


## Article

# Thermochemical Modelling and Experimental Validation of In Situ Indium Volatilization by Released Halides during Pyrolysis of Smartphone Displays

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**Abstract:** The present study focuses on the pyrolysis of discarded smartphone displays in order to investigate if a halogenation and volatilization of indium is possible without a supplementary halogenation agent. After the conduction of several pyrolysis experiments it was found that the indium evaporation is highly temperature-dependent. At temperatures of 750 °C or higher the indium concentration in the pyrolysis residue was pushed below the detection limit of 20 ppm, which proved that a complete indium volatilization by using only the halides originating from the plastic fraction of the displays is possible. A continuous analysis of the pyrolysis gas via FTIR showed that the amounts of HBr, HCl and CO increase strongly at elevated temperatures. The subsequent thermodynamic consideration by means of FactSage confirmed the synergetic effect of CO on the halogenation of indium oxide. Furthermore, HBr is predicted to be a stronger halogenation agent compared to HCl.

**Keywords:** pyrolysis; smartphone; displays; halogenation; indium; volatilization; thermodynamics; recycling

## 1. Introduction

During the last decade, the role of waste electric and electronic equipment (WEEE) as a feedstock has become increasingly important for European metal refineries. Both its significant domestic supply and its high metal content compared to primary resources have made it an attractive raw material for the recovery of valuable metals—especially copper and precious metals (Au, Ag). Moreover, WEEE contains a broad variety of several other metals, ranging from base metals (Fe, Zn, Sn, Al, Pb) to special metals (Ga, Ge, In, Ta, rare earth elements), whereby the content and the actual occurrence of the individual metals depend on the particular kind of WEEE. The metal content of a smartphone, for instance, differs strongly from that of a washing machine, resulting in a high heterogeneity of the total WEEE stream. Following the example of the smartphone, which represents a contemporary, widely distributed type of electronic consumer product, it can be stated that this kind of device exhibits a high complexity—not only in terms of various metals, but also regarding other sorts of materials, like glass, ceramics and plastics. This complexity makes holistic recycling and metal recovery a big challenge. Currently, WEEE with a high content of copper and precious metals is introduced into

the pyrometallurgical copper route which is able to handle larger amounts of feedstock. However, the chance of an easy recovery of precious metals is hindered by the high diversity of additional materials and elements, which leads to an increased input of impurities into the copper phase and requires an extensive slag design during the smelting process. Simultaneously, less noble trace metals, such as indium, tantalum and gallium, are lost in the slag and cannot be recovered [1,2]. From the environmental point of view, the processing of WEEE in copper smelters makes high demands of the off-gas treatment because the combustion of adhering plastics releases harmful substances such as dioxins and halides. The regard of all these aspects induces the consideration of appropriate techniques that can be applied prior to the smelting process in order to remove unwanted substances or separate particular elements which cannot be recovered in the smelter. Existing mechanical disassembling and sorting processes reach their limit when they are faced with composite materials and miniaturized components, i.e., smartphones and printed circuit boards. At this time, a thermal pretreatment of the electronic scrap via pyrolysis is a promising way to overcome these barriers. In this context, the work of Diaz et al. [3] shows that the pyrolysis of adhering plastics has several benefits:

- breakup of plastic-metal composites, so that a mechanical separation of a concentrated metal fraction is possible;
- removal of harmful organic substances and corrosive halides;
- production of a high-caloric pyrolysis gas that can be used as fuel or reduction agent.

Additional to these aspects, the process of pyrolysis enables not only the volatilization of hydrocarbons and halides, but also specific metals because of their affinity to form volatile metal halides. Thus, this work focusses on the case of indium in terms of a complete indium separation during the pyrolysis of indium-containing WEEE.

### 1.1. ITO Displays

As soon as electronic devices equipped with a flat panel display are discarded, indium is introduced into the stream of WEEE. Incorporated into the structure of indium tin oxide (ITO), indium is an indispensable compound to realize the functionality of different types of flat displays which are used for televisions, PCs, tablets and smartphones [4]. In 2017, the European Commission confirmed indium's status as critical because of its insecure import reliance and a recycling rate of 0% [5]. Regarding the latter, and keeping in mind that there is a domestic indium supply by way of discarded flat panel displays, an uncomplicated and cost-efficient way to include a pyrolytical indium separation step into the pyrometallurgical recycling route for WEEE by keeping all the other mentioned benefits of pyrolysis should be considered.

The most widespread technology for flat panel displays in electronic consumer products (i.e., televisions) is LCD technology (liquid crystal display). However, with respect to other more modern devices such as smartphones, OLED technology (organic light emitting diode) is becoming more established as a standard. In both cases, the displays are composed of several glass and polymer layers: lid (glass), polarizer film (polymer), active layer (LCD or OLED), ITO film (glass or polymer substrate), thin film transistors (glass substrate) and optical layers (polymer) [6]. A visualization of this sandwich construction is shown in Figure 1. The exact number and combination of layers depend on the technology, as well as the manufacturer, and will not be examined further. Nevertheless, the organic polymer films, and especially the brominated flame retardants (BFR) enclosed in the polymer structure, play a fundamental role for this work, which is why their chemical composition is taken into account. Due to their high transparency and their good mechanical and electrical properties, polyethylene terephthalate (PET), polycarbonate (PC), polyethylene naphthalate (PEN) and polymethyl methacrylate (PMMA) are appropriate materials to be used in flat displays [7,8]. For the polarizer film, a polymer based on cellulose triacetate (CTA), is state of the art [9]. With regard to PC, PET and PEN, it has been reported that their structure allows the application of BFR [10]. Coming back to the idea of

the pyrolytic pretreatment of WEEE, the question of using bromine, originating from the BFR, as a halogenation agent for the formation of volatile indium bromide remains.

