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*Plenary Lecture*

# THE ROLE OF THERMAL ANALYSIS IN ENVIRONMENTAL PROTECTION

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## Abstract

In the past industry has developed chemicals and products, optimized for the best suitable properties concerning different application fields. Now, ideas of environmental precaution are arising, on the one hand looking for reduction of materials flow to avoid or minimize the waste, on the other hand following the idea of process and product integrated environmental protection. That means to develop processes and products which are safer and more tolerant regarding the environment and its organisms.

In this connection thermal analysis is a very successful tool for predicting the risk of burning processes or fire accidents. Thermal analysis in this context means the classical thermal analysis methods like DTA, TG, DSC and its couplings with gas analysis methods as well as the simulation of burning processes in different kind of furnaces with identification and quantification of the evolved gases.

**Keywords:** environmental protections

## Introduction

Industry and human beings are producing air pollutants, solid wastes and waste water. For not stiffing in the increasing amount of these "by products" of human activities, a re- or down cycling of materials should be done if possible, and only a minimum of waste should be dumped in a more or less save way. For that, the amount of waste has to be reduced and brought into an inert state, which is normally done by thermal processes. Here thermal analysis can help to study these processes and the risks arising from them.

In the past, the industry has developed and optimized products and processes, regarding economy as well as quality and properties of the products. During the last years, in Germany some ideas of environmental precaution

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arose. For this reason, today also aspects of ecology have to be respected. That means minimization of materials flow and production of waste. Under the title of process and product integrated environmental protection, processes and products should be developed which are saver and more tolerant to the environment and its organisms. Live cycle analysis, including the simulation of fire accidents and waste incineration should be done. Potential exposure of humans and the potential impact of hazardous compounds should be taken into account.

Under the headline "combustion: emissions and residues" we are studying physical and chemical properties of chemicals and products, looking for the environmental fate and impact caused by emissions and residues. Therefore, mainly laboratory scale experiments, using different methods of thermal analysis and combustion techniques were carried out.

## Methods

The task, to simulate industrial processes or real fire accidents for a great variety of materials is very difficult. To realize the great variety of real burning conditions as residence time in the hot zone, amount of oxygen at the sample, etc. a variety of different test methods have to be involved in these investigations.

### *Vapor pressure measurements*

Regarding the preparation of legal rules for chemicals in Europe, Japan and the United States, the exposure analysis and estimation of ecological behavior of chemicals get more and more important [1]. Among others, the exposition analysis of chemicals and products covers the distribution of substances in soil, water and air, as well as their degradation and transportation within these compartments.

One of the most important parameters for the calculations of the distribution of substances in soil, water and air is the vapor pressure of the substance as measure of volatility [2]. In combination with the solubility in water, the exposition potential of hazardous substances to human beings and environment can be evaluated.

### *Gas saturation method*

Within this method, the sample is stored in a saturation stove and heated to a defined temperature. A slow inert gas flow, normally nitrogen, passes over the sample and is saturated by it. Since the flow rate, the sampling time and the temperature are known the vapor pressure can be determined. The limits of the method are in the range of $10^4$ to $10^{-6}$ Pa. Two disadvantages have to be mentioned. Only substances, processable by gas chromatography can be investigated and the method has to be calibrated new for each substance.

The vapor pressure and the enthalpy of sublimation are ecological important values. For that we are interested in a relation between the structure of a substance and its thermodynamic values.

