Literature survey of Dioxins and Poly Aromatic Hydrocarbons in combination with waste combustion

-for the summer course “Organic Aerosols”

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Introduction

Background

The technology of waste combustion has been a subject for development over recent decades. According to the International Panel on Climate Change (IPCC) report AR4 (2007) the waste sector causes almost 5 % of the Green House Gas (GHG) emissions globally. Most of it is attributable to methane (CH_4) from landfills [1]. This means that the techniques of recycling and producing energy from wastes are in need of improvement. Sweden has a long tradition of waste combustion and is one of the most successful countries in the world when it comes to diverting waste from landfills to energy recovery, partly because of strict regulations of landfill.

Municipal Solid Waste (MSW) is a heterogeneous fuel, consisting of various elements rather than just carbon and hydrogen. MSW is known to contain various ash forming matters and trace elements [2].The composition of this fuel inhibits complete combustion and can cause formation of compounds like polychlorinated dibenzo-*p*-dioxin (PCDD) or polychlorinated dibenzofurans (PCDF). The high rate of dioxin formation in MSW combustion is due to the highly sooting flames, high metal contents and unsteady-state of the fuel composition [3].

Incomplete combustion also gives rise to Poly Aromatic Hydrocarbons (PAHs), a toxic air polluting compound either in gas form or in solid form bound in fine aerosol particles. For example, the PAHs can attach to soot, which itself is also a sign of incomplete combustion [4]. PAHs are emitted from many different sources but combustion is thought to be one of the major contributors. When it comes to combustion it is also a fact that PAHs are present in small amounts in the ash, which should be taken into account in the landfill debate [5].

Method

This essay intends to give an overview of the current status of the research concerning dioxins and PAHs. This is a part of the summer course “Organic Aerosols” given in Gothenburg in the summer of 2008 by University of Gothenburg.

Project outline

1. Define limitations for literature survey
2. Make a literature search
3. Write a compilation over gathered information

Limitations

This literature survey was done with some limitations. Two databases were used, Compendex and ScienceDirect. In these databases the same words were used as search words (listed below). Two doctoral dissertations [3,7] have been used, as well as personal communication with Ph.D. Evalena Wikström Blomqvist. To keep this summary informative and concise a selection of articles were chosen for this work by reading the abstracts.

Search words and search combinations* used in the databases Compendex and ScienceDirect

Waste combustion + dioxins	Waste combustion + PAH
Waste incineration + dioxins	Waste incineration + PAH
Dioxin + formation	PAH + formation
Dioxin + degradation	PAH + degradation
Dioxin + decomposition	PAH + decomposition
Dioxin + destruction	PAH + destruction
Dioxin + prevention	PAH + prevention
Dioxin + emission	PAH + emission
Dioxin + aerosol	PAH + aerosol

*Some searches were made with combinations of several of the words above.

Results of literature search

The literature search gave an enormous amount of articles and from this a number of articles were chosen and this summary is based on these articles. The method of selection was to keep the information as basic as possible, treating dioxins and PAHs as groups rather than looking at one specific type of dioxin or PAH. Specific articles were chosen based on relative information found in several of the abstracts that were regarded as interesting for this survey.

More articles were found in the reference lists of the two theses mentioned above as well as in the reference lists of the articles we collected from our literature search. More literature than the references were studied but not included in this compilation.

Dioxins

There are over 200 different types of chlorinated derivate of dibenzo-*p*-dioxin ($C_{12}H_8O_2$) and dibenzofuran ($C_{12}H_8O$) and the denomination for these compounds are dioxins [8].

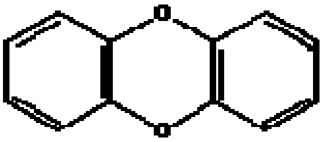

Fig. 1: Dibenzo-*p*-dioxin

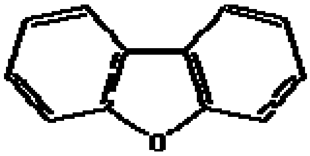

Fig. 2: Dibenzofuran

As mentioned in the introduction of this survey dioxins are formed from incomplete combustion of wastes, predominantly plastic waste. Dioxins have never been produced for technical or commercial use but are a side product of not just waste combustion but several industrial processes [7,9]. They are of interest because of their high chemical stability and the fact that they are also lipophilic in nature, which can cause accumulation in food chains [7].