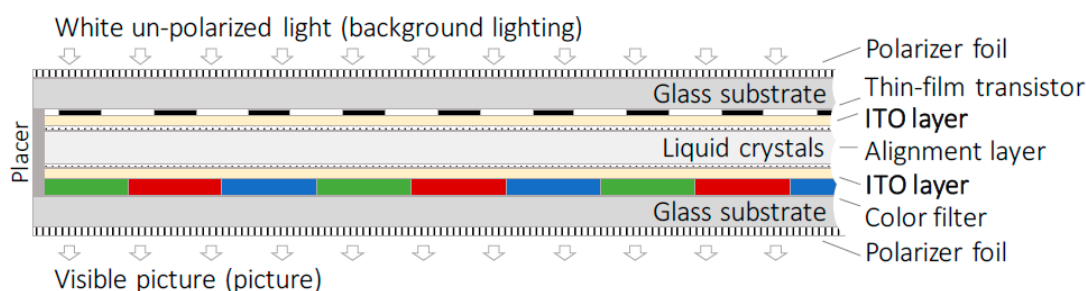


Figure 1. Sandwich construction of a liquid crystal display (LCD) [9].

### 1.2. Halogenation of Metals

Generally, there are several types of halogenation reactions, depending on the number and nature of reactants in the system. Nonetheless, all have the transformation of a metal oxide to a metal halide in common, which can be seen in the following equations, where the chlorination of a bivalent metal oxide is carried out [11]:



As can be seen from Equations (1)–(3), both the use of pure chlorine (halogenation) or gaseous HCl (hydrohalogenation) is possible. Furthermore, chlorine can be replaced by bromine without changing the stoichiometry of the reaction agents, however, it has to be taken into account that the thermodynamics of the reactions are slightly different. As it will be explained later, the halogenation reactions are strongly affected by temperature and other gas components occurring in the system. In this context, the formation of so-called subhalides plays an important role.

### 1.3. Current Research on Indium Volatilization from Displays through Chlorination

So far, there have been several scientific works on the halogenation and volatilization of indium from flat screens. All of these were conducted by using HCl as the halogenation agent. Ma et al. [12] examined the vacuum chlorination of LCD glass powder, whereby HCl was generated by the thermal decomposition of  $\text{NH}_4\text{Cl}$ , which was blended with the glass powder. Prior to the chlorination process, the polymers from the displays were removed via a pyrolysis step. The results of the chlorination showed that the indium recovery increased with the applied temperature due to the higher vapor pressure of  $\text{InCl}_3$ . As a second significant influencing factor, a smaller particle size of the LCD powder was identified to increase the indium recovery.

Similar investigations were carried out by Terakado et al. [13], who also used  $\text{NH}_4\text{Cl}$  and concluded that high temperatures support the chlorination/volatilization. For this work, the input material was synthesized by covering soda glass with ITO, so that no polymers were involved. The temperature was adjusted between 400 and 800 °C under normal pressure. Additionally, Terakado et al. found that the addition of small amounts of carbon powder had a beneficial effect on the indium recovery. In contrast to Ma et al., a longer milling time of the glass and thus a smaller particle size lowered the rate of indium recovery.

Another concept of HCl generation for the chlorination was followed by Kameda et al. [14], who used the products of the thermal decomposition of polyvinyl chloride (PVC) to create a HCl-rich atmosphere. The experiments of Kameda et al. were conducted under air as well as under an

inert nitrogen atmosphere, resulting in a higher indium volatilization when nitrogen was applied. Furthermore, the In recovery from pure  $\text{In}_2\text{O}_3$  was lower than using LCD powder as input material.

Similar to Me et al., Takahashi et al. [15] removed the polymer fraction from the milled LCD displays via incineration. Afterwards, the LCD powder was moistened with aqueous HCl and dried so that water was removed and HCl remained in the solid material. The thermal process was executed between 400 and 700 °C. Like the previous research, high temperatures and a nitrogen-rich atmosphere promoted the formation and evaporation of  $\text{InCl}_3$ .

#### *1.4. Motivation and Innovative Approach of this Work*

In each of the papers presented above, a supplementary chlorination agent was used without consideration of the polymer fraction from the LCD displays. However, this polymer fraction probably contains BFR, which can influence the whole process and act as a halogenation agent in situ unless the polymers are not removed. In one of our preceding papers, we investigated the temperature dependence of the gaseous and solid pyrolysis products during the thermal decomposition of printed circuit boards (PCB) [16]. It was found that elevated temperatures and a high heating rate have a considerable influence on the decomposition mechanism of the organics and thus on the composition of the pyrolysis gas. One important aspect was the formation of HBr at 700 °C during the decomposition of BFR in the epoxy resin. Hence, it is expected that this HBr generation will also occur during the pyrolysis of LCDs.

Therefore, this work focuses on the possibility of an in situ halogenation of indium oxide by HBr. A special point of interest is the influence of other gaseous pyrolysis products on the halogenation reaction. At this point, carbon monoxide (CO) is a matter of particular interest because its formation increases with higher temperatures. According to Peek [11] and Grabda et al. [17], the presence of CO has a synergetic effect on the thermodynamics of the halogenation reaction.

