Thermodynamic Evaluation for the Formation of Dioxins/Furans during the Combustion of the Organic Fraction contained in Electronic Scrap

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Introduction

Electronic scrap is a complex material containing various recyclable fractions. This material contains mainly copper, aluminium and steel, attached to, or mixed with various types of plastics and ceramics [1]. Generally, small amounts of precious metals are incorporated in this mixture. The electronic scrap comes from the manufacture of electronic hardware and the discarding of used electronic products such as old computers, printed circuit boards and connectors [2]. Three options are currently available to proceed the organic parts contained in these scraps.

1. Deposit in landfill,
2. Recycling them in manufacturing of new plastics,
3. Use them as combustibles in process metallurgy.

According to the regulations and under the opinion pressure, the storage of these plastic wastes is limited. Only 25 % of these wastes are recyclable according to some Swedish companies. Currently, the best option about how to manage these wastes is to use them as combustibles during smelting of electric and electronic scrap to recover copper and precious metals like gold and silver. However, during combustion of the plastic contained in electric and electronic scraps, different organic compounds can be formed in the gas mixture. The chemical composition of gas mixtures after combustion of the electric and electronic scrap is given in Ref. 3.

Method of evaluation

Thermodynamic analysis on the formation and decomposition of dioxins and furans, the effects of temperature and gas compositions in quaternary C-O-H-Cl system derived from oxygen are evaluated under assumptions of homogeneous gas phase equilibria at ambient pressure. Although there exist 210 isomers altogether, seven dioxins and ten furans are classified as 2,3,7,8 type toxic species of which molecular formulae and toxic equivalent factors (TEF). Thermodynamic data of these species were taken from Barin [4], "HSC"[5], and estimated from the literature [6 - 12]. The equilibrium composition was calculated using the Gibbs free energy minimization method. In this study, only PCDD/Fs isomers were used for the thermodynamic calculations.

Calculation Parameters

The formation of the dioxins can depend on the quantities of carbon, hydrogen, chlorine and oxygen reacting in a given system, as well as on parameters such as temperature and pressure. Process variables used in the calculations were:

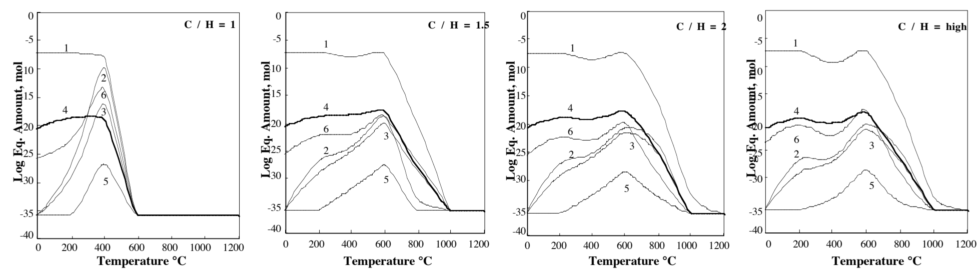
C/H ratio	(corresponding to different fuels and organic wastes),
Cl content	(corresponding to the chlorine present in organic wastes),
O_2 content	(corresponding to different possible gas atmospheres),
Temperature	(corresponding to temperatures encountered in combustion and after post combustion and cooling steps).

C/H/Cl and O_2 input values are always expressed in terms of mole. The temperature range investigated was from 25 to 1200 °C. In the present paper, the influences of C/H ratios, chlorine, oxygen and temperature on the dioxin-furan formation are revealed.

Results and discussion

Influence of C/H ratios on the PCDD/F formation.

Tetr4CDD, Pent5CDD, Octa8CDD (dioxins) and Pent5CDF, Hex6CDF, Hept7CDF (furans) were selected for this work. 1E-5 mole of O_2 were chosen for the calculation of conditions producing dioxins and furans at various C/H ratios and different temperatures. Figure 1 illustrates the behaviour of dioxins and furans for various C/H ratios. At the selected O_2 content of 1E-5 mole and chlorine content of 1.15E-7 mole, dioxins and Furans decompose at 600 °C.



