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GASIFICATION–POST-COMBUSTION OF WASTE MATERIALS; INFLUENCING PARAMETERS AND ON-LINE MONITORING OF ORGANIC SUBSTANCES

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Abstract

Gasification of waste materials on grate systems with independend post-combustion is a newly developed processing for thermal waste treatment. The proposed paper shows investigations of influencing parameters concerning decomposition of organic trace components in the post-combustion process at a pilot plant in conjunction with the application of an on-line analysis method. The applied analysis method is a combination of laser induced Resonance-Enhanced Multi Photon Ionization (REMPI) and Time-of-Flight Mass Spectrometry (TOFMS) which represents a useful tool for the detection of trace quantities of organic substances.

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1 Introduction

Plants for thermal waste treatment may basically be subdivided into two parts. The first part is the so-called thermal main process, with stoker firing systems being frequently applied. The second part includes all additional treatment steps as for example purification of exhaust gases, post-treatment of ash or generation of electrical power. With regard to the reduction of pollution concentrations, in the past the emphasis was on the development of an efficient purification of flue gas and the post-treatment of residuals (i.e. secondary measures). Currently equipped plants now generally comply to the legally required limits concerning the discharge or the disposal of noxious matter in air, water and soil.

Further reduction of stack emissions is expected by optimizing the thermal main process by primary measures. Among investigations at research facilities, pilot plants etc. and mathematical modeling, on-line detection of inorganic as well as organic pollutants is an important prerequisite. While the on-line detection of NO, SO_2 or CO belonged for a long time to the state of the art the on-line detection of organic trace components has still to be developed. As far as speed and chemical preparation of the sample are concerned the conventional GC-MS has reached its limits of performance.

The proposed paper shows the application of an on-line analysis method for organic trace components in conjunction with the development and optimization of a multi-staged process which consists of

- gasification with air on a grate followed by
- an independent post-combustion of the gases generated [1, 2].

The applied analysis method is a combination of laser induced **R**esonance-**E**nhanced **M**ulti **P**hoton **I**onization (REMPI) [3] and **T**ime-**o**f-**F**light **M**ass **S**pectrometry (TOFMS) which represents a useful tool for the detection of trace quantities of organic substances [4-6].

The application as an environmental analysis method will be discussed with reference to test results at a pilot plant (thermal capacity 0.5 MW) using the above-mentioned multi-staged gasification/combustion process. Special emphasis lays here on the investigation of the independent post-combustion of the gases generated in the grate process concerning organic trace compounds. The pattern of organic substances in the flue gas depending on the combustion conditions (temperature, residence time and mixing conditions) can be detected by the REMPI-TOFMS. So this leads to a better understanding of pollutant formation and decomposition mechanisms and beyond this an on-line optimization of the process will be possible.

2 Gasification – Post-Combustion Process

2.1 General Aspects

A concept of thermal treatment of waste should guarantee a low level of pollutants. Before secondary measures are expanded further, the main thermal processes must be optimized above all by primary measures. The process conditions are chiefly determined by the level of main influencing parameters (fig. 1). The distribution of these parameters along the reaction path is important together with the different reaction steps.

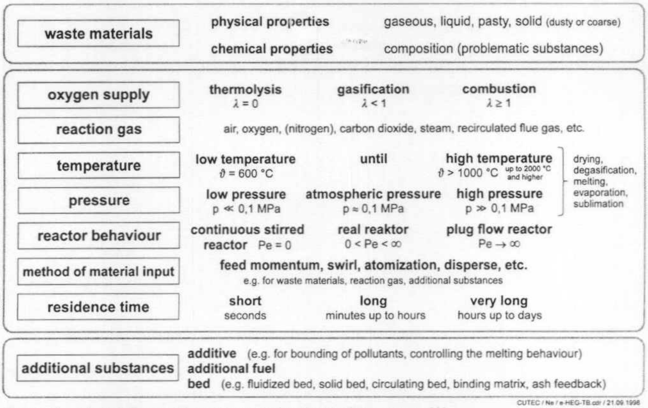

Figure 1. Main influencial parameters for thermal treatment [2].