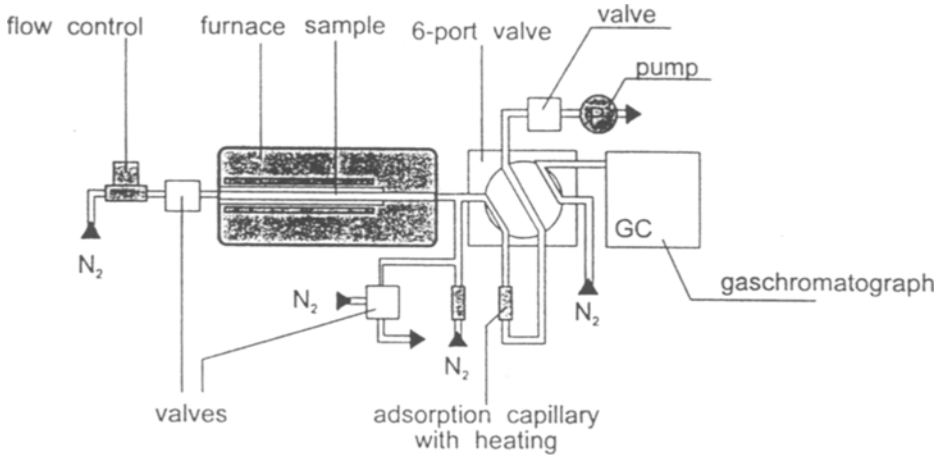

**Fig. 1** Gas saturation method (scheme)

From a series of 30 polycyclic aromatic hydrocarbons we developed a general incremental procedure for the calculation of the vapor pressure and enthalpy of sublimation for this class of substances [3, 4].

Using naphthalene or fluorene as basic substances, every higher homologous can be derived by use of different structural elements as

- linear ortho annelation
- angular ortho annelation
- angular pri annelation
- phenyl group substitution

From this, the vapor pressure ($T$=25°C) and the enthalpy of sublimation for a homologous substance can be determined as follows:

$$p_{(25^\circ C)} = A\ X_1^{n_1} X_2^{n_2} X_3^{n_3} X_4^{n_4} \tag{1}$$

$$\Delta H_s = B + n_1 Y_1 + n_2 Y_2 + n_3 Y_3 + n_4 Y_4 \tag{2}$$

$n_1$, $n_2$, $n_3$, $n_4$ number of structural elements 1, 2, 3 and 4; $A$=10.86 Pa, $B$= 71.7 kJ mol$^{-1}$ naphthale; $A$=1.1·10$^{-1}$ Pa, $B$ =84.9 kJ mol$^{-1}$ fluorene; $X_1$, $Y_1$=incremental factors

### *Vapor pressure balance/Mass spectrometry*

With respect to indoor air quality, the evaporation of individual substances from mixtures is of great importance [5].

Nevertheless, within all methods, used so far, the vapor pressure values of pure substances were determined, that means far off realistic, natural conditions.

To get reliable information of possible risks, a determination of the partial vapor pressure of a substance in its mixture (for example formulation) is required.

