Value-added products from thermochemical treatments of contaminated e-waste plastics – A review

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Abstract

The rise of electronic waste (e-waste) generation around the globe has become a major concern in recent times and their recycling is mostly focussed on the recovery of valuable metals such as gold (Au), silver (Ag) and copper (Cu) etc. However, a significant weight fraction of e-waste consists of plastics (25 – 30%) that are either discarded or incinerated. There is a growing need for recycling of these e-waste plastics majority of them are made from high-quality polymers (composites) such as acrylonitrile butadiene styrene (ABS), high impact polystyrene (HIPS); polycarbonate (PC); polyamide (PA); polypropylene (PP); and epoxies. However, these plastics are contaminated with hazardous materials such as brominated flame retardants (BFRs) and heavy metals (such as lead and mercury). Under any thermal stress, the bromine element (Br) present in the e-waste plastics produces environmentally hazardous pollutants, such as hydrogen bromide or polybrominated diphenyl ethers/furans (PBDE/Fs). The discarded plastics can lead to the leaching of toxins into the environment. Therefore, removal of the toxic chemicals from the e-waste plastics is pre-requisite before considering any thermal process. This review article gives a detailed account of e-waste plastics recycling and recovery using thermochemical processes, such as extraction and pyrolysis. A basic framework of the existing processes has been established by reviewing the most interesting findings in recent times and the prospects that they open in the field recycling of e-waste plastics.

Key words: e-waste plastic, brominated flame retardants, pyrolysis, extraction and solvothermal treatment

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1 Introduction

Plastics are considered as synthetic and semisynthetic materials that are produced from large organic molecules, mixed with different additives, like flame retardants, stabilizers, plasticizers, colours and pigments. Additives improve the physical and chemical properties of the plastic end products. Extensive use of plastics in the manufacturing industry could be attributed to their superior physical and chemical properties, such as high tensile strength, durability, lightweight, flexibility, heat and chemical resistance etc. A recent report estimated that till date the production of virgin plastics amounted to 8300 million metric tons (MMT) and out of which 6300 MMT becomes waste (Geyer et al., 2017).

Both plastic production and plastic generation have been increasing due to wide spread application of plastics and its low life span such packaging plastics. Sector wise demand of plastics in Europe is shown in Fig. 1. It was estimated in 2015, that around 55 percent of global plastic waste was discarded, 25 percent was incinerated and only 20 percent was recycled (Fig. 2). Out of the total plastic waste produced between 1950 and 2015, only 9 percent was recycled (Geyer et al., 2017). Most of the discarded plastics are non-biodegradable and take hundreds of years to degrade naturally. The majority of plastics waste can be traced back to its original source such as packaging, building material and automobile waste. However, only 6-7% of plastic waste comes from the e-wastes. The presence of e-waste plastics in the waste stream makes it problematic since they may contain contaminated toxins, such as brominated flame retardants (BFRs) and heavy metals (Wang, 2018; Forum, 2019).

Fig. 1: Distribution of plastics demand by segments in Europe 2017 (Europe, 2018; Forum, 2019)

Fig. 2: Global disposal of plastic waste from 1980 to 2015 (Geyer et al., 2017)

Due to the rapid technological advancement in the field of household appliance, mobile communication and computers, the global generation of e-waste keeps on increasing and becomes a burden to the waste management systems. The quantity of e-waste generation varies with countries based on the economy and lifestyle of the country (Wang et al., 2016). The per capita generation of e-waste is highest in Norway which was estimated to be 28.5 kg/person (2016). The countries, like China, India, Philippines and African nations, hugely processed the electronic wastes generated in developed countries. Electronic waste contains a variety of substances including precious gold, silver, copper along with toxic substances, such as lead (Pb), polybrominated diphenyl ethers (PBDEs), polychlorinated and polybrominated dioxins and furans (Tsydenova and Bengtsson, 2011). The emission of these toxic substances during recycling may cause serious health hazards to the lives of workers and other livelihoods present in the surrounding (Grant et al., 2013).

The generation of electronic and electrical waste increases continuously in recent years due to the fast growth of the use of home appliances, consumer electronics gadgets, like cell phones, tablets, video game consoles, music player, digital camera, laptops, set-top boxes, etc. E-wastes definition usually comprises of discarded electronic, electrical pieces of equipment, light bulbs, and batteries. The waste generator can be the manufacturer (due to defect or obsolescence) or the consumer when the equipment reached its end of their service life (Robinson, 2009). Fig. 3 shows the trends of generation of electronic and electrical waste in recent years. An increase of 47% of e-waste generation has been observed from the year 2010 to 2018 (Baldé et al., 2017). The United Nation's recent assessment reported that about 44.7 MMT of e-waste was generated globally in the year 2016 and only 20% (8.9 million metric tonnes) was recycled. The amount of e-waste generation was projected to reach 52.2 MMT by 2021 (Forum, 2019). Of these discarded e-waste, 80% go either in landfills or incineration. An extra amount of complexity in the treatment of these e-wastes arises from their toxic content and potential hazardous

emissions which makes it paramount to search for sustainable solutions for their recycling. Most of modern electrical and electronic pieces of equipment use engineering plastics in the manufacturing of their outer body. Inner components also use plastics/epoxy, such as insulating foams, printed circuit boards (PCBs), component's packaging, cables insulators, wirings, connector, switches etc. To ensure both safety and longevity of electronic devices, additives like BFRs, bromine bearing hydrocarbons, are added to the plastics to improve their fire resistance (Altarawneh et al., 2019). But if BFRs are efficient flame retardant they may also produce toxins during waste treatment. Apart from BFRs, e-waste plastics may contain trace amounts of metals and heavy metals, such as Pb, Cu, Ni, Al, Zn, Ba, Ag, Au, Sn, etc. These are very profusely present within plastics from PCBs, their soldered components or in plastics in their near vicinity (Nnorom and Osibanjo, 2009). Heavy metals are also sometime added as additive (for example as pigment) to the plastics (Cherif Lahimer et al., 2017). Heavy metals contamination also limits the recovery of the e-waste plastics for the recycle and reuse.

Fig. 3: Trend of worldwide e-waste generation in recent years (Wang, 2018)

The plastic used in Waste Electrical & Electronic Equipment (WEEE) are fabricated from polymers that are produced from fossil fuels (petroleum/coke) and are rich in carbon and hydrogen. Depolymerisation or control degradation can revert back plastics into useful feed stock or in last resort into fuel for transport industry. The latter being the least favourable from an entropy point of view, it allows to recover the contained energy but waste all the chemical treatment that has been put into its manufacturing process. Common plastics used in WEEEs with respective calorific values are listed in Table 1. The utilization of plastics as energy source is significant as a vast quantity of plastics goes into the waste stream every day.