From the technical point of view of the combustion process, coarse waste materials are more difficult to treat than regular gaseous, liquid and powdered fuels. For very different successive tasks, like:

- conversion of solid matter and
- combustion of gases generated,

the separation into different process units provides opportunities for individually optimizing each task. Depending on the supply of oxygen or air the conversion of solid matter can be run as a pyrolysis, gasification or combustion. The so called classical process of waste treatment is the combustion–post-combustion process with grate systems. With regard to optimization an additional leeway arises if the first process is operated as a gasification. A almost complete conversion of organic solid matter is possible both at gasification and at combustion (avoiding of pyrolysis coke). The gasification leads among others to a combustible gas which makes an independent post-combustion without additional fuel possible in comparison to the combustion. Furthermore primary measures to reduce pollutants can be applied [e.g. 7-10]. The way of conducting the processes

- gasification of solid matter on the grate with air ($\lambda_g \approx 0.4$ to 0.8),
- post-combustion of the gases almost stoichiometrically ($\lambda_{tot} \approx 1.2$ to 1.4) and
- heat exchange

separately, is shown schematically in fig. 2. There are many possibilities available with grate systems for controlling the main acting variables [e.g. 1]. In contrast to shaft furnaces, rotary kilns and fluidized bed reactors, grate systems enable a control of reaction steps (drying, degassing, gasification, burn-out) over the reaction path. Gaseous, liquid and powdered fuels are mostly burned in combustion chambers.

This gasification–post-combustion concept, currently examined on a test-size scale, appears promising, as, in comparison to the conventional incineration processing in grate systems,

- the flue gas mass flows are significantly reduced,
- combustible gases which enable an independent post-combustion process are generated,
- the post-combustion process itself can be optimized regardless of the process on the grate with the help of familiar primary measures for reducing the NO_x-emissions and at the same time achieving high burn-out results,
- emission loads can be reduced considerably [2, 11, 12].

As mentioned before here the optimization of the post-combustion, especially the minimization of organic compounds and the on-line monitoring of this trace compounds are of special interest.

2.2 Pilot Plant

The flow diagram of the pilot plant, including the scheme of the corresponding process measuring and control equipment, is presented in fig. 3. The plant consists of the main components

- 5-zone reverse acting grate or, alternatively, 3-zone advancing grate,
- combustion chamber system,
- heat exchanger and
- flue gas purification unit.

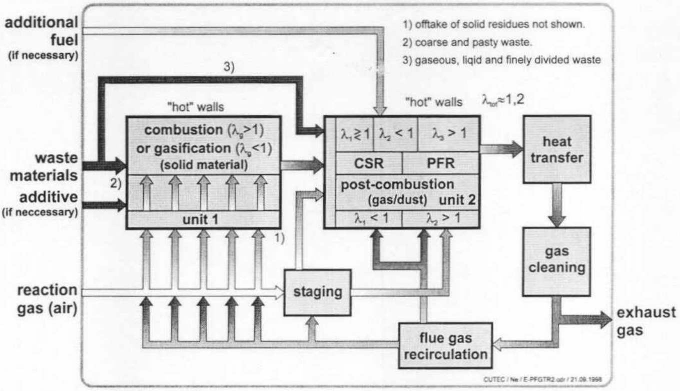

Figure 2. Block flow diagram with independent units of thermal treatment for coarse waste [1].

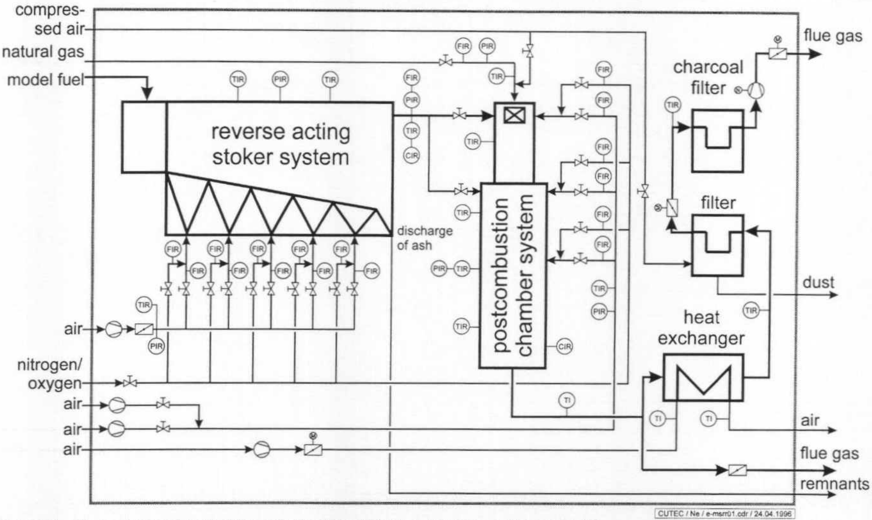

Figure 3. Measuring and control flow chart of the pilot plant (reverse-acting grate) [2].

