$ labeled 2,3,7,8-substituted PCDD/F internal standards (Cambridge Isotope Laboratories, Inc., USA, purities >98%). Extraction was carried out for 24 h in a Soxhlet apparatus using 250 mL toluene. Sample clean-up was achieved by a multi-layer silica gel column and an alumina column as described in JIS K 0311 [9]. The final clean extract was stepwise transferred into a micro-vial and evaporated to dryness with a stream of nitrogen. Ten micro liters of tetradecane containing the recovery standard (1,2,3,4- $^{13}\text{C}_{12}\text{Cl}_4\text{DD}$, 100 pg/ μL) was added to a micro-vial for HRGC/HRMS analysis.

The purified extract was analyzed using an Autospec Ultima high resolution mass spectrometer (Micromass, U.K.) interfaced with a Hewlett-Packard (Palo Alto, CA, USA) 6890 Plus gas chromatograph. A capillary GC column Rtx-2330 (made by Restec) (60 m \times 0.25 mm \times 0.1 μm) was used. Samples were injected in a splitless mode at an injector temperature of 280 °C and at an initial column temperature of 90 °C. After 1.5 min, the temperature was programmed at 25 °C min $^{-1}$ to 180 °C, then at 3 °C min $^{-1}$ up to 260 °C and held for 25 min. The injection port and transfer line temperatures were 280 °C and 250 °C, respectively. The ion source was operated at 250 °C, the electron energy was 37 eV, ionization current was 0.5 mA, ion accelerating voltage was 8 KV and the mass spectrometer was tuned to a mass resolution of 10000 under positive EI conditions. All data were obtained in the selected-ion monitoring (SIM) mode.

Table 1 Main process parameters for operating conditions of MSW incinerator

	Normal combustion	Oxygen-enriched combustion
Refuse feed rate (t/h)	17.4 \pm 1.1	17.2 \pm 1.2
Primary air (km 3 N/h)	28.2 \pm 2.3	27.9 \pm 3.6
Secondary air (km 3 N/h 3)	6.0 \pm 1.2	5.0 \pm 1.6
Furnace temp. (°C)	793.3 \pm 30.2	786.8 \pm 43.3
Superheater inlet temp. (°C)	619.6 \pm 18.7	613.9 \pm 22.3
Economizer inlet temp. (°C)	338.1 \pm 5.4	337.1 \pm 6.1
Boiler outlet temp. (°C)	193.4 \pm 3.5	194.0 \pm 4.9
Semi-dry scrubber inlet temp. (°C)	159.8 \pm 0.3	159.5 \pm 2.4
AC injection rate (mg/Nm 3)	80	80
Bag filter outlet temp. (°C)	151.0 \pm 0.7	151.2 \pm 0.9

Results and discussion

Oxygen enrichment effects on MSW burning efficiency and flue gas composition

The experiment of oxygen-enriched combustion was conducted for 40 h. The primary air was enriched with 23 vol.% (dry basis) oxygen content. A small part of oxygen gas was directly injected into secondary combustor. Main process parameters for operating conditions of MSW incinerator is shown in Table 1. Although the added amount of cotton straw during oxygen-enriched combustion was less by 40 t than during normal combustion, refuse feed rate, air supply and flue gas temperatures at various positions during oxygen-enriched combustion did not show significant differences from those during normal combustion, and also the recovery heat energy during oxygen-enriched combustion was identical to that during normal combustion. These results indicate that oxygen-enriched combustion technology can significantly improve the burning efficiency of MSW.

Oxygen-enriched combustion of MSW obviously increased O₂ level in flue gas. The oxygen content in flue gas was 8.3 vol.% (dry basis) during normal combustion and 9.3 vol.% (dry basis) during oxygen-enriched combustion, respectively (Table 2). The fluctuation ranges of SO₂ and HCl contents in flue gas were larger and oxygen-enriched combustion did not result in the significant changes of their emissions to atmosphere. However, with oxygen enrichment, CO content in flue gas became significant lower and NO_x content in flue gas obviously increased from 330.8±49.9 mg/m³N to 358.5±75.0 mg/m³N. These results further indicate that oxygen-enriched combustion technology significantly improves MSW burning efficiency. In addition, oxygen-enriched combustion of MSW did not give rise to significant variations of the contents of CO₂ and H₂O in flue gas.

Table 2 Composition of flue gas.

	SO ₂ mg/m ³ N	CO mg/m ³ N	CO ₂ %	HCl mg/m ³ N	O ₂ %	NO _x mg/m ³ N	H ₂ O %
Normal combustion	17.9±21.6	13.3±15.0 a ^a	12.0±0.9	65.1±40.6	8.3±0.9	330.8±49.9	29.6±1.1
Oxygen-enriched combustion	16.7±22.0	7.6±14.8 b	12.1±1.4	71.3±48.1	9.3±1.4	358.5±75.0	30.4±1.6

^a SAS ANOVA procedure was run, the difference was significant at 0.05 level when different alphabet attached to the mean value and standard error.