Table 1: Heating values of plastics found in solid waste stream (Walters et al.; Othman et al., 2009)

Plastics	Calorific value (MJ/kg)
PE (LD/HD)	47.7
PP	45.3
PET	24.1
PS	41.4
PVC	14.1
PC	26.7
PMMA	24.1
PA	26.5
ABS	35.2
HIPS	37.8

Indeed, the global energy consumption increases constantly and it was estimated to be around 20,000 million tons of oil equivalent by the year 2050 (Coyne, 2018). In the year 2018, the rate of growth of energy consumption to the previous year was 2.9% which was the highest rate of growth compared to the previous seven years and double the average of last 10 years along with 2% growth of carbon emission due to energy production (Global, 2019). Due to carbon emission and the shortage of fossil fuel resources, the world is moving towards renewable and sustainable energy sources, such as solar, wind, tidal, hydropower, geothermal, bio-energy, etc.

About 80% of the current global energy demand is currently provided by fossil fuel and 90% of world transportation runs on petroleum oil (Jefferson, 2016). Around 14% (total) of global energy demand is supplied by renewal sources (Fig. 4). The fraction of energy supplied by renewal energy sources increases continuously over the years to minimize the energy dependency on fossil fuel.

Fig. 4: Primary global energy consumption by sources (Agency, 2014)

In this critical review of thermochemical conversion of WEEE plastic wastes, their use as an alternative source for useful mono- or oligomers or for fuel, such as gasoline and diesel, is discussed in details. The effect of WEEE plastics' contamination in their production is investigated on the basis of the most relevant previous studies. It should be noted that plastics used in electric and electronics devices are not similar to those of commodity plastics or single-use plastics present in the Municipal Solid Waste (MSW). The presence of toxins and

contaminants like BFRs and heavy metals in e-waste plastics makes their thermochemical conversion process more complex and challenging.

Previous review articles mostly focused on the impact of toxins present in e-wastes on the environment as well as on the recovery of metals from e-waste. Therefore, in addition to the impact of e-waste plastics on the environment, we will compare here the different recycling processes enabling their transformation into valuable products, discuss the significance of recycling e-waste plastics, the effect of the toxins present in the plastics and the complexity involved in the removal of toxins to recover original polymers. Hence, this review article addresses the gaps in the current status quo of the industrial recycling of e-waste plastics and the latest developments in this field. This critical study will furthermore help future researchers and engineers to choose how to process and recycle their mixed stream of plastic wastes containing e-waste plastics including their possible conversion into energy.

2 Plastic waste and its environmental impact

The global generation of plastic waste keeps on increasing as the production of new plastics keeps on increasing. In the year 2015, an estimated amount of 381 MMT of plastics (polymer resin and fibre) was produced globally (Geyer et al., 2017). Around 44% of global plastic production consumed in packaging application such as single-use containers, bottles, bags etc. (Geyer et al., 2017). The life span of plastics products varies, from weeks for packaging plastics to several years for electronics, electrical equipments and building appliances (Buekens, 2006; Lazarevic et al., 2010).

Most plastics are non-biodegradable and the growing plastic waste generation leads to huge garbage accumulation in landfills as well as various natural surroundings like rivers and oceans. In 2010 an estimated amount of 4.8 to 12.7 MMT of plastic waste debris entered in to the oceans from 192 coastal countries(Jambeck et al., 2015). This situation is worsening due to the

global increase of plastic waste generation, which raise the concern regarding the adverse consequences to marine life, ecosystem sustainability and potentially to human health (Lebreton et al., 2017). This threat is even more significant than initially estimated due to the mechanical degradation of plastics into microparticles (Hurley et al., 2018). Solid waste plastics are also responsible for many socio-environmental complications in many developed as well as developing countries, such as soil contamination, ground water pollution, floods, deadly diseases, animal death due to direct consumption or strangling and surface water pollution (Rigamonti et al., 2014).

WEEEs are generally treated separately from MSW as they contain many toxic substances, such as mercury (Hg), lead (Pb), selenium (Se), cadmium (Cd), hexavalent chromium (Cr(VI)), polybrominated diphenyl (PBD) and BFR. Sorted out e-wastes undergo separate treatments for dismantling, separation of metallic and non-metallic fractions. Non-metallic fractions, mainly containing plastics, undergo recovery and recycling processes. E-waste plastics have diverse composition but are mostly made up of ABS, HIPS, HDPE, PA, PP, PC, etc. Flame retardants are essential to electronic and electrical pieces of equipment due to meet requirements from fire safety codes. Most common form of flame retardants used in the plastics of electronic products are BFRs. Most abundantly used commercial flame retardants were polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), hexabromocyclodecane (HBCD), Decabromodiphenyl ether (deca-BDE) etc., however, due to environmental safety, use of these BFRs was restricted and they have been replaced by less harmful ones based on nitrogen, phosphorous and other inorganics (Singh and Jain, 2009). Polybrominated diphenyl ethers (PBDEs) were some of the most commonly used BFRs over the last few decades. More specifically, BFRs such as HBCDs and TBBPA are still extensively used despite being considered as persistent organic pollutants (POP) and referred as novel BFRs (Covaci et al., 2011). During any thermal stress, the BFRs in the e-waste plastics can produce brominated

aromatic compounds which are precursors to the polybrominated dibenzo-p-dioxins (PBDD) and polybrominated dibenzo furans (PBDF) (Weber and Kuch, 2003; Zhang et al., 2016). Trace amount of PBDD and PBDF can cause severe health hazards. Toxicity profiles of different isomers of PBDD/Fs depend on the number of Bromine atoms and what positions they attached to. Basic PBDE and PBDF structures are given in Fig. 5.

Fig. 5 : Molecular structure of PBDD and PBDF

Metal hydroxides, such as Gibbsite (aluminium trihydroxide, ATH), magnesium di-hydroxide (MDH), and Boehmite (Aluminium-oxide-hydroxide, AOH), are among the most common inorganic ones (Qian et al., 2014). Flame retardants are also used based on their compatibility with polymer resins such as melamine cyanurate and melamine phosphate which are compatible with polyamides and polypropylene, respectively (Liu et al., 2006). Although most European countries restricted the use of halogenated flame retardants, a worldwide replacement

with non-halogenated FR is not yet achieved and BFRs are still the primary source of flame retardants in various regions of the world. Due to the huge volume accumulation of e-waste most European countries and USA export the e-waste to Asia or Africa for recycling, where e-waste recycling workers often put themselves into high health risk due to the lack of sustainable technology and safe practice know-how (Zhu et al., 2008; Muenhor et al., 2010; He et al., 2012; Malliari and Kalantzi, 2017; Li et al., 2018). Open burning of e-waste to recover metals is a common practice in African countries (Cao et al., 2020) resulted the emission of harmful dioxins, furans, polycyclic aromatic hydrocarbon (PAHs), polyhalogenated aromatic hydrocarbon (PHAHs) and hydrogen halides. E-waste can further be a source of soil and ground water contamination due to lixiviation and leaching as well as air pollution due to burning. Tang *et al.* (Tang et al., 2010) investigated the soil sample near Wenling, an e-waste recycling city of Taizhou province in China and reported concentrations ranging from 371.8 to 1231.2 µg/kg of polycyclic aromatic hydrocarbons (PAHs) and 52 – 5789.5 µg/kg of polychlorinated biphenyls, which are significantly higher than the permissible limit set by the governmental bodies and legislatures. Tue et al. (Tue et al., 2017) reported high concentration of Cl-PAH and Br-PAH in the range 160 – 220 ng/g and 19 – 40 ng/g respectively in the soil samples from the soil samples collected from the open e-waste burning area of Agbogbloshie's e-waste recycling site in Ghana.. Reports of soil contamination with heavy metals at the e-waste recycling sites have been reported (Luo et al., 2011; Wu et al., 2015; Damrongsiri et al., 2016; Zhang et al., 2019).

