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Microwave assisted pyrolysis of halogenated plastics recovered from waste computers

Luca Rosi ^{a,b,*}, Mattia Bartoli ^a, Marco Frediani ^{a,b}^a Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia, 3-13, 50019 Sesto Fiorentino, Florence, Italy^b Consorzio Interuniversitario Reattività Chimica e Catalisi (CIRCC), Via Celso Ulpiani 27, Bari, Italy.

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ABSTRACT

Microwave Assisted Pyrolysis (MAP) of the plastic fraction of Waste from Electric and Electronic Equipment (WEEE) from end-life computers was run with different absorbers and set-ups in a multimode batch reactor. A large amount of various different liquid fractions (up to 76.6 wt%) were formed together with a remarkable reduction of the solid residue (up to 14.2 wt%). The liquid fractions were characterized using the following different techniques: FT-IR ATR, ¹H NMR and a quantitative GC-MS analysis. The liquid fractions showed low density and viscosity, together with a high concentration of useful chemicals such as styrene (up to 117.7 mg/mL), xylenes (up to 25.6 mg/mL for p-xylene) whereas halogenated compounds were absent or present in a very low amounts.

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1. Introduction

The EU-28, plus Norway and Switzerland (EU28+2), currently generates around 10 million tons of WEEE each year (UNEP, 2005; FISE UNIRE, 2015), and this is rapidly increasing (Huisman et al., 2015).

WEEE consists of a complex mix, including a wide range of different materials such as polymers and metals, and organic molecules which are included as flame retardants (Dalrymple et al., 2007; De Marco et al., 2008; Alston et al., 2011; Muhammad et al., 2015). It has been estimated that roughly 20–30 wt% of WEEE consists of plastics (FISE UNIRE, 2015). The composition of WEEE depends also on the age of the item produced, as the manufacturing process has changed over the years (Martinho et al., 2012).

The 17% of Italian WEEE derives from small appliances and significant proportion of this comprises of the plastic casing from computer bodies and typewriters (FISE UNIRE, 2015).

The large and ever increasing production of electrical materials and electronic devices in the EU has created an imperative towards the proper management and disposal of WEEE. Over the last decade, remarkable efforts have been devoted to the development of a recycling chain for WEEE. This starts from WEEE collection, through the sorting of various components, to their separation

and extraction by traditional methods. WEEE sorting methods have improved significantly recently, but the complexity and the diversity of the WEEE mix hampers a complete and useful recycling of the individual components. (Kiddee et al., 2013). The recycling of WEEE also presents several environmental problems connected with the high quantity of metals contained within it, and also because of the presence of various halogenated and non-halogenated flame retardants (Schlummer et al., 2005). The most widespread halogenated are brominated organic compounds, primarily polybrominated diphenyl ethers (PBDEs), of which the most common are penta-BDE, octa-BDE and deca-BDE, that have been classified as Persistent Organic Pollutants (POPs). Furthermore, yet more polymers have been found and identified in WEEE, such as poly(acrylonitrile-butadienestyrene) (ABS), high impact polystyrene (HIPS), polypropylene (PP), polycarbonate (PC), polyvinyl chloride (PVC), and polystyrene (PS) (Alston et al., 2011).

The pyrolysis process can potentially be exploited to convert plastics into fuel or other more valuable chemicals (Sharuddin et al., 2016), and can be considered a potentially worthwhile process in the recovery and re-use of the polymeric material content of WEEE (Al-Salem et al., 2009; Alston et al., 2011; Martinho et al., 2012; De Marco et al., 2008; Muhammad et al., 2015).

In the realm of pyrolysis, MAP is an established process which offers some advantages over conventional pyrolysis methods- for example, it involves the rapid heating of the material involved and increased production speed- and so provides a volumetric heating that improves heating efficiencies as compared with conventional techniques (Appleton et al., 2005). Most recently, MAP

* Corresponding author at: Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia, 3-13, 50019 Sesto Fiorentino, Florence, Italy.

E-mail address: luca.rosi@unifi.it (L. Rosi).

has been used to convert different polymeric materials such as tires (Undri et al., 2013a), polyolefin (Undri et al., 2014b), polyesters and biomasses (Bartoli et al., 2016a, 2016b), into fuels and liquid fractions with some efficiencies, and some studies have already been devoted to the MAP of WEEE (Andersson et al., 2012). Andersson and co-workers (Andersson et al., 2012) were focused on the influence of some reaction parameters on oil, gas and a solid residue from the treatment MAP of WEEE, and on the mass reduction during the process but no analysis of the fractions were provided.

In this study MAP of WEEE was investigated as a function of two different absorbers and experimental set-ups as possible source of liquid fuels and chemicals. WEEE was in essence processed in a multimode microwave batch reactor. Different set-ups and MW absorbers were tested to enhance the quantity and quality of the liquid fraction, and to reduce the solid residue. Liquid fractions were analyzed through a quantitative GC–MS method, ^1H NMR, and FT-IR. Furthermore, the presence and nature of the resulting halogenated compounds was checked in the liquid fractions after pyrolysis.

