ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 12, 1998

*Werner Beckers**, *Dieter Schuller**

THERMOLYTICAL WORKING-UP OF CONTAMINATED SEWAGE SLUDGES AND COMPARABLE WASTE MATERIALS IN A THREE-STEP BATCH PROCEDURE

A three-step batch procedure for thermal treatment (drying, pyrolysis, gasification = thermolysis) of contaminated waste materials is suggested - for one reactor and regulated by temperature. Contaminated sewage sludges have been investigated under technical criteria and material management criteria. Technical processing yields gases from a pyrolytic step (823 K, C_1–C_4-fraction) and from a steam gasification step (1173 K, H_2, CO, CO_2, CH_4). A solid residue has been leached with water and compared with contemporary legal restrictions. Catalytic treatment (723 K) of volatiles from the pyrolytic step yields a liquid fraction – including btx-compounds. Contaminated intermediate fractions (water from drying and from reaction in a pyrolytic step, contaminated solid residues) should be gasified under definite conditions. The process adapted to contaminated material may be applied to conventional organic feedstocks, too.

INTRODUCTION

Three-step batch procedure

If one talks of advanced and clean gasification and incineration the process itself has to yield good results (primary measures). Secondary measures may be the regulation of input material (in our case: addition of burnt lime to sewage sludges) or the cleaning of gases afterwards (cleaning of raw gas from gasification or flue gas). With each step of processing resulting products (solids, fluids, gases) should be less dangerous or – ideally – less hazardous than the input material or neutral to the environment at all – with the exception of very small amounts of e.g. sludges from cleaning steps. Reduce volume, produce an inert material, produce if possible a reusable material or gas! Our approach to the problem, advanced and clean gasification as derived from our experiments, is a three-step batch procedure in a fluidized bed reactor system. Open handling of hazardous waste is not necessary. Figure 1 shows the whole process as flow chart. The boundary of the system is depicted by a box.

---

* Ökochemie und Umweltanalytik, Department of Chemistry, Carl-von-Ossietzky University Oldenburg, Postbox 25 03, D-26111 Oldenburg, Germany.

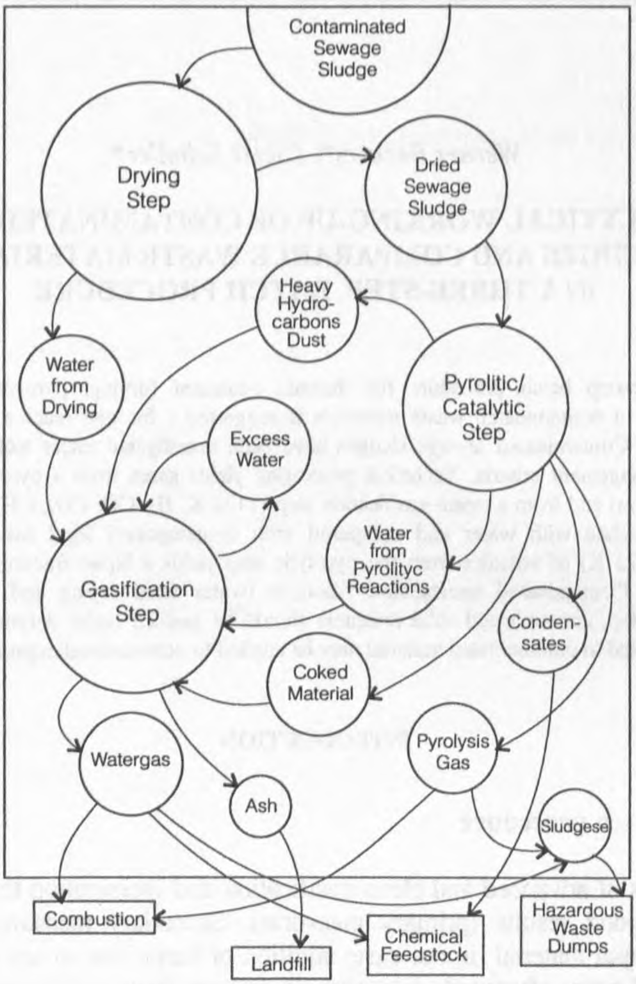

Fig. 1. Flow Chart of the Thermolysis

First step. In the first step organic waste (contaminated sewage sludge) is dried in order to be suitable for thermal treatment.

– The drying process yields a water fraction which can be used for the gasification under neutralization of organic compounds (e.g. organic acids). At least the water is suitable for treatment in waste water facilities.

– The drying should be performed under mild conditions to keep VOC's very low if they are not absorbed into the water.

Second step. In a second step the dry organic waste (contaminated sewage sludge) is pyrolized at temperatures around 823 K. The volatile compounds are treated in a catalytic step (723 K) and in the following steps fractionally condensed to liquids. The following results may be obtained in this step:

– A solid fraction results from the pyrolytic step – a coked material – with good qualities for steam gasification.

– Heavy hydrocarbons should be collected. Contemporary markets do not accept such material.

– Light hydrocarbons, especially small aromatic structures, (benzene, toluene etc.) are a fraction worth processing. They are a potential chemical feedstock.

– A water fraction is collected and decanted (separation from organic liquids).

– Resulting gases are available for heat production.

– Volatile heavy metals may be collected in a gas cleaning facility.

– Chlorinated hydrocarbons are destroyed.

Third step. The steam gasification yields the gas and trace components typical of the process at 1173–1273 K. The following results may be derived from gasification:

– The solid residue – coke – from pyrolytic treatment is gasified. Hydrogen, carbonmonoxide and carbondioxide and small amounts of methane are available. The water gas may be cleaned with leachates of the solid residues.

– Water from original or natural moisture of the input material of the process, the water from pyrolytic reaction and the excess water from gasification should be injected to the steam gasification process.

– Heavy hydrocarbons and solid residues (dust from cyclones) may be measured to the steam gasification under well defined conditions

Sewage Sludges - Amounts - Background Information

In the Federal Republic of Germany sewage sludges are available in amounts of 3 Million metric tons a year. Exact numbers for the amounts of sewage sludge coming from public waste water treatment for 1991 are 2.956 million tons on a dry basis [1]. These masses also contain the amounts of material used for flocculation (e.g. iron sulfates) and for making the sludges hygienic (burnt lime) and for reducing the moisture content. The sludges itself are a product of intensive waste water treatment in Germany. In Germany the degree of connection to centralized waste water treatment plants is relatively high. Because of intensive attempts to hold back phosphates the amounts of sludges will increase until the year 2000. Table 1 shows the percentages of sludges disposed of on landfills, incinerated or put to other use.

Sludges resulting from industrial processes were available in amounts of 1.707 mio. tons on a dry basis. Table 2 lists the amounts of industrial sludges and their utilisation [2]. These sludges may have specific components or contaminations.