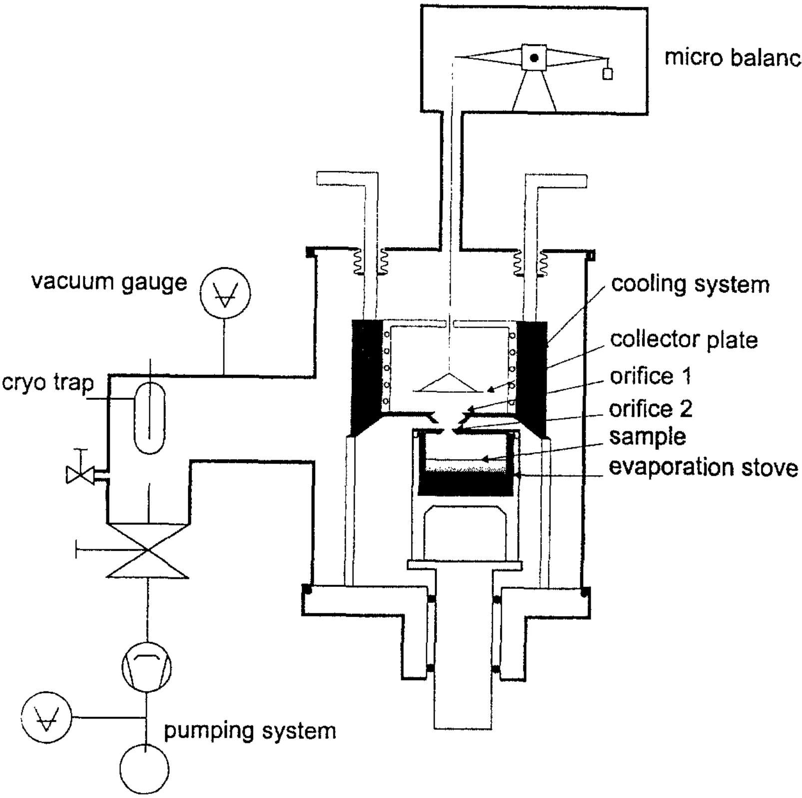

**Fig. 2** Vapor pressure balance (scheme)

Due to matrix- and adsorption effects' correlation methods as known for pure substances are not available [6]. For that reason, a new method for the determination of single compound vapor pressure in mixtures was developed [7, 8].

For the measurement of the partial vapor pressure of an individual substance in a mixture, first the mass spectrometer has to be calibrated. The calibration of the mass spectrometer is done by a vapor pressure curve measurement with the pure substance while recording the mass spectra at each temperature. From this measurement a calibration curve (intensity of selected fragments *vs.* vapor pressure) can be calculated.

In the next step a vapor pressure curve measurement of the mixture is carried out while also recording mass spectra at each temperature. From the

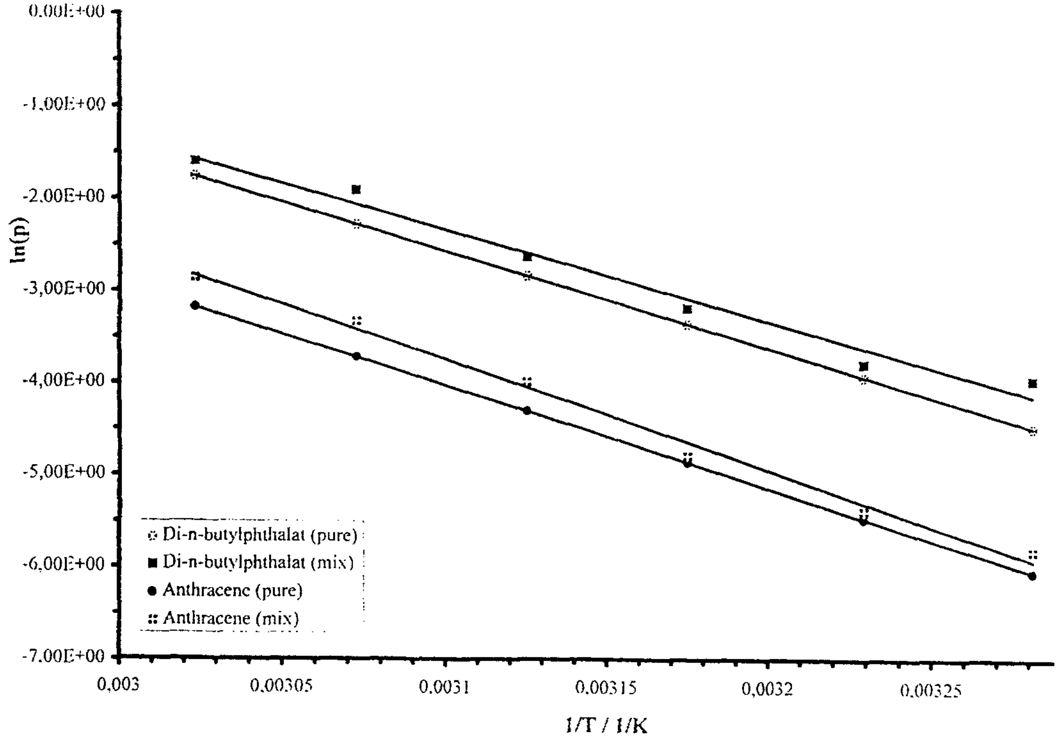

**Fig. 3** Vapor pressure curves of anthracene and di-*n*-butylphthalate (pure and in mixture)

intensities of the selected fragments the partial vapor pressure of the individual substance can be determined. In Fig. 3 the vapor pressure curves of anthracene and di-*n*-buthylphthalate as pure substances and in a mixture are given.

