

**Implementation of thermal processes for feedstock recycling
of bromine, with energy recovery, from plastics waste of
electrical and electronic equipment (WEEE)**

**Phase 2: Production of bromine salt in staged-gasification to
determine technical feasibility of bromine recovery**

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Revisions		
A	Concept version, 27 July 2001	
B	Review EBFRIE (Mr. L. Tange), 3 October 2001	
C	Final version, 4 October 2001	
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Account

The work described in this report is performed by the Unit ECN Biomass of the Energy research Centre of the Netherlands (ECN) under ECN project number 8.20214. ECN is the leading institute in the Netherlands for energy research. The project was fully sponsored by the European Brominated Flame-Retardant Industry Panel (EBFRIP), a sector group of the European Chemical Industry Council (CEFIC).

Keywords

European Brominated Flame Retardants Industry Panel (EBFRIP), Waste of Electrical and Electronic Equipment (WEEE), Brominated Flame-Retardants (BFR), bromine, chlorine, antimony, energy recovery, thermal processes, staged-gasification, gasification, pyrolysis, Pyromaat, Sustainable Bromine Production.

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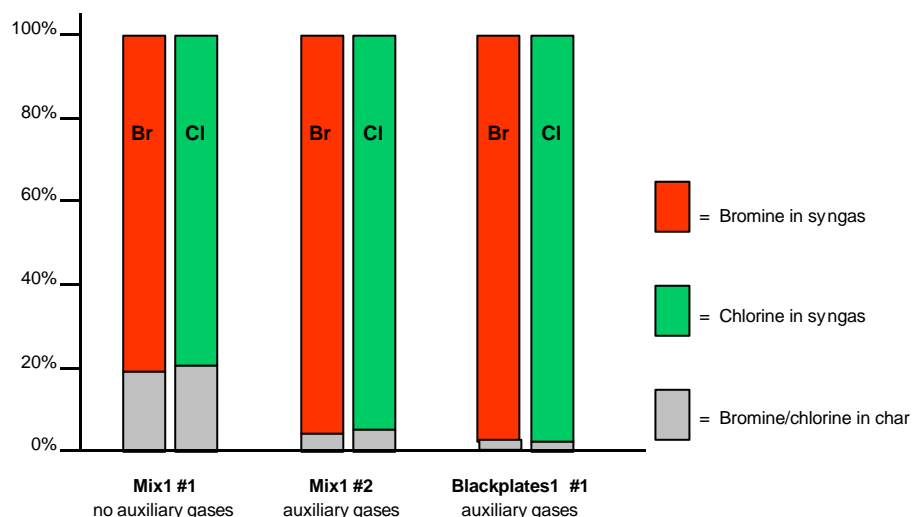
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SUMMARY

The bromine industry wants to process plastics Waste from Electrical and Electronic Equipment (WEEE), containing brominated flame-retardants (BFRs), in order to recycle bromine and recover the energy content. This will improve the sustainability of the production and close the bromine loop at the End-of-Life. Staged-gasification is a thermal process that is potentially suitable for this purpose.

The issue that has to be resolved is whether the bromine that is recovered as a salt in the staged-gasification process, is suitable for recycling. Or more specifically, does the bromine-containing salts satisfy the specifications of the bromine producing industry, *e.g.* concerning contaminants. Representative samples of recovered bromine-containing salts are required to be able to test their suitability for recycling. This report describes processing of the WEEE plastics fractions WEEE Mix1 and TV Backplates1 in the ECN two-stage gasifier 'Pyromaat' and the production of bromine-containing salts by wet alkaline scrubbing of the syngases.

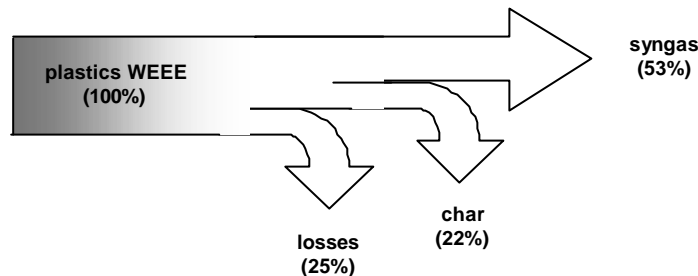
The 'Pyromaat' consists of a low temperature pyrolysis reactor (550°C), a high temperature gasifier (>1230°C), and a 'wet' alkaline scrubber. Upon pyrolysis of the WEEE plastics fraction a lot of soot is formed that ultimately may result in blockage of the installation. Therefore, the runs were periodically shutdown to remove the soot. Furthermore, auxiliary gases were used in most test runs to minimise soot formation and fouling. Utilising auxiliary gases resulted in lower char flows, and resultantly, in higher percentages of bromine (and chloride) and antimony that are volatilised. Under these conditions the desired partitioning of the elements to the gas phase is favoured (see Figure below; on mass basis).



Due to the high temperature of the gasifier all organic compounds were destructed, preventing contamination of the scrubber water. The two bromine containing alkaline scrubber solutions of the test runs with WEEE Mix1 and TV Backplates1 were concentrated to 20 L. From both concentrated solutions four 5 L batches were made and shipped to the addresses provided by EBFRIIP. The bromine to chlorine mass ratios in the concentrated solutions of 0.4 and 1.6 for WEEE Mix1 and TV Backplates1, respectively, are comparable to the ratios in the feed materials.

Based on the lab-scale staged-gasification test runs and the achieved bromine recovery, it can be stated that from a volume of 300,000 tonnes of plastics WEEE (3.7 wt% bromine) at least 10,000 tonnes of bromine can be recovered (*i.e.* 95% from the bromine in the feed). Due to the feeding of pure plastics from WEEE it is possible to produce highly concentrated bromine solutions. It is expected that the concentration of possibly present dioxins and furans is at least twelve times lower than in the case of combustion of WEEE plastics, due to the absence of oxygen in the syngas.

For full-scale staged-gasification installations (input of 4 ton/h) it is expected that plastics from WEEE can be processed to produce char and syngas with 75% efficiency (see Figure below). The char contains 22% of the energy input and is used as energy carrier and reducing agent to produce synthetic basalt in a connected smelter. The approximately 10,000 Nm³/h syngas (bromine content of 14 g/Nm³) represents 53% of the energy and, after cleaning, it can directly be used to generate electricity in gas engines. From the char the (heavy) metals can be recovered while a synthetic basalt can be produced from residual inorganic material.