## **2. Materials and Methods**

### *2.1. Materials*

The input materials for the experimental work were displays from 20 discarded smartphones of different brands. First, the devices were dismantled manually so that the multi-layer displays, having an overall mass of 458 g, could be removed. To obtain a bulk material with a homogenous chemical composition, the displays were processed in a Fritsch Pulverisette 25/19 cutting mill, which resulted in a maximum particle size of 4 mm. The final comminution was completed via cryogenic grinding in a SPEX 6870D Freezer/Mill. Concerning the chemical analysis, the concentrations of most elements were measured by means of an ICP–OES (Perkin Elmer Optima 8300, Waltham, MA, USA), whereas Br and Cl were analyzed via RFA (PANalytical Axios, Malvern Panalytical, Almelo, The Netherlands). The total carbon (TC) was measured in a LECO R612 (LECO, St. Joseph, CT, USA) multiphase carbon determinator. Table 1 contains the results of the elemental analysis. Concerning the results for bromine and chlorine, a certain discrepancy has to be accepted because no appropriate standard material is available to fulfil an appropriate calibration and thus a precise analysis.

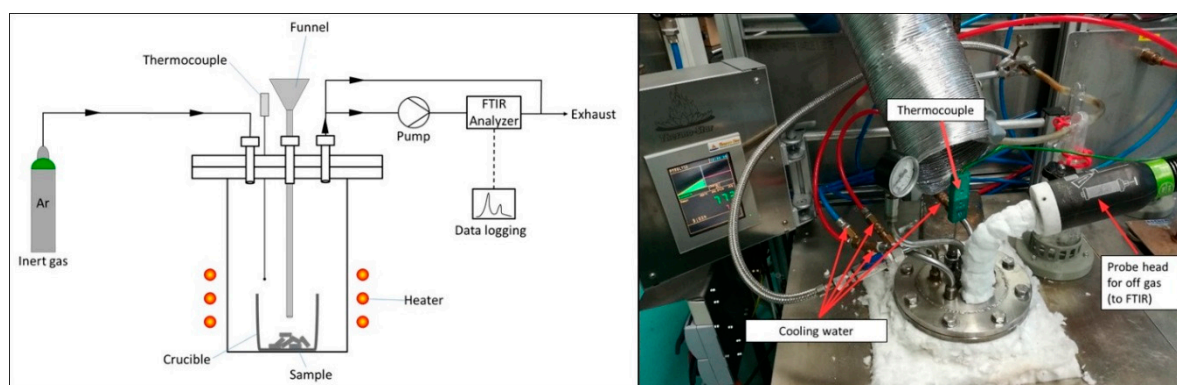
Due to the high share of polymer films, the comminuted product was not a flowable powder but a dense, rubbery fluff. In order to ensure smooth feeding, the material was compressed to pellets with a diameter of 6 mm and a length of 20 mm. For the second test series, pure ammonium chloride was mixed with the display fluff, adjusting to a ratio of 1:100, which means that 10 g display fluff was mixed with 0.1 g  $\text{NH}_4\text{Cl}$ .

**Table 1.** Chemical analysis of milled smartphone displays.

Element	conc./ppm	conc./wt.-%	Method
In	130	0.013	ICP-OES
Sn	470	0.047	ICP-OES
Ba	2000	0.2	ICP-OES
Ca	18,200	1.82	ICP-OES
K	5500	0.55	ICP-OES
Mg	11,800	1.18	ICP-OES
Na	35,500	3.55	ICP-OES
Sr	1400	0.14	ICP-OES
Al	41,100	4.11	ICP-OES
Si	17,400	17.4	ICP-OES
Br	50	0.005	RFA
Cl	100	0.010	RFA
C	231,000	23.100	TC

## 2.2. Experimental Setup and Procedure

The pyrolysis experiments were performed in a closed 1.5 L stainless steel reactor, which was placed in an electric resistance furnace, as can be seen in Figure 2. To prepare for the insertion of further equipment (thermocouple, charging tube and probe head for the off-gas analyzer) the lid was equipped with four gastight lead-throughs. Additionally, the lid was water-cooled to avoid any damage of the rubber seals by thermal impact.

**Figure 2.** Schematic figure (left) and photo (right) of the experimental setup.

For the temperature measurement, a type K thermocouple was chosen. In order to maintain an oxygen-free atmosphere, the reactor was purged with a constant argon stream of 3 L/min. The test runs were conducted at various temperatures between 300 and 800 °C, raising the temperature in steps of 50 °C with each trial. After heating the reactor up to the desired temperature, 10 g of display pellets were charged into the hot reactor using a densely sintered alumina pipe and a funnel. On the bottom of the reactor, an alumina crucible was placed to collect the pellets. Subsequent to feeding, the pipe and the funnel were removed and the lead-through was closed with a steel plug to avoid any leakage of pyrolysis gas. For each temperature step, the above outlined procedure was repeated twice. Following the pyrolysis, it was necessary to let the reactor cool down slowly, before the solid residue could be removed from the crucible and homogenized in a ball mill. Finally, the concentrations of indium and tin were measured via ICP-OES. One separate series of trials was performed to measure the composition of the pyrolysis gas at 300, 500 and 700 °C. For this purpose, a gas pump, manufactured by Ansyco, was used to extract an off-gas volume of 2.0 L/min from the reactor. Downstream from the pump, the gas flew through a Gaset DX4000 FTIR (Gaset Technologies Oy, Helsinki, Finland) (Fourier transform infrared) gas analyzer which allowed the continuous detection and quantification



of various compounds in the pyrolysis gas. Compounds of special interest were HBr, HCl and CO. The overrun gas flow was released from the reactor through a bypass.