## *Thermal analysis*

By means of the simultaneously working combined methods, thermal analysis and mass spectrometry, the thermal characteristics such as melting point and temperature of degradation as well as the released volatile degradation products can be determined [9–13]. Through a two stage orifice system, a part of the gases directly above the sample will be introduced continuously into the mass spectrometer and then being analyzed. Thus the temperature depending release of hazardous substances can be followed. Further features of this equipment are the automatic pressure regulation in the mass spectrometer and a gas control unit to operate under special atmospheric conditions.

Due to the simultaneously and continuously registration of some selected fragments, the temperature depending evolution of some hazardous substances can be determined.

Due to the continuously gas inlet the registrated mass spectra always represent gas mixtures. For this reason and the special fragmentation of the molecules in the MS (EI ionization and thermal treatment) it is sometimes difficult to interpret the on-line mass spectra. To overcome these problems, an adsorption tube is connected to the furnace at the gas outlet and after the TA/MS experiment the adsorbed substances are analyzed by means of GC–MS. With this information of all the substances, being evolved during the thermal treatment the MS data from the on-line experiment are much easier to interpret [14].

The investigation of wastes, pollutants, contaminated soil, etc. in preparation of their thermal disposal or decontamination is related with several problems. Due to the heterogeneity of the sample materials, thermoanalytical measurements, using standard sample amounts of about 20–50 mg do not lead to reliable results. For that reason, we are developing a new thermoanalytical device for about 100 g sample amount. For more detail of this development see our contribution on that scope within this issue.

### *Combustion experiments*

Another way of identifying thermal degradation products is to burn the sample in standardized combustion furnaces under standardized conditions. In the following two of these furnaces are described.

#### VCI- Furnace

The VCI combustion device [15] is to simulate burning processes of solid and liquid high boiling substances at different preselected temperatures. From the charging device, the sample, placed in a quartz crucible, gets directly into the hot zone of the furnace. The decomposition products pass two times through the hot zone and are then adsorbed on suitable resins as XAD-4 and charcoal that are connected in series. Due to this technique the sample is heated rapidly to the preselected temperature and distillation processes will be suppressed. The burning process normally has finished after 2 min. For quantitative collection of the degradation products it is necessary to collect the gases for about 10 min. Subsequently the products will be desorbed and being analyzed by means of GC and GC–MS. A new, improved construction of this furnace type is now available from the Netzsch company.

#### BIS-Furnace

The (Bayer/ICI/Shell) BIS combustion device consists of a horizontal arranged furnace with a quartz tube as reaction chamber. For the investigation at different preselected temperatures, the sample is first placed in the quartz tube outside the preheated furnace. After closing the reaction chamber and adjusting the gas flow (residence time) the furnace is moved over the sample and the degradation products will be adsorbed on suitable materials (XAD-4 and charcoal, connected in series) [16]. Due to this technique the sample is heated slowly and

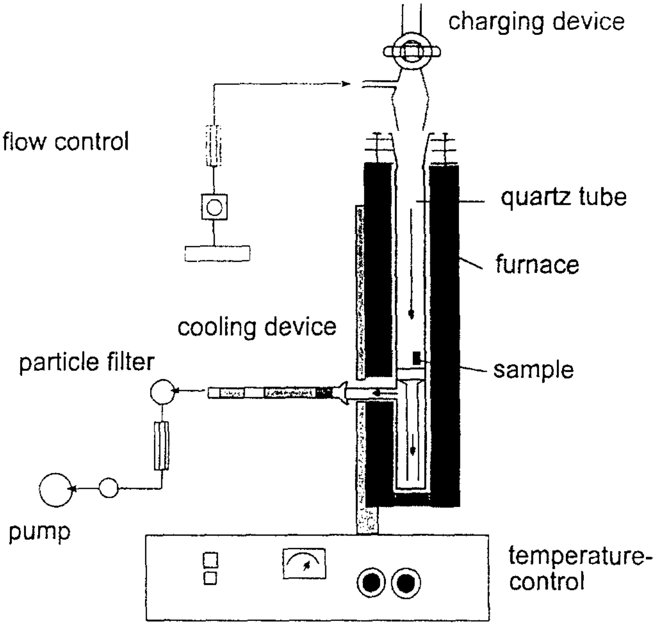

**Fig. 4** VCI combustion device

evaporation and distillation processes will be passed through. After finishing the degradation process at about 5 min the gases are collected for at least additional 5 min. Then the degradation products are desorbed and analyzed by means of GC and GC–MS.