Within the framework set here, the essential aspects are briefly outlined. Complete details on plant technology, data logging system and analysis are reported elsewhere [11].

The model combustible solid or waste material is supplied in intervals to the first grate zone via a feeding ram located at the lower end of the feeding hopper. The reaction gas (usually air; recycling of flue gas or oxygen enrichment is possible) is supplied to the underside of the grate.

The combustion gas generated in a sub-stoichiometrical operation of the grate process (gasification) is fed to the combustion chamber unit for an independent, multi-staged post-combustion. Depending on the primary measures to be examined in the area of the combustion chamber unit, a staging of the air and, if necessary, of the combustible can be provided for the setting of the required conditions of temperature, oxygen-concentration and residence time along the reaction path.

The scheme of the process measuring and control equipment in the flow diagram in figure 3 gives an outline of the quantities measured during the test operation. The mass flow and composition of the input material, the mass flow and the composition of the fuel gas and the exhaust gas: CO_2, O_2, CO, H_2, CH_4, NO, SO_2, HCl, temperatures in the grate and the combustion chamber are important concerning balancing and evaluation of the experimental investigations and belong to the standard program. If indicated not differently, all gas concentrations are referred to $\psi_{O2} = 11$ vol-% (i.s.s. dry). The sampling of the organic trace compounds (**p**oly**c**hlorinated **d**ibenzo-p-**d**ioxines and polychlorinated dibenzo**f**uranes (PCDD/F), **p**olycyclic **a**romatic **h**ydrocarbons (PAH) , **p**oly**c**hlorinated **b**iphenyles (PCB), **p**oly**c**hlorinated **b**en**z**enes (PCBz) etc.) was carried out first of all discontinuously recording VDI-guideline 3499, page 3. For absorption a condenser followed by 2 series of gas bubblers filled with methoxyethanole as absorptive solution were used. The compounds were measured by conventional GC-MS after corresponding clean up of the sample. The PCDD/F-concentrations are indicated as toxicity equivalents (TEQ) referred to the sucked gas volume at $\psi_{O2} = 11$ vol-% (i.s.s. dry). About the on-line measurements with REMPI-TOFMS will be reported below separately.

3 Decomposition of Organic Trace Compounds in the Post-Combustion Process

3.1 Variation of Influencing Parameters

First of all there was the aim to indicate trends on the decomposition of organic trace compounds depending on the process conditions in the post-combustion process. In the context of first grope tests five clear different adjustments of the main influence parameters temperature, oxygen concentration and residence time respectively residence time behavior were provided (table 1) [13].

Striving temperatures of $\vartheta \approx 1200\,°C$ at the first stage of the combustion chamber the first trial (T1) was carried out at near stoichiometric conditions ($\lambda_{pc,1} \approx 1{,}0$). To improve the mixing conditions in the first stage of the combustion chamber the air supply was increased in a second test run (T2). A further improvement of the mixing conditions should be achieved by additional supply of nitrogen (simulation of flue gas recycling) (T3). At the two last test runs a decrease of the temperature was intended. Therefore the mass flow of air was increased (T4) and nitrogen was supplied additionally (T5).

test number (T)			1	2	3	4	5
mass flow rate of fuel supply (grate)	$\dot m_{F,g}$	[kg/h]	60	60	60	80	80
mass flow rate of air supply (post-combustion)	$\dot m_{A,pc,1}$	[kg/h]	110	153	129	202	118
mass flow rate of nitrogen supply (post-combustion)	$\dot m_{N_2,pc,1}$	[kg/h]	0	0	146	0	146
mass flow rate of air supply (post-combustion)	$\dot m_{A,pc,2}$	[kg/h]	134	61	54	314	279
mixture ratio	δ		0,61	0,85	1,63	1,00	1,33

Table 1. Parameter variation of the tests T1 to T5 [13].

