ARTICLE IN PRESS

Waste Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Possibilities and limits of pyrolysis for recycling plastic rich waste streams rejected from phones recycling plants

B.M. Caballero *, I. de Marco, A. Adrados, A. López-Urionabarrenechea, J. Solar, N. Gastelu

Chemical and Environmental Engineering Department, School of Engineering of Bilbao, University of the Basque Country (UPV/EHU), Alda. Urquijo s/n, 48013 Bilbao, Spain

ARTICLE INFO

Article history:
Received 1 October 2015
Revised 31 December 2015
Accepted 1 January 2016
Available online xxxx

Keywords:
Recycling
Pyrolysis
Electrical & electronic equipment
Waste
Landline phone
Mobile phone
WEEE

ABSTRACT

The possibilities and limits of pyrolysis as a means of recycling plastic rich fractions derived from discarded phones have been studied. Two plastic rich samples (⩾80 wt% plastics) derived from landline and mobile phones provided by a Spanish recycling company, have been pyrolysed under N_2 in a 3.5 dm^3 reactor at 500 °C for 30 min. The landline and mobile phones yielded 58 and 54.5 wt% liquids, 16.7 and 12.6 wt% gases and 28.3 and 32.4 wt% solids respectively. The liquids were a complex mixture of organic products containing valuable chemicals (toluene, styrene, ethyl-benzene, etc.) and with high HHVs (34–38 MJ kg^{-1}). The solids were composed of metals (mainly Cu, Zn, and Al) and char (≈50 wt%). The gases consisted mainly of hydrocarbons and some CO, CO_2 and H_2. The halogens (Cl, Br) of the original samples were mainly distributed between the gases and solids. The metals and char can be easily separated and the formers may be recycled, but the uses of the char will be restricted due to its Cl/Br content. The gases may provide the energy requirements of the processing plant, but HBr and HCl must be firstly eliminated. The liquids could have a potential use as energy or chemicals source, but the practical implementation of these applications will be no exempt of great problems that may become insurmountable (difficulty of economically recovering pure chemicals, contamination by volatile metals, etc.)

1. Introduction

The worldwide production of Waste of Electrical and Electronic Equipment (WEEE) has been estimated in 20–50 million tons per year (Wang and Xu, 2014; Ongondo et al., 2011). In Europe around 10 million tons WEEE are generated each year (ITRE Committee, 2014) and it is expected that by 2020 the amount generated in the EU-28 will reach a total annual tonnage of 12.3 million (Muhammad et al., 2015; Alston et al., 2011; Ortuño et al., 2014). In 2012 approximately 35% of the WEEE generated in the EU (≈3.5 million tons) were collected and appropriately managed, having increased this percentage at about 7% per year from 2007 to 2012 (Eurostat, 2015; Hense et al., 2015).

Until recently most of the discarded electrical and electronic equipment (televisions, computers, telephones, etc.) were landfilled or incinerated and both of these alternatives can cause serious damage to the environment and have adverse effects on human health, due to the hazardous products contained in WEEE such as, Pb, Cd, Hg, PVC, and halogenated flame retardants.

In 2002 the European Commission launched the so-called WEEE Directive 2002/96/EC which has recently been replaced by the new WEEE Directive 2012/19/EU that introduces an increase in the collection targets of this waste. From 2016 the annual collection target is defined as the ratio between the collected amount and the average weight of EEE (electrical and electronic equipment) placed on the market in the three preceding years. The collection target is set at 45% in 2016 and will rise to 65% in 2019, a quota that will be very difficult to reach since WEEE is a very complex mixture of many and very different materials (metals, different plastics, glass, rubbers, etc.). As a general rule, WEEE contains about 40% of metals, 30% of plastics and 30% of refractory oxides and the typical composition of metal scrap is copper (20%), iron (8%), tin (4%), nickel (2%), lead (2%), aluminum (2%), zinc (1%) and small percentages of precious metals as silver, gold and palladium (Gramatyka et al., 2007; Yang et al., 2013; Salbidegoitia et al., 2015). With respect to the plastic fraction the most common constituents are acrylonitrile–butadiene–styrene copolymer (ABS), high impact polystyrene (HIPS), polycarbonate (PC), blends of ABS and PC, polypropylene (PP), polyphenylene (PPE) and HIPS, polyvinyl chloride (PVC), polyamide (PA) and polystyrene (PS) (Yang et al., 2013; Alston et al., 2011).

Information and Telecommunication Technologies (ITT) equipment is one of the most predominant WEEE in the EU (≈16–18%

* Corresponding author.
E-mail address: blancamaria.caballero@ehu.es (B.M. Caballero).

http://dx.doi.org/10.1016/j.wasman.2016.01.002
0956-053X/

of collected WEEE) (Eurostat, 2015; Ongondo et al., 2011). This category includes computers, printers, speakers, web cameras, etc., and also phones which are the subject of this study.

The 2014 statistics showed that the number of landline telephones subscriptions in the world was about 1100 millions, which means about 15 subscriptions per 100 inhabitants (ITU, 2015). In Europe fixed phone landline subscriptions decreased from 42.8 (per 100 inhabitants) to 38.3 (per 100 inhabitants) from 2010 to 2014 (ITU, 2015), and will continue to decrease and to give rise to phone waste, due to the advantages of mobile phones and Internet-based alternatives; therefore landline phones are now discarded more and more frequently.