The next activities comprise determination of optimal process layout and operational conditions. With these data the technical and economical feasibility has to be determined with supporting information from additional lab-scale tests in the ECN installation 'Pyromaat'.

1. INTRODUCTION

1.1 Background

In a sustainable society the need for virgin materials and fossil fuels should be minimised. To realise this, waste must be optimally converted into energy and products. In case of waste from electrical and electronic equipment (WEEE), containing brominated flame-retardants (BFRs), this means recycling of bromine, antimony, and other valuable metals, and recovery of the energy content. ECO-impact studies in the Netherlands and Germany have demonstrated that there is a limit to the amount of household plastics waste that can be mechanically recycled with environmental benefits. The maximal amount is 18% [1], or even as low as 15% according to a more recent study [2]. Further mechanical recycling requires relatively many efforts that annul the environmental gain. This means that the majority of the remaining waste must be recycled by other techniques. Combustion, gasification, and pyrolysis-based technologies have in principal the possibility to realise this.

The bromine industry, united in the European Brominated Flame retardant Industry Panel (EBFRIP), needs to find accepted processing routes and have them implemented before the year 2004. In the year 2004 there will be an EU ban on landfilling plastics of WEEE. EBFRIP has concluded that for the realisation of this the above-mentioned thermal processes (combustion, gasification, and pyrolysis) are promising. Aiming at implementation in 2004 the following phased approach is necessary:

- Phase 1: Literature survey/status update, evaluation and ranking of available (existing on full-scale) combustion, gasification, and pyrolysis-based technologies.
- Phase 2: Feasibility study on selected technologies. An economic assessment will be performed based on lab/bench-scale tests and detailed mass and energy balance calculations.
- Phase 3: Implementation scenario's. Existing facilities and implementation initiatives will be summarised and checked with respect to availability for WEEE, also in relation with optimal logistics.
- Phase 4: Design and construction.
- Phase 5: Operation.

Phase 1 was carried out in 2000 and comprised a study performed by ECN Biomass [3]. Eight processes were evaluated on the suitability for the feedstock recycling of bromine and antimony with energy recovery, from WEEE, based on the criteria:

- Energy efficiency,
- Bromine recovery,
- Antimony recovery,
- Emissions,
- Quality of secondary products,
- Operational Experience,
- Profit expectations and ROI (Return on Investment).

The four processes of Austrian Energy, ALSTOM/Ebara, Von Roll RCP, and Gibros PEC were evaluated in detail versus the defined criteria with the conclusion that all four processes are possibly suitable for the treatment of WEEE.

As first step in Phase 2, the technical feasibility has to be assessed of using bromine salts produced in thermal processes as feedstock for the bromine industry. For this purpose, two WEEE processing experiments are issued by EBFRIIP: a co-combustion test in TAMARA pilot-plant of FZ Karlsruhe and a staged-gasification test in the 'Pyromaat' installation of ECN Biomass. This report describes the results of the staged-gasification test.

1.2 Definition of the Issue

The issue that has to be resolved is whether the bromine that is recovered as a salt in the staged-gasification process, is suitable for recycling. Or more specifically, does the bromine-containing salts satisfy the specifications of the bromine producing industry, *e.g.* concerning contaminants. Representative samples of recovered bromine-containing salts are required to test their suitability for recycling.

1.3 Objective

The objective was to produce bromine-containing salts by wet alkaline scrubbing of the syngas from two-stage gasification. Intended was to process three fractions of plastics from WEEE in the 'Pyromaat'.

1.4 Approach

In the ECN offer to EBFRIIP (TH/A.00330) activities were agreed on. However, due to new information and insights in the period between the acceptance of the offer and the test runs, the work approach was slightly modified after discussion and in agreement with EBFRIIP.¹

The main change in the activities was the reduction of the number of materials to be tested from three to two. The programme was altered for two reasons. Firstly, the supplied WEEE plastics feed materials contained less bromine than expected and indicated during the preparation of the offer. Secondly, the planned one-day (8 hours) operation of the staged-gasifier per feed material was insufficient to recover sufficient bromine. This was caused by the necessity for periodical shutdowns, resulting in effective operational times of less than 8 hours.

The materials WEEE Mix1 and TV Backplates1 were selected for the test runs. The test runs with WEEE Mix1 were continued until almost all material was processed. The test runs with TV Backplates1 were continued till more than 100 g bromine was produced.

The final approach that was agreed on is:

1. Four pre-treated fractions of plastics from WEEE of 20 kg each were delivered to ECN by EBFRIIP. The analysis data of all WEEE fractions were made available to ECN.
2. Determination of process conditions and evaluation of safety aspects in discussion and agreement with EBFRIIP.
3. Test runs with WEEE Mix1 and TV Backplates1 to produce bromine containing scrubber solutions. For the test runs with TV Backplates1 the desired amount of bromine was >100 g.
4. Analysis of input and output products during the test runs: mass flows, gas composition, and char analysis.
5. Determination of fate of the relevant elements, bromine, chloride, and antimony in the test runs.

¹. The contact at EBFRIIP was Mr. L. Tange.

6. Concentration of the two produced bromine-containing scrubber solutions and shipping the batches of the concentrated solutions to the four addresses designated by EBFRIIP (agreed on in a separate offer, CND/A.00350).
7. Reporting.

1.5 Intended results

- Two 20 L concentrated alkaline solutions from the scrubber with bromine-containing salt – divided into four 5 L batches.
- A final report in the English language with the main findings of the tests. Five hard copies and an electronic version in Word will be made available to EBFRIIP.

2. EXPERIMENTAL

2.1 WEEE feed material

EBFRIP collected four plastics fractions of WEEE: WEEE Mix1, WEEE Mix2, TV Backplates1 (BP-black), and TV Backplates2. The WEEE fractions were pre-treated by FZ Karlsruhe and on specifications as desired by EBFRIP, and in addition, the particle size was <1 cm. ECN did not further pre-treat the material. The ultimate and proximate analyses of the materials as provided by EBFRIP are summarised in Appendix 2. In discussion with EBFRIP the materials WEEE Mix1 and TV Backplates1 were selected for the test runs. These materials have a bromine content of 1.30 and 3.56 wt%, respectively.