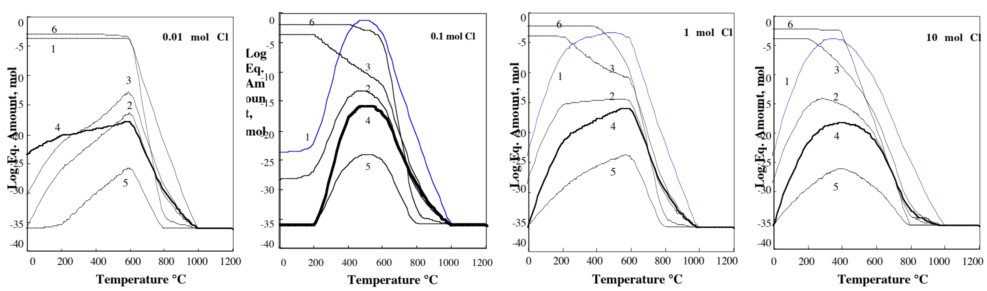
1. PentaCDF 2. HeptCDF 3. HexaCDF 4. TetraCDD 5. PentaCDD 6. OctaCDD

Figure 1. Calculated dioxin & furan potentials as function of temperature for various C/H ratios and O_2 content of 1E-5 mole and a Cl content of 1.15E-7 mole in the system.

In this case, no formation of these molecules occurs at temperature higher than 1000 °C. It seems to show that, at low O_2 and chlorine contents, dioxin and furan amounts increase while increasing C/H ratio up to about 1000 °C.

Effect of chlorine on the PCDD/F formation.

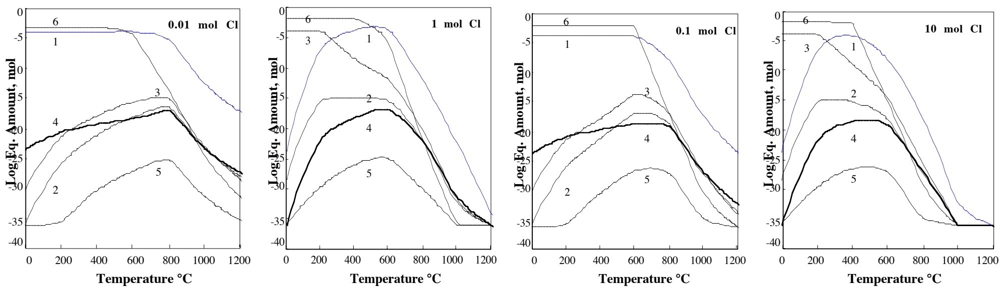
The influence of chlorine on the PCDD/F formation was investigated for different O_2 contents (1E-1 and 1E-5 mole). The concentrations of chlorine were 0.01, 0.1, 1, and 10 moles. Figures 2 shows that, for a O_2 content of 0.1 mole, dioxins and furans can not be formed at a temperature higher than 1000 °C, and that the effect of chlorine is negligible.



1. PentaCDF 2. HeptCDF 3. HexaCDF 4. TetraCDD 5. PentaCDD 6. OctaCDD

Figure 2. Calculated dioxin & furan potentials as function of temperature for various chlorine amounts with a higher C/H ratio and a higher oxygen content of 0.1 mole in the system.

At about 600 °C, the majority of these compound concentrations decreases for chlorine contents less than 1 mole. For 10 moles of chlorine, their concentration decreases at 400 °C. Figure 3 presents the effect of chlorine content on the formation of dioxins and furans at high C/H ratio, for O_2 of 1E-5 mole, and at various chlorine contents as function of the temperature. In this case, it seems that for a lower chlorine contents, the majority of dioxins and furans starts to decompose at about 800 °C. However, for chlorine contents of 10 moles, their amounts decrease from 500 °C. Figure 4 summarizes the various conditions of the dioxin and furan formation. This figure shows that the amounts of dioxins can be decreased at low temperatures for a higher O_2 contents, and the presence of chlorine in the given system can promote the formation of PCDD/Fs (see figure 4).



1. PentaCDF 2. HeptCDF 3. HexaCDF 4. TetraCDD 5. PentaCDD 6. OctaCDD

Figure 3. Calculated dioxin & furan potentials as function of temperature for various chlorine amounts with a higher C/H ratio and a O_2 content of 1E-5 mole in the system.

