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Experimental investigation of the influence of reaction atmosphere on the pyrolysis of printed circuit boards ☆

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HIGHLIGHTS

- Pyrolysis enables the efficient separation of the organic and inorganic fraction.
- Steam influences the thermal decomposition of PCBs.
- The energy recovery potential of PCBs pyrolysis gas is limited.
- Antimony (Sb) migration to gas phase is favored in presence of steam.

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ABSTRACT

Printed circuit boards (PCB) are one of the most challenging fractions of waste electrical and electronic equipment (WEEE) in terms of recycling due to their complexity and diversity. Pyrolysis seems to be a promising alternative for production of energy carriers from its organic fraction with simultaneous recovery of metals. Reaction atmosphere is among the process parameters that affects the thermal decomposition as well as the products' formation and distribution. In this study, the decomposition of two different PCB fractions in inert and steam atmospheres has been investigated by means of thermogravimetric analysis (TGA) and lab scale fixed bed reactor experiments. It was found that the decomposition of the tested materials in steam atmosphere starts at lower temperatures and proceeds slower compared to the N_2 atmosphere. Moreover, a two-step decomposition has been observed on the PCB sockets fraction due to the fact that high amount of antimony oxide was present, a common additive for improving the flame retardancy, which have been also observed on previous studies (Wu et al., 2014). The presence of steam influence the pyrolysis gas composition and promotes additional vaporisation of antimony as verified by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). Finally, the liquid fraction has been qualitatively analysed using a GC/MS in order to determine the brominated compounds as well as other compounds that are produced from this process.

1. Introduction

The world's constantly increasing energy demand, as well as recent statistics from 2016 showing the first increase in oil consumption since 1999, has made energy research more up-to-date than ever before [1]. At the same time, the scientific community is focusing on finding new fuel alternatives proportional to the population growth in order to fulfil the society's growing energy demand. Waste generation is always proportional to the population, with some waste fractions being difficult to recycle, fractions which the utilization for energy purposes should be further investigated. Moreover, recycling of metals can highly contribute on energy savings in comparison to the high energy consuming extraction processes of mining and extraction.

During the last decades it has been a revolution of the informatics technology and as its result, the demand of electrical and electronic equipment is increasing globally while at the same time their total life span is decreasing [2]. Alongside the quantity of the waste electrical and electronic equipment (WEEE) fraction has increased and will continue to increase according to recent predictions to 49.8 Mt by 2018 [3]. Printed circuit boards (PCBs) are the main component for most electronic and electrical devices

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and represent 6 wt% of the total WEEE fraction in Europe, which is almost 500,000 tons annually [4].

Recycling of PCBs has attracted the attention of the scientific community over recent years because of its complex composition and packed size which decreases their material's recovery rate. The three main material types used for the manufacturing of PCBs are: a fibre mesh made from either silica or alumina fibres, a metallic laminated sheet, and epoxy resins or cyanate esters plastic material. The separation of these components seems to be challenging by mechanical means and the degree of their liberation is limited [5]. Thermochemical recycling of waste's organic fraction, such as pyrolysis and gasification, seems to be a valuable option, both for recovering the energy content of the organic part and for enhancing the separation of the metallic and ceramic materials [6].

Most of the research on thermochemical conversion of PCBs has been focusing on the drawbacks and the limiting factors of these processes such as pollutants with high health risks on human exposure which can be found in the liquid, gas and solid residue acquired by pyrolysis of PCBs. On previous experimental investigation on pyrolysis of PCBs done by the authors [7], the primary products of pyrolysis of PCBs according to the temperature conditions has been revealed as well as reaction pathways of the phenolic and the brominated compounds has been proposed based on the findings. This study concluded that temperature conditions are of high importance since it influences the reaction pathways and the decomposition mechanism in order to yield specific products. Lin et al. [8] investigated the production of organic compounds and the chemical form of the elements in the solid residue according to the temperature conditions of the process. The work concluded that the pyrolysis oil obtained could be utilised for energy after being upgraded. Chiang et al. [9] focused on the exhaust emission factors and their control because some of the produced volatile organic compounds might escape from conventional exhaust treatment systems and thereby a new control of the exhaust treatment was proposed. Salbidegoitia et al. [10] has also investigated the influence of steam on thermal decomposition of phenolic PCBs in the presence of metal oxides in order to verify if the catalytic effects of metallic powder can improve the production of hydrogen at low temperature range (550 °C). This study concluded that the higher the temperature conditions of the process, the lower is the catalytic effect of the metals contained in the mixture for hydrogen production. Ahmed et al. [11] have investigated the thermal treatment of waste paper in both nitrogen and steam atmospheres in order to evaluate their energy yield under different temperatures. Hall et al. [12] have investigated the effect of antimony trioxide on the pyrolysis of styrenic polymers and its influence in the decomposition reactions' pathways. They concluded that the plastic fractions contain antimony trioxide, produce lighter oils during their pyrolysis than the ones that did not contain antimony trioxide.

