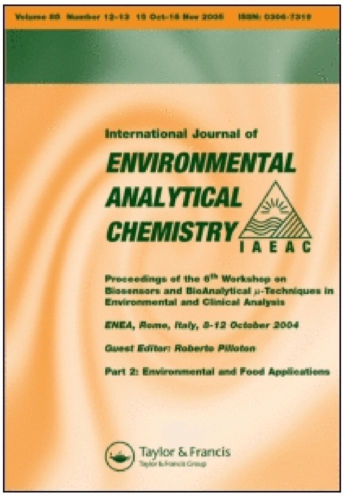

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Combustion of Waste Waters Containing Organic Alkaline Salts

H. Bartz[a]; H. Fissan[a]; D. Dolan[a]
[a] Univesität Duisburg, Aerosolmeßtechnik, Duisburg 1, F.R.G.

To cite this Article Bartz, H. , Fissan, H. and Dolan, D.(1983) 'Combustion of Waste Waters Containing Organic Alkaline Salts', International Journal of Environmental Analytical Chemistry, 13: 3, 193 — 203

To link to this Article: DOI: 10.1080/03067318308071593

URL: http://dx.doi.org/10.1080/03067318308071593

Intern. J. Environ. Anal. Chem., 1983, Vol. 13, pp. 193–203
0306-7319/83/1303-0193 $06.50/0

Printed in Great Britain

Combustion of Waste Waters Containing Organic Alkaline Salts†

H. BARTZ, H. FISSAN and D. DOLAN
Univesität Duisburg, Aerosolmeßtechnik, Bismarckstr. 81, 4100 Duisburg 1, F.R.G.

(*Received May 13, 1982*)

The biological treatment of waste waters from chemical industry containing organic and inorganic salts causes problems because these materials inhibit the metabolic activity of the bacteria. One possible and economically feasible way to convert the organic materials into less toxic forms is a thermal oxidation process, which can take place either in a fluidized bed combustor or in a vertical combustion chamber.

The process is described and parameters of the process are discussed. Results from particle measurements on a vertical combustion chamber for the combustion of various artificial waste waters are presented. The chemical analysis of the particulate matter from different stages of the process allows a detailed characterization of the decomposition of the organic material. Conclusions are drawn both with respect to the process and the environment.

KEY WORDS: Waste water, combustion, alkaline salts, aerosols, chemical oxygen demand.

INTRODUCTION

Water pollution is not only caused by human activities. Industrial processes are also a major source for waste waters. Their compositions are as different as the variety of products. Problems arise from organic pollutants as well as inorganic compounds such as nitrates and phosphates and toxic substances which can have either an organic or inorganic basis.

---

†Presented at the 12th Annual Symposium of the Analytical Chemistry of Pollutants, Amsterdam, April 1982.

Highly polluted waste waters are originated in different branches. For example the plastic industry and herein mainly the fibre production is one of the most important sources. The waste waters of this group contain organic alkaline salt compounds, mainly sodium compounds.

Waste waters from the dye industry and from pulp mills contain phosphates and hydrocyanic residues which cannot be treated biologically and thus require physical-chemical methods. Organic and inorganic salts are also present in waste waters from desulfurization plants as well as from the production of pharmaceuticals, explosive materials and insecticides.

The quantity of these waste waters depends on the production method as well as on the output of products. However even small quantities can cause a damage in the environment if these waters are emitted without any treatment.

From a legislative point of view the water pollutants are characterized with respect to their impact on the environment by overall parameters which either describe the oxygen demand of the pollutants or indicate their carbon contents. The biological oxygen demand within a time period of five days (BOD_5) has been internationally accepted.

Because of the time consuming determination method, the chemical oxygen demand (COD) instead of BOD_5-value is favoured for many practical applications.

In Table I the organic load of different waste waters is listed. For municipal waste waters, the BOD_5 value is about 350 mg/l.[1]

The most common treatment method for these waters is biological

TABLE I

Comparison of different waste waters.

