CRANFIELD UNIVERSITY

LUISA CANOPOLI

UPCYCLING OF PLASTICS RECOVERED FROM ENHANCED LANDFILL MINING THROUGH PYROLYSIS

SCHOOL OF WATER, ENERGY AND ENVIRONMENT
Energy and Power

PhD Thesis
Academic Year: 2019 - 2020

Supervisor: Dr Stuart Thomas Wagland
Associate Supervisor: Prof. Frédéric Coulon
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This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

ABSTRACT

Since 1950 the global plastics production increased at a compound annual growth rate (CAGR) of about 8.5 % and it is expected to grow in the next 5 years at a CAGR of about 4 %. The estimated amount of plastics that ended up in landfill and natural environment in the past 70 years is 4.9 billion tonnes. Most of this comprises of thermoplastics which can be potentially recycled and reintroduced in the new circular plastic economy reducing the use of virgin fossil resources. To achieve this, more information is needed on recovered plastics physico-chemical characteristics and their suitability for conventional recycling processes. Due to the expected contamination and degradation of excavated plastics, potential upcycling routes need to be explored to produce marketable products. The plastic recycling, fresh waste or excavated, needs to fit into the circular economy strategy which aims to maximise service life and minimise waste. In the case of recovered plastics, the starting material is unused and must be renovated to become useful again. Between common recycling routes for fresh plastic waste, chemical recycling was found in line with the circular economy concept. Specifically, the pyrolysis method leads to the production of chemical compounds that can be used in the plastic industry. This PhD investigates the feasibility of producing valuable products from the pyrolysis of excavated plastics from municipal solid waste (MSW) landfill. Firstly, the physico-chemical characteristics of genuine plastic from landfills were analysed. The chemical and mechanical properties of buried plastics were hypothesised to be affected by the chemical, biochemical and physical parameters within a landfill environment. Secondly, the potential valuable products from the pyrolysis of recovered plastics were investigated. Polyethylene and polypropylene represented 64 wt% of total recovered plastics. The samples with storage of more than 10 years in landfill showed a general greater extent of degradation compared to newer samples. The pyrolysis of excavated plastics at 500°C and 650°C produced the highest level of hydrocarbons and most of the pyrolysis products fitted within the naphtha range (C6-C10) which has a high potential to be used in the petrochemical cluster. The findings from this PhD bring to the attention that buried plastics have hidden potential. These plastics have, in the past, been considered useless by virtue of being landfilled and are potentially harmful to the environment and ecosystem long-term in closed landfill sites. This work demonstrates the potential of recovering value from excavated plastics as part of an enhanced landfill mining project, reducing the need for virgin fossil fuel, preventing long-term pollutants release and producing valuable and useful products.

Keywords: Recycling, waste, circular economy, excavated plastic, secondary raw material.

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile–butadiene–styrene copolymer
APCr	Air pollution control residues
ASPEN	Advanced System for Process Engineering
ATR-FTIR	Attenuated total reflection-Fourier Transform-Infrared Spectroscopy
BOD	Biochemical oxygen demand
BPA	Bisphenol A
BTX	Benzene toluene xylene
CAGR	Compound annual growth rate
CI	Carbonyl index
COD	Chemical oxygen demand
DEHP	Diethyl-hexyl phthalate
DLM	Dynamic landfill management
DMP	Dimethyl phthalate
DoU	Degree of unsaturation
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetric
ELFM	Enhanced landfill mining
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
LFM	Landfill mining
MRF	Material recovery facilities
MSW	Municipal solid waste
NIR	Near infrared
NP	Nonylphenols
PAHs	Polycyclic aromatic hydrocarbons
PC	Polycarbonates
PCDFs	Polychlorinated dibenzofurans
PE	Polyethylene
PET	Polyethylene terephthalate
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polystyrene

PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinyl chloride
Py-GC-MS	Pyrolysis-Gas Chromatography coupled to mass spectrometry
RDF	Refuse derived fuel
REACH	Registration Evaluation Authorisation and Restriction of Chemicals
SEM/EDS	Scanning electron microscopy/energy dispersive x-ray spectroscopy
SRB	Sulphate-reducing bacteria
SRF	Solid recovered fuel
TDPA	Totally degradable plastic additives
TGA	Thermogravimetric analyser
UN	United Nations
VOCs	Volatile organic compounds
WtE	Waste to energy
WtM	Waste to material
XRF	X-ray fluorescence

1 INTRODUCTION

This chapter provides an overview of the research background, the research aim and objectives, and the thesis structure.