### 3. Results and Discussion

In contrast to earlier studies on the pyrolytic volatilization of indium, the experimental setup used in this work did not allow the characterization of volatilized indium compounds. The water cooling of the lid resulted in the condensation of pyrolysis oil on its underside. Hence, in any case of indium halide vaporization, indium must occur in the condensed oil. However, there currently exists no successful procedure for an elemental analysis of the oil. Regarding a structural analysis of the solid pyrolysis residue via XRD, no satisfying results were obtained due to the high amount of carbon and glass, as well as the low content of indium compounds, in the powder. Therefore, the following results refer to the elemental analysis of the solid residue (via ICP-OES) and the off-gas analysis.

#### 3.1. Mass Loss and Volatilization of ITO

The mass loss of the pyrolyzed materials can be seen in Figure 3. Apart from slight discrepancies at the beginning and the end, both graphs show an almost identical trend, reaching their maximum at 650 °C (35% for pure display powder) and 800 °C (39% for  $\text{NH}_4\text{Cl}$ -addition).

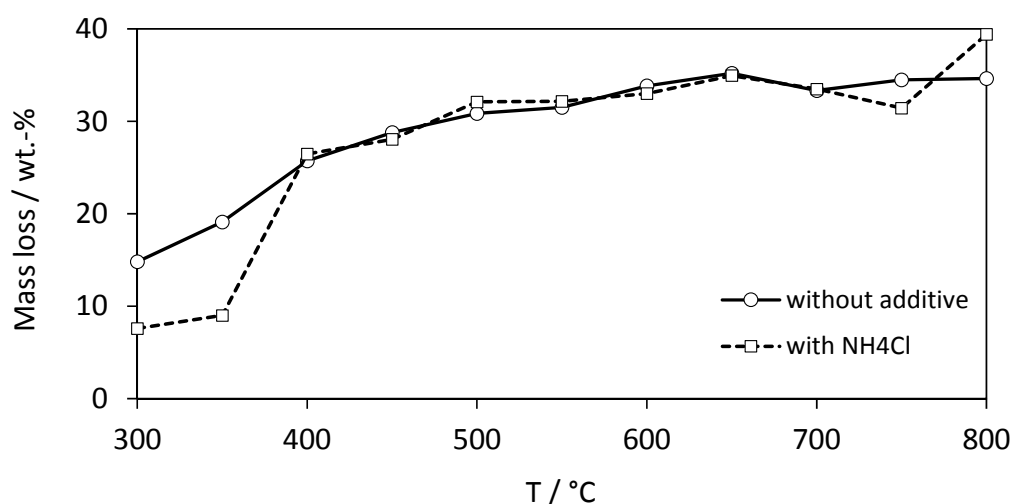
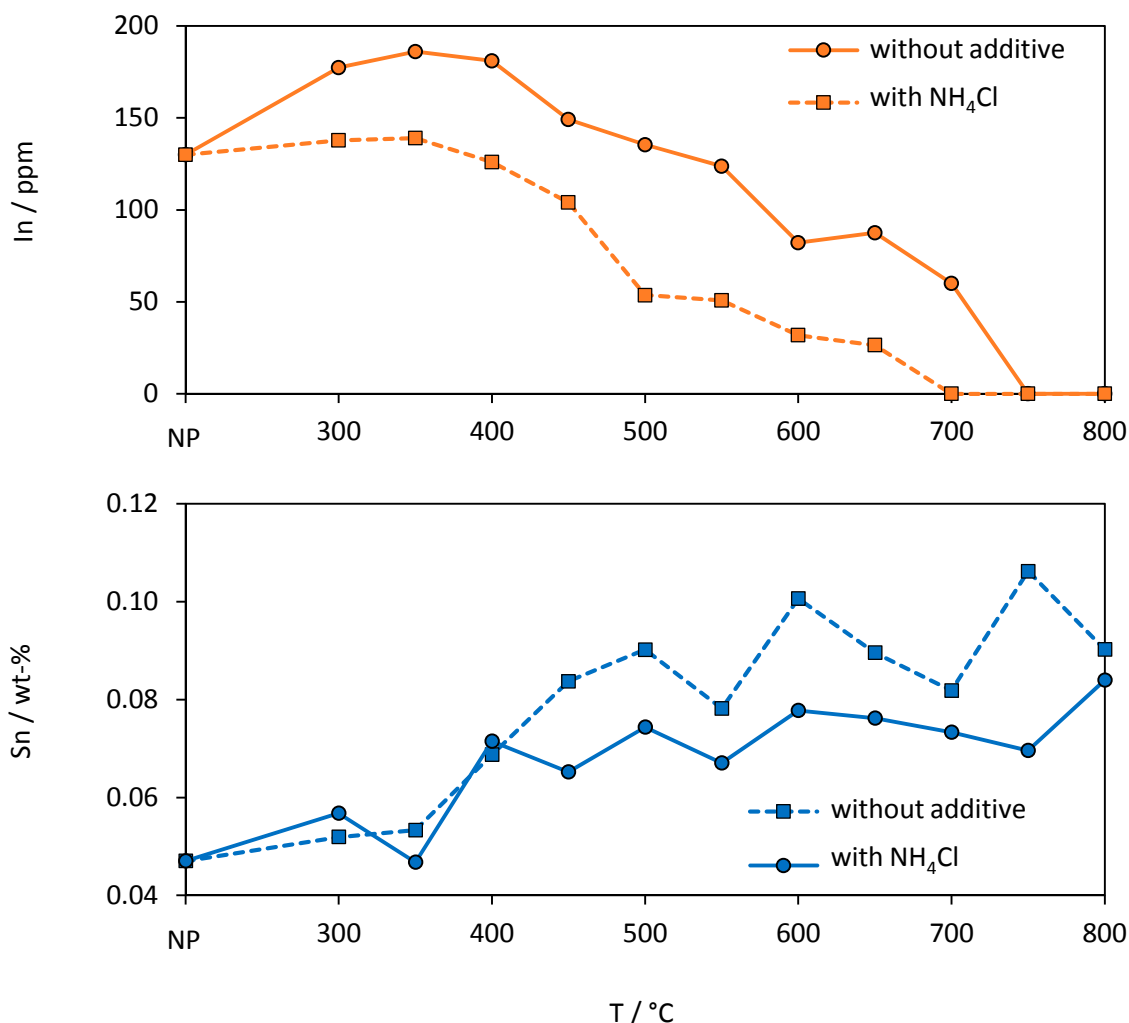


Figure 3. Mass loss during the pyrolysis of ground smartphone displays.