Surface water contamination due to non-regularised and un-licensed e-waste recycling facilities is also a major concern. Leaching and lixiviation of toxic chemicals (PAHs, heavy metals) from e-waste landfilling and waste acidic waters from recycling sites led to significant surface and ground water contamination (Wu et al., 2015). Air borne pollutants are also generated by open burnings, incinerations and combustions. Heating or burning of e-waste that

contain halogenated compounds, such as BFRs, may lead to the emission of environmentally hazardous substances, like polybrominated, diphenyl ethers (PBDEs), polychlorinated dibenzodioxins (PCDDs), polybromochlorodioxins and polychlorobenzofurans (PBCDD/Fs) (Vehlow et al., 2000; Vehlow et al., 2003; Wang et al., 2010). Such toxins from e-wastes can cause chronic and acute health conditions to human (Kiddee et al., 2013). Traces of toxic substances like brominated or chlorinated fire retardants and heavy metals were found in the human (recycle workers) blood, urine, and milk and hair samples (Grant et al., 2013). These pollutants and toxic chemicals can cause serious health risk to human as well as animals. The recycling processes of plastic wastes from different sources require sincere attention in removal of toxics and contaminants before converting the waste into useful resources.

3 Plastic waste management and disposal techniques

Physical properties of plastics vary with polymer types, class of additives and manufacturing techniques employed. Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS) etc. are widely used for packaging and single use plastic products. On the other hand, polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), Nylon 6, Nylon 6,6, polyamide (PA), polybutylene terephthalate (PBT), polycarbonate (PC), polyetheretherketone (PEEK), polyetherketone (PEK), polysulphone (PSU), polytetrafluoroethylene (PTFE/Teflon), etc, are known as engineering plastics used as building materials and in automobile parts. The service life of most engineering plastics are higher than that of single use or packaging ones. ABS, HIPS, PC, PP, PA, etc., are also found in electronic or electrical plastic wastes. Due to the turnover rate of lifestyle electronic goods like mobile phones, computers, tablets, etc., there is a significant increase in e-waste plastic generation in recent years.

Around 10 – 12 % of MSW of the world consists of plastic waste (Diaz et al., 2020). The recycling of solid waste like plastics depends of efficient collection and segregation which is influenced by the economic status of the country(Joshi and Ahmed, 2016). The techniques of plastics recycling can be classified into primary secondary and tertiary recycling, which we will review in subsequent sections.

3.1 Primary and secondary (mechanical) recycling

Primary and secondary recycling deal with the mechanical means of recycling of plastic wastes, such as grinding, washing, separating, drying, re-granulating, extrusion and compounding (Al-Salem et al., 2009). Mechanical processes are utilized to produce recyclates from plastic waste. Primary recycling is the process of producing the same or similar products, whereas secondary recycling produces products with substandard quality, such as dustbins, furniture, plastic vases, etc. Primary recycling needs pure and homogenous plastic wastes (in-plant scrap), while secondary recycling uses post-consumer plastic. High production costs are the concern in the implementation of primary and secondary recycling. Mechanical processing is at the basis of any recycling process, especially for electronic wastes that comprise of a complex mixture of many materials (valuable and hazardous, or not) including metals (ferrous or non-ferrous) and non-metals like plastics, glass, ceramics with various sizes and shapes. Hence, it is important to utilize cost effective sustainable mechanical processes to separate the different components of e-wastes as best as possible. WEEEs undergo dismantling and sorting steps at the beginning of the recycling process. Complex components, such as PCBs, after being extracted from their original equipment usually undergo grinding and the separation of metallic (ferrous and non-ferrous) and non-metallic fractions. In Fig. 6, a process flowchart is shown that is rigorously followed in many waste PCB recycling industries. Separation processes include screening (Wilson et al., 1994), shape separation (Furuuchi and Gotoh, 1992; Furuuchi et al., 1993), magnetic separation (Veit et al., 2005), electric conductive base separation (Meier-Staude and

290 Koehnlechner, 2000), density base separation (Schubert, 1991), etc. Wäger *et al.* (Wäger et al.,
291 2011) confirmed that mechanically recycled electronic and electrical waste plastics have five
292 times lower environment impact than virgin plastics in the manufacturing of plastic products.
293 However, past studies suggested that 25 – 30 wt% of the collected e-waste plastics have BFR
294 as additive and it is difficult to recycle them mechanically (Brennan et al., 2002; Stenvall et al.,
295 2013; Baldé et al., 2017). The e-waste plastics with BFR are not suitable for primary and
296 secondary recycling. Pre-treatment processes like solvent extraction, chemical leaching and
297 other chemical treatment (with acid/alkalis) can remove the toxic chemicals from e-waste
298 plastics and convert them into mechanically reusable plastics. BFRs that are not chemically
299 bound to the polymer chain can be removed from the plastic matrix by the solvent extraction
300 processes. Efficient and sustainable solvent extraction process assisted by microwave, ultra-
301 sonication or supercritical CO₂ extraction processes can be developed for BFR extraction from
302 e-waste plastics. On the other hand, thermal degradation can remove chemically bonded Br in
303 the plastics.

Fig. 6: schematic representation of the physical separation process of MF and NMF of PCB

3.2 Tertiary (chemical and thermal) recycling

Tertiary or chemical recovery of plastic waste is a promising aspect in the recovery of valuable chemicals and fuels (Achilias et al., 2007; Yildirim et al., 2014; Zhou et al., 2014). Its principle lies behind the alteration of the polymer's chemical structure by depolymerisation. Major advantages of chemical recycling over mechanical recycling is that it allows processing of heterogeneous and contaminated plastics with limited pre-treatment opportunities. Chemical recycling can convert plastics like polyethylene terephthalate (PET) and nylon into their monomer units (feedstock recycling) (Veregue et al., 2018; Choi and Choi, 2019; Jehanno et al., 2019; Vesnin et al., 2020), while the polyolefin type of plastics produce a mixture that can be precursor to liquid fuel (Coates and Getzler). Processes, such as dissolution, hydrogenation, gasification, pyrolysis, and catalytic cracking, come under chemical recycling of plastics.