Oxygen enrichment effects on dioxin formation and emission

PCDD/Fs are mainly formed in post-combustor and air pollution control devices at the temperature of 650 °C –200 °C through three main pathways: (i) pyrosynthesis, i.e., high-temperature gas phase formation [10]; (ii) *de novo* mechanism, occurs essentially by a process of the oxidative degradation of unburned carbon species in the presence of a chlorine source [11, 12]; and (iii) precursor mechanism, i.e., formation from most chlorinated aromatic compounds (chlorobenzenes, chlorophenols, PCBs, and chlorinated diphenylethers, etc) [13, 14]. Therefore, the PCDD/F level in flue gas at boiler outlet, where the temperature of flue gas is below 200 °C, can indicate the total formation of PCDD/Fs [15]. PCDD/F concentrations in the flue gases at boiler outlet are shown in Table 3. During oxygen-enriched combustion, the total amount of tetra- to octa- PCDD/Fs in flue gas at boiler outlet was 112.06 ng/m³N, with a TEQ value of 1.883 ng/m³N. Compared with normal combustion, the

formation rate of PCDD/Fs during oxygen enriched combustion decreased by 9.2% according to TEQ value. The formation factor of PCDD/Fs for oxygen-enriched combustion was calculated to be 3.599 $\mu\text{g TEQ/t}$, which was lower by 11.4% than that for normal combustion (4.060 $\mu\text{g TEQ/t}$).

Table 3 Formation and emission of PCDD/Fs under normal combustion and oxygen-enriched combustion

	Formed PCDD/Fs at boiler outlet ng /Nm ³	Emission factor $\mu\text{g TEQ/t}$	Emitted PCDD/Fs at bag filter outlet ng /Nm ³	Emission factor $\mu\text{g TEQ/t}$
<i>I-TEQ</i>				
Normal combustion	2.073 \pm 0.254	4.060	0.099 \pm 0.013	0.194
Oxygen-enriched combustion	1.883 \pm 0.232	3.599	0.082 \pm 0.011	0.157
<i>Total tetra- to octa- CDD/F</i>				
Normal combustion	120.06 \pm 18.45		2.86 \pm 0.45	
Oxygen-enriched combustion	112.06 \pm 12.23		2.66 \pm 0.34	

PCDD/F level in flue gas at bag filter outlet can represent the PCDD/F emission from MSW incinerator to atmosphere. PCDD/F concentrations in the flue gases at bag filter outlet are also shown in Table 3. During oxygen-enriched combustion, the total amount of tetra- to octa-CDD/Fs in flue gas at bag filter was 2.66 ng/m³N, with a TEQ value of 0.082 ng/m³N. Compared with normal combustion, the emission rate of PCDD/Fs during oxygen enriched combustion decreased by 17.1% according to TEQ value. The emission factor of PCDD/Fs for oxygen-enriched combustion was calculated to be 0.157 $\mu\text{g TEQ/t}$, which was lower by 19.0% than that for normal combustion (0.194 $\mu\text{g TEQ/t}$).

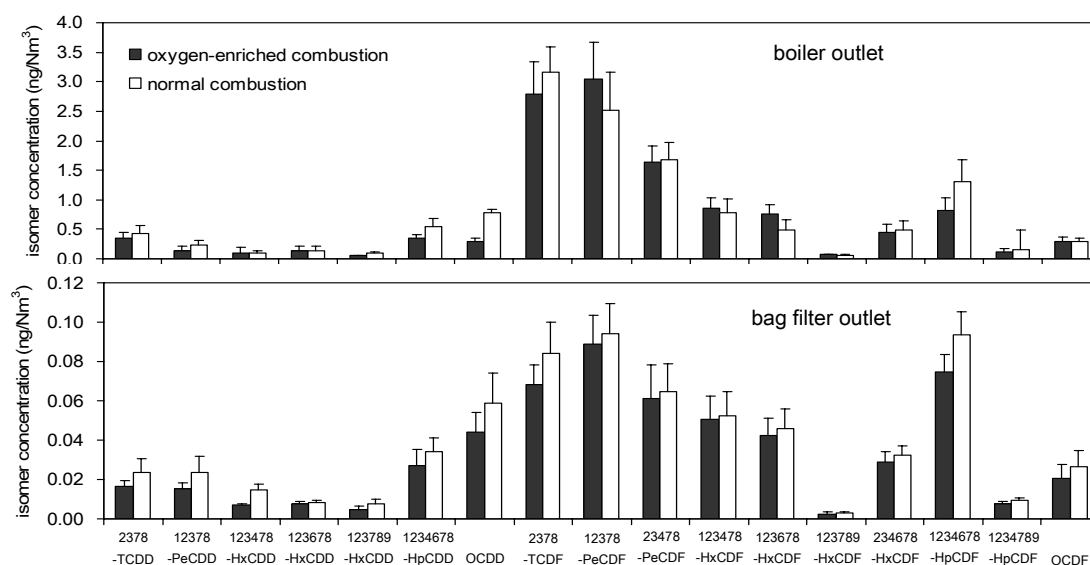


Figure 2 Levels of 2,3,7,8-substitued PCDD/Fs in the flue gases at the bag filter outlet and boiler outlet.

To get a better understanding of the effect of oxygen-enriched combustion on the PCDD/F formation, we analyzed all congeners of tetra- to octa-CDD/Fs. Levels of 2,3,7,8-substituted PCDD/Fs in the flue gases are shown in Figure 2. The distribution patterns of 2,3,7,8-substituted PCDD/Fs for oxygen-enriched combustion were almost identical to those for normal combustion. Oxygen-enriched combustion did not give rise to a systematical change of the distribution pattern of PCDD/F congeners. One of the reasons for this independence can be that the major precursor synthesis (condensation of CPhs) can operate independently of changes under oxidization conditions [13]. Another reason can be that the *de novo* synthesis has the statistical properties [16], and thus oxygen enrichment can only significantly decrease the quantity of formed tetra-to octa-CDD/Fs but not alter the distribution pattern.

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