Source	Waste water quantity m^3/h	C O D mg/l	BOD_5 mg/l
City with a population of 100.000	850	n. d.	350
Varnish color industry	100	700	500
Paper mill	700	n. d.	500
Ethylenoxide and Polypropylen production	100	n. d.	2500
TREVIRA production	6	200.000	90.000

n. d. - not determined

cleaning. Examples for industrial waste waters show the range of BOD_5-values as well as the range of possible quantities. As can be clearly seen, the waste waters from the production of synthetic fibres (in this case TREVIRA[2]) differs considerably from the others. The BOD_5-value is more than 250 times that of a municipal waste and considering the quantity of $6\,m^3/h$ the daily waste water production equals that of a city with a population of nearly 200,000 people.

Biological treatment plants are no longer economically favourable in such cases because large areas and long treatment times are required. Problems also arise because of toxic agents or inorganic salt compounds which inhibit the metabolic activity of the bacteria.[3]

It appeared that thermal decomposition of these waste waters is an alternative method both with respect to economy and to ecology. The water is burned with or without additional fuel either in a fluidized bed combustor or in a vertical combustion chamber. Organic substances are oxidized and in the ideal case the end product contains only water and carbon dioxide as well as inorganic compounds (salts) which can either be deposited or recycled.[4]

The real process however behaves different. The decomposition of organic material depends upon the combustion conditions and may be incomplete, for example if reaction temperature is too low or reaction time is too short. Aerosols are formed in the combustion chamber and the exhaust gas contains particles which are difficult to precipitate because of their submicron size.[5]

The investigation of this process has two main points of view:

1) How must the combustion parameters be chosen so that a complete decomposition of the organic material in the waste water is guaranteed?

2) What are the physical and chemical properties of the emitted particles?

Thus far, technological aspects such as construction of burner and combustion chamber,[6-8] operating conditions,[9,10] field of application,[11,12] and economical aspects such as energy consumption and maintenance costs[13-15] have been studied. Recent investigations deal with the NO_x-production from fuel-N[16] and the formation of aerosols in this process.[17] Here experimental results are presented concerning the rate of decomposition of organic materials.

EXPERIMENTAL SET-UP

Combustion chamber, measurement system and artificial waste waters

The thermal oxidation of the waste water can generally be accomplished in a fluidized bed combustor at temperatures of about 700–800°C or in a vertical combustion chamber at about 900–1300°C. If the combustion products contain alkali salts, the vertical combustion chamber is prefered because the melting point of these salts lies within the range of the fluidized bed combustion and so the bed material easily becomes encrusted.

In the vertical combustion chamber (Fig. 1) the waste water is introduced through a burner on top. In this research project a flame evaporation burner was used which means that all of the components involved in the combustion are brought into the chamber at the same point. The waste water is introduced through an air-blast atomization system and then reacts in the gas/air flame.

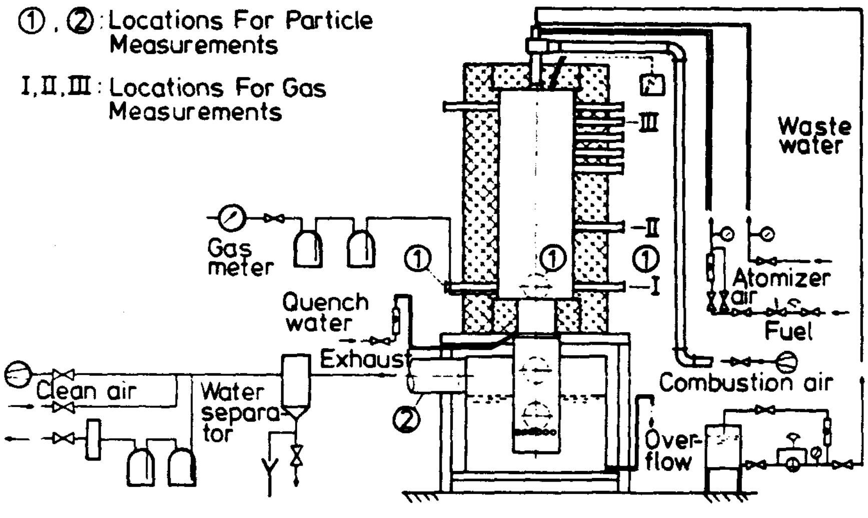

FIGURE 1 Experimental system for waste water combustion.