Table 1

Ways of Utilisation (mio. tons, dry matter)
of Municipal Sewage Sludge

Landfill	1.236	41.8%
Incineration	0.266	9.0%
Agriculture	0.819	27.7%
Other*	0.635	21.5%

* i.e.: intermediate deposition.

Table 2

Ways of Utilisation (mio. tons, dry matter)
of Industrial Sewage Sludge

Landfill	0.982	57.5%
Incineration	0.295	17.3%
Agriculture	0.027	1.6%
Other*	0.403	23.6%

* i.e.: intermediate deposition.

Besides the amount of sludges (how much is accepted) the contamination of the sludges is important for their use in agriculture. If they are contaminated they have to be put on landfills or have to be incinerated in combustion plants – especially built for sewage sludges – or they are combusted together with coal or municipal solid waste. Incineration is unpopular but alternatives are not in use. Our approach to the problem dates back to the late seventies. The contamination of sewage sludges turned out to a problem, as soils and agricultural products were contaminated with heavy metals. In the middle of the eighties limits to concentrations of heavy metals were set by legislation. New methods had to be found to handle these materials. Besides incineration thermal treatment under exclusion of oxygen seemed to make sense. The working group Ökochemie und Umweltanalytik, Department of Chemistry at the new Carl-von-Ossietzky University did one of the first experiments. Meanwhile legislation on allowed concentrations of inorganic and organic pollutants has been changed. The contemporary status includes organic pollutants along with heavy metals [3]. The development in waste water treatment has not stopped, especially the management of waste waters has been improved. Therefore the resulting sludges contain less inorganic and organic pollutants. Nevertheless not all sludges are acceptable for agricultural use according to the restrictions given by the law. Possible organic pollutants which can't be easily controlled and the limits for actual contaminants are being frequently discussed. Because of this situation work on thermal treatment of sewage sludges is still going on in our working group with emphasis on the production of organic fractions fit for reuse and stabilisation of solid residues.

RESULTS OF EXPERIMENTS ON A LABORATORY SCALE

In the beginning of our work sewage sludges have been investigated without previous treatment with burnt lime. The resulting organic fraction (condensates) polymerized and was not suitable for reuse. One reason was the occurrence of organic acids and unsaturated organic compounds. This complex mixture always had the tendency to polymerize. Other efforts report of similar difficulties [3, 4]. One promising attempt is to reduce the percentage of the organic acids by addition of burnt lime. The sludge originally used had been without lime. By treatment of the hot pyrolysis gas in a catalytic step the results improved. Table 3 shows the percentages of different organic fractions which were yielded by the chosen treatment [5].

Table 3

Composition of a Pyrolysis Oil Yielded at 873 K
(Pre-treatment with Burnt Lime, Catalytic Treatment)

n-alkanes	36%
1-alkenes	29%
Aromatic compounds	14%
Isomeric hydrocarbons	9%
Heteroaliphatic compounds	5%
Organic acids	6%
Phenolic compounds	<1%
Other compounds	<1%

This process had been performed with small laboratory facilities. A larger facility has been built. Some details of the small plant are shown in Tab. 4.

Table 4

Technical Data
of the Laboratory Scale Facility for Pyrolysis

Fluidized bed	
Width	42 mm
Height	100 mm
Fluidization medium	nitrogen
Temperature	823–923 K
Condensers	288–268 K

The flow diagram (Fig. 2) shows the whole process.

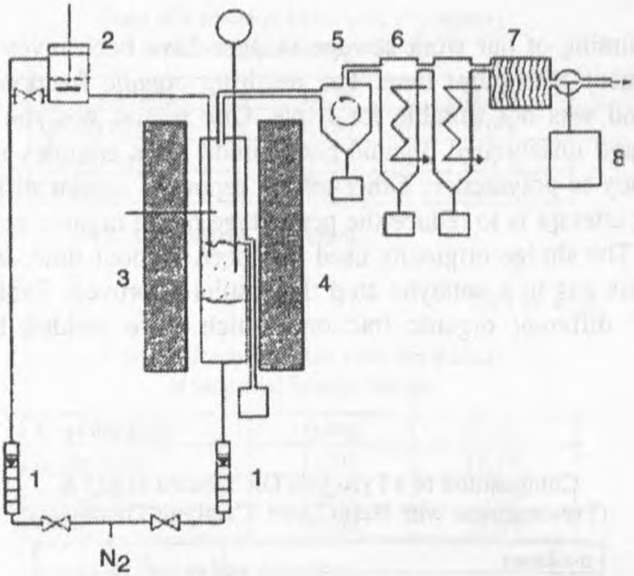

Fig. 2. Flow diagram of the pyrolysis apparatus
1 – Flowmeter; 2 – Feeding System; 3 – Reactor; 4 – Heating; 5 – Cyclone; 6 – Condenser; 7 – Filter; 8 – Vessel for Gas

Table 5

Technical and Analytical Data of the Feed-stock

Dried sewage sludge	
Density	1570 kg/m^3
Bulk density	450 kg/m^3
Particle size	250–350 µm
Analytical data	
Moisture	8.7%
Elemental analysis (wt %)	
Carbon	17.85%
Hydrogen	2.05%
Nitrogen	1.7%
Volatile matter	
Under air up to 823.15 K	44.2%

Dried sewage sludge is fed via a feeding system (entrained flow) to the fluidized bed reactor. The hot raw gas is separated from dust in a cyclone. Afterwards the roughly cleaned uncondensed gas flows through two condensers (temperature: 288, 268 K). The heat is supplied by electric heating, the regulation is done by a transformer. The fluidization is realised by nitrogen. A mixture of pyrolysis gas and the original nitrogen leaves the system. The cleanness of the resulting gas mixture was not the aim of this work.

A mass balance is presented in table 6 which was obtained by Brat [6].

The results were obtained with a municipal sludge which had been treated with relatively high amounts of burnt lime (nearly 30%). The decarboxylation process obviously was very good. But are these high concentrations necessary ?

Table 6

Wt% of Pyrolysis Products at Various Temperatures on Dry and Ash Free Basis

Temperature	823 K	833 K	888 K	923 K
Condensates	41.1	39.4	41.4	38.3
Coke	28.8	31.2	30.2	32.4
Water	21.3	18.6	12.8	12.2
Gas	8.8	10.8	15.6	17.1

The mass balance offers some insights into certain tendencies during the pyrolysis process. The higher the temperature of the pyrolysis the lower the percentage of water and the higher the temperature the higher the percentage of gaseous components among the resulting organic fractions. The calorific value of the pyrolysis gas is of interest too. This gas offers the opportunity to burn it and produce the necessary heat. Table 7 presents the main components. Traces have not been investigated because the main results are more relevant for determination of the important technical processing data at this stage.