1.1 Background

The global annual plastic production between 2005 and 2018 almost double reaching 359 million tonnes of which a third was produced by China (PlasticsEurope, 2019). In the meantime, the European packaging demand reached 20 million tonnes which represented about 40 % of the total converted demand (PlasticsEurope, 2019). The plastic production is expected to grow at a compound annual growth rate (CAGR) of ~4 % by 2025 (Grand view research, 2019). Besides this growth, the concern about plastic waste mismanagement is increasing. It has been estimated that ~4.9 billion tonnes of plastics ended up either in landfill or in the natural environment in the past 70 years (Geyer et al., 2017). Further to this, there is a substantial amount of plastics still disposed of in landfills because of the lack of feasible valorisation routes. For example, it is estimated that 7.2 million tonnes of plastics were still disposed of in landfill across Europe in 2018 (PlasticsEurope, 2019). The reuse and recycling of plastics and cut of single-use plastics were introduced into the European circular economy strategy (European Commission, 2018). The circular economy is based on closed-loop recycling where the product is designed to maximise its service life and minimise the waste. The Ellen MacArthur Foundation in collaboration with the United Nations (UN) Environment Programme launched the new plastic economy global commitment, covering the production, consumption and reuse or recycling (Ellen MacArthur Foundation and UN Environment Programme, 2019). This project establishes a new circular economy for plastic, reducing the use of fossil fuels which are the main sources of plastic production. This view fits into the enhanced landfill mining (ELFM) concept which was developed since 2008 by Flemish ELFM Consortium (Jones et al., 2013) and focuses on the valorisation of buried waste. Through ELFM the excavated plastics could be upcycled and reintroduced in the circular economy as secondary raw materials (Canopoli et al., 2018; Fox and Stacey, 2019). However, plastics from landfill likely present contaminants such as wood, textile and fines fractions (Breyer et al., 2017; Canopoli et al., 2018). In addition, buried plastics are subjected to weathering and degradation due to the nature of the landfill environments where acidic leachate, corrosive chemicals and relatively high temperature are dominant. These aspects need to be considered for recycling recovered plastics from landfill sites. The integrity and the composition of excavated plastics are likely to be different from fresh plastic materials that are directly recycled through material recovery facilities (MRF). Fresh plastic materials recycling methods include reuse (primary), mechanical recycling (secondary), chemical recycling (tertiary) and energy recovery via incineration (quaternary) (Al-Salem et al., 2009). Due to the likely altered physico-chemical properties of excavated plastics and the presence of contaminants, mechanical recycling is not suitable for upcycling this material (Canopoli et al., 2018). Similarly, energy recovery via incineration does not embrace the circular economy concept and therefore is not seen as a valuable recycling route for plastics. In contrast, chemical recycling was found in line with the circular economy view and capable of offering marketable products from fresh plastic waste (Fox and Stacey, 2019). From this, it can be supposed that a similar approach should be followed for obtaining valuable products from excavated plastics. Different researchers have identified the pyrolysis of fresh plastic waste as a valuable method to produce chemical building blocks (Al-Salem et al., 2009). However, the limited number of studies on pyrolysis of recovered plastics from landfill mostly focused on fuel production without considering the recovering of high valuable chemicals (Breyer et al., 2017; Santaweesuk and Janyalertadun, 2017). This route needs to be investigated in order to evaluate the potential upcycling of excavated plastics and their introduction into the new plastic economy. Some studies mined plastics with a storage age of about thirty years which were made around the ‘80s or before and for this reason likely to present more dangerous substances than new plastics (Quagherbeur et al., 2013; Zhou et al., 2014). Indeed, this plastic is likely to contain more cadmium and phthalates than new plastics because the introduction of European regulation REACH (Registration, Evaluation, Authorisation and restriction of Chemicals) about these compounds started in 2007 (European Parliament, 2009). In addition, landfill environments can lead to plastic degradation which needs to be analysed in order to evaluate the potential value of this material (Webb et al., 2013). For these reasons, the upcycling of excavated plastics needs to pass through the investigation of their physico-chemical characteristics and products obtained through pyrolysis. Thus, in this study, the main research question was: Can closed municipal solid waste (MSW) landfills be introduced in the circular economy loop by recovering plastic waste and producing added value and sustainable products?

1.2 Research aim and objectives

The aim of this research was to investigate the feasibility of producing valuable products from the pyrolysis of excavated plastics from MSW landfills. In order to achieve this, the following objectives have been identified:

1. Critically review the literature on plastics from MSW landfills and the possibility of recovery through pyrolysis.
2. Characterise the extent of degradation of recovered plastics from MSW landfills according to the age of the buried waste and landfill conditions.
3. Develop a pyrolysis model for recovered plastics from MSW landfills to predict valuable product outputs from the pyrolysis.
4. Perform and assess the effects of thermochemical conversion operating conditions on recovered plastics and product outputs.
5. Evaluate the quality of the pyrolysis products in relation to feedstock characteristics.