After the combustion process the exhaust gas can either be passed through a steam generator or, if there is no need to use this enthalpy as in the case of the research plant, is passed through a closely coupled water quench. The quench both cools the gases down and removes part of the reaction products such as molten salts and aerosol particles. Dissolved salts can be recycled from the quench water and either be deposited or possibly reused as raw material.

In this project the experiments were conducted on a pilot plant at the L. and C. Steinmüller Company. Gummersbach, West Germany. The inside diameter of the combustion chamber is 0.6 m. In order to minimize heat losses, the chamber wall consists of 275 mm of high temperature insulation with an inner fireproof casing. The rated output of the chamber is 250 kW.

Samples for the characterization of the combustion products were taken from an opening located at the end of the chamber. At this point the combustion process is terminated by the quench. It is assumed that no further chemical conversion occurs. Therefore measurements at this point also characterize the entrance conditions for the quench.

A second sample was taken from behind the quench. This is the point where the exhaust gas, which is already partially cleaned, is released into the environment or if necessary is introduced into further cleaning devices.

The measurement system used consists of a cooled probe to ensure complete condensation of salts in the flow. To prevent water condensation, the sample is diluted with nitrogen. One leg of the system goes directly to a filter or size fractionating cascade impactor. A chemical analysis was performed to determine COD-values and sodium concentration corresponding to the mass loadings of these filters. In the second leg there is a flow measurement orifice followed by a second stage of dilution. At this point the Electrical Aerosol Analyzer (TSI Model 3030) was used to determine the size distribution in the diameter range 0.01–1.0 μm.[18]

Because of the heterogeneous and complex nature of real waste waters, artificial waste waters were used. Their properties (chemical compounds and COD-values) are typical for real waste waters (see Table I) and they could be easily reproduced. Table II gives an overview for combinations which are studied.

The measurements reported here refer to a composition according to the second line. The waste water flow was 15 kg/h, the equivalence ratio λ

TABLE II

Artificial waste waters.

	Organic Compound	Inorganic Compound		Scope
I	10% C_2H_7NO	10% Na_2CO_3	80% H_2O	formation of: - nitrogen oxides
II	10% C_6H_5COONa	10% Na_2CO_3	80% H_2O	-salt particles
III	10% $C_7H_8O_3S$	10% Na_2CO_3	80% H_2O	-SO_x
IV	10% $C_5H_8NNaO_4$	10% Na_2CO_3	80% H_2O	-NO_x and particles

was set at 1.3. For a measured chamber temperature of 950°C a residence time *t* in the combustion chamber of 2.14 s was calculated.

RESULTS

The combustion is terminated when the combustion products enter the quench. Measurements of the sodium content in the quench water and the exhaust gas behind the quench showed that only 50% of the sodium introduced at the atomizer is found before the quench, or, in other words, 50% stay inside the combustion chamber. It is assumed that this material deposits on the chamber walls which is supported by the fact that samples from the fireproof insulation contained several Na-Al silicates. A saturation state for this reaction was not yet observed.

The decomposition of organic material is characterized by the ratio of COD-values for the combustion products and the input waste water. The COD value for the waste water is 200 g/l which corresponds at a given water flow rate of 15 l/h to a value of 3000 g/h. At the quench entrance only 7.4 g/h were found, which is the sum of values for the quench water and exhaust gas. Assuming a complete decomposition for the wall losses, this gives a decomposition rate of more than 99%.