Table 7

Wt% of Pyrolysis Gas at Various Temperatures

Temperature Gas	823 K	833 K	888 K	923 K
H_2	2.0	2.5	2.8	2.5
CH_4	5.4	3.6	5.9	8.0
CO	17.8	16.9	27.1	40.6
CO_2	66.3	70.2	54.4	37.3
C_2H_4	4.0	1.7	3.5	4.7
C_2H_6	0.6	0.7	0.9	1.4
C_3H_6	1.7	1.3	2.5	1.8
C_3H_8	0.3	0.3	0.4	0.4
ΣC_4-HC*	1.3	2.8	2.5	3.3
MJ/Nm^3	12.8	11.6	14.5	19.0

* HC denote hydrocarbons.

The condensates have not been investigated any further, because of the reasons mentioned above (no catalytic step had been installed). The solid residue – a coked material – results from Pyrolysis. The gasification is discussed in the next section.

Gasification by Water Gas Reaction

The solid material is nearly free of volatile organic carbon effluing at low temperatures (823 K). A coked material is gasified with nearly a zero production of light and heavy organic compounds. Within the water gas reaction we have to deal with the typical components influenced by the water gas shift reaction (H_2, CO, CO_2). The trace components have not been investigated at this stage (i.e. NH_3, COS, H_2S and others). Table 8 lists up the basic parameters of the input material. For the gasification experiment a pressurized vessel had been installed to produce the necessary steam.

Table 8

Technical and Analytical Data of the Feedstock

Cocked residue of the pyrolysis	
Density	2090 kg/m^3
Bulk density	640 kg/m^3
Particle size	<350 µm
Analytical data	
Moisture	1.6%
Elemental analysis (wt %)	
Carbon	15.6%
Hydrogen	0.3%
Nitrogen	0.7%
Volatile matter	
Under air up to 1123 K	26.0%

Table 9 presents the fractions of the different gases which yield from the gasification process with steam. The main components have been determined (CO, CO_2, H_2 and CH_4).

Table 9

Wt% of Gasification Products at Temperatures of 1173 K

Gas	
H_2	3.8
CO	42.6
CO_2	53.3
CH_4	0.3
Calorific value MJ/Nm^3	8.7

Distribution of Heavy Metals after Thermal Treatment in the Pyrolytic and Gasification step

In the beginning we talked about contaminated sewage sludges. If you have material which contains heavy metals and organic contaminants small amounts of gas should be processed and cleaned. Therefore the fate of some heavy elements was of interest. Among them in our experiments were elements of relatively high toxicity (Hg, Cd). Figures 3–14 show the distribution of the elements iron, chromium, lead, mercury, cadmium and zinc in the resulting products after the pyrolysis (890 K) respectively after gasification (1173 K). The percentages after the pyrolytic and after the gasifcation step are listed. The percentages for each row adds up to 100%. A loss of metal is listed too, because no adsorption system had been installed. The loss of elements indicates after which thermal step emphasis has to be put on which elements.

Looking at both figures for iron, no loss into condensates or water can be identified. No volatile compounds have been formed and possible amounts of very fine dusts which may occur in the other fractions did not transport any iron into them. Dust collected by the cyclones obviously is the material containing the iron.

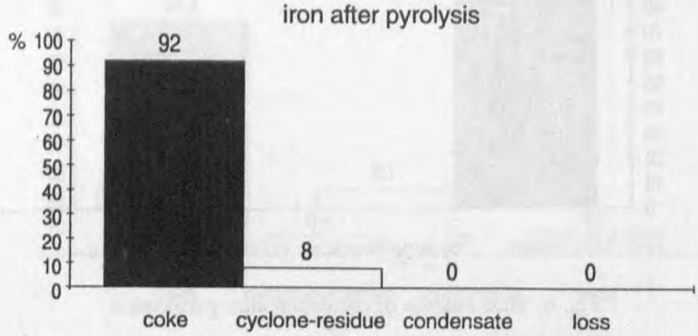

Fig. 3. Mass balance of iron after pyrolysis

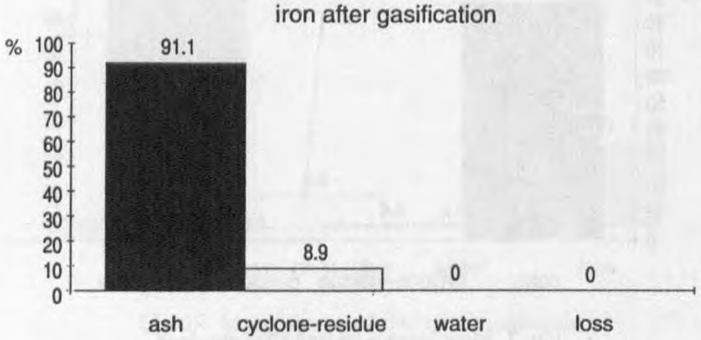

Fig. 4. Mass balance of iron after gasification

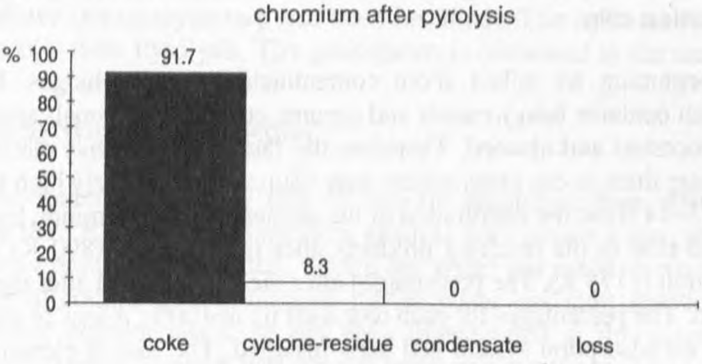

Fig. 5. Mass balance of chromium after pyrolysis

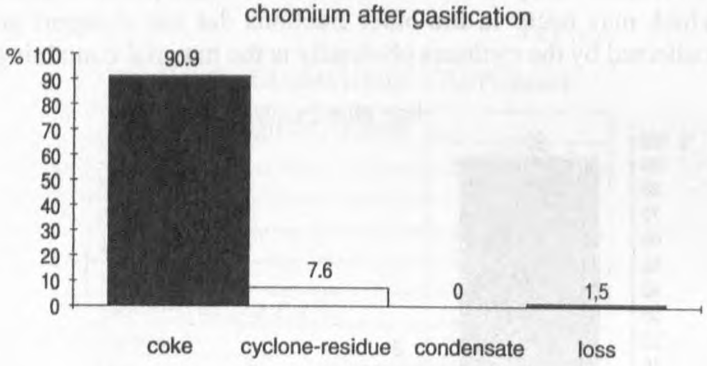

Fig. 6. Mass balance of chromium after gasification

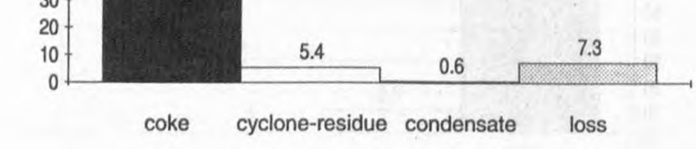

Fig. 7. Mass balance of lead after pyrolysis

The situation is different for chromium. A small percentage is lost after the gasification process. Volatile compounds must have been formed.