1.3 Thesis outline

This thesis follows a paper-style format and comprises of six chapters (Figure 1.1).

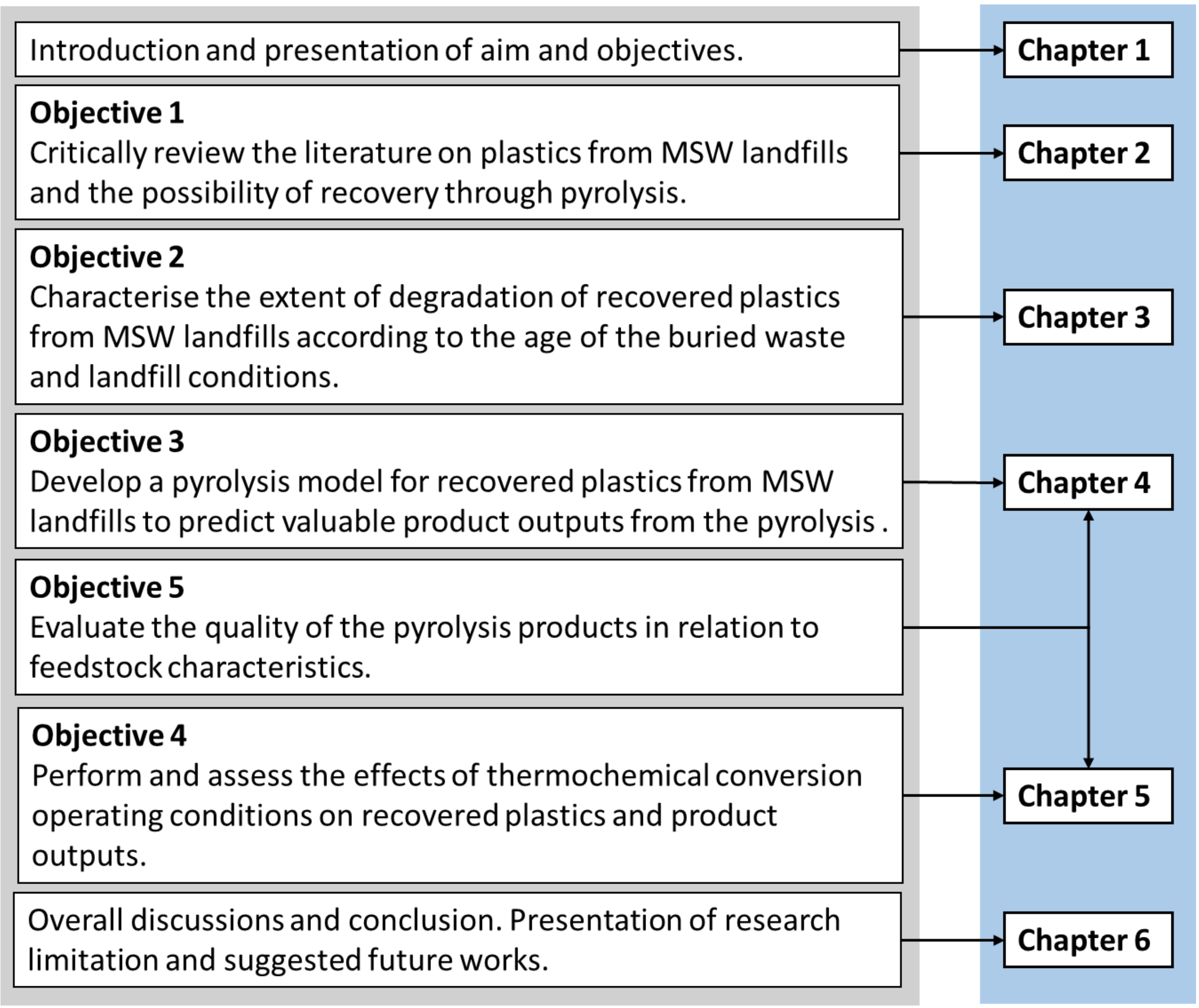

Figure 1.1 Schematic diagram of the thesis structure.

Chapter 1 – Introduction. It presents the background of the thesis project, aim and objectives.

