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Pyrolysis and catalytic pyrolysis as a recycling method of waste CDs originating from polycarbonate and HIPS

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ABSTRACT

Pyrolysis appears to be a promising recycling process since it could convert the disposed polymers to hydrocarbon based fuels or various useful chemicals. In the current study, two model polymers found in WEEEs, namely polycarbonate (PC) and high impact polystyrene (HIPS) and their counterparts found in waste commercial Compact Discs (CDs) were pyrolysed in a bench scale reactor. Both, thermal pyrolysis and pyrolysis in the presence of two catalytic materials (basic MgO and acidic ZSM-5 zeolite) was performed for all four types of polymers. Results have shown significant recovery of the monomers and valuable chemicals (phenols in the case of PC and aromatic hydrocarbons in the case of HIPS), while catalysts seem to decrease the selectivity towards the monomers and enhance the selectivity towards other desirable compounds.

1. Introduction

Waste electrical and electronic equipment (WEEE) appears to be one of the faster growing waste streams, mainly due to their variety of applications and their relatively short life. The lack of efficient recycling technologies of WEEE is posing an increasing problem of managing this specific waste stream. In the EU, 9.5 million tonnes of WEEE were disposed in 2008, and this is expected to rise to 12.3 million tonnes by 2020 (Alston et al., 2011; Kantarelis et al., 2011). EU, in an attempt to deal with the problem and at the same time to face the potential oil and fossil fuels reserves depletion, has introduced the 2002/96/EC directive (Kantarelis et al., 2011), which demands 70–80% of the WEEE generated to be recovered in terms of energy and materials (Kantarelis et al., 2011). The directive clearly aims to minimize the percentage of solid wastes that will be landfilled or combusted and states that by 2020, all solid waste streams (including plastics) should be diverted towards thermal and/or mechanical treatment and energy recovery.

Recycling WEEEs is rather difficult because such wastes are composed of many and very different materials: metals, glasses, rubbers, plastics. The plastics usually have metals or other materials embedded in them and for this reason the separation and mechanical recycling of the individual components of many plastic WEEEs streams faces significant technical and/or economical challenges (De Marco et al., 2008; Tarantili et al., 2010; Rousis et al., 2008). A typical WEEE contains 20–30% plastics (Kantarelis et al., 2011). The composition can vary, but an example of the breakdown from actual collected WEEE is: acrylonitrile–butadiene–styrene (ABS) 30%, high impact polystyrene (HIPS) 25%, polycarbonate (PC) 10%, PC/ABS 9%, polypropylene (PP) 8%, poly(phenylene ether) (PPE)/HIPS 7%, poly(vinyl chloride) (PVC) 3%, polystyrene (PS) 3%, polyamide (PA) 3%, poly(butylene terephthalate) (PBT) 2% (Dalrymple et al., 2007).

The pyrolysis of several types of electrical and electronic wastes has been studied in the recent literature (Triantou and Tarantili, 2012; Achilias, 2009). Kowalska et al. (Kowalska et al., 2006) have reported thermogravimetric studies of two types of electronic wastes: a mixture of three types of printed circuit boards and a mixture of electronic junctions with metal wires. Despite the brominated and chlorinated flame retardants present in the two samples (which remain one of the main challenges in the pyrolysis process (Peeters et al., 2014)), preliminary HPLC analysis of the liquid fraction produced indicated that it consists of a series of two to four unsaturated ring hydrocarbons and it could potentially be used as a fuel. Another group (De Marco et al., 2008) has reported the pyrolysis in an autoclave of four types of real WEEEs streams: wires of polyethylene (PE), table phones, mobile phones and printed circuit boards (PCB). They found that pyrolysis liquids vary significantly depending on the WEEE pyrolysed. Other researchers (Molto et al., 2011) have reported the pyrolysis and

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combustion of different parts of a mobile phone (printed circuit board, mobile case and a mixture of both materials) at 850 °C in a horizontal laboratory furnace. They found the liquid fraction to consist of mainly phenols and hydrocarbons. Another group (Acomb et al., 2013) has studied the pyrolysis–gasification of a plastic waste collected from a commercial WEEE recycling plant, mainly consisting from waste computer monitors and television sets, by using a two-stage reaction system in order to produce hydrogen. Hall et al. pyrolysed fire retarded high impact polystyrene using a fluidised bed reactor (Hall and Williams, 2006). Although the emphasis was on the bromine distribution on the pyrolysis products, the yields and compositions of the main fractions were also reported. In a later study of the same research group, three different plastic fractions from a commercial waste electrical and electronic equipment (WEEE) processing plant were collected and investigated through batch pyrolysis. The first plastic was from equipment containing cathode ray tubes (CRTs), the second was from refrigeration equipment, and the third was from mixed WEEE. Analysis of the pyrolysis products was provided and the pyrolysis oils were found to contain valuable chemical products while the pyrolysis gases were mainly halogen free, making them suitable as a fuel (Hall and Williams, 2007). Molto et al. (Molto et al., 2009) studied the pyrolysis and combustion of mobile phones and printed circuit boards at 500 °C in a horizontal laboratory furnace and the analysis of the gas and semivolatile fractions presented. More than 100 semi- volatile compounds were identified: mainly hydrocarbons, straight chain and of aromatic origin. A similar study (Pinto et al., 1999) investigated the influence of several catalysts on product distribution from plastic waste pyrolysis. The waste under study had the typical composition of Portuguese municipal solid wastes (68% PE, 16% PP and 16% PS) while the catalysts selected were zeolites and a series of metallic catalysts. Similar results were obtained from the catalytic and non-catalytic runs, in terms of total conversion, product yields and composition. Finally, Guan et al. (Guan et al., 2010) studied the recycling of waste PC-main board by pyrolysis. No significant effect of temperature on the products was observed for values over 400 °C. In the volatile products several types of phenols were identified together with some lower alkanes.