2.2 ‘Pyromaat’

The ECN lab-scale unit ‘Pyromaat’ is a bench-scale staged-gasification installation with a capacity of 5 kg/h. Comparable full-scale installations are marketed by Gibros PEC. A short description of the PEC process is given in Appendix 3. The basic process layout with the functional units of the ‘Pyromaat’ is shown in Figure 2.1. Feed material is introduced with a screw feeder into the externally heated pyrolysis reactor. The material is transported through the reactor by a screw with an open flight. The processing is similar to a rotary kiln. Upon pyrolysis the material decomposes in a solid residue (char) and a gas. The pyrolysis gas comprises CO, H₂, CO₂, H₂O, CH₄, C_xH_y, BTX (benzene, toluene, and xylenes), and tars (larger organic compounds). After the pyrolysis reactor the char falls into a char container.

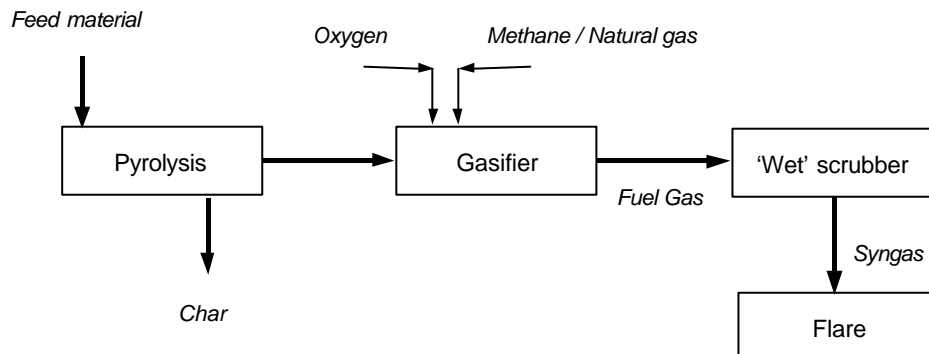


Figure 2.1. Schematic representation of the functionalities of the ECN lab-scale staged-gasification installation “Pyromaat”.

The gases go into the high temperature gasifier (*i.e.* tar cracker). The gasifier is generally operated at temperatures between 900 and 1400°C. Due to the relative small size of the gasifier (*i.e.* large surface over volume ratio) the heat loss is significant, therefore, methane or natural gas is used as additional fuel. Depending on the applied temperature and residence time in the gasifier most of the tars will decompose, where at temperatures >1200°C generally all tars are broken down.

The syngas from the gasifier consisting of CO, H₂, CO₂, and H₂O is washed with water in the wet scrubber. Depending on specific feed materials a basic or acidic solutions can be used. The solution is sprayed in the scrubber column and circulated. The scrubber system consists of a buffer tank, a pump, and a filter to remove dust and soot in the water. In the WEEE tests the tank was equipped with a feeding point to add concentrated NaOH to the scrubber solution to

control the pH. The syngas leaving the scrubber is flared or can be utilised for other experiments.

2.3 Experimental conditions and safety aspects

The experimental conditions and safety aspects were discussed with Mr. L. Tange from EBFRIIP on 18 October 2000. The relevant safety issues and precautions were reported to the involved personnel [4].

2.3.1 Experimental conditions

In the WEEE test runs the conditions as presented in Table 2.1 were applied in the ‘Pyromaat’. In addition to the description in the previous section, auxiliary gases were added to the installation. The purpose of these gases was to minimise formation of soot and to minimise deposition in the connection between the reactor and gasifier. The auxiliary gases had an effect on the amount of char and gases formed during pyrolysis. These effects will be discussed in the next Chapter.

Table 2.1. *Experimental conditions of WEEE Mix1 and TV Backplates1 test runs in ‘Pyromaat’.*

Condition	Value
Feed material	WEEE Mix1 or TVBackplates1
Feed flow rate	1.5 – 1.65 kg/h
Pyrolysis temperature	550°C
Pyrolysis residence time	> 15 min
Gasifier temperature	> 1230°C
Gasifier (oxygen blown)	methane
Auxiliary gases	steam, air, and/or nitrogen
Initial NaOH concentration in scrubber solution	0.06 mol/L

2.3.2 Safety aspects

The WEEE fractions contain large amounts of the halides bromine and chlorine. Upon pyrolysis these compounds in the feed material are released as mainly HBr and HCl, and to a lesser extent Br₂ and Cl₂, while also part of the bromine and chlorine remains inorganically bound in the char. For comparison, in pyrolysis experiments with printed circuit boards ~75% of the sum of both halides was found in the product gas and the remainder in the char [5]. All four compounds have serious health hazards and for the test runs (additional) measurements were taken:

- Safety Data Sheets were made available to all personnel involved in the test runs;
- the ‘Pyromaat’ is located in a closed space in the laboratory hall under air suction and the air is filtered before releasing into the atmosphere;
- spray bottles with sodium bisulphite were available in the laboratory to neutralise possible halide emissions;
- pressure in the installation was monitored and the test runs were discontinued at elevated pressure (to prevent gas emissions with the halide compounds from the installation);

- NH_3 was injected into the flared gas to neutralise all halide compounds present in the gas. The flow of NH_3 was based on a 100% emission of all halides present in the feed assuming the NaOH scrubber failed.

3. RESULTS OF TEST RUNS

3.1 Overall test impression

3.1.1 Pyrolysis reactor

Plastics materials have in general a high carbon content - for the two tested WEEE materials the carbon content is 67 and 84 wt%, respectively, for WEEE Mix1 and TV Backplates1. Upon pyrolysis this gives rise to the formation of large amounts of soot (*i.e.* pure carbon dust). This soot has a low density and is dragged with the gas instead of remaining in the solid phase (*i.e.* the char). High soot loads of the gas may result in fouling and blockage of the system. In installations dedicated to the treatment of this type of materials special features are present that, in combination with suitable operational conditions, minimises fouling. The 'Pyromaat' is not dedicated for one type of feed material but is a test installation designed to process many different feed streams.

In the 'Pyromaat' test runs with WEEE Mix1 as well as TV Backplates1, due to the soot formation, blockage of the system occurred in the pipe connecting the pyrolysis reactor and the gasifier (Figure 3.1) resulting in overpressure in the reactor. Without additional measures blockage of the connection started to occur within 30 (TV Backplates1) or 60 minutes (WEEE Mix1). At those moments the test runs were terminated and the soot was removed.