Achilias et al. (Achilias et al., 2009) carried out chemical recycling of PC, PABS, and PS from WEEE by means of dissolution/re-precipitation and pyrolysis. More than 90% recovery of polymers was reported by the dissolution process where pyrolysis converted the model PC sample into 63% liquid product. Pyrolysis or thermolysis of plastics is a process of thermal decomposition of plastics under inert or oxygen-starved conditions. These processes are able to convert high molecular weight plastics into low molecular weight hydrocarbons and chemicals (Kaminsky et al., 1995; Adrados et al., 2012). The process of plastic waste into oil (fuel) through pyrolysis has been developed and practiced. Processes like ThermofuelTM (Ozmotech Pty Ltd), Smuda process, Royco process (EZ-oil generator), Reentech process, Hitachi process, Chiyoda process (Chiyoda corp. Japan), Blowdec process, Conrad processes are some of the processes available for the commercial utilization (Scheirs and Kaminsky, 2006). These processes are mostly handled polyolefin types of plastics available in MSW. By reducing the process cost and up-scaling the present capacity of the technologies may lead to a wide-scale industrial application of plastic pyrolysis. The heat recovery processes like combustion, incineration and gasification are also considered as tertiary recycling processes, however, these techniques are sometimes separately identified as quaternary recycling processes (Al-Salem et al., 2009).

Regarding PCBs' epoxy resin, they are usually used as fuel in pyrometallurgy plants that recover precious metals. Since they are made of cross-linked polymers with the aim of high chemical, time and temperature stabilities their up-cycling is a difficult problem. In the field of depolymerisation, it is worth noting that in 2019, Chen et al. (2019) reported an original process enabling the dissolution of anhydride epoxy thanks to a transesterification reaction occurring between the -OH group in ethylene glycol, used as solvent, and the ester bond within the epoxy network. To be efficient, the reaction uses the transesterification catalyst (1,5,7-Triazabicyclo[4.4.0]dec-5-ene). Also, a diffusion solvent (N-Methyl-2-Pyrrolidinone) allows

for the swelling of the resin, allowing for both the ethylene glycol and catalyst to penetrate within the cross-linked epoxy network. Reaction time varied from 6h to 40 min when using reaction temperatures of 100 °C and 180 °C, respectively.

4 Removal of toxic molecules from e-waste plastics

E-waste plastics are notoriously known to be tainted with toxic compounds such as BFRs and heavy metals (Tange and Drohmann, 2005; Das et al., 2009; Li et al., 2009; Peng et al., 2010; Damrongsiri et al., 2016; Debnath et al., 2018). Over the years, the European Union regulated and restricted various substances in plastics particularly in the case of electronics and electrical goods (E.U., 2015). Table 2 lists restricted substances and their permissible limits in such goods. The science of removal of the toxic chemicals from e-wastes has been explored and a number of technologies were investigated that optimize energy and material consumptions. The removal of metal contamination at the molecular level is difficult by mechanical and physical means described in section 3.1 (Kurose et al., 2006; Li et al., 2007). Although hydrometallurgical processes like leaching assisted with cyanide, thiourea, thiosulfate or halide have been developed mainly for to recover precious metals from waste PCBs (Cui and Zhang, 2008; Zhang et al., 2012), they can also be used for the removal of contaminated metal from e-waste plastics. Regarding PCBs, they are an essential part of any electronic equipment and represent between approximately 2-3% of total e-waste generated worldwide (Vats and Singh, 2014). PCBs are also abundant in small electronic devices, such as mobile, tablets and other smart devices. A typical PCB is constructed with a Cu-clad laminate which consists of glass fibre reinforced with epoxy resin, plastics and metals (Hsu et al., 2019). It was approximated that a PCB contains roughly 40% metals, 30% organics and 30% refractory (ca. fibre glass) (Shuey and Taylor, 2005). PCBs are generally treated for the extraction of some of the valuable metals they contain, such as Cu, Al, Ag and Au (Oh et al., 2003). The pre-treatment process follows the common processes stated in section 3.1 (Fig. 6) to separate the metallic fraction

(MF) and the non-metallic fraction (NMF). The MF then undergoes intense chemical treatment to recover valuable chemical components. The non-metallic part of the PCBs is most toxic as it contains traces of solders made from Pb/Sn and BFRs. Although, recent PCBs are lead free solder most old PCBs have 2-5% of Pb in their solder (Ghosh et al., 2015).

Table 2: Restricted substances used in the electronic and electrical goods by EU (E.U., 2015)

Toxic substance	Permissible limit (wt%) [†]
Lead (Pb)	0.1
Mercury (Hg)	0.1
Cadmium (Cd)	0.01
Hexavalent Chromium (Cr ⁶)	0.1
Polybrominated biphenyls (PBB)	0.1
Polybrominated diphenyl ethers (PBDE)	0.1
Bis(2-ethylexyl)phthalate (DEHP)	0.1
Butyl benzyl phthalate (BBP)	0.1
Dibutyl phthalate	0.1
Diisobutyl phthalate (DIBP)	0.1

[†]0.1 wt% = 1000 ppm and 0.01 wt% = 100 ppm

4.1 Removal of BFR from e-waste plastics

The BFRs are relentless and bioaccumulative toxins in nature, and their decomposition pathways during thermal treatment have been previously reported (Ma et al., 2016a). The treatments to recover BFR free plastics or products are discussed in the subsequent sections.

4.2 Solvothermal processes to remove BFRs from e-waste plastic

High extraction efficiencies can be achieved with conventional solvent extraction with organic solvents (Suzuki et al., 2002; Zhang and Zhang, 2012b). Toluene, methanol, 1-propanol, isopropanol, acetonitrile, and ethanol are some of the common organic solvents used (Altwaig et al., 2003; Evangelopoulos et al., 2019). Different extraction processes, such as pressurised

liquid extraction (PLE), ultrasonic assisted extraction (UAE), microwave assisted extraction (MAE) and simple Soxhlet extraction have been proposed and investigated for BFRs extraction (Vilaplana et al., 2008).

Chandrasekaran *et al.* (Chandrasekaran et al., 2018) recovered 89% of pure PC from the mixture of PC/PA (from waste cell phones) by solvent extraction using N-methyl-2-pyrrolidone (NMP). NMP was preferred to dichloromethane (DCM) for selective dissolution of PC and to avoid the use of the chlorinated solvents. The study also emphasize the important of the factors such as solid matrix, initial BFR content, solvent polarity, solid liquid ratio, temperature and pressure affecting the BFR removal efficiency and temperature being the most dominant factor in the extraction process. Vilaplana et al. (Vilaplana et al., 2008) reported the use of mixed solvent systems (isopropanol/hexane and isopropanol/methanol) and achieved a high recovery of BFRs. Complete recovery of TBBPA and HBCD was reported by the process of MEA, using isopropanol/n-hexane as solvents at 130°C for 60 min, however UAE gives recovery rates that are strongly temperature dependant and that increase with temperature (Vilaplana et al., 2008; Romarís-Hortas et al., 2009). Hence, optimal conditions for extraction processes vary for different types of feedstock. carried out extraction of deca-BDE from HIPS matrix using an ionic liquid (IL) prepared with by the mixture of 1-bromobutane, 2-(2-chloroethoxy) ethanol and 3-bromopropionitrile. The IL was able to achieve 92.7% of BDE recovery from the HIPS. ILs can be designed based on the material property and improve the extraction efficiency, however in plastic waste recycling processes, operational costs play a vital role which as yet precluded the industrial use of ILs so far. Zhang and Zhang (2012a) studied three alcohols (methanol, ethanol and isopropanol) as solvent for the extraction of TBBPA from e-waste plastics inside a pressurised vessel reactor, and reported that methanol was the most suitable one under optimum conditions of 90°C, 2h of extraction time and liquid to solid ration of 15:1, respectively. It should be noted that at high extraction temperature it

was observed that plastics underwent marginal swelling, but this did not seem to affect its properties.

