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A two step Procedure to Investigate the Importance of Combustion Parameters in the Formation of Products of Incomplete Combustion.

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Abstract

An artificial municipal solid waste (MSW) was combusted in a laboratory scale fluidized bed reactor to investigate the influence of different combustion parameters on the formation of products from incomplete combustion. Three parameters were studied; total amount of air, the air distribution between the primary and secondary inlet in the reactor and the temperature of the secondary air. The experiments were planned according to experimental factorial design (MODDE). The investigation consists of one survey study and one complete study. The survey study was performed to verify the experimental domain and its suitability and practicability for combustion efficiency studies. The study consists of online measurements of inorganic gases; CO₂, O₂, CO, NO and total hydrocarbons. This variable enables a quick evaluation of the data. Online measurements and flue gas sampling of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) was performed during the complete study. The procedure with an inexpensive and fast evaluated factorial experimental designed survey study before a complex complete study is a very useful instrument to reduce the time and cost of investigations. The formation of CO, CO₂ and hydrocarbons was very much related to the total amount of air in the system, and the formation of PCDD/F was more correlated to the air distribution between the primary and secondary air inlet.

Introduction

Formation of PCDDs/Fs during combustion processes have been known for a long time. How they are formed are not completely understood, due to a very complex formation mechanism. A correlation between combustion efficiency (CE) and the formation of PCDD/F are known^{1,2}, but exactly which combustion parameters that are involved in the formation are not fully understood. A correlation between the reduction of coplanar PCBs and PCDDs/Fs and the efficiency of the secondary combustion has been found in earlier studies³. I. Fängmark *et al.*⁴ studied the influence of oxygen level (CE), temperature in the bed, flue gas temperature at the sampling point, residence time in the convective section, HCl and H₂O levels on the formation level of PCDDs/Fs. The results show that the most important parameter was the residence time in the convective section, and not the oxygen level in the flue gas. But, the influence of the CE was not studied during extreme low conditions in these experiments, the oxygen level was never lower than 4.9 %.

The aim with this study was to investigate which of the combustion parameters that influence CE and how the formation of PCDDs/Fs was effected. The experiments were performed in a laboratory scale fluidized bed reactor fed with an artificial municipal solid waste (MSW) fuel. The main advantages with the reactor and fuel are that they simulate full scale MSW incinerators very well and experiments with low CE, 96 % can be performed during controlled conditions.

Materials and Methods

The laboratory scale fluidized bed reactor and the artificial MSW

The combustion reactor used in this study is a laboratory scale (5 kW) fluidized bed reactor. It was constructed in order to achieve reproducible and well controlled combustion experiments combined with low costs. The operating parameters of the reactor such as feeding rate and gas flows are all computer controlled. The primary and secondary air can be pre-heated to a temperature around 500°C, with a flow rate between 0-120 dm³/min. The convective of the reactor consists of five horizontal sections. The sampling port for inorganic combustion gases, CO₂, O₂, NO and NO₂ was located at the end of section two and the sampling for hydrocarbon was located at the beginning of the same section. The reactor is easily cleaned between different experiments in order to minimize the memory effects.

The inorganic gases CO₂, CO, NO, NO₂, and O₂ were continuously measured in the flue gas. CO₂ and CO (0-1000 ppm) were detected by an IR-instrument and the NO, NO₂, O₂ and CO (1000-10000 ppm) levels by electrochemical sensors. A flame ionization detector was measuring the level of incomplete combusted hydrocarbons in the flue gas; the level was afterwards recalculated as hexane. The sampling of PCDD/F, was done isokinetically at the end of section five and the gas volume was normalized to 1 atm dry gas at 0 °C. The extraction and clean-up procedure was performed according to standard methods^{5,6} and analysed with a HRGC/HRMS. An artificial MSW with same proportion of the main components as in a normal MSW in Sweden was composed to facilitate studies on MSW combustion. The content in a MSW in Sweden was characterized and divided into 8 material categories; Paper, Plastic, Laminate, Textile, Glass, Kitchen and garden sweepings, Remaining combustible and Remaining incombustible⁷.