Dioxins were first discussed by Olie et al. in 1977 [5]. In this article the authors point out the connection between dioxins and toxification causing serious health problems. In 1978 Buser et al. [10] also attracted attention to the dioxins when detecting them in incinerator fly ash. Today, the largest release of dioxins is related to open burning of household waste, municipal waste, medical waste, landfill fires, agricultural fires and forest fires [11]. Abad et al [12] have made dioxin mass balance calculations and showed that only 2 % of the yearly production from a MSW grate incinerator was emitted as air pollution while 74 % was emitted by the slag and 22 % as fly ash.

Formation of dioxins

In Wikström's thesis [7] it is explained that the formation of dioxins from high temperature processes has been thought to occur because of one or more of the following theories:

- Incomplete degradation of dioxins already present in the waste.
- Formation from related chlorinated precursors such as PCPhs, PCBzs and PCBs.[1]
- De novo synthesis from the elements C, H, Cl and O.

Of these three theories, the first one is not considered as an important pathway for dioxin emissions nowadays. Dickson et al. [13] showed that the two latter mechanisms transpire independent of each other but it is yet to be concluded which of the mechanisms is the fastest. This is probably due to difficulties related to the examination of them individually [7].

Hunsinger et al. [14] studied the formation of dioxins in a grate furnace and showed that formation depends on fuel composition, temperature in the boiler and burn out characteristics of the fuel bed. High levels of chlorine and metal content (Cu) in the fuel will cause dioxin

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[1] PCPh: Polychlorinated phenols, PCBz: Polychlorinated benzene, PCB: Polychlorinated biphenyl

formation as well as “Cold strands” of unburned flue gas, caused by incomplete or disturbed combustion. Deposits, containing residual carbon, in the boiler section are also a source for the formation reaction [14].

Degradation of dioxins

Degradation of dioxins can occur via dechlorination/hydrogenation reactions where one or more of the chlorine atoms are replaced by hydrogen atoms [3]. Hydrogen and water vapour, proposed by Yazawa et al. [15], are to be quite effective in degradation of dioxins to form benzene and hydrocarbons. Another way to decompose dioxins is by breaking the oxygen bond which causes the degradation to smaller chlorinated molecules like PCBzs, and ultimately to CO_2 [3].

Dioxins decompose at high temperatures while degradation starts at 400 °C and after one second in 1000 °C the dioxins are totally destroyed [7]. Hunsinger et al. [14] concluded that a controlled combustion and complete burnout of especially soot keeps the amount of dioxins low in the flue gas. In an article from 2005, Lundin and Marklund [16] investigate the degradation of dioxins from MSW ashes. They showed that temperatures below 200 °C are too low to achieve degradation of the total amount of dioxins during thermal treatment of the ash, regardless the composition of the fly ash. Moreover, they showed that the degradation reactions are favoured in temperatures over 600 °C [16].

Song et al. [17] studied the dechlorination and destruction of dioxins in fly ashes from a MSW incinerator using low temperature thermal treatment finding that the total destruction efficiency was above 95 % at the treatment temperature of 450 °C for 3 h. However, they also concluded that the removal efficiency of different types of compounds varied and in some cases increased. Additionally, Lundin and Marklund [16] show in their article that the composition of fly ash, treatment type, and atmosphere are important when studying if formation or degradation occurs during thermal treatment of fly ashes, even if temperature is the most important factor.

PAH

PAH (Polycyclic Aromatic Hydrocarbons) is a generic term for a large number of chemical air pollutants formed during incomplete combustion of organic matter [6]. There are a number of PAHs that are considered as "Priority PAH Pollutants" by U.S EPA [18]. Among these we find, for example, Naphthalene (C_8H_{10}), Pyrene ($C_{16}H_{10}$) and Chrysene ($C_{18}H_{12}$), which show an example in the variety of their structure.

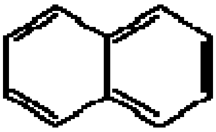

Fig. 3: Naphthalene, C_8H_{10}

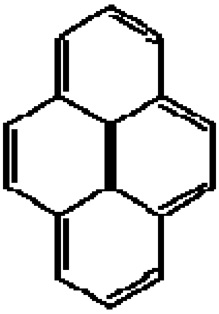

Fig. 4: Pyrene, $C_{16}H_{10}$

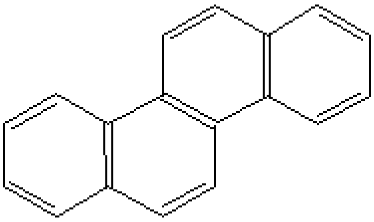

Fig. 5: Chrysene, $C_{18}H_{12}$

Around 100 PAHs are stable enough to outlive the combustion process and enter the atmosphere as primary air pollutants. PAHs are toxic and related to the public health discussion [6, 18-27].