The gasification process put in front was operated with crushed waste wood (mixture of coated woods, pallets, plastic materials, window wood etc.) and remained unchanged concerning the air ratio $\lambda_g \approx 0.6$. The mass flow rate of input material was constant in the test runs T1 to T3 and T4 and T5.

3.2 Results and Discussion

The results of the above mentioned parameter variations are summarized in table 2 [13]. The temperatures were measured at the first stage of the combustion chamber ($\vartheta_{pc,1}$), at the second stage behind the secondary air supply ($\vartheta_{pc,2}$), and at the outlet of the combustion chamber ($\vartheta_{pc,3}$). The gas concentrations have been detected at the outlet of the combustion chamber. To characterize the mixing conditions at the first stage of the combustion chamber a simplified mixture ratio δ is introduced here: the sum of the primary air mass flow rate $\dot m_{A,pc,1}$ and the nitrogen mass flow rate $\dot m_{N_2,pc,1}$ ($\dot m_{RG,pc,1} = \dot m_{A,pc,1} + \dot m_{N2,pc,1}$) is referred to the mass flow rate of the fuel gas from the gasification $\dot m_{G,g}$.

With regard to the PCDD/F-concentrations three summarized aspects seem to be important:

- All TEQ-concentrations are below 0.1 ng/m^3 (TE) (limit value [14]).
- The sum concentrations for the test runs T1 to T3 are on the same level in the context of analysis precision.
- The sum concentrations for the test runs T4 and T5 are on the same level too, however in comparison with T1 to T3 around a order of ten higher.

This allows the following conclusions. High temperatures alone like in the first test T1 of about $\vartheta \approx 1200\,°C$ do not represent any mandatory prerequisite for a high decomposition of organic trace compounds. Also at lower temperatures of about $\vartheta \approx 950\,°C$ according to better

test number (T)			1	2	3	4	5
temperature in the post-combustion chamber	$\vartheta_{pc,1}$	[°C]	1200	1050	1050	1050	750
	$\vartheta_{pc,2}$	[°C]	950	1000	950	750	750
	$\vartheta_{pc,3}$	[°C]	900	900	900	700	750
residence time	τ_{pc}	[s]	2,8	3,1	2,2	2	2,4
mixture ratio	δ	[-]	0,615	0,855	1,627	1,005	1,333
O$_2$-concentation	$\psi_{O2,pc}$	[vol.-%]	4,34	4,31	2,76	10,2	6,47
CO-concentration	$\psi_{CO,pc}$	[mg/m^3]	<10	<10	<10	<10	<10
NO$_2$-concentration	$\psi_{NO2,pc}$	[mg/m^3]	265	357	254	409	297
PCDD-concentration	$\psi_{PCDD,pc}$	[pg/m^3]	224	201	204	1046	89
PCDF-concentration	$\psi_{PCDF,pc}$	[pg/m^3]	333	180	605	2322	2774
PCDD/F-concentration	$\psi_{PCDD/F,pc}$	[pg/m^3]	556	381	810	3368	2862
PCDD/F (TEQ)	$\psi_{PCDD/F,pc}$	[pg/m^3]	21	10	20	59	32

Table 2. Selected results of the tests T1 to T5 [13].

mixing conditions (T2, T3) a high decomposition is possible. The PCDD/F-concentrations of test runs T4 and T5 are comparatively to the test runs T1 to T3 about one order of ten higher, which can be referred to the clear lowering of the temperature level below $\vartheta < 800\,°C$. Nevertheless the PCDD/F-concentrations are also at this low temperature level below $0.1\,ng/m^3$ TEQ. This is remarkable, if one takes into account, that even at gasification of waste wood several organic compounds are produced. This will be shown by the REMPI-TOFMS spectrum below.

A further important task, also in connection with the development of the on-line analysis, is the investigation of so called indicator compounds for PCDD/F. Previous investigations have shown that the chlorinated benzenes and phenols are good dioxin indicators [e.g. 15-18]. Also at the here mentioned investigations a good correlation between chlorinated benzenes and PCDD/F was recocnized (fig. 4) [13]. However polychlorinated biphenyles shows not such a behavior. The PCB varies in a range of about $\psi_{PCB} \approx 1000$ to $3000\,ng/m^3$. A direct dependence on process conditions was not detectable.