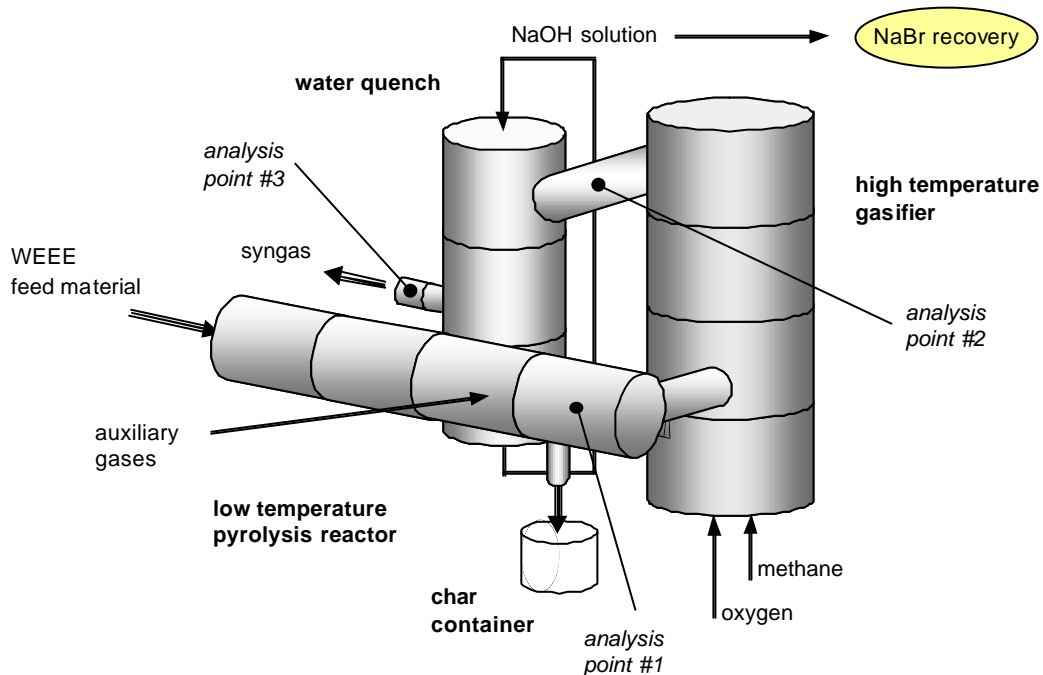


Figure 3.1. Impression of the 'Pyromaat' with the material flows and analysis points indicated.

During the test runs it was attempted to minimise the fouling by the addition of auxiliary gases to the system, which indeed resulted in lower dust loads in the gas and minimised soot deposition. With these measures for the WEEE Mix1 feed material test runs of four hours could be made. For TV Backplates1, with a much higher carbon content, these measures were only lightly beneficial and typical test runs were 30 to 45 minutes. To produce the desired amount of

bromine salts several runs were performed with both feed materials. In this report the conditions of selected runs are reported in detail.

3.1.2 Gasifier

The gasifier was operated with flows of oxygen and methane sufficient to maintain a temperature $>1230^{\circ}\text{C}$. At these conditions all organic compounds are destructed. Major constituents of the syngas leaving the gasifier are CO , H_2 , CO_2 , and H_2O . The gasifier operated stable in all test runs and was not effected by the soot load of the gases.

3.1.3 Scrubber

The scrubber was operated with an initially 0.06 M NaOH solution ($\text{pH} >10$). After the start of a test run the pH dropped rapidly to $\text{pH} \sim 7$ due to dissolving of CO_2 in the solution. During the test runs the pH remained ~ 7 by the buffering nature of the CO_2 in the solution. Periodically additional NaOH was added to compensate for the OH^- consumption by the dissolved bromine and chlorine. The bromine and chlorine stripping efficiency of the scrubber was determined during some test runs by measuring the bromine and chloride concentrations at the inlet and outlet of the scrubber. The initial stripping efficiencies were found to be above 97%.

In the scrubber also large amounts of the soot were recovered. Most of the soot was removed from the water in the filter of the circulation system. However, the fine particles remained in the water phase and also ended up in the 'product', the final concentrated scrubber solutions.

3.2 Analysis of products

The staged-gasifier 'Pyromaat' affords two products: the solid char fraction and the syngas. An intermediate product is the pyrolysis gas, which can be subdivided into GC-detectable gases, tars, and H_2O . In Table 3.1 the pyrolysis conditions are shown given for five runs during which char flows were determined, the char samples analysed, and syngas compositions determined.

Table 3.1. Process conditions during test runs of which analyses are discussed.

Condition		Mix1 #1	Mix1 #2	Backplates #1	Backplates #2
Feed flow	[kg/h]	1.50	1.50	1.65	1.65
Char flow	[kg/h]	0.45	0.30	0.14 ¹	0.14 ¹
Char as fraction from feed	[-]	0.30	0.20	0.08	0.08
Auxiliary gases	[-]	no	yes	yes	yes

¹. Char flows are an estimate based on the average char production during several runs.

3.2.1 Pyrolysis gas

The composition of the pyrolysis gas was analysed in point #1 (see Figure 3.1). In Table 3.2 representative compositions of pyrolysis gas for runs with WEEE Mix1 and TV Backplates1 are shown. In the test runs auxiliary gases were used. The concentrations of bromine in the pyrolysis gases were between 15 and 30 g/Nm^3 (wet gas), depending on the feed material and the process conditions.

Table 3.2. Representative composition of pyrolysis gases for WEEE Mix1 and TV Backplates1. Values are on dry and tar free basis. Process conditions as shown in Table 3.1.

Compound		WEEE Mix1	TV Backplates
		#2	#1
benzene	[ppmV]	0.48	0.57
toluene	[ppmV]	0.90	0.88
H ₂	[vol%]	1.2	0.0
N ₂	[vol%]	73.6	77.1
CH ₄	[vol%]	2.3	1.5
CO	[vol%]	12.4	11.8
CO ₂	[vol%]	7.8	7.5
ethene	[vol%]	0.98	0.54
ethane	[vol%]	0.33	0.16
<i>Control total</i>	<i>[vol%]</i>	<i>100.0</i>	<i>100.0</i>

3.2.2 Syngases

The syngas composition was measured at analysis point #2, as after the scrubber (point #3) some leak of gases (*i.e.* N₂ and CO₂) from the combustor (not shown) disturbed the analyses. Analyses were only performed when the process was in stable operation (Table 3.3). All higher carbons in the pyrolysis gas (*i.e.* CH₄, ethene, ethane, BTX, and the tars) are decomposed. The concentrations of bromine in the wet syngases were approximately 2 and 5 g/Nm³, respectively, for the WEEE Mix1 and TV Backplates test runs.