Figure 4 shows the concentration of indium and tin in the solid residue at several pyrolysis temperatures. The first value on the abscissa, which is labelled “NP”, represents the indium content of the non-pyrolyzed material. It should also be taken into account that the detection limit of indium in the ICP-OES was 20 ppm. In the case of five samples (between 700 and 800 °C), the analysis resulted in indium concentrations below this limit. To illustrate these points in the diagram, the values were set to zero but it must be assumed that the actual indium concentrations are located somewhere between 0 and 19 ppm. Apart from that aspect, it can be seen clearly that the processing temperature has a strong influence on the volatilization of indium from the material whether or not  $\text{NH}_4\text{Cl}$  was added as a supportive chlorination agent. Looking at both graphs, no decrease of indium in the material can be observed up to 350 °C. After the application of higher temperatures, an increasing amount of indium left the material. The increase before can be due to the mass loss referring to the pyrolysis of polymers. Both graphs exhibit a similar course, where the graph showing the experiments with  $\text{NH}_4\text{Cl}$  addition keeps an average distance of 57 ppm below the graph without any additive. Therefore, the detection limit of 20 ppm was already reached at 700 °C, whereas the samples without  $\text{NH}_4\text{Cl}$  had to be processed at least at 750 °C to bring the indium content to the same level. Obviously, a complete volatilization of indium without any extra halide-providing substance is possible and it

follows that there must be sufficient halides in the polymer fraction of the displays. According to Figure 4, a significant indium vaporization starts between 350 and 400 °C because the enrichment of indium by the act of pyrolysis of polymers is balanced.



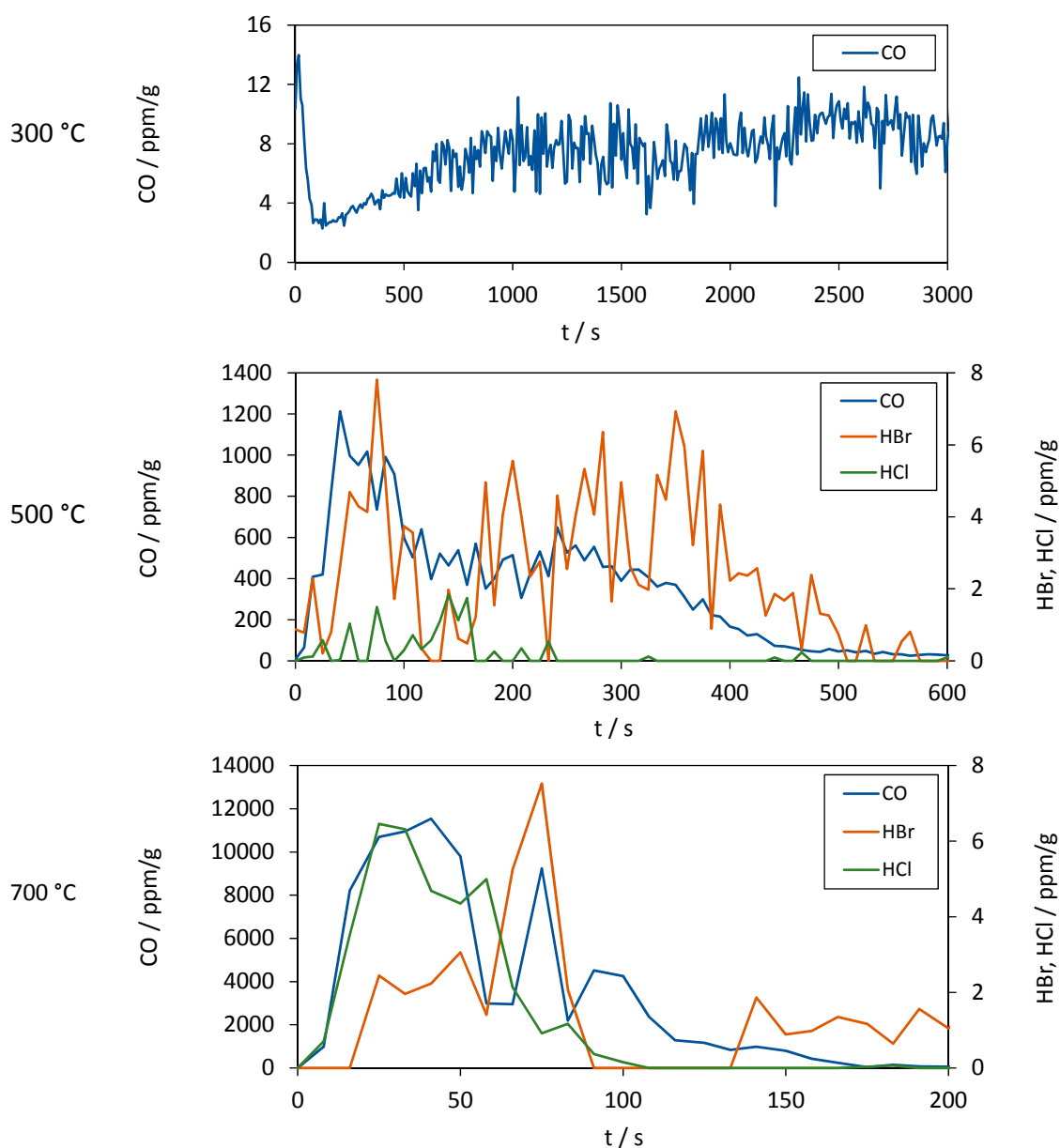
**Figure 4.** Concentration of In and Sn in the solid residue at different pyrolysis temperatures.