Next to the organic pollutants consideration should be given to CO- and NO-concentrations. In all cases the CO-concentrations are below $\psi_{CO} < 10\,mg/m^3$. As reported elsewhere [e.g. 19] the results point out that CO is not any indicator for more stable organic compounds like PCBz, PCDD/F etc.

The staged processing in test run T3 with external flue gas recycling (simulated by nitrogen) leads to low NO-concentrations. At the tests mentioned here no minimization of NO was scheduled. However, if the process is optimized as reported in [2, 20], results lower than $\psi_{NO2} \approx 200\,mg/m^3$ can be obtained.

The results altogether lead to the conclusions, that also at gasification–post-combustion processing of contaminated waste wood the temperature, residence time and residence time behavior in the post-combustion process contribute all together to a decomposition of organic trace substances. A temperature level of about $\vartheta \approx 950\,°C$ accompanied by a high mixing intensity in a first sub-stoichiometrical stage (continuously stirred tank reactor) followed by near plug flow conditions in a second overstoichiometrical stage is well suited to achieve a high decomposition rate both of organic trace substances and NO.

Optimization tests with regard to organic substances require a high expenditure of time and money if the detection of these compounds is performed off-line–as reported until now. An on-line monitoring of organic trace substances would open the possibility of an on-line optimization too. So a new set of process parameters can be evaluated immediately after transition into a new steady state. The following attempts with a on-line measurement method are of special interest both concerning on-line optimization and a better understanding of pollution formation and decomposition mechanisms.

4 Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometer

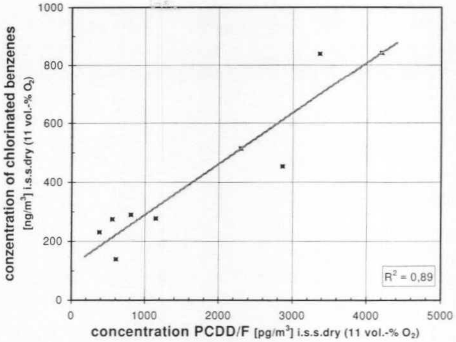

Figure 4. Concentration of chlorobenzene referring to concentration of PCDD/F [13].

4.1 Experimental Method

While the on-line detection of NO, SO_2 or CO belonged to the state of the art for a long time the on-line detection of organic trace components has still to be developed. The conventional GC-MS has reached its limits of performance as far as speed and chemical preparation of the sample are concerned. The results are available hours or even days after the sample has been taken.

On-line measurements of trace compounds in exhaust gases of combustion processes require methods that combine selectivity with sensitivity. Laser spectroscopic techniques, like e.g. the absorption spectroscopy, the laser induced fluorescence (LIF), the matrix assisted laser desorption and ionization (MALDI) or the light

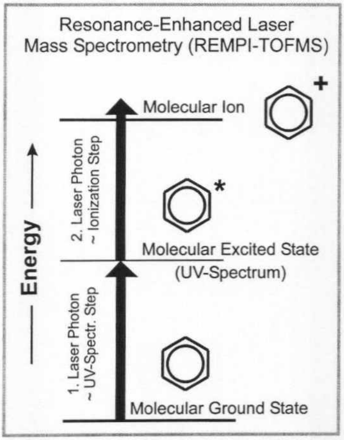

Figure 5. Ionization process.

detection and ranging (LIDAR), find more frequently practical application. A promising possibility for a species selective on-line detection is given by a newly developed, mobile laser mass spectrometer (Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometer, REMPI-TOFMS). REMPI-TOFMS combines the optical selectivity of Resonance-Enhanced Multiphoton Ionization with a Time-of Flight Mass Analysis to a two-dimensional analytical method.

For the REMPI detection of aromatic compounds, usually a one photon resonante /two photon ionization process is used (fig. 5). The first photon is absorbed and the molecule is in an exited state. This step is similar to gas phase UV absorption spectroscopy. In the measurements described below a second photon is absorbed, ionizing the molecules of interest. For strong transitions in the first excitation step the ionization yield can be in the range of several per cent of the illuminated molecules.