Properties of the solvent play a critical role in the solvothermal treatment in removal of BFRs from plastic. The solvents must have swelling capacity without dissolving the plastic and at the same time must have the affinity to dissolve the BFRs. Mixed solvents with polar and non-polar solvents tend to increase the efficiency of the extraction if we are dealing with different types of analytes having contrasting polarity and molecular weight (Vandenburg et al., 1998). Temperature plays a crucial role in the extraction process. The optimum temperature for the extraction of additives from the plastics should not exceed the glass transition temperature (Lateef et al., 2008). High temperature may result in excessive swelling and collapse of the polymer structure.

Supercritical carbon dioxide (Sc-CO₂) extraction processes have also been proposed, as early as 2000 (Gamse et al., 2000), as possible advanced sustainable processes for BFR removal (Altwaiq et al., 2003; Wang et al., 2004) and the decontamination and recovery of pure plastics from the contaminated e-waste plastics (Gamse et al., 2000; Nakajima et al., 2002; Ma et al., 2016a; Ben Said et al., 2017; Egerer et al., 2019). The interest in using Sc-CO₂ resides in its intermediate properties between liquid and gas which enable for fast diffusion within polymer and reasonable solubilizing capacity. High extraction efficiency has however only been reported when using organic co-solvents which significantly reduce the environmental advantage as well as increase running costs. More research is therefore needed to enable a pure ScCO₂ based extraction process allowing for plastics decontamination and reuse.

In 2020, Zhang and Zhang (2020) reported a high efficiency Sc-CO₂ based process for dehalogenation of e-waste plastics into halogen-free products without the need of any catalysts or additives. When temperature in the range of 375-550°C dehalogenation of up to 99.51%

could be achieved producing halogen-free products (solid carbon materials as well as organic chemicals). This study performed at the laboratory scale will still need further investigations to prove its industrial potential and economic viability.

These results indicate that significant amount of work is required for the development and optimization of large scale extraction processes adapted to additive BFRs. In cases of reactive BFRs, which cannot be lixiviated out, a thermochemical treatment is usually required. Bromine or its derivatives must be separated during the pyrolysis process from the oil/gas products, ideally into solid residues, by using suitable catalysts. The following sections will discuss the thermochemical treatment of plastic waste and role of high temperature processes, such as incineration, combustion and pyrolysis in the recycling of e-waste plastics.

5 Thermochemical treatment of plastic waste

Thermochemical approaches of recycling e-waste plastics entail processes, such as incineration, combustion or pyrolysis. Incineration and combustion involve burning the waste (oxidation) and pyrolysis is here referred as a process of degradation by heating the material under an oxygen-starved environment (Das and Tiwari, 2018b).

5.1 Incineration/combustion process for plastic disposal:

Incineration and combustion of MSW are usually carried out to reduce the amount of waste to landfill as well as whenever possible to recover some of its chemical energy, to convert it into electricity (Liu and Liu, 2005). As most plastics are produced from petroleum resources, they intrinsically have high calorific value. Up to now, incineration/burning of post-consumer plastic waste is one of the traditional ways of retrieving energy from waste, and incineration plants are successfully operated in many developed countries. A major advantage of incineration of plastics is the solid volume reduction by 90 – 99% (Arvanitoyannis, 2013). With reduced volume, it is easy to dispose of the solid residue. The major plastic types found in the

waste stream are highly carbonaceous and have a very high heat of combustion (Table 3). Within well controlled incineration chambers an efficient burning can produce heat energy that can be utilized to produce steam and subsequently the electrical energy. Contrary to the latter, pyrolysis processes convert highly carbonaceous materials (like plastics) into useful chemicals and fuels, in the solid, liquid and gas forms. Both incineration and pyrolysis have advantages and disadvantages. Incineration destroys the plastic to produce energy that can be utilized as electrical power, which is not sustainable. Whereas, pyrolysis can transform the material into other useful forms and therefore is more sustainable. However, both incineration and combustion lead to toxic emissions through gas and the residues.

Table 3: Heat of combustion some of the plastics found in waste stream

Waste Plastic (s)	Heating value (MJ/kg)	Reference
PE	47.74	Lyon et al. (1998)
PP	45.8	
PS	43.65	
PVC	18	Costiuc et al. (2011)
PET	24.13	
ABS	39.84	
PC	31.30	
PMMA	26.81	
PCB	24.12	Areeprasert and Khaobang (2018)
ABS/PC	37.5	

Proper gas filtration systems and careful handling of residual solids or ashes can make incineration processes an acceptable solution to dealing with a large spectrum of plastic wastes. On the contrary, narrow process windows coupled with consumption of energy for heating and

471 sorting out suitable feed restrict pyrolysis process to more specific and precisely defined
472 feedstock.

473 Hence, an in-situ generated supply of product fuel gas from the pyrolysis furnace could lead to
474 a cost effective pyrolysis process for the disposal of plastic waste. Pyrolysis products, such as
475 plastic derived oil, may fulfil a fraction of petroleum product demand due to the continuous
476 depletion of fossil fuel reserves. Thus, producing value-added oil and chemicals from plastics
477 waste by pyrolysis could be an efficient way to dispose of plastic wastes.

478 Heating the plastic under inert condition may lead to depolymerisation, breaking of long chain
479 polymeric chain into small chain hydrocarbons, which can be a source of petroleum products
480 and chemicals (Das and Tiwari, 2018b). Presence of plastics improves the MSW quality as it
481 improves the overall heating value of the MSW. Although garbage burning is not encouraged
482 due to emissions, it is one of the viable solutions for the huge accumulation of solid waste in
483 the natural habitats, especially when land is scarce and therefore landfilling is not an option.
484 The incineration/burning of e-waste plastics is or should not however be practiced as they
485 contain brominated and chlorinated components, such as BFRs, which may lead to severe toxic
486 emissions.

487 Vehlow *et al.* (Vehlow et al., 2000) mixed e-waste plastics with household MSW to find out
488 the toxic emission in the different exit streams from an incineration plant. Increasing the e-
489 waste plastic fraction in the feedstock increases organic compounds related to flame retardants,
490 such as poly brominated diphenylethers (PBDPE), polybrominated biphenyls (PBB), tetra-
491 bromo-bisphenol A (TBBA), as well as active elements like bromine (Br), chlorine (Cl) or
492 phosphorous (P). The chlorine and bromine elements were found more in the flue gas stream
493 than in the other exit streams, such as fly ash, grate ash, boiler ash, etc. The process' combustion
494 temperature influences the production of PCDD/Fs and PBDD/Fs. It was found that incomplete

combustion may results in more PCDD/Fs and PBDD/Fs than what is measured when it is complete. The chances of emission of PCDD/Fs and PBDD/Fs are more when the combustion takes place at low temperature whereas at a very high temperature ($>600\text{ }^{\circ}\text{C}$) the Cl and Br get reduced to HCl and HBr (Duan et al., 2011). Since incineration is a high temperature operation, Cl and Br containing plastic may produce hydrogen halides which may corrode the equipment and create serious problem in downstream plants.