Table 3.3. Representative composition of syngas gases for WEEE Mix1 and TV Backplates1. Values are on dry basis. Process conditions as shown in Table 3.1.

Compound		Mix1	Mix1	Backplates	Backplates
		#1	#2	#1	#2
H ₂	[vol%]	32.1	25.6	21.4	19.4
N ₂	[vol%]	1.99	14.9	23.3	23.1
CH ₄	[vol%]	0	0	0	0
CO	[vol%]	34.5	28.4	24.0	19.8
CO ₂	[vol%]	31.4	31.2	31.4	37.7
<i>Control total</i>	<i>[vol%]</i>	<i>100.0</i>	<i>100.0</i>	<i>100.0</i>	<i>100.0</i>

3.2.3 Char

During a test run the char was collected in a container, which was replaced periodically. In stable operation (excluding start-up and shutdown periods) the char flow can be determined from the collected amount. Due to the discontinuous nature of most test runs (*cf.* section 3.1.1), and especially for the TV Backplates1 test, the determination of the flows is not very precise.

In run #1 with WEEE Mix1, without auxiliary gas, 30 wt% of the feed was converted into char. When auxiliary gases were used the amount of char decreased to 20 wt% as char and soot partly reacted and were converted into gas. In runs with TV Backplates1 8 wt% of the feed is converted into char. The lower production of char in the TV Backplates1 runs originates from

the lower ash content of the material and to the use of relatively more auxiliary gas. The ultimate and proximate analyses of the char samples are shown in Table 3.4.

Table 3.4. Ultimate analysis of pyrolysis chars. Analysis of two chars from pyrolysis runs with WEEE Mix1 and two chars from runs with TV Backplates1.

Char sample run #		Mix1 #1	Mix1 #2	Backplates #1	Backplates #2
% C	[wt%]	42.64	36.55	53.17	58.39
% H	[wt%]	2.13	1.60	1.77	1.55
% O	[wt%]	7.32	7.53	4.32	3.94
% N	[wt%]	1.38	1.20	1.09	0.98
% S	[wt%]	0.28	0.28	0.18	0.15
% Cl	[wt%]	3.60	1.59	0.54	0.80
% F	[wt%]	0.04	0.06	0.03	0.02
% Br	[wt%]	1.35	0.51	0.97	2.04
% ash (by difference)	[wt%]	41.27	50.69	37.94	32.15
HHV	[MJ/kg]	17.11	19.79	21.09	
ratio Br/Cl in char sample	[-]	0.37	0.32	1.81	2.55
ratio Br/Cl in feed (Appendix 2)	[-]	0.60	0.60	1.94	1.94
Al	[mg/kg]	20914	19336	12208	
As	[mg/kg]	23	27	198	
B	[mg/kg]	3354	3261	1332	
Ba	[mg/kg]	1735	1761	2548	
Ca	[mg/kg]	56153	53504	30906	
Cd	[mg/kg]	220	224	512	
Co	[mg/kg]	34	26	14	
Cr	[mg/kg]	120	256	672	
Cu	[mg/kg]	104327	45428	41664	
Fe	[mg/kg]	4978	4116	3545	
K	[mg/kg]	1456	1292	2385	
Li	[mg/kg]	18	17	25	
Mg	[mg/kg]	3820	3720	3605	
Mn	[mg/kg]	181	200	232	
Mo	[mg/kg]	1	2	2	
Na	[mg/kg]	1289	1392	2756	
Ni	[mg/kg]	200	1387	596	
P	[mg/kg]	2971	3295	2656	
Sb	[mg/kg]	653	668	1201	
Se	[mg/kg]	23	21	137	
Si	[mg/kg]	42783	41929	28810	
Sn	[mg/kg]	757	691	202	
Sr	[mg/kg]	301	289	254	
Ti	[mg/kg]	267	248	159	
V	[mg/kg]	6	7	2	
Zn	[mg/kg]	3590	6014	15231	
TOTAL elements	[g/kg]	250	189	152	

3.3 Fate of bromine, chloride, and antimony

Based on the ultimate and proximate analysis of the feed materials and the chars the recovery rates in the char fraction were constructed for the compounds, bromine, chlorine, and the metals including antimony (Table 3.5). Most values for the metal elements are well above 100%, which originates from the uncertainties in the mass flows of char and the inhomogeneity of the char. For example, the high copper (Cu) recovery values most likely result from a copper wire present in the char sample. In the Table the values significantly below 100% recovery are indicated in grey. Here, only recovery of the relevant elements bromine and chlorine in combination with antimony (Sb) is evaluated.

Table 3.5. Weight percentage of elements recovered in the char. Numbers significantly below 100% are indicated in grey. Elements not included, or indicated with ~, are not analysed in the feed. Process conditions as shown in Table 3.1.

Element	WEEE Mix1 #1	WEEE Mix1 #2	TV Backplates1 #1
Br	19%	4.0%	1.5%
Cl	21%	5.2%	1.5%
As	40%	31%	31%
Ba	138%	93%	~
Ca	174%	111%	~
Cd	97%	66%	63%
Cr	53%	76%	~
Cu	1186%	345%	~
Fe	98%	54%	~
K	56%	33%	~
Mn	93%	69%	~
Mo	3.2%	7.5%	2.5%
Ni	56%	260%	~
Sb	2.9%	2.0%	0.4%
Sn	40%	25%	10%
Sr	133%	85%	~
Zn	131%	146%	~

In test run #1 with WEEE Mix1 19 wt% of the bromine and 21 wt% of the chlorine remained inorganically bound in the char phase. Especially calcium (Ca), present in the feed in 10 g/kg as CaCO₃, is known to form stable halide salts. The remainder of the halides volatilised mainly as HBr and HCl and, possibly, to a minor extent as Br₂ and Cl₂. Furthermore, part of the halides was volatilised with antimony in the form of the (mixed) halide salts SbX₃ (SbBr₃, SbBr₂Cl, SbBrCl₂, and SbCl₃). Antimony bromide boils at 280°C and the mixed halide antimony compounds have a similar chemical behaviour (*e.g.* boiling point of SbCl₃ is 283°C) [6]. This volatilisation accounts for the low recovery of antimony in the char. In contact with water in the scrubber or the syngas component CO₂ at lower temperatures SbX₃ salts hydrolyses to the trioxide (Sb₂O₃) [3]. The higher mass percentage of chloride recovered in the char compared to bromine might be explained by the higher stability of the inorganically bound chlorides compared to the bromides.