Fig. 6 shows the REMPI-TOFMS equipment schematically. A very important part of the instrumental design is the setup of the probing and sample inlet system for real-time on-line measurements. The exhaust gas of waste incineration processes consists of corrosive inorganic substances e.g. HCl, NO, SO_x, a variety of organic substances of different volatility up to low volatile compounds (e.g. tar) and is loaded with dust particles. The requirements for direct probing of PAHs from the combustion flue gas are:

- avoiding of condensation of low volatile compounds,
- minimization of memory effects for the semi-volatile compounds,
- reduced catalytic activity of the surface and
- a rugged and reliable design.

The sample system inlet is built with quartz glass surface from the sampling point to the MS. It consists of a quartz glass tube, a quartz glass wool filter paper and a capillary. The whole system is heatable up to 200 °C to avoid memory effects for larger PAHs. The flue gas is sucked with a flow rate of about 100 l/h and the residence time in the system is about 3 sec [6].

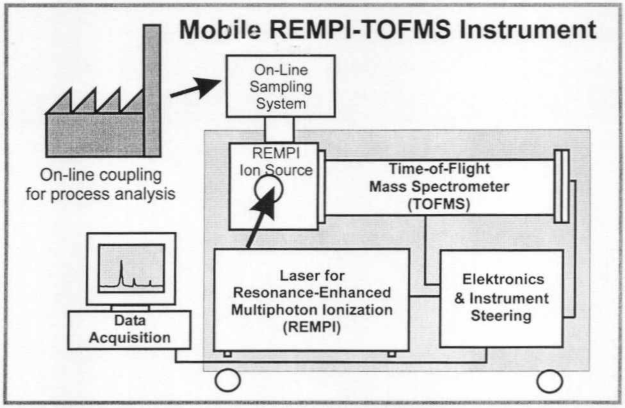

Figure 6. Schematic presentation of the REMPI-TOFMS instrument.

The applied KrF excimer laser (248 nm) supplying laser pulses with 10 ns duration, up to 50 Hz repetition rate und up to 10 mJ pulse energy (MINEX, Lambda Physics Inc., Germany). The laser wavelength of 248 nm is well suited for detection of benzene and its alkylated derivates as well as for many PAHs and theirs alkylated derivates. The ionization yield is proportional to the laser intensity, however an adequate calibration procedure is necessary for analytical application. The calibration and adjustment of the laser mass spectrometer were performed with ppb standards prepared dynamically with permeation and diffusion devices. Details of the in-house designed micro-devices will be published elsewhere. Naphthalene can be quantified directly using the external calibration standard. Quantitative results are given in reference. The calibration factors for other PAHs have been adapted in combination with naphthalene calibration from other experiments [6]. For naphtalene@248nm using the KrF excimer laser a detection limit of 86 ppt was achieved.

4.2 Results and Discussion

Because of its unique selectivity, combined with high sensitivity, the REMPI technique is ideally suited for real-time applications. Simultaneous to the above mentioned investigations of the process conditions of the post-combustion process on the decomposition of organic trace substances first on-line measurements with the REMPI-TOFMS were carried out at the gasification–post-combustion pilot plant. The results discussed here were obtained at the outlet of the combustion chamber.

The selectivity and sensitivity of this method analyzing complex flue gases from a waste incineration process can best be evaluated with non stationary test conditions. Fig. 7 shows a REMPI@248nm mass spectrum recorded after partly extinguished post-combustion due to reduced air supply. The measurement time was 500 milliseconds, corresponding to 25 averaged mass spectra with a laser repetition rate of 50 Hz. The mass spectra shows a large number of monocyclic and polycyclic aromatics and their alkylated derivates. A tentative assignment of the peaks is given in fig. 7. It is interesting to note the very low intensity of toluene (m/z = 92) and higher alkylated benzene derivates in the mass spectrum. Benzene, naphthalene, its methylated derivates, anthracene and pyrene are typical products of incomplete combustion. The spectrum also shows phenol (m/z = 94), a typical product of wood gasification. The REMPI-sensitivity for phenolic compounds is lower compared with benzene, since the introduction of the hydroxyl group causes a large red shift of the first UV transition.