Polycarbonate, poly(bisphenol A carbonate) (PC) appears to be one of the most significant fractions of WEEEs mainly due to a series of desirable properties such as optical clarity, high mechanical and thermal resistance etc, and for this reason it finds a variety of applications in digital storage media (e.g. CD, DVD), in electrical and electronic equipment, in the automobile industry etc. Because of its resistance at high temperatures it is also used in bottles for storage of water and liquids. PC, due to its increasing number of uses, high melting point and low biodegradation has started accumulating at high quantities at the points of disposal, which makes the need for a meaningful recycling method more immediate (Katajisto et al., 2003; Antonakou and Achilias, 2013). High Impact Polystyrene (HIPS) is a composite material that consists of a polystyrene phase and a dispersed polybutadiene (PB) phase (Grause et al., 2010). It is produced by the free-radical polymerisation of styrene in the presence of polybutadiene (PB) to improve the impact strength and toughness of glassy polystyrene (PS). The properties of the produced composite material mainly depend on the percentage of the butadiene in the initial polymer, which varies between 3 and 10 mol%. It is widely used in electrical and electronic equipment, in construction and packaging materials and in storage bottles, appliance parts, housewares, and interior parts in household electronics (Beigbeder et al., 2013). In one of the few studies on the HIPS catalytic thermal decomposition, it is reported that there was a marked increase in yield of gas with the introduction of nickel catalysts (Acomb et al., 2013). Marcilla et al. (Marcilla et al., 2007) also reported the thermal decomposition of mixtures of Al-MCM-41 and different polymers and copolymers involving styrene by means of thermogravimetric data and they concluded that mesoporous catalysts can be promising for the decomposition of the HIPS copolymer. The same authors (Marcilla et al., 2006, 2009) have also studied the influence of several acid catalysts, including Al-MCM-41, on the pyrolysis of different polymers.

The main problems related to the traditional treatment methods of WEEEs are complexity of the waste and presence of additives of various chemical compositions. They also usually end to a polymer fraction with deteriorated properties and limited end uses. Thermal cracking (pyrolysis) of WEEE streams is receiving increasing attention, due to the potential recovery of either monomer(s) or secondary valuable materials, leading to a more sustainable waste management. Disadvantages of pyrolysis are related to the variable product composition and the low selectivity concerning the respective monomers and/or products of commercial value. The use of suitable catalysts in the pyrolysis process can offer the possibility to control the selectivity towards the desired products.

Following our recent work on the pyrolysis of several waste polymers (Achilias et al., 2007a,b, 2008), in the current study, two model polymers found in WEEEs, namely PC and HIPS and their waste counterparts found in commercial Compact Discs (CDs) were pyrolysed in a bench scale reactor. The particular polymers were selected due to their wide variety of uses and their high abundance in the waste stream. The research in the area of catalytic pyrolysis of both polymers is very limited but of significant interest, since the understanding of the thermal degradation mechanism and the correlation between the catalyst's functional characteristics and the production of desirable products will open the area for the treatment of more complicated waste fractions. For these reasons both thermal and catalytic pyrolysis in the presence of two different catalytic materials, one with basic and one with acidic properties was studied in all four types of materials. According to our knowledge, thermal and catalytic pyrolysis of waste CDs containing either PC or HIPS is presenting for the first time in literature.

2. Materials and methods

2.1. Materials and catalysts

Commercial poly(bisphenol A carbonate) and HIPS (Aldrich) were used for the experiments (for PC: Tg (DSC, onset) 149.0 °C and melt index 7.00 g/10 min and for HIPS: Poly(styrene-*co*-butadiene) 4 wt.%, melt index 6 g/10 min (200 °C/5 kg)). A mill was used to treat the PC-pellets, the HIPS material and the two commercial CDs and particles less than 2 mm were used for the pyrolysis experiments. No heat was produced during the milling process.

Carbon and hydrogen content was determined using a LECO-800 elemental analyser, while S content was determined using a LECO CHNS-932 elemental analyser. Ash content was determined by oxidation of a small sample (2 g) in air at 600 C for 16 h. Results showed for the PC: 91.58% C, 7.08% H, 0.047% S, 0% Ash for HIPS: 75.41% C, 3.40% H, 0.051% S, 0.06% Ash and for the two commercial products 92.39% C, 6.65% H, 0.038% S, 0.13% Ash (CD PC) and 75.06% C, 4.09% H, 0.054% S, 0% Ash (CD PS).

The two catalysts were selected based on their distinctly different textural and surface properties. More specifically, the catalysts tested were an acidic commercial equilibrium ZSM-5 zeolite diluted with silica-alumina (containing ~30 wt.% crystalline zeolite) and a basic magnesium oxide (MgO), which was produced industrially via calcination of natural magnesite at temperatures between 700 and 1100 °C (Grecian Magnesite S.A.). The ZSM-5