In the WEEE Mix1 test run #2 auxiliary gases were used and the char production was ~30% lower (*cf.* Table 3.1). The decreased recovery of antimony is in line with the lower char flow. However, the effect on the halide recovery in the char is much bigger, *i.e.* that is approximately 5 times lower (*cf.* Table 3.5). The addition of auxiliary gases and the reaction with the char leads to locally higher temperatures in the material, which results in more volatilisation of the halides as HBr and HCl. In the test run with TV Backplates1 only <2 wt% of the halides and antimony remained in the char. This is a result of the combination of the low calcium content in the feed, a low char production, and the utilisation of auxiliary gases.

3.4 Scrubber solutions

The syngas containing most of the halides (81 to >98 wt% bromine and 79 to >98 wt% chlorine) was washed with a NaOH solution in the 'wet' scrubber. For test runs with the same feed material the same solution was used resulting in increasing concentrations of bromine and chlorine in the water. The concentrations were periodically analysed to determine if the desired amount of bromine was recovered. After the experiments the two scrubber solutions were concentrated by evaporation of water at 100-120°C from the final volume of the scrubber solutions of 150-190 L to less than 20 L. Upon heating most of the dissolved CO₂ was released and the pH of the solutions decreased from pH ~ 7 to the original pH ~ 10. The two concentrated scrubber solutions were each divided into four fractions of ~5 L. From both concentrated solutions 5 L samples are shipped to the addresses provided by EBFRIIP (Mr. L. Tange; see Appendix 4). Indicative compositions of the samples are shown in the Table 3.6. The bromine-chlorine ratios in the concentrated solutions are comparable to the ratios in the feed materials. Prior to evaporation the carbon content of both solutions was analysed to check for the presence of organic compounds in the water, *i.e.* possible tar residues. In both solutions no organic compounds were present: Dissolved Organic Carbon concentration DOC = 0 mg/kg.² The Dissolved Inorganic Carbon concentration (DIC), due to the presence of carbonate (CO₃²⁻) salts originating from dissolved CO₂, was 678 and 350 mg/kg for the WEEE Mix1 and TV Backplates1 solution, respectively.

Table 3.6. Indicative composition of the two concentrated scrubber solutions.

Feed material		WEEE Mix1	TV Backplates1
pH	[-]	~10	~10
concentration Br ⁻	[mg/kg]	3232	14060
		(totally approx. 60 g)	(totally approx. 280 g)
concentration Cl ⁻	[mg/kg]	8893	8713
concentration Na ⁺	[mol/L]	~0.5	~0.5
mass ratio Br/Cl	[-]	0.4	1.6
DOC, excluding soot	[mg/kg]	0	0

Upon pyrolysis of the two fractions a lot of soot was formed. Most of the soot was removed in the filters of the scrubbing system. However, as the filters are not specifically designed for the soot loads encountered, a lot of soot remained in the scrubber solutions. To obtain samples rep-

². Analysis performed prior to concentration of the solutions. Detection limit is 5 mg/kg. Suspended soot was removed by filtration prior to analysis. Remaining trace amounts of organic compounds might have been adsorbed to the soot).

representative for dedicated commercial installations filtering of the soot is advised prior to recycling experiments.

3.5 Implications for industrial scale

3.5.1 Process layout

In a full-scale (industrial) installation the process layout is comparable, however, the syngas cleaning will be more extensive (*cf.* Appendix 3). The gas cleaning will consist of standard units like a scrubber to recover the HBr (efficiency >99.9%) and dust, followed by a bag filter to remove the remaining dust, and an alkaline and a biological washer to remove H₂S. Finally, an active coal filter to absorb remaining impurities, dioxins, furans, and Hg. The clean syngas can be used without further treatment to generate electricity (and heat) in gas engines.

Due to the relative small size of the 'Pyromaat' and especially the gasifier (*i.e.* large surface over volume ratio) the heat loss is significant and not representative for a full-scale installation. In a full-scale installation no additional fuel is used for the gasifier. Extrapolation of the 'Pyromaat' results to a full-scale installation with a capacity of 4 ton/h gives the indicative data as presented in Table 3.7.

Table 3.7. Indicative parameters for full-scale processing of plastics WEEE.

Parameter		Value & Remarks	
Feed plastics WEEE material	[-]	WEEE Mix1 and TVBackplates1	
Average bromine content	[wt%]	3.7	
Feed flow	[ton/h]	4.0	
Energy input	[MJ/h]	132	(LHV of feed: 33 MJ/kg)
Char flow production	[ton/h]	0.7	(=18 wt% of input)
Energy value of char flow	[MJ/h]	29	(LHV of char: ~40 MJ/kg)
Syngas production	[Nm ³ /h]	10,000	
Syngas composition	[vol%]	CO (30); H ₂ (30); CO ₂ (25); N ₂ (15)	
Bromine concentration in syngas	[g/Nm ³]	14	(5 wt% of input remains in char)
Energy value of syngas	[MJ/h]	70	(LHV of syngas: 7.0 MJ/Nm ³)
Bromine recovery	[kg/h]	133	(95 wt% recovery in scrubber)

3.5.2 Energy recovery

In this extrapolated case, the overall energy efficiency of the process from the feed material to the char and syngas is 75% (*cf.* Figure 3.2). The syngas represents 53% of the energy input and can after cleaning directly be used to generate electricity in gas engines. The char contains 22% of the energy input that can also be recovered, for example, in the metal recycling process. In a metal recycling step carried out a high temperature smelter, a concentrated metal stream can be recovered while a synthetic basalt is produced from the remaining inorganic material.

3.5.3 Volume of bromine recovery

Based on the bromine partitioning data collected in the staged-gasification test runs an extrapolation can be made for the possible recovery on larger scales. Assume a total annual volume of

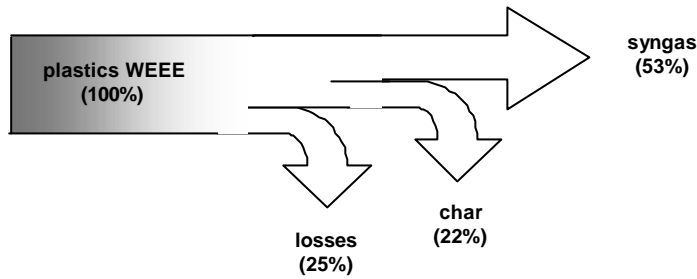


Figure 3.2. Indicative energy flow diagram for the full-scale processing of plastics WEEE.

