HALOCLEAN AND PYDRA - A DUAL STAGED PYROLYSIS PLANT FOR THE RECYCLING WASTE ELECTRONIC AND ELECTRICAL EQUIPMENT (WEEE)

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ABSTRACT
In the context of an European project - "Halocleanapplication" - a dual-stage thermal-chemical treatment pilot plant of two gas tight rotary kilns has been developed to transfer halogen containing materials like WEEE into “clean” fuels and residues for noble metal recovery.
In this work the process parameter, temperature and residence time were optimised. The temperature has been varied between 250 °C and 450 °C. The residence time was changed between one hour and four hours. The bromine content of all products was determined and correlated with the different temperatures. The content of the pyrolysis oil was specified by GC-MS. In particular the changes of bromine components in the pyrolysis oil were investigated.

INTRODUCTION
Plastics in electrical devices are equipped with different additives like phosphates, brominated compounds, chlorinated substances or antimony oxides in order to suppress the evolution of flames and the development of heat in case of fire.
However, especially brominated flame retardants are creating problems when electronic and electrical equipment reach end of life. If landfilled, toxic brominated flame retardants may slowly leach out into the ground water, where they persist for several years or they can be evolved into the air. If waste materials are burned toxic polybrominated dioxins and furans can be formed [i,ii].
Although phosphates are replacing more and more brominated additives there is still a wide range of manufacturers around the world using them. So waste will continue to contain these substances. At the moment there are two main possibilities for the recycling of those bromine containing electronical devices. On the one hand some devices are mechanically dismantled, on the other hand metal rich fractions are treated in the copper smelters where copper and

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noble metals are regained. But on the background of the European directive for waste electrical and electronic equipment started at 13.02.2003 in the future recycling rates of 50 or 75 % are required depending on the type of waste [iii]. Hence, an innovative technology to come along with bromine containing electronical devices is required. That is why a European project of 10 European partners from industries, universities and research centers developed a process called “ Haloclean ”pyrolysis procedure. To separate brominated additives from inert and valuable materials in electronic scrap the pyrolysis process Haloclean has been examined.

**PROCESS CONCEPT**

The Haloclean process recovers electronic scrap in order to obtain halogen free fuels and a residue for noble metal recovery.

![Fig 1: Staged pyrolysis of electronic scrap.](image)

The electronic scrap is shredded into pieces of about 25 mm size and mixed with stainless steel spheres which allow for a good heat transfer and grinding of the material. Then the material is transported into a first reactor. The reactor operates at a temperature level of 300 to 400 °C. It is very important that the volatile products are able to leave the reactor
immediately. The typical characteristics of the oil produced in the first reactor are dependant on the feed used.

The material and spheres are then transported into a second reactor operating at a temperature level of 400 to 550 °C. Again different oils occur depending on the feed material used. Using melted polypropylene as a source for hydrogen the oils from both steps can then be dehalogenated, hydrogen bromide is obtained. Due to the fact that electronic scrap consists of a mixture of different polymers the oils will not be useful for recycling plastic, but it is possible to use them for methanol synthesis.

The next step is the separation of residues, spheres and the additives. As the residue is non tacky and dry different fractions can be gained by mechanical treatment. The metal containing fraction can be used in electrolysis to regain precious metals [iv].

For the Haloclean process it is absolutely necessary that both temperature and residence time in the different reactors are exactly adjusted. Furthermore, an optimal heat transfer to the feed and short residence times for volatile products to prevent secondary reactions are required. Rotary kilns, widely used in incineration and pyrolysis and studied by many researchers [v], may provide the necessary features. In the European project Haloclean a complex system of modified rotary kilns has been developed.

**Haloclean Reactor** [vi]

The Haloclean reactor is an externally heated pilot-scale rotary-kiln pyrolyser (Fig 2).
In the kiln a screw for material transport and mixing is mounted. With the help of this screw the mean residence time in the reactor can be infinitely varied and adjusted exactly. The shaft of the screw is hollow and equipped with approximately 200 sinter metal plates. Through these plates gas can stream into the reactor. Therefore, a good transport of volatile products out of the reactor is given. In the inner core of the screw two heating tubes are installed for preheating the gas before flowing into the reactor and the reactor is heated not only from outside but also from inside. It is possible to drive the screw forwards and backwards for a good mixing of the material. The three zones of the oven can be driven separately and on both sides gas can be let in.

**THE HALOCLEAN & PYDRA PLANT**

Figure 3 shows the schematic view of the Haloclean plant realised at the research centre, Forschungszentrum Karlsruhe GmbH, Institut für Technische Chemie - Thermische Abfallbehandlung. The Haloclean reactor is situated right next to the PYDRA, a standard pyrolysis rotary kiln. Therefore, it is possible to use an existing burner and other installations and the infrastructure.
The pyrolysis gases of PYDRA and Haloclean can be burned in a combustion chamber or cooled down with a cooling device. Both pyrolysis oils can be cooled or burned. After the burning chamber there are some purification devices for waste gases. There is also the possibility to condense small amount of pyrolysis oil for off-line analysis.

Both rotary-kilns are pressure controlled. When pressure will be too high a valve will open and the pyrolysis gases will cooled down by a condenser. The remaining gaseous fraction will be burned outsight with help of a security flame. With the PYDRA rotary kiln it is also possible to test filtration of the pyrolysis gas at high temperature.

**Results and discussion**

In the Haloclean rotary kiln different fractions of electronic scrap were tested and pyrolysed. One of these fractions was a fraction consisting of circuit boards from computers. This
fraction had a gold content of 300 g/t and a bromine content of 5 % due to the brominated flame retardants.

This fraction was treated with temperatures between 250 and 400 °C and a residence time of one respectively two hours. After this first step the residue was cooled down and then again transported into the Haloclean rotary kiln and pyrolysed at 450 or 550 °C for 2 hours. The pyrolysis products, oil and residue, were analysed by means of GC-MS, RFA ... The organic components of the pyrolysis oil were found to be phenol mainly. The content of phenol and substituted phenols was up to 80 %. But there were also brominated compounds found in the oil, mostly being characterised as bromophenol and dibromophenol. In other words, the bromine content – quantified with the help of an oxidative decomposition followed by ion chromatography – after the second step was still too high to use the pyrolysis oil in further chemical processes like methanol synthesis of phenol recovery. A post-treatment with e.g. polypropylene is necessary [vii].

Concerning the pyrolysis residue, it could be shown that after the two pyrolysis steps approximately 45% of the material remained in the residue independent of process temperature or process time. The concentration of bromine in the residue was nearly the same then in the feed whereas the gold concentration was twice as big as in the feed. In other words all gold could be found in the residue.

**Conclusion**

The directive on WEEE of the European community makes it necessary to recycle electronic scrap in the future. The Haloclean process – a complex system of different rotary kilns - is the first process which allows for a chemical treatment of electronic scrap and therefore the first process which gets along with the problems due to the high bromine content of electronic scrap. It could be shown that electronic scrap can be converted into gaseous hydrogen bromine, a nearly debrominated oil and a residue, that contains the noble metals in a more concentrated form. All three fractions are suitable for further usage.

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[iii] Elektronik 4/2003, 40-44


[vi] European Patent Application, No 00830831.4, filed on 19.12.2000, in the name of Sea Marconi Technologies di Wander Tumiatti Sas