A B C D

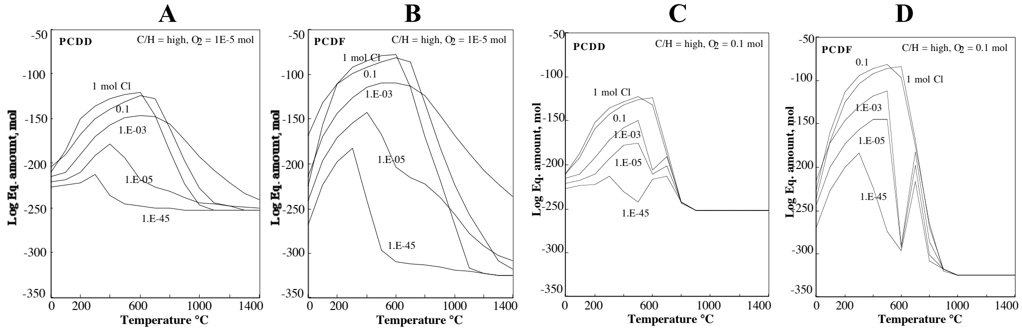
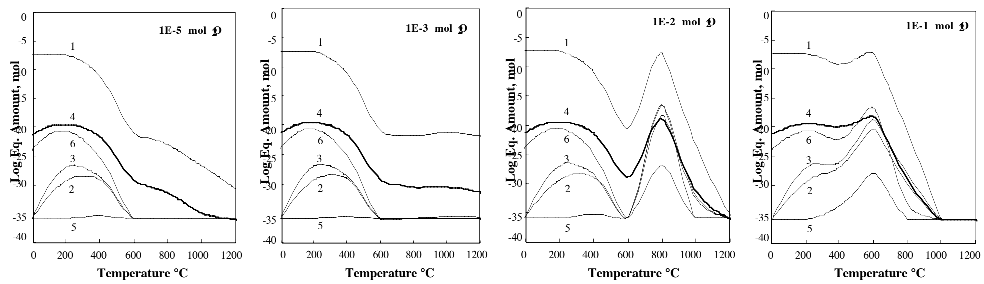


Figure 4. Decomposition of PCDD/Fs for different oxygen and chlorine contents. **A**. & **B** - for low oxygen content respectively. **C** and **D** - for high oxygen content.

Effect of oxygen on the PCDD/F formation.

The influence of O_2 contents on the formation of dioxins and furans was studied at high C/H ratio and for 1.15E-7 mole of chlorine between 1E-5 and 0.1 mole of oxygen at ≤ 1200 °C. As shown by figure 5, at temperature ≤ 200 °C, these compounds can be formed, while the effect of oxygen is negligible. However, they decrease between 200 and 600 °C, for oxygen content less than 0.01 mole. Until 600 °C, dioxins and furans are stable for a O_2 - content of 0.1 mole. The majority of these substances cannot be formed at high temperature, with a lower chlorine and a higher C/H ratio.



1. PentaCDF 2. HeptCDF 3. HexaCDF 4. TetraCDD 5. PentaCDD 6. OctaCDD

Figure 5. Calculated dioxin & furan potentials as function of temperature for various oxygen amounts with a higher C/H ratio and a chlorine content of 1.15E-7 mole in the system.

Temperature dependence of formation

The thermodynamic calculations were realised using temperatures of 300 °C, 600 °C, 900 °C and 1200 °C at high C/H ratio between 1E-45 and 1 mole of chlorine, and for 0.1 and 1E-5 mole of oxygen. No dioxins and furans can be formed at 900 °C and 1200 °C for a high oxygen content of 0.1 mole. However, their amounts increase between 1E-3 and 1 mole of chlorine for a low oxygen content in a given system. In the temperature range of 300 °C to 600 °C, the dioxins and furans start to decrease from 0.1 mole of chlorine in both cases. It seems to indicate that dioxins and furans can be formed at low temperature for high oxygen content and even at high temperatures for low level of oxygen content.

Conclusions

The present results must be useful as one of the keystones for basic understanding of formation of these toxic species because there exist no systematic thermodynamic survey in this field and no trial to bridg a gap between equilibrium and kinetic predictions. The thermodynamic analysis of several organic compounds resulting from combustion of plastic contained in electric and electronic scrap show that, the formation of dioxins and furans strongly depend on oxygen, chlorine contents, temperature, residence time of gas mixture and on the feed material (C/H ratios).

Acknowledgements

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