Statistical experimental design

By changing all factors (variables) simultaneously in a systematically way by factorial design instead of "one variable at a time" (OVAT) approach, the experimental domain will be scanned more efficiently⁸. The experiments in this investigation were planned according to experimental design (MODDE 3.0 by Umetri). This investigation was performed in two steps, one survey study before the complete study, two kinds of experimental designs were therefore used. One central composite face (CCF) design in the survey study and one complete factorial design (CFD) in the full study. A complete factorial design with three factors studied in two levels contains of 2³ experiments, one in each corner of a cube. Three experiments in the middle of the experimental domain "cube" were added to determine the experimental bias. A CCF design is an expanded CFD design with experiments on each surface of the cube i.e. the factors was investigated in three levels instead of two⁹. Figure 1 shows two schematic pictures of a CFD and CCF design. All experiments were performed in random order to minimise the effect of systematically errors.

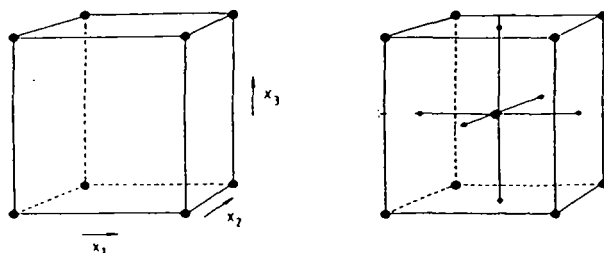


Figure 1a, schematic pictures of a CFD and 1b a CCF design.

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Results and Discussions

Survey study

The aim with the survey study was to quickly examine if the selected experimental domain was suitable and practicable for CE-studies, without any expensive and time consuming analysis, such as PCDD/F analysis. Three factors were selected to be investigated, total air in to the reactor (Air), distribution of the air between primary and secondary inlet (Sec) and the temperature of the secondary air (Tep). Table 1 list the factors and levels and Table 2 each experiments actual setting.

Table 1 The selected factors and theirs three levels.

Factors	-	0	+
Total air flow (l/min)	90	120	150
%-flow in the secondary air (%)	20	45	70
Temperature of the secondary air (°C)	50	200	350

The residence time in the post combustion zone is of importance for the PCDD/F formation but not so essential for the inorganic gases. To minimise the effect of different residence time due to different total air flow in the experiments, nitrogen was added to the bed to a constant flow of 150 dm³/min. The survey study consist only of online measurements: temperatures, CO₂, O₂, CO, NO and total hydrocarbon, no flue gas sampling was performed. When the settings of each experiment were obtained, the measurments was performed during 30 minutes, afterwards the seetings were changed for the next experiments. The results from the survey study is listed in Table 3, each data is an average value during 15 minutes of combustion. The variation within the emission data, of the frequency of the CO-peaks in the experiments was rather high, which bring a CE (CE (%)=100*CO₂/CO₂+CO) variation between 100 and 96.9 %

Table 2 The settings of the experiments in the survey study (CCF-design).

Exp. No	Run Order	Total air (dm ³ /min)	Secondary air (%)	Nitrogen flow (dm ³ /min)	Temperature (°C)
1	8	90	20	60	50
2	10	150	20	0	50
3	7	90	70	60	50
4	1	150	70	0	50
5	15	90	20	60	350
6	2	150	20	0	350
7	16	90	70	60	350
8	3	150	70	0	350
9	9	90	45	60	200
10	12	150	45	0	200
11	4	120	20	30	200
12	13	120	70	30	200
13	5	120	45	30	50
14	14	120	45	30	350
15	17	120	45	30	200
16	6	120	45	30	200
17	11	120	45	30	200

Table 3 Data from the survey study, each data is an average of 15 minutes.