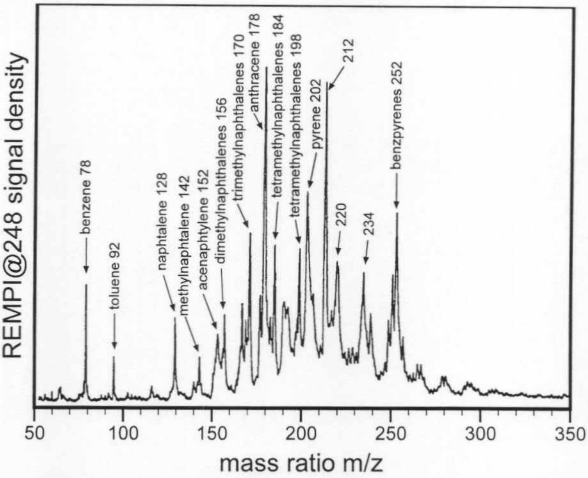

Figure 7. REMPI@248 TOFMS mass spectrum [5].

The relatively prominent peak at m/z = 212 may be due to hexamethylated naphthalene. The m/z = 252 peak corresponds to the ensemble of pentacyclic PAH isomers (perylene, benzoflouranthenes and benzypyrenes). The highly carcinogenic benz[a]pyrene (BAP) molecule represents an indicator compound for the toxicity of complex PAH mixtures. A selective on-line BAP monitoring is possible with a two-laser REMPI scheme and a supersonic inlet valve for sample cooling [21].

5 Summary and Further Investigations

The first part of the paper deals with the optimization of a newly developed gasification–post-combustion process. Special emphasis is given to the decomposition of organic trace compounds depending on the conditions at the post-combustion process. Thereby the main influential parameters temperature, oxygen concentration, residence time and residence time behavior have to be considered coherently. Not only a high temperature of $\vartheta \approx 1200\,°C$ is the prerequisite of a good burn-out, even if high concentrations of aromatic substances and pre-cursors for PCDD/F occurs in front of the post-combustion. A temperature level of about $\vartheta \approx 950$ °C accompanied by a high mixing intensity in a first sub-stoichiometrical stage (continuously stirred reactor) followed by near plug flow conditions in a second overstoichiometrical stage is well suited to achieve a high decomposition rate both of organic trace substances and NO.

However, optimization of the post-combustion concerning organic decomposition is expensive due to the high effort of discontinuously sampling and analyzing. A promising possibility for a species selective on-line detection is given by a newly developed, mobile laser mass spectrometer (Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometer, REMPI-TOFMS). REMPI-TOFMS combines the optical selectivity of Resonance-Enhanced Multiphoton Ionization with a Time-of Flight Mass Analysis to a two-dimensional analytical method. The results presented here prove that a REMPI-TOFMS device is applicable under rough environmental conditions (dust, temperature changes, vibration etc.). A highly time-resolved, on-line analysis of organic compounds in flue gases of industrial incinerators (waste incinerators, power plants, industrial thermal processes) is possible. It allows on-line detection of PAHs with molecular mass of 252 and higher with sensitivities in the low ppb region and better. The direct monitoring of process-caused concentration fluctuations in the post-combustion chamber at high temperatures opens additional leeway for on-line optimization of the process.

One future aim is the on-line detection of indicator compounds for PCDD/F. Previous investigations have shown that the chlorobenzenes and phenols are good dioxin indicators. Next to the further improvement of the REMPI-TOFMS there is the task of on-line optimization of the post-combustion process. With regard to further minimization of the experimental effort the optimization should be accompanied by mathematical modeling.

6 Acknowledgements

Here we would like to give special acknowledgement to the "Deutsche Bundesstiftung Umwelt", Osnabrück, Germany. With the financial help of this foundation the pilot plant was erected, the majority of the tests presented here were carried out and the REMPI-TOFMS device was developed.

7 Nomenclature

Symbols

ϑ	temperature
λ	air ratio, stoichiometric ratio
ψ	concentration (volume related)
δ	mixing index
τ	residence time
m	mass
m/z	mass ratio

CSR	continuously stirred tank reactor
PFR	plug flow reactor
PAH	polycyclic aromatic hydrocarbones
PCB	polychlorinated biphenyles
PCBz	polychlorinated benzenes
PCDD/F	polychlorinated dibenzo-p-dioxines and poychlorinated dibenzofuranes
TEQ	toxicity equivalent

Indices

1,2,3	staging index
A	air
F	fuel
g	grate
G	combustible gas
i.s.s.	in standard state
pc	postcomustion chamber
RG	reaction gas (air)
tot	total
.	flux

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