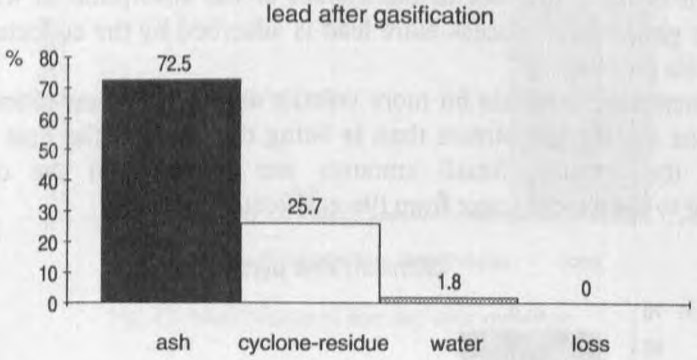

Fig. 8. Mass balance of lead after gasification

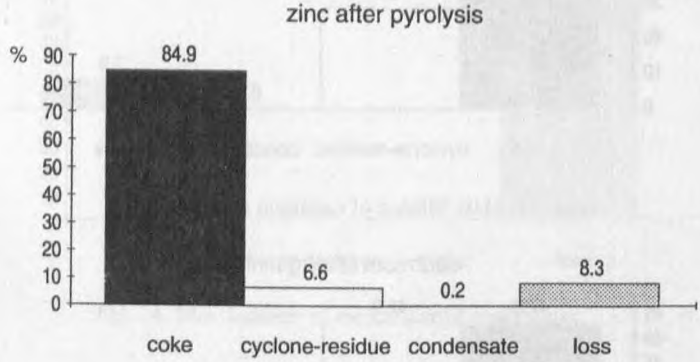

Fig. 9. Mass balance of zinc after pyrolysis

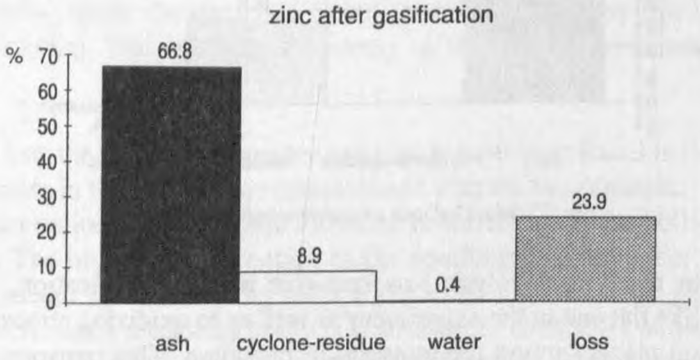

Fig. 10. Mass balance of zinc after gasification

Lead is the first volatile metal in this row volatile in the pyrolysis process. Besides adsorption on fines (finest particles) transport by discrete compounds or by fines is the reason for loss out of the system or the absorption in water (maybe fines). In the gasification process more lead is adsorbed by the collected dust than in the pyrolysis process.

The element zinc is a little bit more volatile under chosen conditions. A larger amount is lost via the gas stream than is being collected in the dust – the solid residues in the cyclone. Small amounts are collected in the condensates, coresponding to the excess water from the gasification process.

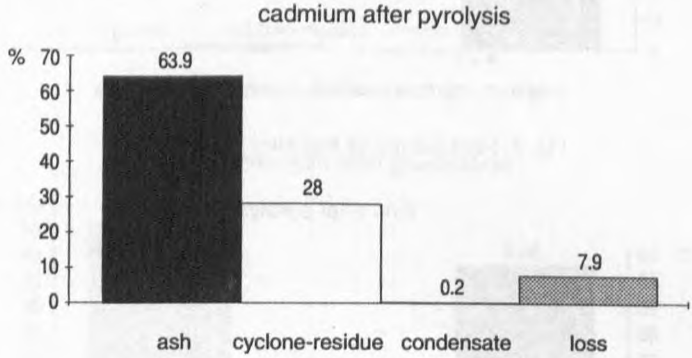

Fig. 11. Mass balance of cadmium after pyrolysis

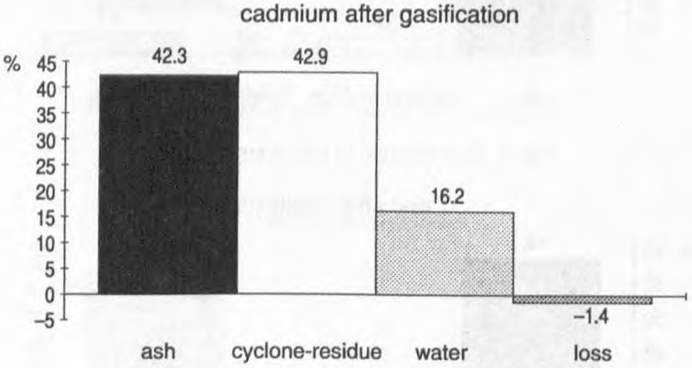

Fig. 12. Mass balance of cadmium after gasification

Cadmium reacts to pyrolysis less sensitive than to gasification. A reducing atmosphere like the one in the experiment as well as in oxidizing atmosphere found in incineration plants support the transport of cadmium. This transport takes place from the input material via fines or definite compounds in the gas phase. The excess water from the gasification absorbes the cadmium, too (difference to zinc). Cleaning systems have to take that into account.

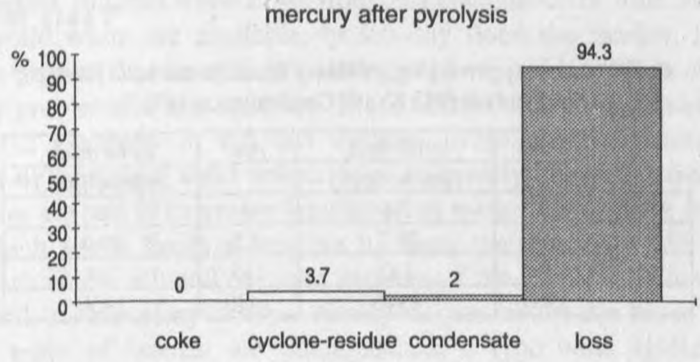

Fig. 13. Mass balance of mercury after pyrolysis

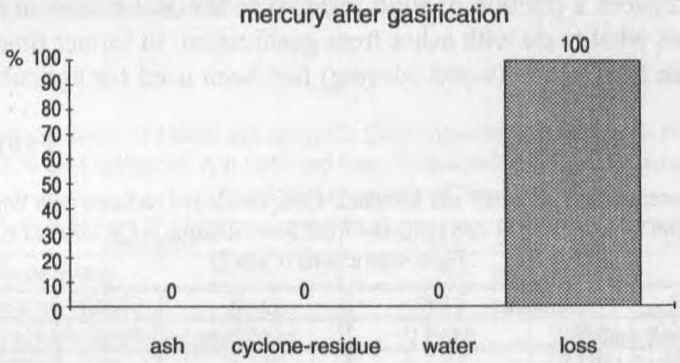

Fig. 14. Mass balance of mercury after gasification

Mercury turns out to be the most volatile heavy metal. The pyrolysis process alone sets free all the mercury. Thus Figure 13 is just the proof that all the mercury has left the coke during the pyrolysis. Small amounts of mercury can be found in the organic fraction. The analysis of mercury in the organic condensates is very complicated.