Exp. No	Bed (°C)	F1 (°C)	O ₂ (%)	CO ₂ (%)	CO (ppm)	CO >4000 ppm (peaks/h)	NO (ppm)	FID (ppm)	CE (%)
1	738	772	3.4	8.8	2691	1.6	137	14	97.0
2	779	797	11.9	8.6	67	0	295	2	99.9
3	724	875	3.8	13.1	3257	2.0	457	112	97.6
4	814	846	9.7	10.4	377	0.2	374	0	99.6
5	795	878	4.9	10.5	3283	2.0	273	201	97.0
6	853	856	10.9	9.2	32	0	231	3	100
7	800	1066	3.3	12.8	4079	3.0	841	4	96.9
8	838	999	9.0	11.1	671	0.2	802	3	99.4
9	757	913	3.8	12.8	3401	2.2	377	178	97.4
10	833	836	11.5	8.9	23	0	274	1	100
11	804	820	8.7	8.4	243	0.1	295	2	99.7
12	781	883	6.5	10.1	74	0	618	2	99.9
13	785	828	7.2	10.8	1316	0.5	172	2	98.8
14	830	904	7.1	10.5	399	0.1	537	6	99.6
15	845	883	7.3	11.0	196	0.1	237	0	99.8
16	799	847	7.0	10.6	519	0.1	228	5	99.5
17	715	838	6.6	10.5	624	0.2	485	3	99.4

An evaluation of the data with the statistical program MODDE was then performed to study if there was any systematic variation within the data. MODDE was using partial least square (PLS) regression to fit a model between the emission data "responses" and the factors. With PLS all responses are fitted simultaneously to one model. The factors are orthogonal and scaled to unit variance. The results from the calculation are shown in Figure 2.

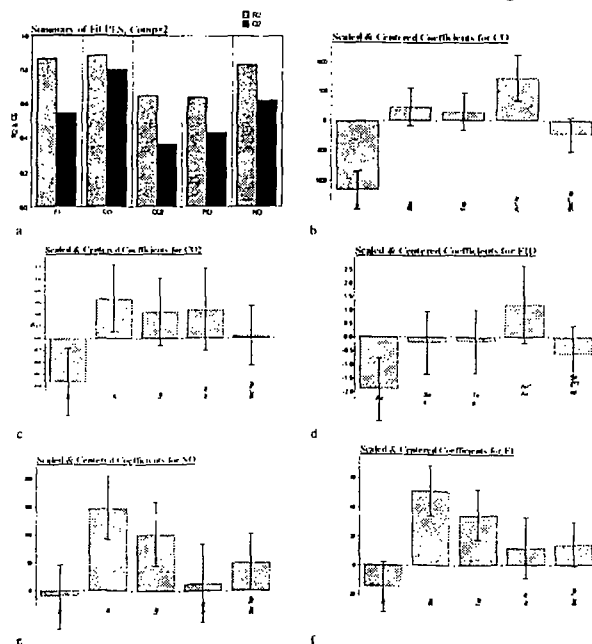


Figure 2 Significant factors and the model explanation and prediction for the formation of CO, CO₂, hydrocarbons, NO and temperature in freeboard 1.

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Figure 2a show the explanation (R2) and prediction (Q2) capacity of the responses in the model. The CO, CO₂ and FID hexane emission were strongly negative correlated with the total amount of air added to the combustion (Figure 2b-1d) i.e. low level of air supply and the formation levels of CO, CO₂ and hexane will increase. The temperature of the secondary air was not significant for any of the three compounds but the distribution of the air between primary and secondary air inlet was a slightly significant for the CO₂ emission. The NO emissions and the temperature 350 mm above the bed, free-board 1 (F1) were distinct positive related with the temperature of the secondary air and the distribution of the air (Figure 2e and 2f); i.e. a important flow of preheated secondary air will give rise to higher formation levels of NO.