300,000 tonnes of plastics WEEE with average bromine content of 3.7 wt% to be processed in several dedicated staged-gasifiers. Furthermore, the materials are processed in installations using auxiliary gases and the gas cleaning with (a) alkaline scrubber(s). In that case at least 95 wt% of the bromine will volatilise of which at least 95 wt% will be captured in the scrubber (this is a careful estimate as industrial scrubbers do reach >99.9% recovery). The annual amount of bromine that is recovered under these assumptions is $300,000 \times 0.037 \times 0.95 \times 0.95 = 10,000$ tonnes. A further 550 tonnes remain in the char phase and might (partly) be recovered by leaching from the char [7] or from the flue gas after combustion.

4. CONCLUSION AND CONTINUATION

4.1 Conclusion

Staged-gasification test runs were performed with two plastics WEEE fractions: WEEE Mix1 and TV Backplates1. Upon pyrolysis of these material a lot of soot is formed that ultimately may result in blockage of the installation. Therefore, the runs were periodically shutdown to remove the soot. Due to the absence of oxygen in the syngas it is expected that the concentration of possibly present dioxins and furans is at least twelve times lower than in the case of combustion of the WEEE materials [8].

Furthermore, auxiliary gases were used in most test runs to minimise soot formation and fouling. Utilising auxiliary gases resulted in lower char flows, and resultantly, higher percentages of bromine (and chloride) and antimony that are volatilised. For WEEE Mix the bromine volatilisation increases from 81 to >98 wt%, while for TV Backplates1 the volatilisation is >98 wt%. Recovery of more than 95% of the bromine in the feed can be achieved based on conservatively estimated scrubber efficiencies of 99%). When using auxiliary gases the (desired) partitioning of the elements to the gas phase is favoured. The partitioning (in wt%) of the halides in the test runs is illustrated with Figure 4.1.

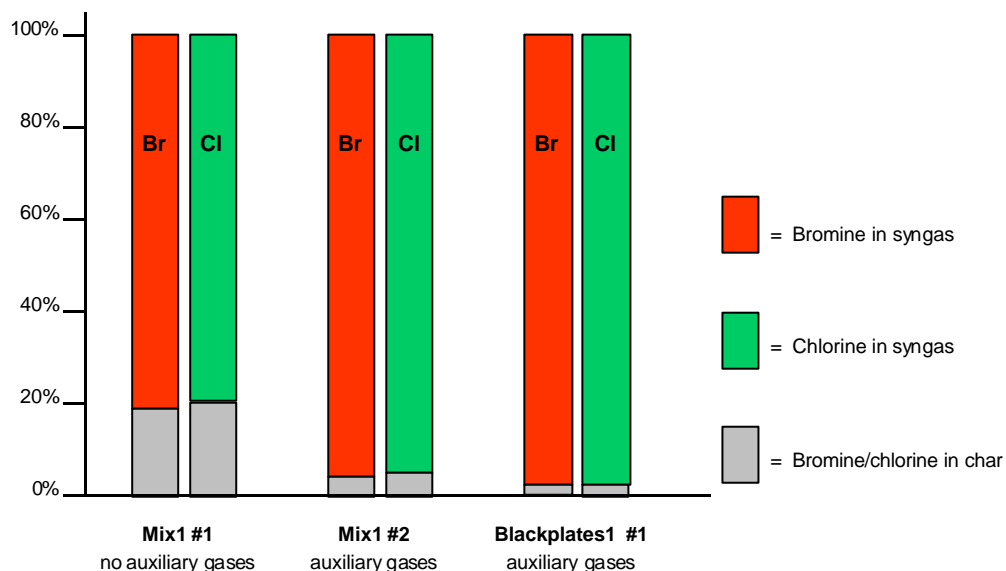


Figure 4.1. Partitioning (wt%) of halides in feed over the output syngas and char phase in staged-gasification test runs with WEEE Mix1 and TV Backplates1.

The gasifier was operated with oxygen and methane to maintain the temperature >1230°C. At these temperatures all organic compounds (*i.e.* the pyrolysis tars) are destructed. In the 'wet' scrubber the syngas from the gasifier is washed with a NaOH solution to remove most of the bromine from the gas.

The two alkaline scrubber solutions of the test runs with WEEE Mix1 and TV Backplates1 were concentrated to 20 L. From both concentrated solutions four 5 L batches were made and shipped to the addresses provided by EBFRIIP. The bromine-chlorine ratios in the concentrated solutions of 0.4 and 1.6 for WEEE Mix1 and TV Backplates1, respectively, are comparable to the ratios in the feed materials.

4.2 Continuation

Based on the lab-scale staged-gasification test runs and the achieved bromine recovery it can be stated that from a volume of 300,000 tonnes of plastics WEEE (3.7 wt% bromine) at least 10,000 tonnes of bromine can be recovered (*i.e.* 95% of the bromine in the feed). In full-scale installations (input of 4 ton/h) it is expected that plastics WEEE can be processed with 75% energy efficiency affording 10,000 Nm³/h syngas (dry basis, LHV of 7MJ/Nm³) with a bromine content of 14 g/Nm³. From the char the (heavy) metals can be recovered while synthetic basalt can be produced from the residual inorganic material.

EBFRIP has to determine whether the bromine that was recovered as a salt in the staged-gasification process, is suitable for recycling. If this question is answered positively, the first part of Phase 2 of the implementation of bromine recycling in 2004 is successfully finished. The next activities comprise determination of optimal process layout and operational conditions, as it is clear from the current study that processing plastics WEEE fractions brings about specific technical issues. With these data the technical and economical feasibility has to be determined with supporting information from additional lab-scale tests in the ECN installation 'Pyromaat'.