On the other hand the use of mobile phones is at present outrageously widespread. There are around 7000 million mobile phone subscriptions in the world, which means around 96 per 100 inhabitants (ITU, 2015). Mobile phones are continuously being replaced by newer ones with higher performance or more novel designs. The average life span of a smart phone is less than 2 years.

It is evident that phones, either landline or mobile ones, currently constitute an important and increasing waste stream, which has the advantage of being easily and selectively collected. For this reason this paper has been centred in the study of an alternative for recycling waste streams coming from discarded landline and mobile phones.

1.1. Waste of electrical and electronic equipment management

Recycling companies are almost exclusively focussed in recovering metals from WEEE. Typical WEEE recycling methods include a first step in which hazardous or valuable components (batteries, printed circuit boards, casing, external cables, etc.) are separated, and a second mechanical or metallurgical process to upgrade the content of desirable materials and obtain marketable output streams. Mechanical processes include shredding or crushing and then sorting based on the size, shape, density, and electrical and magnetic characteristics (magnetic separation, Eddy current separation and gravity separation), while metallurgical processes involve either melting (pyrometallurgical processes) or dissolving (hydrometallurgical processes) the metals (Tsydenova and Bengtsson, 2011).

Concerning discarded phones, WEEE recycling companies recover a great part of the metals from landline phones (base, card phone and wire included) and mobile telephones (including terminal transmitter/receiver, battery and accessories such as transformer/battery charger, and cover) by shredding them and then subjecting them to magnetic and Eddy current fields. After this process a waste stream with a very high proportion of different plastics (PC, ABS, PVC, etc.) mixed with some metals and other materials (glass, fillers ...) is left. In order to achieve the targets of the recently renewed WEEE Directive, these types of rejected waste streams have to be, as much as possible, recycled. However, the plastics in these streams are very much intermingled and also have some remaining metals or other materials embedded in them. Therefore because of their complexity and heterogeneity, and also due to their content of hazardous substances, the separation and mechanical recycling of the individual components of these waste streams is not technically and/or economically feasible.

For this reason this paper has focussed on the study of the possibilities and limits of pyrolysis as an alternative route for recycling plastic rich fractions rejected from phone recycling industrial plants. In the pyrolysis process the organic volatile matter of the material (plastics, rubbers, etc.) is decomposed to gases and liquids. The inorganic components (metals, fillers, glass, etc.) remain almost unaltered during the process, and consequently their valuable components can be recovered and reused. The pyrolysis process is therefore especially appropriate for complex waste, which contain many different plastics mixed with other materials, as is the case of the plastic rich waste streams coming from landline and mobile phones considered in this study.

There are several references in the literature dealing with the pyrolysis of plastic fractions contained in WEEEs. Some authors have investigated plastics from cathode ray tubes (televisions and computer monitors), refrigeration and freezers equipment (Hall and Williams, 2007a; Muhammad et al., 2015), and from computer bodies and monitor cases (Hall and Williams, 2006). Other studies have focused on printed circuit boards from waste computers, televisions and mobile phones (Hall and Williams, 2007b). Mixtures of WEEE plastics have been studied by Hall and Williams (2007a), Alston et al. (2011) and Acomb et al. (2013). However there are no studies devoted specifically to the pyrolysis of plastic rich streams derived from mobile phones and landline phones. There do are some references dealing with pyrolysis of certain components of mobile phones, in particular with printed circuit boards or mixtures of printed circuit boards and cases from mobile phones (Hall and Williams, 2007b; Ortuño et al., 2014; Moltó et al., 2009, Moltó et al., 2011), but only the latter of this references devotes some attention specifically to a plastic rich fraction (the casing) of the mobile phones.

In 2008 the authors published a preliminary study about the pyrolysis of different electrical and electronic WEEEs (de Marco et al., 2008), in which the pyrolysis yields obtained and a light and incomplete characterization of pyrolysis products were included. The main conclusions were that the yields and characteristics of the pyrolysis products depended very much on the type of WEEE pyrolyzed, and that all three products may find useful applications. Many scientific papers dealing with pyrolysis of plastic waste claim the goodness of pyrolysis products without considering the limitations that arise when it comes to the applications of these products in practice especially if the plastics come from WEEE. In this paper a thorough characterization of the solids, liquids and gases obtained by pyrolysis of plastics-rich fractions derived from phones is presented, which enables the ability to assess the possibilities and limits of pyrolysis as a means of recycling plastics-rich waste streams rejected from phone recycling plants.

2. Material and methods

2.1. Origin of the samples

The landline and mobile telephone samples pyrolysed were provided by a Spanish recycling company devoted to recovering metals from WEEE. Such samples are the waste streams that are obtained in the mentioned company after grinding the landline and mobile telephones (base, card phone and wire included) once the magnetic parts have been magnetically removed. Both samples were provided with a particle size of $\approx$ 2 cm and were pyrolysed as they were received. Homogeneous and representative 100 g samples were separated for the pyrolysis experiments by successively dividing the original samples and subsamples into fourths. Fig. 1(a) y (b) shows a picture of the landline phone and mobile phone samples. Two of the 100 g samples (one of each type of phone) were finally ground to a particle size <0.5 mm, which is the appropriate size for the different analytical techniques used to characterize the samples, which will be described in Section 2.3.

2.2. Pyrolysis experiments

The pyrolysis experiments were carried out at 500 °C in a nitrogen atmosphere, using an unstirred stainless steel 3.5 dm^3 reactor in a semi-batch operation at atmospheric pressure.