Both types of burning devices have been used from us in several cases for the identification and quantification of degradation products of polymers and selected chemicals [17–23].

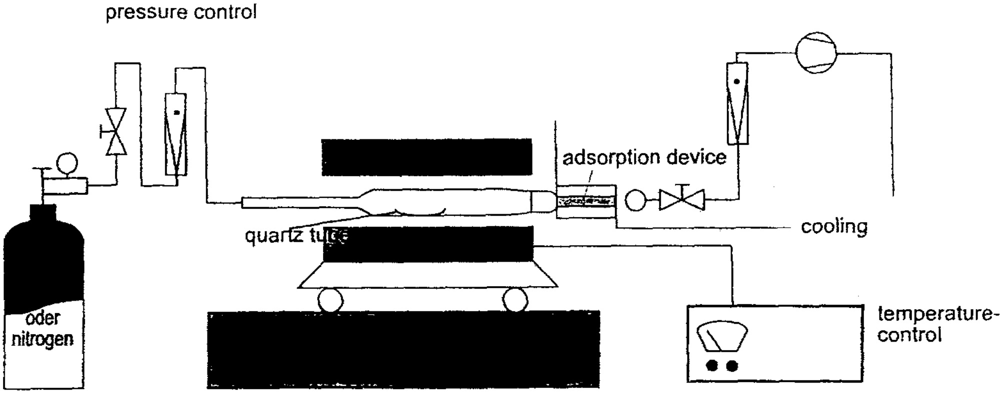

**Fig. 5** BIS combustion device

For a better simulation of real burning processes that means control of the atmosphere during the experiment we are developing a new, more sophisticated system. In this system, the atmosphere can be changed during the experiment from oxidizing to reducing conditions as it can happen during real burning processes.

## Results

On the base of former results [24–31 ] it is obvious, that there is a need for environmental precaution by process, respectively product integrated environmental protection.

We have performed for example studies on polybutylene phthalate containing 10% decabromo diphenylether and 2.5% of metal stearate or 6% of metal oxide (used as stabilizers, pigments, fortifiers and synergists in flame retardance) in polymers [32]. As it can be seen from Figs 6 and 7, metals and metal oxides influence the yield of brominated dioxins and furanes. These laboratory results are consistent with those obtained from copper cable recycling plants who observe high concentrations of PBDF as well as PBDD.

For that, the normal use, fire diseases and waste disposal as well as waste incineration has to be simulated, regarding the toxicological and ecotoxicological risks. For this purpose, we are co-operating in joint venture projects with the industry. In the following, one example of such cooperations is given.

Due to the formation of polyhalogenated dibenzo-*p*-dioxines and -furanes from flame retardant polymers, using halogenated flame retardants, in 1989 the Siemens Corporated Research Development took up the challenge of developing halogen free duroplastics.

Investigations of the processes during the combustion of plastics served as starting point for the chemical concepts. To ensure the same level of flame resistance without use of halogenated materials, the other approaches were:

- to reduce the percentage of generated combustible gases,
- to change the composition of the pyrolysis products, and
- to prevent heat transfer to the remaining solid plastics

We participated in the development of all materials by assessing the combustion products of the newly developed materials as well as their toxicity. During the lifetime of the project the composition of the materials was changed according to the results of ecotoxicological respectively toxicological test. For this, the procedure for every new synthesized product was

- Investigation by TA/MS and by burning in horizontal and vertical furnaces.
- Identification and quantification of the pyrolysis products.
- Biological testing of the volatile degradation products as well as the residues using organisms of different levels of the food web (bacteria and small aquatic organisms) as well as mutagenic effects testing.