5.2 Pyrolysis of plastic waste

As previously mentioned, pyrolysis is a process that turns organic material into gas, oil and char thanks to degradation processes induced by the application of heat under an oxygen starving environment. Pyrolysis end products can be valuable petroleum-like feedstock, which can be treated in oil refineries for the synthesis of various chemicals and fuels. Under pyrolysis, macromolecular structures of polymers present in plastic wastes are broken down into smaller molecules and produce a wide range of hydrocarbons. Product distribution and quality of the pyrolytic products depend primarily on temperature, heating rate, feedstock composition, residence time, etc. (Williams and Williams, 1997; Das and Tiwari, 2018a). Furthermore, using a particular type of catalyst and reactor design could influence the reaction rate and product distribution.

The impact of time and temperature on pyrolytic product distribution has been studied extensively (Ma et al., 2002; López et al., 2011a; Xue et al., 2015; Singh and Ruj, 2016; Das and Tiwari, 2018a, b). Pyrolysis temperatures of plastics were determined based on the material degradation temperatures. Degradation temperatures of plastics have been evaluated using thermogravimetric analysis (TGA) (Das and Tiwari, 2017). It was found out that the degradation temperature of plastics increases with an increase in heating rate (Das and Tiwari, 2017). TGA coupled with Fourier transform infrared spectroscopy (TG-FTIR) as well as pyrolysis coupled with GCMS (Py-GC/MS) have been used to determine real-time

compositions of evolved gases during plastics' degradation under thermal stress (Fries et al., 2013; Jin et al., 2016).

The feasibility of pyrolysis technology to convert waste plastics into valuable products has been studied extensively and was adopted for industrial scale production. Hence, polyolefins pyrolysis can produce more than 80% of liquid oil, which can be easily blended with conventional oil (Das and Tiwari, 2018b). The quality of the liquid product can be improved by post pyrolysis distillation to produce petroleum derivatives, including gasoline and diesel grade fuel (Sharma et al., 2014). Dr Heinrich W. Smuda developed the Smuda process for the pyrolysis of polyolefins waste to produce fuel at the temperature range of 300 – 450°C in presence of catalyst made by silicates of iron, cobalt, nickel, magnesium, cadmium, copper, chromium and zinc catalyst (Smuda, 2001). The Smuda process can tolerate high levels of non-polyolefin plastics, such as PET, in which under heat decarboxylation can produce benzoic acid and benzoate (Scheirs and Kaminsky, 2006). The PET increases the aromatic content of the fuel oil. However, the PET is not considered in the pyrolysis process due to the formation of troublesome terephthalic acid (TPA) that makes solid deposits in the downstream pipelines and condensers. The presence of oxygen in the PET molecules results in the acidic component of the liquid oil. Likewise, PVC plastics in the feed causes hydrochloric acid (HCl) production (Williams and Williams, 1999). Material selectivity influences the product distribution of any pyrolysis process.

The e-waste plastic stream is composed of different types of plastic, such as ABS, PS and PC etc. (Fig. 7). Pyrolysis of polycarbonate (PC) produces phenolic components (Antonakou et al., 2014) and pyrolysis of ABS and PS results in aromatic hydrocarbons, like styrene, ethyl benzene (Rutkowski and Levin, 1986; Chaukura et al., 2016). PCBs have plastics as well as organic epoxy in addition to its metallic fraction. Evangelopoulos et al. (Evangelopoulos et al., 2015) investigated the degradation behaviour of PCBs in a temperature range of 400 – 900°C

by TGA and Py-GC/MS. It was observed that PCBs' decomposition starts at ~120°C and around 20 – 25 % of volatile matters was evolved at different temperature programs. Epoxy resins present in the PCBs decomposed along with other non-metallic components. The py-GC/MS detected a wide range of organic compounds that entailed brominated components (e.g. bromomethane, bromophenol), hydrocarbons, phenolic compounds and furans (e.g. benzofuran, 2methyl-benzofuran). Brominated molecules were produced due to the presence of significant amount of BFRs in the PCBs. It should be noted that a detailed analysis of the pyrolysis products from the pyrolysis of individual types of e-waste plastics with or without BFR is still lacking. Availability of such data would have a great influence in future development of processes for the disposal and recycling of e-waste plastics.

Fig. 7: Typical composition of e-waste plastics in UK, 2006 (Keith Freegard; Alston et al., 2011)

Hall and Williams (2006) performed pyrolysis of old computer monitor casing composed of ABS and PVC in a fast fluidised bed pyrolysis setup at 500°C. The pyrolysis reactor was externally heated by an electrical furnace and the fluidized media (N₂ gas) was preheated up to

450°C. To assist the fluidization, the feedstock was mixed with sand particles (300-425 μm) supported over a sieve plate. A schematic representation of the setup is displayed in Fig. 8. The fast pyrolysis of halogenated plastics produces halogenated organic components and hydrogen halides. These molecules are unwanted in the plastic derived oil for its usage as fuel. De-halogenation of the plastic sample seems to be a pre-requisite for fast pyrolysis although fast pyrolysis with catalyst can still be utilized for simultaneous degradation and de-halogenation of e-waste plastics (Sakata et al., 2003).

Fig. 8: Schematic representation of the fluidized bed pyrolysis reactor. Reprinted (adapted) with permission from (Energy Fuels 2006, 20, 4, 1536-1549). Copyright (2006) American Chemical Society (Hall and Williams, 2006)

5.3 Catalytic pyrolysis of plastics

In conventional catalytic pyrolysis, catalysts are used to enhance the production of specific chemical components or to reduce the energy or time needed for degradation. A wide range of catalysts were mentioned in the literature, most of these catalysts are used extensively in the

industry. The catalysts were categorised into homogeneous catalysts, acidic or non-acidic mesoporous materials, zeolites, metallic oxides, smectite clays as well as their pillared derivatives, etc. (Brebua et al., 2005; Lopez-Uribe et al., 2012; De Stefanis et al., 2013b). Zeolites (ZSM5, HZSM etc.) are effective in plastics degradation as discussed in numerous past studies (George Manos, 2000; Ranbir Bagri, 2002).