Chapter 2 – Literature review. The literature review on the excavated plastics covers the first objective of the project. It focuses on the possible impact of landfill environment on plastics characteristics and the viability of excavated plastics for thermochemical recycling. It helped to identify the research gaps, set the research questions and focus, and develop the research plan. This paper has been published in Waste Management journal (Canopoli et al., 2018. Physico-chemical properties of excavated plastic from landfill mining and current recycling routes. *Waste Management*. 76: 55-67).

Chapter 3 – Excavated plastics characterisation. These chapter findings are related to objective 2. They cover the analyses of excavated plastics and the evaluation of degradation and contamination compared to fresh plastic waste. This paper has been published in Science of the Total Environment. (Canopoli et al., 2020. Degradation of excavated polyethylene and polypropylene waste from landfill. *Science of the Total Environment.* 698: 1137-1143).

Chapter 4 – Pyrolysis simulation model. A pyrolysis simulation model was developed in ASPEN Plus for the prediction of products from excavated plastics pyrolysis.

Chapter 5 – Pyrolysis of recovered plastics with Py-GC-MS. This chapter identified the potential recyclable compounds from the pyrolysis of excavated plastics at different temperatures. It presents the comparison between products from different feedstocks such as PE, PP and mixed plastics. Chapters 4 and 5 have been compiled and adapted for journal submission.

Chapter 6 – Conclusion and discussion. The overall conclusion and discussion are presented in this chapter showing the research limitations and suggesting areas of further work.

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2 LITERATURE REVIEW

Physico-chemical properties of excavated plastic from landfill mining and current recycling routes

This chapter critically reviews the literature on plastics from landfill and the possibility of recovering it through pyrolysis. A modified version has been published in the Waste Management journal (see Appendix D).

2.1 Introduction

Over the last two decades, the amount of waste being managed by landfill disposal each year has decreased across Europe and the UK. According to the Eurostat (2016) waste estimation, 473 kg per capita of MSW was generated in 1995 in EU-27, of which 64 wt% was disposed of in landfill and 11 wt% was recycled. In 2015, the EU-27 reported 477 kg of MSW per capita of which 28 wt% was recycled, 26 wt% incinerated (including energy recovery), 25 wt% landfilled, and 16 wt% was processed by composting and digestion (Eurostat, 2016). New legislation, such as Council Directive 1999/31/EC (European Parliament. Council of the European Union 1999) and Waste Framework Directive 2008/98/EC (European Parliament. Council of the European Union, 2008), has driven the changes in the management of landfill, encouraged sustainable waste management and resulted in the closure of many landfills (Hogland et al., 2011). The waste management hierarchy included in Framework Directive 2008/98/EC has become part of the European waste management, defining different aspects of this topic such as waste, recycling, recovery, secondary raw materials and by-products (European Commission, 2016). Recently, Europe has moved towards the 'new' concept of a Circular Economy, aiming to recycle 65 wt% of MSW and reduce the amount of MSW disposed of in landfill by 10 wt% before 2030 (European Parliament. Council of the European Union, 2015). However, there are between 125,000 and 500,000 landfills (EURELCO, 2017) in Europe, many of which are now closed; waste in landfills represents an important legacy that needs to be addressed. It is estimated that over 5.25 billion tonnes of waste were deposited in landfills between 1995 and 2015 across the EU-27 countries