Table 10 lists the levels of concentrations which have been found in the products. The solid residues in the cyclones are contaminated with the heavy metals.

The concentration of the specific elements is correlated to the boiling point of the elements. The higher the percentage in the resulting ash the higher the boiling point of the metal. Because of the reducing atmosphere the metal goes through several oxidative states producing many possibilities for chemical bonding. Volatile compounds may be formed. A gas cleaning has to take that into account. Nearly all mercury is lost. Volatile elements (cadmium, zinc) can be found in the dust, which has been collected in cyclones. This information allows estimating contaminated fractions in respect to masses.

Table 10

Concentrations (ppm=mg/kg) of Heavy Metals in the Solid Products of Pyrolysis (873 K) and Gasification at 1173 K

	Coke	Solid resid. cyclone (pyr.)	Ash	Solid resid. cyclone (gas.)
Hg	0	2.4	0	0
Cd	5.4	27.2	3.3	33.2
Pb	194	147	215	784
Zn	1487	1340	1440	1960

Solid residues

If one produces a fraction of solid residues in thermal treatment of wastes the question arises what to do with ashes from gasification. In former times ashes from incineration in households (wood burning) had been used for agricultural purpose

Table 11

Concentrations of Metals and Inorganic Compounds in Leachates with Water from the Gasification Ash (ash) and from Solid Residue in Cyclone (s.r.c.), Tight Restrictions (Class I)

Parameter	Limit	Ash	s.r.c.
Volatile matter			
Under air (823 K)	<3wt%	0%	4.80%
Extractable lipophilic compounds	<0.4wt%	0.22%	0.34%
pH-value	5.5–13	12.8	12.4
Conductivity	$<10^5$ µS/cm^2	4800	4600
TOC	<20 mg dm^{-3}	n.i.*	n.i.*
Phenolic compounds	<0.2 mg dm^{-3}	<0.1	0.8
Arsenic	<0.2 mg dm^{-3}	n.i.	n.i.
Lead	<0.2 mg dm^{-3}	0.012	0.048
Cadmium	<0.05 mg dm^{-3}	0.01	0.06
Chromium	<0.05 mg dm^{-3}	<0.03	<0.03
Copper	<1.0 mg dm^{-3}	<0.5	<0.5
Nickel	<0.2 mg dm^{-3}	n.i.	n.i.
Mercury	<0.005 mg dm^{-3}	0.001	<0.001
Zinc	<2 mg dm^{-3}	0.02	0.05
Fluoride	<5 mg dm^{-3}	<1	<1
Ammonia	<4 mg dm^{-3}	n.i*.	n.i*.
Cyanide	<0.1 mg dm^{-3}	n.i.*	n.i.*
AOX	<0.3 mg dm^{-3}	<0.01	0.02
Water-soluble percentage	<3wt%	4.0	3.7

* n.i.: not identified.

or for the garden. In times when ashes from coal combustion or from incineration of municipal solid waste are available, or lets say flood the market, legislation is necessary to prevent this material from being used as wild landfill or other possible ecologically problematic management. These considerations have resulted in tight regulations in Germany in the last decades. Regulations on ashes from the incineration of municipal solid wastes have frequently been discussed in the last years and now are part of extensive legislation on wastes. Landfilling is restricted to material which keeps limits in respect to many parameters. Table 11 lists the parameters which the ash and the solid residues of the gasification have to keep in order to fulfil the necessary criteria. Nearly all parameters are based on leaching tests. Two types of landfill are distinguished: a type with tighter restrictions (class I) where less demands are defined concerning the technical construction and a type less restrictive but where the demands concerning the technical construction are more extensive (class II, Tab. 12).

Table 12

Concentrations of Metals and Inorganic Compounds in Leachates with Water from the Gasification Ash (ash) and from Solid Residue in Cyclone (s.r.c.), Less Restrictive Parameters (Class II)

Parameter	Limit	Ash	s.r.c.
Volatile matter			
Under air (823 K)	<5wt%	0%	4.8
Extractable lipophilic compounds	<0.8wt%	0.22%	0.34%
pH-value	5.5–13	12.8	12.4
Conductivity	<5 x10^{4} µS/cm^{2}	4800	4600
TOC	<100 mg dm^{-3}	n.i.*	n.i.
Phenolic compounds	<50 mg dm^{-3}	<0.1	0.8
Arsene	<0.5 mg dm^{-3}	n.i.*	n.i*.
Lead	<1 mg dm^{-3}	0.012	0.048
Cadmium	<0.1 mg dm^{-3}	0.01	0.06
Chromium	<0.1 mg dm^{-3}	<0.03	<0.03
Copper	<5 mg dm^{-3}	0.51	<0.5
Nickel	<1 mg dm^{-3}	n.i.	n.i.
Mercury	<0.02 mg dm^{-3}	<0.001	<0.001
Zinc	<5 mg dm^{-3}	0.02	0.05
Fluoride	<25 mg dm^{-3}	<1	<1
Ammonia	<200 mg dm^{-3}	n.i.*	n.i.*
Cyanide	<0.5 mg dm^{-3}	n.i.*	n.i.*
AOX	<1.5 mg dm^{-3}	<0.01	0.02
Water-soluble matter	<6wt%	4.0	3.7

* n.i.: not identified.

To which extent these parameters are met by the solid residues resulting from thermal treatment (ashes or s.r.c.) decides on the type of landfill. Until the year 2005 these parameters must be kept. Especially solid residues from thermal treatment of municipal solid waste have to meet the parameters given above. The main reason setting such restrictions is to prevent organic material from being landfilled. Many problems have resulted from untreated municipal solid wastes being landfilled. Legislation concerning wastes and residues in Germany tries to install cycles in material management [7]. The list contains some physical parameters, too, which have to be kept. In so far qualities of ashes belong to the problem of advanced and clean management of wastes. Every parameter is described in distinct norms like DIN or EN. In this context it is impossible to discuss them. Materials like ash from gasification have puzzolanic qualities. A stabilizing effect is the result of chemical reaction. Few heavy metals or soluble components of the ash will be leached. Much work has been done on that field to evaluate the risk arising from landfilling of ashes, be it ashes from incineration or ashes from other thermal treatment. By establishing criteria for leaching the contamination of leached water from landfill is reduced; especially heavy metals or phenolic compounds or cyanides have a tremendously toxic effect on aquatic ecosystems.