López et al. (2011b) even used red mud, a Bauxite by-product waste from alumina production industry, as a catalyst for waste plastics pyrolysis as it favours hydrogenation reactions, but the high catalyst activity was only found at high temperatures ($>500^{\circ}\text{C}$). On the other hand, catalyst like ZSM-5 was found to be active at lower temperature (440°C) and also to promote the production of lighter hydrocarbons (gas/liquid) with high aromaticity. Still regarding nanoporous aluminosilicates, De Stefanis et al. (2013a) reported three possible catalysts from restructured smectite clays: saponite, montmorillonite and beidellite. Catalysts were substantiated for their performance in the catalytic pyrolysis of a medium-density polyethylene. Catalysts were able to reduce the temperature of cracking down to 300°C , as compared to 650°C or more for non-catalysed pyrolysis. In comparison to zeolites, clay based catalysts were found superior in producing liquid hydrocarbon from plastic wastes as they favour the production of liquid hydrocarbons in the gasoline and diesel range liquid from the polyethylene plastics.

5.3.1 Bromine fixation from BFR containing e-waste plastics degradation

Hall and Williams (2007) performed pyrolysis experiments with brominated ABS plastics originating from old computer monitor casings in a fluidised bed reactor system heated using an externally heated furnace, an air preheater (450°C) for fluidizing the fine ($300 - 425\ \mu\text{m}$) sand particles used as bed material. The reactor was externally attached with condensers and scrubbing systems. They successfully converted the Br-ABS waste into more than 91% of oil. 98% of the bromide was found in oil fraction and no bromine was found in the solid char one.

In catalytic pyrolysis, it is possible to fixate the bromine into different product stream (Ma et al., 2016b). Hence, catalytic pyrolysis is also utilized for simultaneous de-halogenation and degradation of e-waste plastics. Sakata et al. (2003) proposed iron oxide and calcium carbonate as the catalyst/sorbent for dehalogenation process. The process can follow two approaches (Fig. 9). One approach advocated the degradation of plastics followed by dehalogenation of the halogenated products. In the other approach, both degradation and dehalogenation occurs simultaneously in presence of a suitable catalyst.

Fig. 9: Two steps and single step dehalogenation and degradation of halogenated plastics (Sakata et al., 2003)

Areeprasert and Khaobang (2018) investigated the utilization of char obtained from e-waste as a green catalyst in the process of simultaneous debromination and pyrolysis of ABS/PC, PCB from e-waste. Although it is difficult to separate out Br from the pyrolysis product stream, the use of catalyst, one can modify brominated molecules from one stream (for example gas) in order to shift it to another stream (for example liquid). Chen et al. (2020) use Fe-Ni/MCM-41 catalyst to recover the Br free oil fraction from the pyrolysis of BFR added e-waste plastics. Presence of Fe in the catalyst significantly reduces the HBr in the oil fraction whereas Ni helps in the reduction of SbBr_3 in the oil. Ma et al. (2016b) observed a 50% reduction of Bromine content in the oil product in presence of zeolite catalysts compared with the non-catalytic

thermal pyrolysis. Addition of catalyst resulted in decrease of bromine content in the oil but simultaneously increased in wax and char residue. Table 4 compares the reduction of Bromine content in the oil fraction using different catalysts when compared with non-catalytic pyrolysis. PCB pyrolysis is an energy intensive process since their thermal decomposition is endothermic. Guo et al. (2014) were able to recover 10.17 wt% gas, 18.23% of oil/tar and 71.60% of solid residue by doing the low temperature (~500°C) pyrolysis of FR4 (epoxy composite) type PCBs. The calorific values of gas and tar samples are 2.38 MJ/kg and 4.5 MJ/kg respectively, which amounted around 35% of the total energy consumption for the pyrolysis. Gases such as CO, CO₂ and 2-methyl propene, were major components of the gaseous fraction. Regarding the tar fraction, it consisted of mostly phenols and alkyl aromatics along with brominated hydrocarbons.

632 **Table 4: Effect of catalyst in the reduction of Br from the pyrolysis liquid product compare to the non-catalytic pyrolysis liquid product**

Catalyst	Material	% reduction of Br from the non-catalytic pyrolysis	Reference
Y-Zeolite	Waste ABS+PC (80:20) with BFR	75%	Areeprasert and Khaobang (2018)
	PCB with BFR	8.1%	
ZSM-5	Waste ABS+PC (80:20) with BFR	75%	
	PCB with BFR	7.7%	
Bio-char (BC)	Waste ABS+PC (80:20) with BFR	60%	
	PCB with BFR	54%	
Electronic waste char (EWC)	Waste ABS+PC (80:20) with BFR	81%	
	PCB with BFR	58.6%	
Iron oxide loaded Y-Zeolite (Fe/YZ)	Waste ABS+PC (80:20) with BFR	81%	
	PCB with BFR	19%	
Iron oxide loaded ZSM-5 (Fe/ZSM-5)	Waste ABS+PC (80:20) with BFR	89.1%	
	PCB with BFR	46.3%	
Iron oxide loaded biochar (Fe/BC)	Waste ABS+PC (80:20) with BFR	90.5%	
	PCB with BFR	58.6%	
Iron oxide loaded electronic waste char (Fe/EWC)	Waste ABS+PC (80:20) with BFR	98.1%	
	PCB with BFR	70.9%	
Fe-Ni/MCM-41	Waste ABS with TBPPA+Sb ₂ O ₃	~60%	Chen et al. (2020)
Zeolite catalyst (HY)		~42%	Ma et al. (2016b)
Zeolite catalyst (H β)		~50%	
Zeolite catalyst (HZSM5)	Br-ABS	~39%	
MCM-41 (All silica)		~11%	
Al ₂ O ₃		~40%	

633

5.4 Effect of pyrolysis reactor configuration

We have seen that pyrolysis is a possible solution for e-waste plastics degradation and dehalogenation. As discussed in the previous section, thermal treatment of e-waste plastics with BFR can be carried out in three ways: Firstly, dehalogenation is followed by pyrolysis of e-waste plastics; secondly, both dehalogenation and pyrolysis are performed simultaneously; thirdly, contaminated plastics undergo pyrolysis which is followed by a product up-gradation step to produce more useful products without toxins (Yang et al., 2013). For these approaches, different reactor configurations were used including batch reactor, semi-batch reactor, catalytic bed reactor, two-stage drop down reactor, fluidized bed reactor, rotary kiln reactor, screw kiln reactor, etc. Industrially, batch, fluidized bed and rotary kiln reactors are commonly considered for waste plastic pyrolysis.

5.4.1 Batch/semi-batch reactors

Batch/semi-batch reactors are often used in the laboratory scale studies as they enable to easily maintain reaction conditions, such as temperature and pressure. For example, Hall and Williams (2008) performed catalytic pyrolysis in a batch reactor and examined the potentials of zeolite based catalyst in the process of removing brominated organic compounds from the oil products. They reported that zeolites: (i) significantly reduced the brominated organic components within the pyrolysis oil when treating BFR containing ABS and HIPS; (ii) but at the same time however, deteriorated the overall product quality by reducing the production of valuable chemicals, such as styrene and cumene.

5.4.2 Fluidized bed reactors

Jung et al. (2012) mixed shredded particles of Br-ABS from e-waste plastics with Calcium-based additives, such as calcium oxide, calcium hydroxide and oyster shells, and carried out the pyrolysis experiment in a fluidized bed reactor. The Ca-based absorbents were able to neutralize the hydrogen halide (X) formed due to the pyrolysis at 400°C of halogen containing

659 plastics (Br, Cl). The following reactions (Eq. 1 – Eq. 3) explain the reaction mechanism of the
660 dehalogenation process.