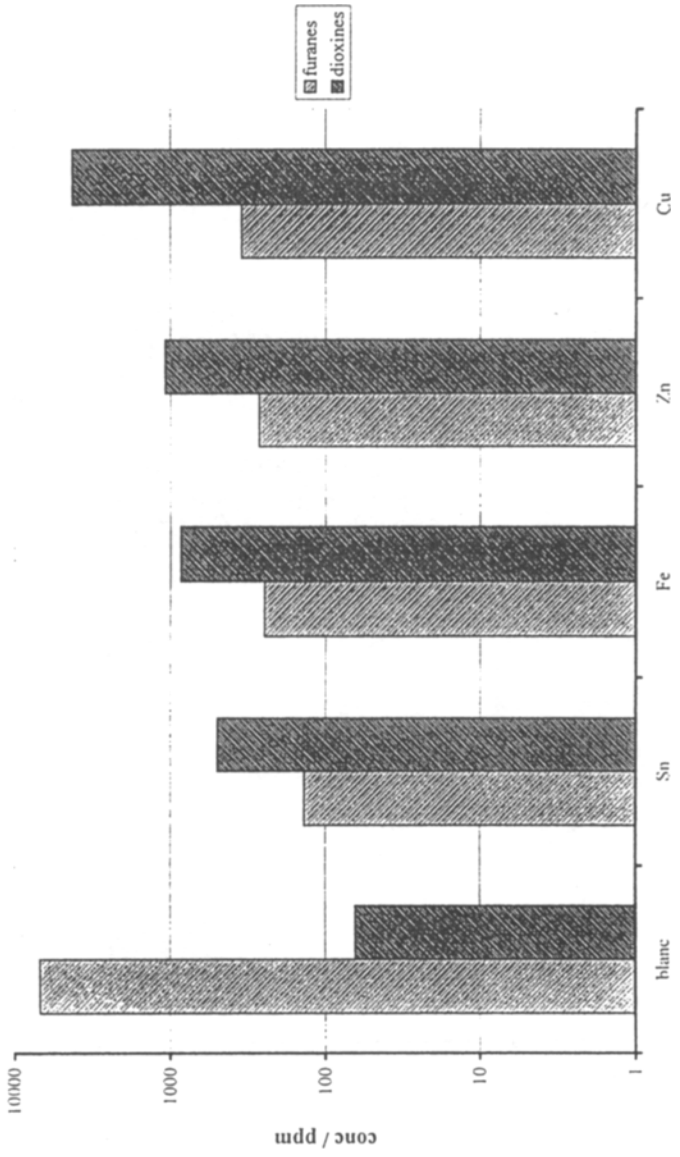

**Fig. 6** Influence of metals to the formation of PBDD and PBDF

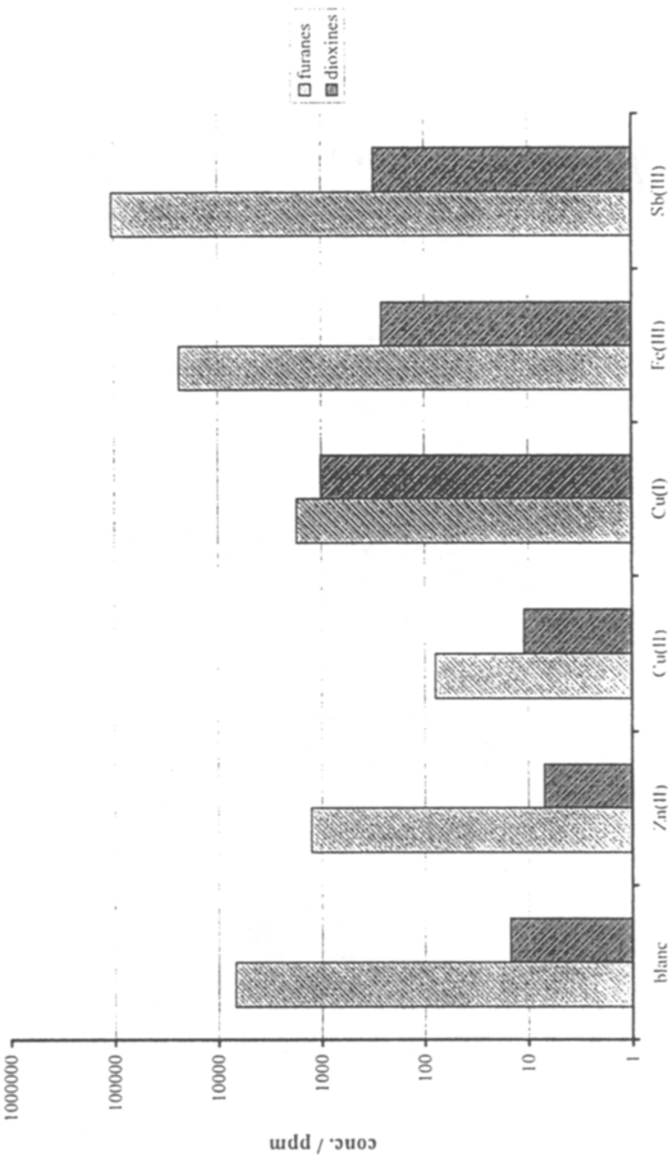

**Fig. 7** Influence of metal oxides of the formation of PBDD and PBDF

The results of toxicity tests with Daphnia magna for example show an increasing toxicity with increasing temperature for all materials. Only beech-wood behaves differently showing the lowest toxicity at 600°C. The toxic effect in all cases is assumed to be due to synergistic effects of the combustion products. A direct correlation between specific combustion products and toxic effects like in the bacterial toxicity test is not possible.

The toxicity's of all newly developed polymers are in the same range like those of the reference materials or even lower. The plastics investigated here contain phosphorus compounds for flame retardancy. As the Daphnia test is known for its high sensitivity to neurotoxic compounds like organophosphates, it can be assumed from relative high $EC_{50}$ values – that no neurotoxic compound was formed during combustion from the phosphorus flame retardant compounds.

In Fig. 8 the results of the toxicity testing with Daphnia of the semi-volatile combustion compounds are given.

Based on this results, the structure and formulation were optimized with respect to the toxicity of the pyrolysis products to archive a final product which pyrolysis products are less or comparable toxic than the pyrolysis products of wood from the beech tree [33].

A second project under this scope was carried out in cooperation with the AUDI car company, which is making a lot of efforts to reduce the car weight for minimizing fuel consumption and at least emissions. This was done by two strategies:

- use of aluminum as materials for car bodies and
- use of sandwich material fixed together by adhesives, e.g. epoxy resins.

In case of sandwich materials, an electrical spot welding of the parts is necessary for getting stable car parts.

Our tasks in the cooperation were investigations concerning the properties of adhesives by thermal treatment, the pyrolysis products formed and the simulation of the welding process as well as field studies in the factory.

We performed a series of experiments for the characterization of thermal and pyrolytic behavior of different types of epoxy resin, PUR and buthyl-chaoutchouc adhesive.

The adhesives used in our experiments were of different trade origin, but pyrolysis at high temperature, modeling the real situation, shows similar patterns that are known for formation of aromatics and polycyclic aromatic hydrocarbon. In Tables 1 and 2 the identified degradation compounds from TA/MS experiments as well as from the combustion experiments in the VCI furnace are given exemplarly for the epoxy resins.

The patterns of pyrolysis products we got from DTA/MS investigations and pyrolysis experiments in the German VCI furnace correlate quite exactly with