5. REFERENCES

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APPENDICES

Appendix 1. List of Abbreviations

Appendix 2. Ultimate and Proximate analyses of WEEE materials as provided by EBFRIIP

Appendix 3. Gibros PEC process

Appendix 4. List of addresses to which samples of the concentrated scrubber solutions were shipped

Appendix I. List of Abbreviations

Ar	Argon
BFR	Brominated Flame-Retardants
Br	Bromine; the element
Br ₂	Bromine; a gas
BTX	Benzene, Toluene, and Xylenes
Ca	Calcium
CEFIC	European Chemical Industry Council
CH ₄	Methane
Cl	Chlorine; the element
Cl ₂	Chlorine; a gas
CO	Carbon monoxide
CO ₂	Carbon dioxide
C _x H _y	Sum of all linear hydrocarbon compounds
DIC	Dissolved Inorganic Carbon concentration
DOC	Dissolved Organic Carbon concentration
EBFRIP	European Brominated Flame-Retardant Industrial Panel
ECN	Energy research Centre of the Netherlands
H ₂	Hydrogen
H ₂ O	Water
HBr	Hydrobromic acid
HCl	Hydrochloric acid
LHV	Lower Heating Value
N ₂	Nitrogen
NaOH	Sodium hydroxide
Sb	Antimony
WEEE	Waste of Electrical and Electronic Equipment

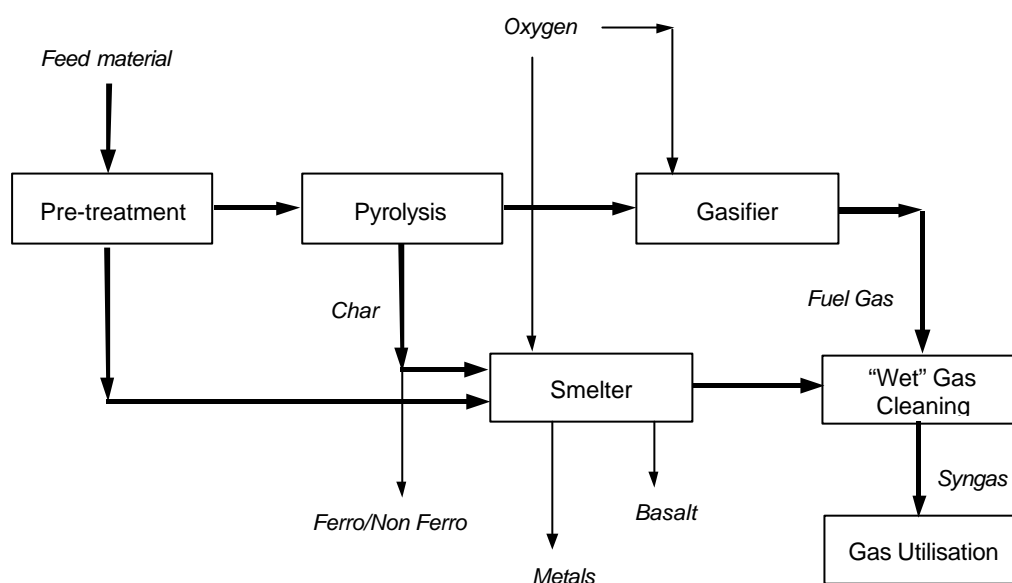
Appendix 2. *Ultimate and Proximate analyses of WEEE materials as provided by EBFRIIP*

Sample ¹		WEEE Mix1	WEEE Mix2	TV-Backplates1	TV-Backplates2 (BP-black)
C	wt%, dry	67.04	56.60	83.78	83.98
H	wt%, dry	6.80	5.97	7.35	7.31
N	wt%, dry	2.92	2.81	1.01	0.68
S	wt%, dry	0.11	0.10	0.03	0.02
Cl	wt%, dry	3.12	5.64	1.94	0.71
Br	wt%, dry	1.30	1.74	3.56	2.74
O	wt%, dry	8.16	8.24	1.09	3.34
ash	wt%, dry	10.54	18.90	1.24	1.23
LHV	MJ/kg	31.0	25.4	38.0	35.7
ratio Br/Cl	-	0.42	0.31	1.83	3.88
As	[mg/kg	18	15	55	30
Ba	[mg/kg	390	<25	<20	120
Ca	[mg/kg	9980	1260	<10	500
Cd	[mg/kg	70	110	70	20
Cr	[mg/kg	70	6	<1	<16
Cu	[mg/kg	2720	80	<1	20
Fe	[mg/kg	1570	80	<2	145
K	[mg/kg	810	70	<20	540
Mn	[mg/kg	60	4	<1	7
Mo	[mg/kg	6	95	6	5
Ni	[mg/kg	110	8	<1	16
Pb	[mg/kg	3500	1010	220	145
Rb	[mg/kg	<10	~	<1	<20
Sb	[mg/kg	6950	7190	23980	14540
Sn	[mg/kg	580	935	170	70
Sr	[mg/kg	70	4	<1	<7
Zn	[mg/kg	850	40	<1	210

¹. Measured wt% data normalised to 100%.

Appendix 3. Gibros PEC process

General aim of the PEC (Dutch acronym: Product en Energiecentrale) process is to produce syngas, metals and high quality construction material from different waste streams. The Gibros PEC process is a combination of pyrolysis, gasification (thermal cracking), and smelting (see Figure below). The pyrolysis takes place in a rotating kiln (500-600°C; residence time of approximately one hour) that is externally heated with part of the gas produced in the process. The pyrolysis gases containing tars are subsequently gasified (cracked) in a high temperature (1200-1300°C) gasifier by the addition of oxygen [9].



Larger pieces of ferrous and non-ferrous metals are removed from the solid product from the kiln. The remaining solids (char) are smelted (at 1400-1500°C). The heat is generated by partial oxidation of the char with oxygen (under reducing conditions). In the smelter a layer can be formed of molten metals under the molten slag, allowing separation of both fractions. The off-gas is combined with the gas from the gasifier. The mineral slag can be used as construction material (synthetic basalt) [9]. Due to the high temperatures in the gasifier and the smelter no organic compounds are present in the syngas.

Gas cleaning is performed prior to the gas utilisation and it consists of a washer to remove HCl, HBr, HCN, NH₃ (if present) and dust, followed by a bag filter to remove the remaining dust, and a basic and a biological washer to remove H₂S. Finally, an active coal filter to absorb dioxins, furans, and Hg (Hg concentration is reduced from ppm to ppb levels) [9]. The syngas is used to generate electricity (and heat) in a gas engine.

Appendix 4. *List of addresses to which samples of the concentrated scrubber solutions were shipped*

Albemarle

Attention: James E. Boone
R&D Albemarle Corp.
8000 GSRI AVE
Baton Rouge
U.S.A.

Dead Sea Bromine Group

Attention: Dr. Ron Frim
Industrial Chemicals Dept.
IMI - Institute for Research and Development
P.O. Box 10140
Haifa Bay 26111
ISRAEL

Great Lakes Chemical Corporation

Attention: David Bartley
1801 Highway 52, NW
West Lafayette
Indiana 47906
U.S.A.

Transbrom

Attention: Mr. L. Tange
Mercuriusstraat 2
4551 LB Sas van Gent
The Netherlands