The hot combustion products have to be cooled down before they are emitted. Here they are introduced into a water quench. The particles which are formed during this cooling were studied using the sampling probe described earlier.

In Fig. 2, a typical size distribution, as measured with the EAA and the cascade impactor, is shown. The mass mean diameter is in the submicron

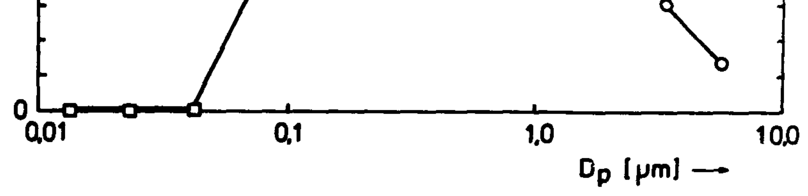

FIGURE 2 Relative particle mass distribution (combustion chamber).

range and the distribution covers about two decades. The formation of this kind of aerosol has been characterized by a model[17] with the following main steps:

- generation of a waste water aerosol with particles in the size range 5–200 μm by the air blast atomization system (coarse mode aerosol);
- evaporation of volatile material such as water and other constituents; the remaining particles still comprise a coarse mode aerosol;
- evaporation of the remaining salt particles with a rate according to chamber temperature and residence time within the chamber;
- nucleation, recondensation and coagulation within the sampling probe. An accumulation mode aerosol is formed.

According to this model it should be expected that two separate types of particles with respect to their composition are present in the combustion chamber: those which have undergone chemical reaction in the gas phase and which are now present in the submicron size range and those which remain after partial evaporation consisting mainly of unburned material.

In Fig. 3 the specific COD-values for the material collected during two different sets of conditions in the combustion chamber (the one described earlier and another with a higher temperature and shorter residence time) are plotted vs. particle size. The COD-values decrease drastically with decreasing particle diameter. The decomposition rate for submicron

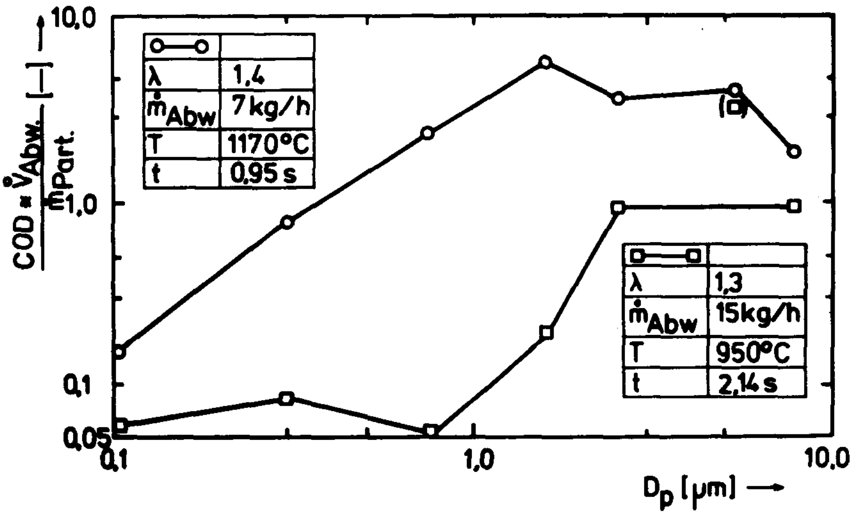

FIGURE 3 Specific COD-values vs. particle size.

particles is better than for those which didn't undergo complete evaporation. Particles with diameter 10 μm still have specific COD-values in the range 1–3 whereas for 0.1 μm particles this value is about 100 times smaller.

The differences between the two curves support the aerosol formation model.

The decomposition rate for particles which had a longer residence time inside the combustion chamber is greater than for those which were introduced with about half the mass flow of water into a chamber with a higher temperature. Residence time is thus a parameter which has a stronger influence on the reactions inside the chamber than temperature.