Concerning the analysis results of tin, the graphs in the second diagram of Figure 3 show an unsteady performance which is contrary to the results of indium. All in all, tin tends to be enriched in the material and no volatilization seems to happen. Comparing the tin concentration of the non-pyrolyzed material and the residue from the 800-°C trial, there is an increase of more than 90%, which is consistent with the mass loss of 35% (pure display powder) and 39% (NH<sub>4</sub>Cl-addition) as can be obtained from Figure 2.

### 3.2. Off-Gas Analysis

The results of the off-gas analysis for CO, HBr and HCl during the pyrolysis of display powder at 300, 500 and 700 °C are depicted in Figure 5. While the off gas contained numerous other gaseous species—especially organic substances—for this work, the three named compounds appear to be the most important ones. The concentrations of each component are normalized to one gram of charged material. By comparing the three diagrams, the changing scale of both axes has to be respected. Basically, the course of the curves resembles the results from our previous work where printed circuit boards were pyrolyzed (Diaz et al. [2]). At 300 °C, little gas formation could be measured, at which no detection of HCl and HBr happened. The oscillating CO concentration around 8 ppm proves that

there is a slow thermal decomposition which lasts for at least 50 min. With increasing the temperature to 500 °C and 700 °C, the amount of all gas components rose rapidly, particularly in the case of CO. Different to Diaz et al., a significant release of HBr was already observed at 500 °C but did not increase at 700 °C. This is different for HCl, which exhibits a strong increase from 500 °C to 700 °C. Concerning this temperature increase, the period from the first time of gas evolution to the last point of significant concentrations was reduced to a third. However, the graphs for HBr reveal some challenges regarding its detection in the gas phase. It must be kept in mind that the detection of HBr using FTIR is possible but is strongly affected by the sampling. From practice it is known that HBr tends to adhere to the inside surface of the sampling equipment so that the molecules reach the FTIR detector with a certain delay. Thus, its concentration–time record, as it is shown in Figure 5, is drawn-out as against the records for CO and HCl. It was also observed that the concentration of HBr continued to oscillate between 0 and 2 ppm although the formation of all other compounds, and therefore the pyrolysis itself, were finished.



**Figure 5.** Concentrations of CO, HBr and HCl during the pyrolysis of display powder at 300, 500 and 700 °C.

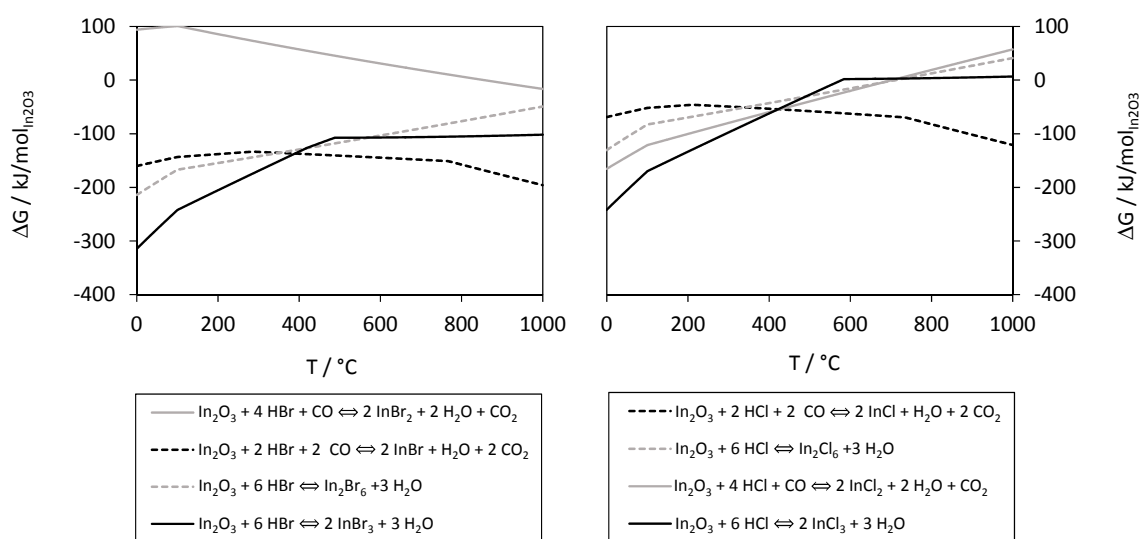


Despite the limited HBr measurement, it can be stated that higher pyrolysis temperatures favor the formation of CO, HBr and HCl. On the one hand, this aspect confirms the results of the indium decline with increasing temperature (see Figure 4), but on the other hand, it is not known yet which compound—HBr or HCl—acted as the major halogenation agent. Although the pyrolysis reaction at 700 °C is three times faster compared to 500 °C, there seems to be no limitation in terms of kinetics of the volatilization. In other words, the halogenation reaction and evaporation are fast enough and do not require residence times of HBr/HCl and CO longer than 100 s.