Discussion in Detail

Only few parameters may be problematic. Phenolic compounds and cadmium are leached from the solid residue collected in cyclones in amounts which can't keep the concentrations given by the class I landfill. Conductivity is far below the limits (concerning the tighter restrictions) but is explicable. The sludges had been treated with relatively high amounts of burnt lime. The resulting ash reacts strongly alkalic and obviously sets free conductible components into the water. The pH-value is 12.8 for the ash and 12.4 for the residue from the cyclones. The percentages of soluble matter are compatible with these results. But nevertheless much of the original burnt lime seems to be fixed in the material. Sulphates and chloride add to the conductivity, too, but most of it results from OH^--concentration. To redu-ce the percentages of burnt lime seems to be necessary in order to further reduce the parameters discussed above and perhaps the percentage of water-soluble matter.

Organic pollutants

Besides heavy metals organic pollutants are subjected to control concerning the agricultural reuse of sewage sludges. The heavy metals are persistent pollutants in geological time perspectives. Organic pollutants do not belong to this group. But nevertheless they have to be controlled because they are persistent in terms of human time perspectives. Normally these parameters (organic pollutants) are not a problem in respect to agricultural reuse. But what happens to organic pollutants in case of thermal treatment ? Are they concentrated in products, destroyed or do they increase over the whole process? Another research in our group deals with this subject [8]. A small reactor was added to the laboratory facility, which was filled with a fixed bed of catalyst. In principle the whole apparatus was not modified. Two groups of organic pollutants were investigated in respect to the question mentioned above. The fixed bed reactor was installed with the aim of producing an organic liquid fraction for reuse. The problems with these fractions have already been described above. The possible use of such material is dependant on physical qualities (i.e. viscosity) and important analytical parameters in respect to processing in refineries. We want to be careful. We are far away from putting such material into processing steps of refineries. But nevertheless analytical parameters have been investigated to identify necessary steps in that direction. Figure 15 shows the apparatus with the new catalytic step. The entrained flow is realized with a modified device.

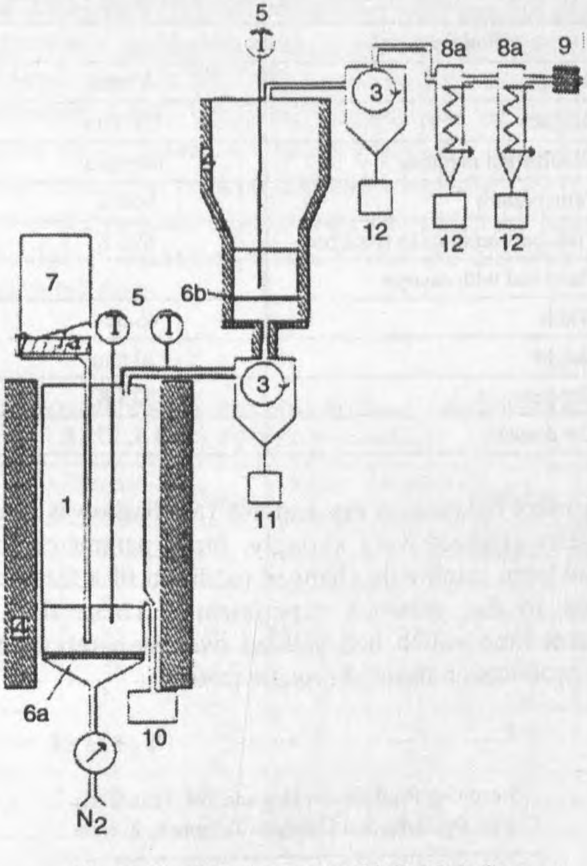

Fig. 15. Pyrolysis Apparatus with Catalytic Step
1 – Pyrolysis Reactor; 2 – Reactor for Catalysis; 3 – Cyclone; 4 – Heating; 5 – Thermocouple; 6a – Distribution Plate; 6b – Distribution Plate; 7 – Feeding System; 7a – Screw Conveyer; 8a – Condenser; 8b – Condenser; 9 – Gas Filter; 10 – Collection (Coke); 11 – Collection (Dust); 12 – Collection (Condensate)

Several groups of organic pollutants were of interest. Besides PCB, PCDD and PCDF have to be controlled in Germany concerning agricultural reuse of sewage sludges. The PAH have been chosen because they are typical trace products resulting from thermal treatment in reducing and non reducing atmosphere. Roughly estimated they are formed in larger amounts under reducing conditions than under oxidizing conditions. Therefore secure knowledge of production, transport in the process and concentrations in products is necessary. PAH are relevant constituents of tar resulting from gasification processes be it gasification with air or steam. Besides the installation of the small reactor the physical and technical parameters of the input material and the apparatus have not been changed.

Table 13

Technical Data of the Laboratory Scale Facility for Pyrolysis

Fluidized bed	
Width	42 mm
Height	100 mm
Fluidization medium	nitrogen
Temperature	903 K
Transport sections to fixed bed	693 K
Fixed bed with catalyst	
Width	45 mm
Height	30 mm
Temperature	723 K
Condensors	293 K, 273 K

The resulting mass balance on dry and ash free basis was interesting in so far that previous results changed very strongly. Input parameters of the processed sewage sludge had been minimally changed (addition of a fraction of fines which had been omitted in the previous experiments). These fines consist almost exclusively of burnt lime which had yielded over preparation of input material. Table 14 lists the products on basis of organic matter.

Table 14

Resulting Products on Dry and Ash Free Basis
after Pyrolysis and Catalytic Treatment in wt%

Coke	12
Solid residue cyclone	4
Condensates	33
Gas/water	51

Filter material has been installed which held back the heavy organics to determine PAH-concentrations. As important result may be derived that the percentage of gas obviously increases very strongly upon catalytic treatment (this is obvious if one thinks of the feedstock for catalytic cracking in industry). The resulting condensate did not react or polymerize in more than one year.

PAH. Polycyclic aromatic hydrocarbons (PAH) are important constituents of volatile organic material which results in coking-plants as well as in combustion processes. As persistent organic pollutants they have been investigated very thoroughly. Especially in Germany benzo-a-pyrene is nowadays a leading parameter for the evaluation of material to be classified as hazardous or not. Thermal treatment of organic material in principle produces such compounds. It does not matter if you look at overstoichiometric or understoichiometric processes or at least at oxygenfree atmosphere. Automotive exhaustive contain PAH in amounts of gram per mile to microgram per mile [9]. This has to be kept in mind to take measures which permit emission levels regarding comparable emission standards. And perhaps one should try to reduce emissions especially in technical processes in comparison to other sources of organic pollutants regarding PAH. Original sewage sludge before processing contains amounts of PAH which are below concentrations which have to be tightly controlled. Table 15 list the amounts of PAH in input material and product fractions.