Formation of PAHs

Combustion is thought to be one of the major sources of PAHs to the atmosphere [18-22]. Different types of combustion, such as domestic, industrial and agricultural, all contribute to the emissions. Waste combustion is (due to the heterogeneous mix) a potential source for different types of PAHs. The chemical and physical formation of PAHs is a very complex and many decades of scientific study have been dedicated to this matter. A few notions are presented in this short review.

Longwell [17] proposes the following different sources of PAH when they are collected in gas produced by practical combustion equipment:

- Unburned fuel and lubricating oil
- Fuel that has undergone pyrolysis but has not assed through a flame zone
- PAHs produced in the flame.

In 1991, Haynes [20] suggested three possible formation mechanisms for PAHs during combustion:

- Slow Diels–Alder condensations
- Rapid radical reactions
- Ionic reaction mechanism

Ravindra et al. [21] state in their article from 2007 that the existing ring structure of cyclic compounds is conducive for PAH formation. Unsaturated compounds are especially susceptible to the reactions involved in PAH formation. The higher alkanes present in fuels and plant material form PAHs by the process of pyrolysis, i.e. the cracking of organic compounds. They also describe that PAHs can be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Furthermore, they suggest pyrosynthesis and pyrolysis as the two main mechanisms to explain the formation of PAHs.

Furthermore, Chagger et al. [22] suggest that PAHs are results of incomplete combustion and are often products of the start up phase of the combustion. They also conclude from modelling a combustion situation, that PAHs are formed in higher concentrations in a fluidised bed, than in a kiln, because of a more unstable combustion in the fluidised bed.

Degradation of PAHs

PAHs are naturally removed from the atmosphere when they are absorbed by particulate matter that later sediment into the soil [23]. According to Johnsen et al. [24] PAHs tend to interact with non-aqueous phases and soil organic matter. This means that the PAHs become potentially unavailable for microbial degradation because bacteria are known to degrade chemicals only when they are dissolved in water [24]. Moreover, Johnsen et al. points out that the aqueous solubility of PAHs decreases almost logarithmically with increasing molecular mass, which means that high-molecular weight of PAHs ranging in size from five to seven rings are of special environmental concern. Wild et al. [4] agrees with the problems of solubility when they state that the PAHs leach very slowly through soils.

In summary it shows that even if PAHs are cleaned from the atmosphere by absorbing on particulate matter or just sediment into the soil, they keep their toxicity and it is not certain that a microbiological degradation can take place. Therefore, it is better to lower the original emissions, i.e. destroy the PAHs before leaving the burner or hinder formation of PAHs.

One example of preventing PAH emissions is suggested by Wang et al. [25] whom have studied the possibilities to decrease the emissions of PAHs by adding an after burner to a MSW-plant. The tests were performed using variations of temperature and oxygen mole fraction. Their results showed that PAH emissions were lowered together with the CO emission when the after burner was used.

Kahlfi et al. [26] performed laboratory tests where they combusted wood from old furniture, which is a common waste in our society today. They suggest that PAHs reach a maximum emission between 900-950ºC, while PAH abatement was recorded over 1000ºC. Furthermore, they noticed a decrease in PAHs when combusting bigger slabs compared to shredded samples of the fuel. Another important observation they made was that the furniture wood did not give rise to much higher emissions of PAHs than natural wood fibres combustion.

Callén et al. [27] used an electron beam technology, which is proven to clean out SO_2 and NO_x, in their test to clean out organic emissions, like PAHs, from the hot flue gas. Their conclusions were that the most volatile PAHs were affected by the beam and decreased in concentration.

Summary

In this compact compilation focus is the formation and degradation of dioxins and PAHs. A lot of material gained from the literature survey was not presented in this text. The study was performed by using databases, doctoral theses and the reference lists from relevant articles.

The gathered information is supposed to give an introduction to the areas concerning dioxins and PAHs from waste combustion. The complexity of both dioxins and PAHs have been studied for decades, hence to cover all opinions would take more time and effort than possible for this survey.

One thing that is evident, from this study, concerning dioxins and PAHs in combination with waste combustion is that it is an important topic which needs further investigation. Both compounds are toxic and in a fast developing society of today, when consumption and use of new materials increases, the combustion of different materials might give rise to different emission potentials when it comes to energy recovery from combustion.

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