Steam is known for its ability to promote the gasification of solid carbon and promote the production of hydrogen through steam reforming reactions [13]. Moreover, it has been used as process gas for thermochemical treatment of plastic waste both for hydrogen and carbon nanotubes production [14]. For industrial scale applications, the utilization of steam is an attractive alternative to nitrogen for process gas since it can be readily available in process because of thermal integration and waste heat recovery at different stages of high temperature industrial processes. Furthermore, previous studies have concluded that steam pyrolysis favours the yield of liquid products on other waste fractions [15] Moreover, the presence of metals together with steam have even shown to promote the conversion of organic matter to liquid or gas products because of their catalytic influence [16]. Zhang et al. [17] has investigate the kinetics of steam gasification of phenolic circuit boards at low temperatures in the presence of molten carbonates for converting the plastic fraction into fuel gas, while on the same time enhancing the recycling of metals. But limited number of studies has been carried out for both investigating all the fractions derived by this process and how the presence of steam influences them. In this study, the influence of steam in comparison with nitrogen atmosphere on the decomposition of PCBs was investigated as well as its influence on the produced gas, liquid, and solid with emphasis on the different phenomena that occur. The experiments have been carried out both using a thermogravimetric analyser (TGA) and a fixed bed reactor.

2. Materials and methods

2.1. Sample handling and composition

Printed circuit boards (PCBs) were collected from recycling facilities and were divided into two different fractions similar to the recycling process used for their separation by recycling companies. The main body of PCBs (hereby referred to as PCBmb) consisted of a glass fibre sheets which act as a base of the PCB, metallic layers used for closing the circuits of the different components, and plastic resins used to glue everything together and enhance the strength of the PCBs. The plastic sockets (hereby referred to as PCBsockets) were the additional parts of the PCBs, and were attached on the surface of the PCBmb used for connecting the independent elements and components of the computers' conductors, such as CPUs and RAMs. Most of the PCBsockets were pure plastic components with a few metallic pins. Both the PCBmb and the PCBsockets were shredded and mixed to achieve high homogeneity prior to testing. Both fractions were characterised by means of proximate and ultimate analyses (Table 1).

2.2. Thermogravimetric analysis

TGA tests were conducted using a NETZSCH STA 449 F3 Jupiter thermogravimetric capable to operate also with water vapour as process gas. Both examined fractions (PCBmb and PCBsockets) were subjected to three different heating rates, namely 5 °C/min, 10 °C/min and 20 °C/min, in two different atmospheres, nitrogen and steam. In the case of steam, nitrogen was used initially to purge the TGA furnace during the heating phase, with a flow of 5 g/h of pure steam being introduced when the temperature had reached 120 °C in order to avoid condensation. For all cases, the starting temperature was set at 50 °C followed by temperature increase at different heating rates with the final temperature set at 850 °C.

2.3. Fixed bed experiments

The two examined fractions (PCBmb and PCBsockets) were also tested in both atmospheres in a fixed bed reactor (Fig. 1). The reactor consists of a 1 in. inner diameter stainless steel tube inserted in a 1 kW electrically heated furnace. Flow of N_2 was controlled by a Brooks flow meter. Produced vapours were condensed in cold traps submerged in liquid bath at 0 ± 1 °C. The volume of noncondensable gases was determined by the water displacement method.

The pyrolysis conditions were designed in a similar way to the conditions used during the TGA experiments in order to obtain comparable results. The reactor was charged with 10 g of solid material and was purged with 50 ml/min of nitrogen in room temperature prior to heating until no oxygen was detected. The reactor was then heated to 600 °C and the sample was held at this temperature for 20 min until no gas was produced in order to make sure

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