2. Materials and methods

Samples of WEEE were recovered from a large selection of plastic waste computer bodies, monitor cases, and keyboards, stored temporarily in our Chemistry Department on their way to being sent to recycling plants. Some of these bodies and monitor cases were subsequently disassembled and reduced into pieces. A representative 5 kg sample of various different plastic components were ground into smaller ‘granules’ of about 1×1 cm and then mixed together to obtain as homogeneous and representative samples as possible (Fig. 1).

MAP experiments in general do not strictly require a powdered sample due to the heating process, which is volumetric. However, the only limitation of this approach is that the thickness of the sample should be more or less comparable to the MW penetrating power in order to avoid the dissipation of MW power, and to prevent the conductive heating transfer process, from the wall of the reactor to the center of the sample, taking place (Farag et al., 2012).

The carbon powder employed as a MW absorber was the solid obtained from the MAP of tires, minus the metal wire component. (C: 89.01%, H: 0.83%, N: 0.48%, S: 2.0%). A detailed characterization of this carbon powder was previously published in 2013 by Undri et al. (2013a, 2014a).

Iron (purity 99.9%) was also employed as a MW absorber, and dimethylsulfoxide- d_6 (DMSO- d_6) (isotopic purity 99.8%) both of which were supplied by Sigma Aldrich and used without any further purification.

Analytical standards for the GC–MS and acetonitrile used in the study (99.99%, GC grade) were purchased from Sigma Aldrich and were used as received.



Fig. 1. WEEE samples from waste monitors cases, keyboards, and computer bodies.

Molecular sieves (4 Å) supplied by Carlo Erba were activated by heating under vacuum (453 K for 30 min) before their use.

Kinematic viscosity was detected according to the ASTM method D 2854-00, using an Ostwald viscometer thermostated at 298.14 K, with a Julabo model ME-18 V. Cyclohexane, chlorobenzene and 1,4-dimethylbenzene were used as standards (Haynes, 2011).

Density was determined with a pycnometer at 298.14 K. Fourier transform infrared spectroscopy (FT-IR) analyses were performed with a Shimadzu model IRAffinity-1, equipped with a Golden Gate single reflection diamond ATR (Attenuated Total Reflectance) accessory supplied by Specac for the analysis of liquids and solids in reflectance mode, and a sapphire cell (10 cm) was used for gas analysis.

^1H NMR spectra were recorded with an NMR Varian Mercury 400, using dimethylsulfoxide- d_6 (DMSO- d_6) as a solvent. Residual hydrogens of the solvent were employed as internal standards, and spectra were referenced to tetramethylsilane (TMS).

Gas chromatographic analyses were performed using a Shimadzu GC–MS QP5050A equipped with a capillary column PetrocolTM DH 24160-U, (100 m length, 0.25 mm diameter, 0.5 μm stationary phase), using a 1:30 split ratio and a quadrupole mass (MS) detector, with a 70 eV electron impact ions generator, operating in the mass range 40–450 m/z . The oven operated at 298 K for 15 min, then was heated at 2.5 K/min up to 523 K, and was then kept at this temperature for a further 15 min.

The total ion chromatography (TIC) was obtained with a signal/noise ratio of five, and the composition was reported as percent peak areas, reproducibility 0.1%. Compounds were tentatively identified using the NIST mass spectral library. Relative response factors were evaluated according to the equation recently reported for GC-FID (Undri et al., 2015) and extended to GC–MS (Bartoli et al., 2016b).

ICP-MS analyses were performed by the Microanalysis Laboratory of the University of Florence on a representative sample of WEEE after acid digestion.

The bromine and chlorine contents of the liquid fractions from pyrolysis were determined by Idro-Consult Laboratori Riuniti s.r.l. in Florence. The samples were prepared according to the EPA method 5050, using the Gallenkamp autobomb bomb calorimeter. The bomb combustate solution was analyzed by ion chromatography according to the EPA method 9056 (coverage factor $k = 2$ with a level of confidence of 95%).

2.1. Pyrolysis details

Pyrolysis were carried out in a MW multimode reactor working at 2.45 GHz, equipped with four external magnetrons, each absorbing an electric power of 2 KW for a total of 8 KW, and as a whole capable of delivering a microwave power of up to 6 KW inside the oven. The reactor was designed and supplied by Bi.Elle s.r.l. (Italy), and equipped with a wide-angle measuring infrared thermometer, which provided information on the overall temperature inside the oven but not the temperature on the sample surface. In fact, temperature measurement during MW heating is quite challenging (Menéndez et al., 2010), because microwaves interact with common probes such as thermocouples or with chemical thermometers. An IR thermometer can be used to evaluate the temperature of the vapor phase during MAP, whereas an optic fiber probe can be employed to measure the temperature of the solid, point by point. In order to monitor the MAP process globally, the temperature was measured with an infrared thermometer and calibration of this thermometer was run with an optic fiber, according to the method reported by Undri et al. (2013b). The calibration curve is provided in the supplementary materials.

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