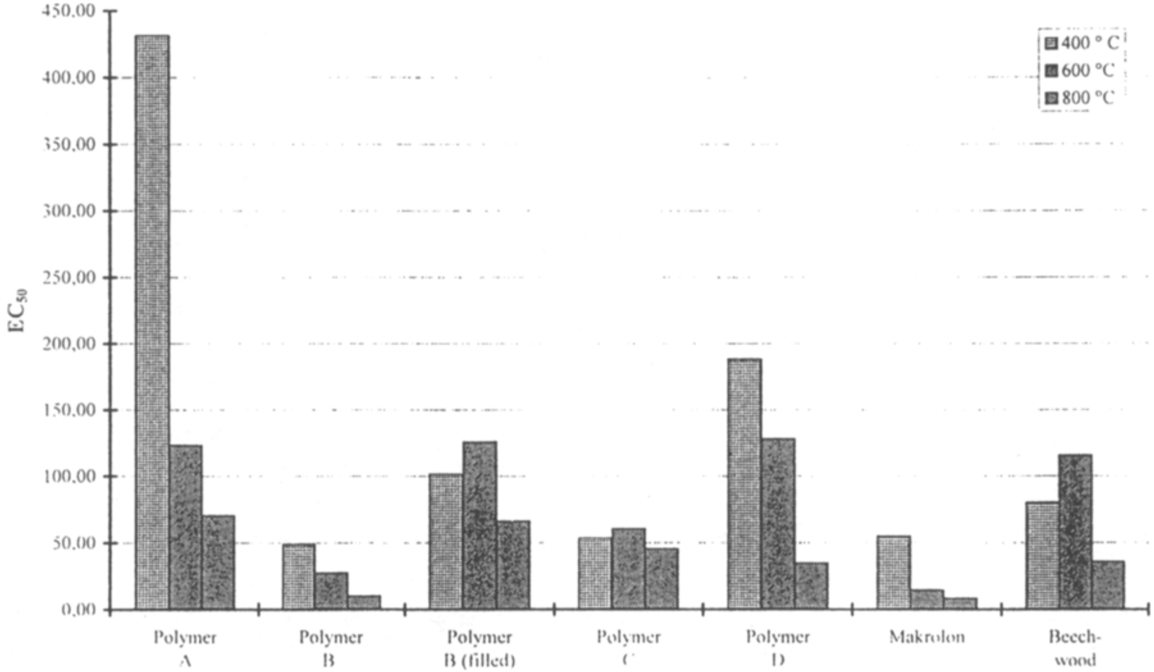

Fig. 8 Results of toxicity testing with Daphnia of semi-volatile combustion products

**Table 1** Selected possible substances and structural elements from samples XB5103, XW 1044-2 and ESP 110

| m/z | Possible substances and structural elements |
|---|---|
| 18 | $H_2O$ |
| 55 | $C_3H_5N$, $C_3H_3O$, $C_4H_7$ |
| 66 | $C_4H_2O$, $C_5H_6$, $C_4H_4N$ |
| 77 | $C_5H_3N$, $C_6H_5$ |
| 91 | $C_6H_5N$, $C_7H_7$ (Tropylium), $C_6H_4O$ |
| 94 | $C_6H_6O$, $C_7H_{10}$ |
| 107 | $C_7H_9N$, $C_7H_7O$, $C_6H_5NO$, $C_8H_{11}$ |
| 121 | $C_7H_7NO$, $C_8H_{11}N$, $C_8H_9O$, $C_9H_{13}$ |

**Table 2** GC-MS results of the VCI-pyrolysis experiment with the Delo ESP-110 epoxy resin adhesive (μg product of pyrolysis/g burned sample)

| T/°C | 400 | 600 | 800 | 1000 | 1200 |
|---|---|---|---|---|---|
| Benzene | 10 | 50 | 420 | 11800 | 650 |
| Toluene | 60 | 90 | 120 | 170 | 30 |
| Phenol | 31 | 26 | 11 | | |
| 2-Methylbenzaldehyde | 9 | | | | |
| 1-Ethyl-4-methoxybenzene | 8 | | 10 | | |
| Biphenylene | | 20 | | 20 | |
| Naphthalene | | | 31 | 87 | |
| 2-Methylnaphthalene | 7 | | 11 | | |
| 9-Methylfluorene | | | 6 | 25 | |

those from the apparatus from welding simulation and the field experiments. Taking into account the number of welding points per experiment respectively per working period and the amount of oil and epoxy resin used, we are able to make trend evaluation for real situations by laboratory scale experiments.

## Conclusions

The task, to simulate real, for example burning processes for a great variety of materials is very difficult. Only the use of a variety of different test methods for these investigations can lead to the desired results. Thermal analysis, especially its couplings with gas analysis methods is a very useful tool in this field of investigations, but still the methods need to be developed and optimized with respect to the special demands.

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