The COD-value for large particles and long residence times is nearly the same as for the artificial input waste water (0.98). A slight increase is due to a split off of CO_2 from the inorganic sodium carbonate which also shows up in an increase in specific sodium content from 0.30 to 0.33. For the other measurement the specific COD values are about 3 times greater than for the input material. This is proposed to be due to the low mass loadings on the impactor stages in this case (less than 0.1 mg) from which one cannot expect a high degree accuracy. The effect of size dependency for the COD-value however is evident in this case, too.

The cooling and partially cleaning of the combustion products is accomplished in this process by the water quench. The emission site thus consists of two mass streams: the continuously flowing quench water and the exhaust gas.

Figure 4 shows the complete result of a material balance based on sodium detection, part of which has already been discussed. Only 2% of the sodium entering the quench are emitted with the exhaust gas; this gives an efficiency for the quench of 98% which surely is supported by the high solubility of sodium in water. The COD value of this sample is 2.3 g/h whereas in the quench water 5.1 g/h have been found (Fig. 5). Calculating a quench efficiency this gives 69% for the organic material, which is not as good as compared to the sodium balance. Because high COD-values are found only for large particles (Fig. 3), the fractional penetration of particles through the quench is better for large particles than for small ones.

CONCLUSIONS

The process of waste water combustion was presented and experimental results concerning the chemical decomposition of organic material were discussed. A nearly complete decomposition can be accomplished only if the organic salts undergo an evaporation and reactions can take place in

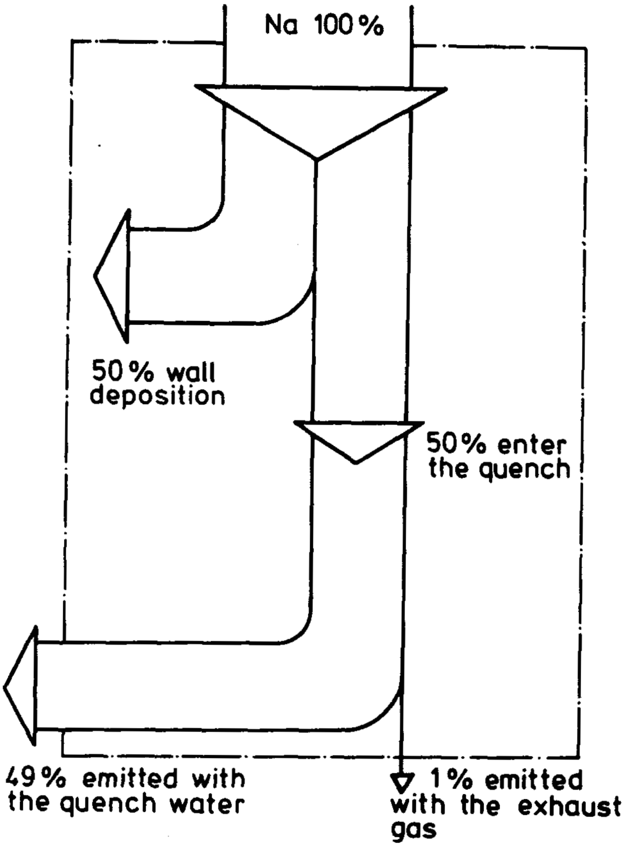

FIGURE 4 Sodium balance.

the gas phase. Partially evaporated salt particles still contain organic material. It was shown that the degree of evaporation is influenced by residence time stronger than by temperature. Roughly 50% of material is lost on the chamber walls, where reaction products of sodium were found.

Emissions from this process occur with the quench water and the exhaust gas. The quench water contains 90% of sodium and roughly 70% of organic material present at the exit of the combustion chamber. The remaining part is emitted with the exhaust gas. Because of the high decomposition rate of organic material, the pollution problem however is considerably reduced.