### 3.3. Thermochemical Modelling

For a more detailed investigation on the halogenation reactions occurring during the pyrolysis of powdered smartphone displays, several thermochemical calculations were executed using the software FactSage™ 7.0 [18], which is provided by GTT Technologies. The background of these calculations are considerations of Ma et al. [3] concerning the formation of indium sub chlorides, which may depend on the presence of a reducing agent.

All calculations in FactSage™ were done by assuming ideal conditions, which means that there are no molecular interactions in the gas phase. The required thermodynamic data was received from the SGPS database for pure substances. As a result, two series of Gibbs free energy lines were obtained: one series for the hydrobromination and the other for the hydrochlorination of one mole  $\text{In}_2\text{O}_3$  (see Figure 6). In fact, a calculation involving ITO would represent the real system rather than only  $\text{In}_2\text{O}_3$ . However, the available data bases of FactSage™ do not provide any data for ITO so a compromise had to be made.

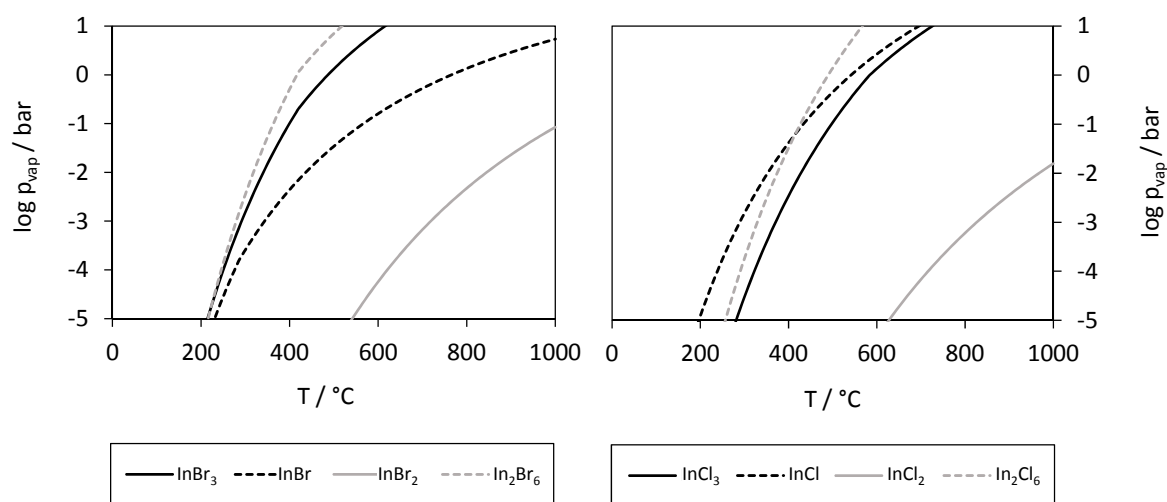


**Figure 6.** Gibbs free energy for hydrobromination (left) and hydrochlorination (right) of indium oxide.

All the graphs exhibit kinks at 100 °C, which indicates a phase change due to the evaporation of water at this temperature. Inflection points at higher temperatures represent the formation of halides in the gaseous state. In the cases of  $\text{InCl}$  and  $\text{InBr}$ , the melting point at 210 and 285 °C can be observed. Comparing the curves of the reactions, there is only a small difference between HBr and HCl, leading to the conclusion that HBr might be a slightly better halogenation agent due to the lower Gibbs free energy. As temperature increases, there are only three halogenation reactions, which become more favorable from the thermochemical point of view—as long as CO is added to the system in order to act as a reducing agent. Thus, if temperatures above 400 °C and sufficient CO is present, the generation of indium in the form of  $\text{InBr}$  and  $\text{InCl}$  seems to be the predominant mechanism. However, at 750 °C the formation of  $\text{InBr}_3$  and  $\text{In}_2\text{Br}_6$  is predicted to be also possible. As seen in Figure 3, 750 °C is the temperature where a complete volatilization of indium from the display powder without any

additional  $\text{NH}_4\text{Cl}$  was achieved. The different courses of the solid grey lines, which represent the formation of  $\text{InBr}_2$  and  $\text{InCl}_2$ , create doubt that the quality of the thermodynamic data is appropriate to reach a conclusion regarding the temperature-dependent formation of these particular compounds.

As a further step, the temperature dependence of the evaporation of the formed halides from Figure 6 will be investigated, because all halides can occur in different aggregate states and the success of the practical work is based on their evaporation. Therefore, the logarithmic vapor pressure lines of the different gaseous indium bromides and chlorides are shown in Figure 7.