Table 15

Absolute Amounts of PAH in Input Material (Sewage Sludge) and in Products of the Pyrolysis Process (µg)

Compound	Sewage-sludge	Coke	Solid-residue	Conden-sate	Oil-filter	Gas-filter	Prod-ucts
Fluoranthene	61	17	13	314	30	90	464
Pyrene	49	15	11	263	32	73	393
Benz(a)anthracene	20	5	5	108	12	35	165
Chrysene	35	22	19	348	43	137	569
Benzofluoranthene	58	n.d.*	7	71	24	27	129
Benzo(a)pyrene	14	n.d.*	3	136	30	n.d.	169
Indenopyrene	12	n.d.*	2	18	n.d.	n.d.	20
Dibenzanthracene	n.d.*	n.d.*	2	n.d.	n.d.	n.d.	2
Benzo(ghi)perylene	15	n.d.*	2	22	12	n.d.	36
Sum	263	59	62	1280	183	362	1946

* n.d.: not detectable.

As the main result one can derive the fact already mentioned above that polycyclic aromatic hydrocarbons are produced under the conditions chosen in this experiment. Theoretically it is possible that very small amounts of PAH have left the system. If this is the case they are very low. The gas phase has been treated in a fluid phase (oil-filter). Most of the PAH obviously are collected in the fluid phase within the condensers (roughly up to 70%). If one sums up amounts of all PAH formation a factor of 7 seems reasonable under the chosen conditions. Now one has to change an important variable. Is the outcome of PAH independent of the input or is it possible to pose following question: Is there a concentration in the input material at which one can predict if the resulting amounts are lower? Transport and new formation of PAH can not be distinguished in this process. If one chooses a concentration and in consequence the sum over all PAH is reduced over the process one can say PAH are destroyed. To get an answer to that we prepared a sewage sludge with an extra amount of PAH. Table 16 presents the results of this experiment.

Table 16

Absolute Amounts of PAH in Input Material (Sewage Sludge) and in Products of the Pyrolysis for the Prepared Form of Sewage Sludge (μg)

Amount	Sewage sludge	Coke	Solid residue	Condensate	Oil-filter	Gas-filter	Products
Fluoranthene	938	54	39	549	5	194	841
Pyrene	727	50	28	436	4	153	672
Benz(a)anthracene	323	16	18	183	2	70	288
Chrysene	348	36	48	504	5	200	793
Benzofluoranthene	484	22	28	158	2	60	271
Benzo(a)pyrene	172	trace	14	78	1	48	141
Indenopyrene	113	n.d.*	7	26	n.d.*	n.d.*	32
Dibenzanthracene	41	trace	3	n.d*.	n.d.*	n.d.*	3
Benzo(ghi)perylene	85	n.d.*	6	28	n.d.*	trace	34
Sum	3231	178	190	1962	20	725	3075

* n.d.: not detectable.

The results from the last table suggest that PAH may be destroyed. One has to be careful to derive such a result. Still most of the PAH are collected in the condensate. The level of concentration is interesting, too. Table 17 presents the concentration of the PAH in the input material and in product fractions - solid products. These numbers (coke, residues in cyclones, condensates) may be specific for the process. Concentrations in ab-/adsorbing material is of less importance (it matters only in case of planning when one wants to calculate break threw volumes or break threw masses).

The amounts of the corresponding concentrations of PAH in the sludge are very low. Naturally the solid residues from the cyclone and the condensates have higher concentrations as expected from the values above. What does the situation look like for the prepared sewage sludge. Table 18 lists up the results.

Table 17

Concentration of PAH in Solid Input Material and in Coke, Solid Residues in Cyclones and Condensates after Pyrolysis and Catalytic Treatment in mg/kg

	Sludge	Coke	Sol. res.	Cond.
Fluoranthene	0.98	0.6	5.2	37.8
Pyrene	0.79	0.5	4.3	31.7
Benz(a)anthracene	0.32	0.2	1.8	13.0
Chrysene	0.57	0.7	7.8	41.9
Benzofluoranthene	0.94	n.d.*	2.8	8.6
Benzo(a)pyrene	0.22	n.d.*	1.1	7.0
Indenopyrene	0.2	n.d.*	0.6	2.2
Dibenzanthracene	n.d.*	n.d.*	0.7	n.d.*
Benzo(ghi)perylene	0.24	n.d.*	0.6	2.6
Sum	4.26	2.0	24.8	154.7

* n.d.: not detectable.

Table 18

Concentration of PAH in Solid Input Material and in Coke, Solid Residues in Cyclones and Condensates after Pyrolysis and Catalytic Treatment in mg/kg for the Prepared Material

	Sludge	Coke	Sol. res.	Cond.
Fluoranthene	7.21	0.9	19.3	44.0
Pyrene	5.59	0.8	14,2	34.9
Benz(a)anthracene	2.49	0.3	8.8	14.6
Chrysene	2.67	0.6	23.8	40.3
Benzofluoranthene	3.72	0.4	14.1	12.6
Benzo(a)pyrene	1.32	trace	16.4	6.2
Indenopyrene	0.87	n.d.*	3.4	2.1
Dibenzanthracene	0.32	trace	1.5	n.d.*
Benzo(ghi)perylene	0.66	n.d.*	3.1	2.2
Sum	24.85	3.2	95.2	153.0

* n.d.: not detectable.

The coke is nearly free of PAH in both cases. The prepared sludge has ten times higher concentrations of PAH. The process conditions make the PAH volatile in so far that they are collected in the cyclone residues and in the condensates. The PAH have been discussed here very intensively but because of that the whole process should not be looked at under the perspective what happens to PAH. An appropriate weight must be applied.

PCB. Polychlorinated biphenyls are another analytical and environmental problem often mentioned. These compounds have been investigated, too. PCDD, PCDF have not been investigated because analytical methods of these compounds are very complicated and expensive. But nevertheless you get the information to which extent chlorinated compounds are destroyed in the whole process. Again original sewage sludge and a prepared sewage sludge have been investigated to get a mass balance for PCB. The following PCB-isomers were investigated: 28, 52, 101, 153, 138, 180. Table 19 gives concentrations of PCB in original and processed sewage sludge and the prepared form of sludge.

Table 19

Concentration of PCB in Solid Input Material,
in Solid Residues of the Cyclones and Condensates after Pyrolysis
and Catalytic Treatment in μg/g

PCB	Sewage sludge	Prepared sewage sludge
28	0.012	≤ 0.06
52	0.013	1.04
101	0.037	2.53
153	0.086	3.88
138	0.077	3.34
180	0.043	1.35

Table 20

Absolute Amounts of PCB in Input Material (Sewage Sludge)
and in Products of the Pyrolysis for the Prepared Form of Sewage Sludge in mg

PCB	Sewage sludge	Solid res.(mg)	Solid res.(%)	Condensate (mg)	Condensate (%)	Percentage sum (%)
28	≤ 0.007	≤ 0.0004		≤ 0.005		
52	0.13	0.001	1	0.04	28	29
101	0.33	0.003	1	0.06	18	19
153	0.50	0.004	1	0.06	12	12
138	0.43	0.003	1	0.04	10	10
180	0.18	0.001	1	0.01	6	6

The important result from Tab. 20 is that chlorinated compounds obviously are destroyed. This result can be derived from the prepared sludge. The concentration of PCB in the uncontaminated sludge was too low to justify a mass balance from an analytical point of view.