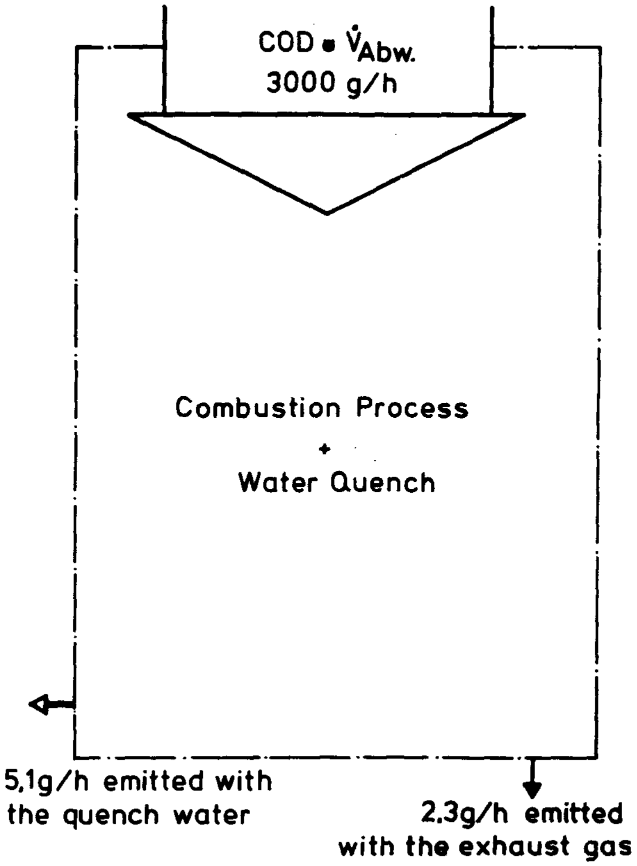

FIGURE 5 Decomposition of organic material (COD-values).

Acknowledgements

This work was supported by the Bundesminister für Forschung und Technologie (BMFT) of the Federal Republic of Germany. The experiments were performed on the pilot plant of L. & C. Steinmüller GmbH, Gummersbach, West Germany. The authors are thankful for this assistance.

References

1. F. Rüb, *Technik der industriellen Abwasserbehandlung* (Krauskopf Verlag, Mainz 1974).
2. H. Salomon, *Jahrbuch vom Wasser* **39** (1972).
3. F. Malz, *VDI-Bericht Nr.* **207**, 69 (1973).
4. Th. Burkard, *Technische Mitteilungen* **71**, 527 (1978).

5. H. A. Herbertz, *Salze and salzhaltige Lösungen, Umweltbundesamt:* Erich Schmidt Verlag, Berlin (1977).
6. K. Hess, W. Leuckel and E. Minx, *Chemie-Ingenieur-Technik* **44,** 325 (1972).
7. K. Leikert, *Wärme* **1/2,** Bd. 78 (1972).
8. E. Ruhl, *VDI Bericht Nr.* **346,** 209 (1979).
9. E. Lavanchy and B. Anderau, *Chemie-Ingeneieur-Technik* **48,** 15 (1976).
10. G. Hoerner and W. Leuckel, Institute of Chemical Engineering, Symposium Series No. 43, 1.1–1.9 (1976).
11. L. Barniske and Chr. Nels, *Brennstoff-Wärme-Kraft* **33,** 166 (1981).
12. H. Tsurata, *Chemical Economy and Engineering Review* **4** (1972).
13. G. Hebbel, *Chemie-Ingenieur-Technik* **48,** 12 (1976).
14. H. Leib, *Chemie-Ingenieur-Technik* **46,** 319 (1974).
15. K. Schlömer, *Chemie-Ingenieur-Technik* **48,** 41 (1976).
16. R. Shamekhi and P. Roth, *VDI Report no. 423,* 55 (1982).
17. H. Bartz, D. F. Dolan and H. Fissan, *VDI Report no. 429,* not yet published.
18. B. Y. H. Liu and D. Y. H. Pui, *J. of Aerosol Science* **6,** 249 (1975).