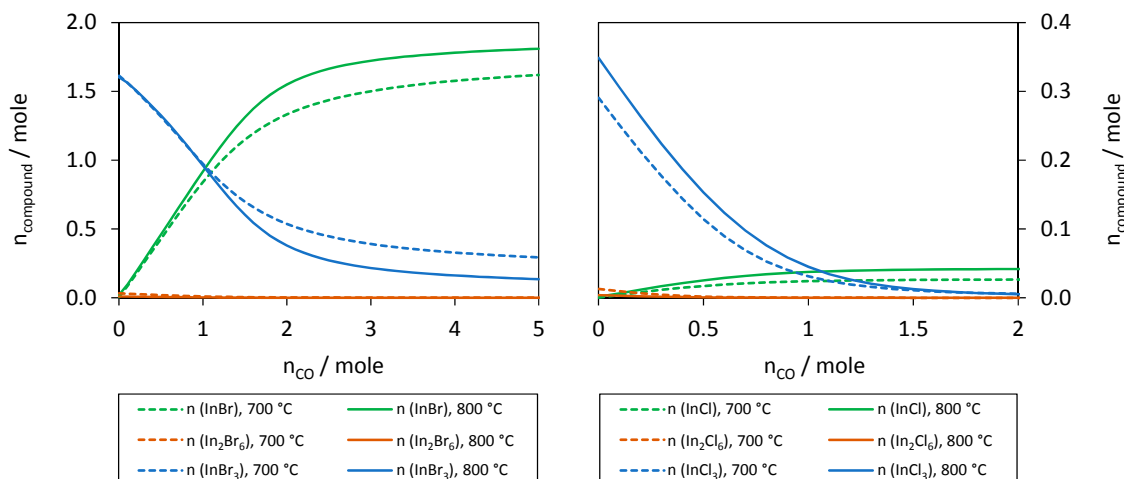


**Figure 7.** Vapor pressure curves of pure indium bromides (**left**) and indium chlorides (**right**).

If the curves are compared to the Gibbs free energy lines (see Figure 6), it becomes clear that there is a competition between the Gibbs free energy and the vapor pressures of the single components, which means that a halogenation reaction with a low Gibbs free energy forms a halide with a low vapor pressure (except  $\text{InBr}_2$  and  $\text{InCl}_2$ ). Therefore, the process of evaporation is another barrier which is strongly influenced by temperature. Assuming that mostly  $\text{InBr}$  is generated (according to Figure 6) it still requires sufficiently high temperatures to bring it to the gas phase.

To complete the contemplation of thermodynamics, we will have a closer look at some equilibrium calculations—especially with respect to the amount of supplied CO and the resulting proportion of the gaseous indium halides. In other words, the results from Figures 6 and 7 are combined in one diagram. For this purpose, a system was defined consisting of 1 mole of  $\text{In}_2\text{O}_3$  and an excess amount of 6 moles each of  $\text{HBr}$  and  $\text{HCl}$ . The quantity of CO was varied from 0 to 5 moles in steps of 0.1 mole and the whole procedure was executed for 700 °C and 800 °C. Finally, Figure 8 illustrates the resulting data from the equilibrium calculations. Also, here attention must be paid to the different scale of the axes. Due to the great difference in their amount, bromides and chlorides are shown in two different diagrams, although they exist in the same system.

As already predicted by the Gibbs free enthalpy lines in Figure 6, the occurrence of indium chlorides in the gas phase is inhibited by the preferred formation of indium bromide and for all amounts of CO, both  $\text{In}_2\text{Br}_6$  and  $\text{In}_2\text{Cl}_6$  play only a minor role. In contrast, the proportion of  $\text{InBr}/\text{InBr}_3$  shifts to higher values as the supply of CO increases. Raising the temperature from 700 °C (broken lines) to 800 °C (solid lines) intensifies this effect. This fact can be also observed concerning the formation of chlorides, but in a much lower scale as was previously mentioned. Again, it is theoretically proven that a CO-rich (reducing) atmosphere supports the formation of gaseous subhalides as well as the halogenation process. Referring to the results from the off-gas measurement (see Figure 5), a preferred formation of  $\text{InBr}$  seems to be the most probable mechanism at 700 °C because there is an enormous excess of CO compared to  $\text{HBr}$  and  $\text{HCl}$ .



**Figure 8.** Proportion of formed indium halides by HBr (left) and HCl (right) depending on the amount of CO.

#### 4. Conclusions

The aim of this work was to assess whether it is possible to volatilize indium from the display material of discarded smartphones without using an additional halogenation agent. This requirement was accomplished at a minimum processing temperature of 750 °C. At this temperature, significant amounts of HBr/HCl and CO were released from the plastic fraction to react with indium oxide. The theoretical study on thermodynamics confirmed the idea of a synergetic effect of CO on the halogenation at which In tends to be evaporated in the form of InBr/InCl rather than InBr<sub>3</sub>/InCl<sub>3</sub> at low CO concentrations. Compared to HCl, HBr is slightly preferred in order to act as a halogenation agent from the thermochemical point of view. Due to the successful decrease of indium and the recorded concentrations of HCl and HBr in the off gas it can be concluded that the amount of halide in the displays' plastics is sufficient for a complete indium halogenation so that no additive is required. Of course, the indium volatilization can also be realized at lower temperatures by adding an excess of NH<sub>4</sub>Cl, as was demonstrated in other papers [12–15], as well as in this work. However, both thermochemical calculations and experiments have shown that even though a successful halogenation would have happened, at least 700 °C is necessary to achieve a complete evaporation of the indium halides from the display material. As a final result, it can be stated that the success of a complete indium volatilization during pyrolysis depends on a chain of several mechanisms which are all promoted by high temperatures:

- thermal decomposition of plastics and the supply of sufficient HBr/HCl and CO;
- halogenation of indium oxide and the formation of (sub) halides depending on temperature and supply of CO;
- evaporation of formed (sub) halides.

Although no product material was collected, the process appears to be selective because the concentration of tin in the pyrolysis residue increased (due to of the mass loss of the material) which means that tin was not volatilized significantly. In this paper, the basic idea is to include the process of indium volatilization into a current recycling concept for WEEE with as little effort as possible. The main requirement for this, indeed, is the application of a pyrolysis step in the WEEE processing route which provides several other—probably more substantial—advantages [3,16]. Based on this fact, however, a simultaneous indium separation would be a great feature.

**Author Contributions:** B.F. (Benedikt Flerus) and T.S. conceived and designed the experiments; T.S. performed the experiments; B.F. (Benedikt Flerus) analyzed the data and wrote the paper with contributions of K.B.; R.S. and B.F. (Bernd Friedrich) supervised the work and contributed reagents, materials and analysis tools.

**Conflicts of Interest:** The authors declare no conflict of interest.

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