664 Where X = Cl or Br

665 5.4.3 Two stage pyrolysis reactors

666 Two-stage reactors were used in which the pyrolysis reaction occurs in the first stage and the
667 evolve gases passes through a catalytic bed in the second stage (Williams and Chishti, 2000;
668 Ratnasari et al., 2017). Ratnasari et al. (2017) performed pyrolysis experiments in a two stage
669 pyrolysis unit where in the second stage, a multi-layered structured mesoporous (MCM41)
670 catalyst stacked on top of a micro-porous catalyst (ZSM5) layer to ensure more gasoline type
671 hydrocarbon production from waste plastics. Two stages reactors are also utilized for the
672 catalytic pyrolysis and bromine removal of the non-metallic fractions of waste PCBs. Ma and
673 Kamo (2018) applied low cost Fe and Ni catalysts in a two stage fixed bed reactor for the
674 pyrolysis of waste PCBs and reported that Fe particles have excellent bromine removal
675 efficiencies from the pyrolysis product. The schematic representation of the two stage fixed
676 bed pyrolysis setup is shown in Fig. 10.

Fig. 10: Schematic representation of the two-stage fixed-bed reactor system.(Ma and Kamo, 2018) [Reprinted from the article: *C. Ma and T. Kamo, Journal of Analytical and Applied Pyrolysis, 134, (2018) 614, with permission from Elsevier*]

5.4.4 Auger (screw kiln) reactor

As reported recently, low temperature pyrolysis of carbonaceous material, such as plastics, with long holding times undergoes consecutive degradation to produce lighter hydrocarbon liquid fractions (Das and Tiwari, 2018b). However, at high temperature, ultra-pyrolysis (flash/fast pyrolysis) indulges more production of gaseous hydrocarbon (Alvarez et al., 2015; Lopez et al., 2017). Slow pyrolysis experiments were conducted mostly in batch or semi-batch reactors. For continuous production, a screw kiln reactors/auger reactors can be used for low to moderate temperature pyrolysis. Auger reactors use a screw to convey the feedstock down

the length of the externally heated tube (Campuzano et al., 2019). The temperature of the reactor can be programmed to vary along the length of the reactor tube. A typical auger reactor used for the pyrolysis of biomass is shown in Fig. 11 (Campuzano et al., 2019).

Fig. 11: Single-auger reactor for pyrolysis of biomass [Reprinted from the article: Campuzano, Felipe Brown, Robert C. Martínez, Juan Daniel, *Auger reactors for pyrolysis of biomass and wastes*, *Renewable and Sustainable Energy Reviews*, 102, (2019) 372, with permission from Elsevier

5.4.5 Microwave assisted pyrolysis

In microwave pyrolysis, microwaves are used as the energy source. Microwave are electromagnetic waves with wavelength ranging between 1 mm and 1 m (Undri et al., 2013). Materials like water, biomass, metals and carbon particles, are considered good microwave absorbers (dielectric materials). Polymers and plastics are transparent to microwave because they have low microwave absorption capacity (Cheng and Hu, 2010). However, these latter

materials can undergo pyrolysis by mixing them with dielectric ones, such as carbon particles or metal particles, in a microwave reactor. The control of pyrolysis temperature in microwave heating is however tricky due to the formation of hot spots during heating caused by localized microwave field that are due to the difference in dielectric properties of the various material and large wavelength of the radiation (Undri et al., 2013).

Microwave heating has been used for pyrolysis of biomass (Zhao et al., 2012; Zhang et al., 2017), waste plastics (Ludlow-Palafox and Chase, 2001), scrap tyres (Undri et al., 2013) and electronic waste (Sun et al., 2011). Aishwarya and Sindhu (2016) successfully carried out the pyrolysis of simulated plastic mixtures in a microwave assisted pyrolyser which had a power of 5 kW and was integrated with 4 magnetron generating microwaves continuously. Ludlow-Palafox and Chase (2001) successfully recovered aluminium and hydrocarbons from high density polyethylene and aluminium/polymer laminates (empty toothpaste tubes) by microwave induced pyrolysis in a semi-batch reactor using carbon particles as microwave absorbing materials. Hussain et al. (2012) used a microwave heating aluminium coil reactor for the pyrolysis of waste polystyrene into useful products. The heating was controlled by changing the size and shape of the metal reactor. Major factors affecting the microwave pyrolysis include the feedstock's properties, feeding pattern, heating program, microwave power, microwave power delivery, reactor design, susceptor type, catalytic properties of the susceptors and other reaction conditions. A typical microwave assisted pyrolysis setup is shown in Fig. 12 (Sun et al., 2011).

Fig. 12: Diagram of the reactor system for microwave-induced pyrolysis of WPCBs: (1) nitrogen cylinder, (2) rotameter, (3) microwave oven, (4) quartz reactor, (5) thermocouple, (6) data collection, (7) condensing system, (8) glass wool trap, (9) deionized water, (10) gas bag [Reprinted (adapted) with permission from (J. Sun, W. Wang, Z. Liu and C. Ma, *Industrial & Engineering Chemistry Research*, 50, (2011) 11763.). Copyright (2011) American Chemical Society.]

6 Conclusion and outlooks

The recovery of toxic free plastics from e-waste plastics is an interesting field of waste utilization and conversion. An extensive amount of studies of thermochemical conversion of waste plastics have been carried out in recent years and many significant technological advances have been achieved. However, a pyrolytic solution is still lacking that is capable of dealing with waste quantities as large as the ones that can be treated using conventional waste treatments, such as incineration and land filling. Major hurdle for plastic pyrolysis is the non-homogeneity of plastic waste. Plastics like PVC and PET in the feedstock can lead to different types of end products compared with polyolefin based plastics. On the other hand, plastic wastes from WEEEs contain various types of plastics including styrene based plastics (ABS, HIPS), polycarbonates, polyamides and polyolefins containing environmentally harmful toxins, such as BFRs and heavy metals. Special attention is needed to recover the non-toxic

plastics from such e-waste plastics. Extraction processes of BFRs from the latter have been studied extensively with different solvents, such as methanol, propanol, hexane, etc., with good extraction efficiencies. However, it is advisable to do extractions of toxins in a sustainable way by using green technology, such as using supercritical CO₂ as solvent, bio solvents, ionic liquids, etc.

Pyrolysis of e-waste plastics have been performed particularly with various catalyst based on different metals, such as Ni, Fe, Ca, Mg etc, which might help in reducing the brominated organic hydrocarbon content in pyrolysis products. Pyrolysis is one of the most recommended technique in the treatment of e-waste plastics to convert them into value added products, however complete detoxification of e-waste plastics by pyrolysis remains the limiting factor. The scope of utilizing thermochemical conversion of e-waste plastic into oil and chemicals is significant and helps to deal with the massive and global problem of plastic as well as e-wastes. The pros

Declaration of competing interest

The Authors have no conflict of interest between them.

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