The results from the survey study verified that the experimental domain was suitable for CE studies, i.e. the factors were selected in interesting levels. The difference between a CCF design and a CFD is that quadratic terms are also calculated in the model together with linear and interaction terms. The only responses that have a significant quadratic term (Air*Air) is CO. The rest of the responses have only linear relationships to the factors. This give rise to a more simplified design, CFD with fewer experiments, 11 instead of 17, was selected to the complete study.

Complete study

Each experiment in the full study was performed during one experimental day. The reactor was cleaned between each experiment to minimize the memory effects. The factor levels were identical with the survey study and the total flow was 150 dm³/min in each experiment to minimize the effect of different residence time for the flue gas. The formation levels of PCDD/F in the different experiments in the CFD are listed in Table 4.

Table 4 The settings of the factors in each experiment in the CFD and the formation levels of TCDD-equiv.

Exp. No	Run order	Total air (dm ³ /min)	Secondary air (%)	Nitrogen flow (dm ³ /min)	Temperature (°C)	TCDD-equiv. (ng/Nm ³)
1	4	90	20	60	50	75.5
2	8	150	20	0	50	142
3	6	90	70	60	50	51.1
4	1	150	70	0	50	53.7
5	7	90	20	60	350	41.4
6	10	150	20	0	350	138
7	9	90	70	60	350	59.7
8	2	150	70	0	350	49.0
9	11	120	45	30	200	76.0
10	5	120	45	30	200	72.9
11	3	120	45	30	200	70.2

The variation of PCDD/F between the three centre points is very small; i.e. the experimental bias in the data is very low. While the variation is three order of magnitude between the eight factorial experiments. Especially two experiments have higher formation levels then the other, experiment 2 and 6. High amount of air added to the reactor and high flow through the primary air inlet are two common parameters yielding high formations value of PCDDs/Fs. A mathematics model was calculated with MODDE, the model was fitted by multiple linear regression (MLR) and the factors were orthogonal and scaled to unit variance. The significant factors from the calculations are shown in Figure 2. The explanation level (R2) and the prediction capacity (Q2) of the variation in PCDD/F of the model is high, 0.94 respectively 0.80. Figure 3 show that formation of PCDD/F is distinct positive correlated to the amount of air in the system and how the air is distributed between primary and sec-

ondary air inlet. The temperature of the secondary air is not a significant factor in the formation of TCDD-eqv according to this study.

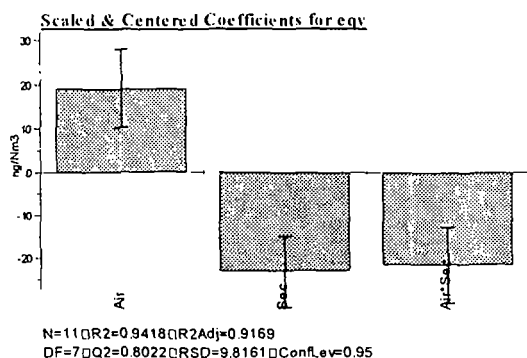


Figure 2 The significant factors for the formation of PCDD/F

Conclusions

- Factorial design is a very useful instrument in the evaluations of complex data. Different combustion parameter importance for the formations of products from incomplete combustion is an example of an application.
- A useful action to minimise the cost and unnecessarily hard work with an investigation is to perform the study in two steps; one survey and one complete study where all important parameters from the survey study are investigated from to investigate.
- Formations of CO and total hydrocarbon are related to the total amount of air in the system but not dependent on how the air is supplied into the combustion chamber. Furthermore the important factors for formation of PCDD/F in this study is almost reversed compared with the CO and hydrocarbons. The amount of primary air is a significant factor in the formation of PCDD/F; it increases with high quantity of primary air. The air in the system has to be distribute to facilitate the oxidation reactions to be complete i.e. the after burning is very important for reduction of PCDD/F

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