Outlook. For further work some modifications will be made:

– For new experiments we will reduce the amounts of burnt lime which are added to sewage sludges.

– A fluidized bed reactor for the catalytic step will be used.

– The amount of PAH in the gaseous products of the gasification will be scrutinized

General and Final Remarks

In principle hazardous intermediates must be introduced to the steam gasification process under optimized conditions. Regulation of the hazardous streams and closed handling (closed loops) are very important goals. Main fractions like solids, fluids and gases should be as clean as possible when they leave the process. Very small amounts of stabilized sludges from gas cleaning containing heavy metals must be deposed of to landfills or stored as hazardous waste on hazardous waste dumps (less than one percent, perhaps less than 1per thousand concerning the masses of input material). Different input material with typical physical and chemical qualities has to be adapted to the process or vice versa. In incineration processes material is very often mixed up to yield a regular calorific value of the input material. This procedure is not convincing at all. As in hazardous waste management specific input material should be collected or perhaps mixed up to definite qualities. Leather or contaminated wood are a good example of such a definite input material. Maybe dimensions of operating plants should be adapted to specific streams of waste. Input material should not simply be thrown together and burnt neither in the landscape nor even in an incineration plant.

ACKNOWLEGMENT

We thank the Ministry for Research and Technology (BMFT) for funding our work (Förderkennzeichen: 02-WS 278, 02-WS 278/5, 02-WS 8902).

REFERENCES

[1] *Statistisches Bundesamt, Umwelt – Fachserie 19 Reihe 2.1 – Wasserversorgung und Abwasserbeseitigung im Bergbau und verarbeitenden Gewerbe und bei Wärmekraftwerken für die öffentliche Versorgung*, Metzler Poeschel, Stuttgart (1995)

[2] *Statistisches Bundesamt, Umwelt – Fachserie 19 Reihe 2.1 – Öffentliche Wasserversorgung und Abwasserbeseitigung*, Metzler Poeschel, Stuttgart (1995)

[3] Bundesministerium für Forschung und Technologie (BMFT), Klärschlammpyrolyse/-konverierung – Klärschlammentsorgung mit Gewinnung von Ölen, Förderkennzeichen: 02-WS 8835 (1992)

[4] Bundesministerium für Forschung und Technologie (BMFT), Konvertierung von Trockengut aus Klärschlamm, Förderkennzeichen: 02-WS 8846/7 (1991)

[5] V. Rosemann, *Gewinnung von Chemierohstoffen durch Pyrolyse von Klärschlamm – Optimierung von Reaktionsbedingungen und Analytik der Produkte durch Gaschromatographie/ Massenspetrometrie*, PhD-Thesis, Carl von Ossietzky University Oldenburg, Oldenburg (1988)

[6] B. Brat, *Umweltverträgliche Verwertung von Klärschlamm durch Pyrolyse und Vergasung in der Wirbelschicht*, PhD-Thesis, Carl von Ossietzky University Oldenburg, Oldenburg (1992)

[7] P. Queitsch, *Kreislaufwirtschafts- und Abfallrecht*, Bundesanzeiger Verlags-Ges. mbh, Köln (1995)

[8] G. Meyer, *Entstehung und Verbleib umweltrelevanter organischer Schadstoffe bei der thermischen Behandlung von Klärschlamm*, PhD-Thesis, Carl von Ossietzky University Oldenburg, Oldenburg (1994)

[9] Sachverständigenrat für Umweltfragen, Umweltgutachten 1994, Bundestagsdrucksache 12/6995 (1994)

Werner Beckers, Dieter Schuller

TERMOLYTISCHE AUFARBEITUNG KONTAMINIERTER KLÄRSCHLÄMME UND VERGLEICHBARER ABFALLSTOFFE IN EINEM DREISTUFIGEN „BATCH"-VERFAHREN

Ein dreistufiges „batch"-Verfahren für die thermische Verarbeitung von kontaminierten Abfallstoffen wird vorgestellt: Trockung, Pyrolyse und (Wasserdampf-) Vergasung – zusammenfassend als Thermolyse bezeichnet – werden in einem zeit-temperaturgesteuerten Wirbelschicht-reaktor durchgeführt. Das Verfahren wurde für kontaminierte Klärschlämme unter besonderer Betrachtung der technischen Durchführbarkeit und des erforderlichen Stoffstrommanagement untersucht. Der technische Prozeß liefert Gase aus der Pyrolysestufe (823 K) die sofort einer katalytischen Behandlung (723 K) unterzogen werden. Es resultiert ein Anteil an kondensierbaren Stoffen unter denen gut verwertbare niedere Aromaten (BTXE) einen bedeutenden Teil ausmachen. Der feste Rückstand und die nicht verwertbaren Anteile des Kondensats aus der Pyrolyse werden unter Verwendung des Schwelwassers aus der Pyrolyse und des Brüdenkondensats aus der Trocknung unmittelbar im Reaktor in einer Wasserdamfvergasung (1173 K) weiter verarbeitet. Das dabei entstehende Gasgemisch (H_2, CO, CO_2, CH_4) wird über Gaswäsche von CO_2 sowie sauren und basischen Spurenbestandteilen befreit und dann entweder zur unmittelbaren Befeuerung des Reaktors oder zur Verstromung eingesetzt. Der feste Rückstand der Wasser-damfvergasung erfüllt die Voraussetzungen zur Deponierung auf einer Deponie für Inertstoffe. Seine Verwendbarkeit im Bausektor wurde noch nicht technisch geprüft. Das für kontaminierten Klärschlamm entwickelte und im kleinen Technikumsmaßstab erprobte Verfahren kann auch für andere biogene Stoffe eingesetzt werden.

Werner Beckers, Dieter Schuller

TRZYSTOPNIOWY PROCES PRZETWARZANIA OSADÓW ŚCIEKOWYCH I PORÓWNYWALNYCH MATERIAŁÓW ODPADOWYCH

W pracy przedstawiono trzystopniowy proces termicznego przetwarzania (odwodnienie, piroliza i gazyfikacja) skażonych materiałów odpadowych. Skażone osady ściekowe przebadano z uwzględnieniem aspektów technicznych i organizacyjnych. Piroliza prowadzona w temperaturze 823 K powadzi do otrzymania gazów frakcji C_1–C_4, a zgazowanie parą w temperaturze 1173 K dostarcza gazu o składzie H_2, CO, CO_2 i CH_4.

Stała pozostałość jest przemywana wodą, w której oznacza się wymywane substancje celem konfrontacji z obowiązującymi normami. Lotne związki tworzące się na etapie pirolizy są przerabiane w procesie katalitycznym w temperaturze 723 K. Proces opracowany w celu termicznego przetwarzania skażonych osadów ściekowych może być stosowany do przerobu konwencjonalnego organicznego materiału.