(Eurostat, 2016). The first landfill mining (LFM) project was carried out in Israel in 1953 (Savage et al., 1993), but only until the late 1980s, interest began to increase, especially in the USA and Europe (Hogland et al., 2004). The concept of enhanced landfill mining (ELFM), which started to develop in 2008 (Jones et al., 2013), focuses on maximising the valorisation of waste found in landfills and dumpsites as material (WtM) and energy (WtE) (Jones et al., 2012). Landfills can be considered as temporary storage for waste while the technologies for their valorisation are improved and achieve large-scale deployment (Bosmans et al., 2013). Landfills operating between the 1950s to the mid-1990s have been identified as the most suitable for ELFM, because they were not affected by the directives that lead to a minimisation and pre-treatment of waste disposed of in landfills and have higher content of valuable and combustible materials (Hogland et al., 2011; Van Passel et al. 2013). A key challenge exists in the recovery of value from materials excavated from landfills, which has been partially addressed in previous academic publications, however this review specifically focuses on plastics. Here there is an opportunity to explore alternative methods of recovering value from plastics as conventional recycling/recovery methods will not be viable. Similarly, recovery of energy from waste and advanced conversion processes require further research and development due to the pollution and the unknown effects of landfill contamination on the chemical transformation pathways. A variety of landfilled materials can theoretically be recycled or used for energy recovery, which can contribute to the security of energy supply and substitute raw materials (Greedy, 2016). For example, recovery of secondary raw materials available within landfills such as valuable metals (Gutiérrez-Gutiérrez et al., 2015) can mitigate the increasing concern about the availability and security of critical raw materials (European Commission, 2017). Opportunities also exist in the recovery of plastics, which represent between 5-25 wt% of the total waste deposited; the proportion increases in landfills during time due to the degradation of organic matter and its consequent weight loss (García et al., 2016; Sel et al., 2016; Münnich et al., 2015; Quaghebeur et al, 2013; Jones et al., 2013; Van Passel et al., 2013; Van Vossen and Prent, 2011). The annual worldwide plastic production has increased from 1.5 million tonnes in the 1950s to 322 million tonnes in 2015 (PlasticsEurope, 2016). In 2014, 59 million tonnes and 311 million tonnes of plastics were generated in Europe and in the world respectively (PlasticsEurope, 2016). In the same year, of 25.8 million tonnes of plastic waste produced, 29.7 wt% was recycled, 39.5 wt% used for energy recovery and 30 wt% was landfilled (PlasticsEurope, 2016). Over the years, the inadequate plastic waste management has led to the accumulation of plastics in the environment, causing pollution and consequent health risks (Singh and Ruj, 2016; Thompson et al., 2009). The conjunction of increasing energy demand and scarce resources such as fossil fuel has resulted in a need for sustainable secondary fuels and chemical resources (Sharma et al., 2014; Singh and Ruj, 2016). Plastics from landfills can potentially be reprocessed to other plastic products, used as part of a waste-derived fuel for energy or used as a feedstock to produce valuable base petrochemicals (Al-Salem et al., 2009; Mastellone, 1999). Because 90 % of the plastic is produced from petroleum, pyrolysis of fresh plastic waste is considered a feasible process to recover chemical building blocks and a valuable alternative to the ordinary plastics disposal routes, such as landfill (Al-Salem et al., 2009; Al-Salem and Lettieri, 2010). Critical reviews and studies on technical and economic aspects of LFM and ELFM have been previously published (Krook et al., 2012; Jones et al., 2013; Bosmans et al., 2013; Van Passel et al.; 2013). However, these do not focus on the excavated plastic fraction and therefore do not consider its chemical characteristics. This paper reviews the research focusing on excavated plastics and the physico-chemical properties of this fraction along with the gaps in scientific knowledge that need to be filled to consolidate and enable the development of upcycling technologies. The aim of the work is to critically review the likely impacts of landfill chemistry on the degradation and/or contamination of recovered plastics and their properties, and assess the viability of using excavated plastics as feedstock for upcycling to valuable chemicals or liquid fuels via thermochemical conversion.

2.2 Plastic components of landfill waste and factors affecting their degradation

2.2.1 Plastic components of landfill waste

Plastics can be thermoplastics, which are capable of melting and flowing at a certain temperature without undergoing chemical changes, and thermosets such as bakelite, which are characterised by irreversible cross-linked polymer chains formed at high-temperature treatments (Jasso-Gastinel et al., 2017). The molecular structure is characterised either by a random arrangement of polymer chains forming an amorphous structure such as polystyrene (PS) and polyvinyl chloride (PVC), or by an alternation of random and regular orders forming semi-crystalline structure such as polyethylene (PE) and polypropylene (PP) (Gilbert, 2017). Thermoplastics have secondary bonding between molecules while thermosets cross-linking often have primary covalent bonds and occasionally hydrogen bonds (Lampman, 2003). Chemical reactivity and thermal stability are related to the primary bonds while the solubility of the polymers is associated with the secondary bonds (Brydson, 1999). Thermoplastics include PE, which can be sub-divided into low-density (LDPE) and high-density polyethylene (HDPE), polyethylene terephthalate (PET), PP, PS, and PVC. Thermoplastics represent approximately 80 wt% of the consumed plastics and constitute most of the plastic fraction of municipal solid waste (Dewil et al., 2006; Andrady and Neal, 2009; Lettieri and Al-Salem, 2011).

2.2.2 Factors affecting plastic waste degradation

Their chemical composition and structure influence their degradation behaviour (Brydson, 1999). Thus, polymers with heteroatoms such as PET, are more susceptible to degradation than polymers with pure carbon backbones (Zheng et al., 2005; Müller et al., 2001). The water permeability of plastics is directly proportional to their polarity; hence nonpolar polymers are less affected by water permeability (McKeen, 2014). Most common plastics can be classified from the most polar to the less polar as follows: PET > PU > PC > PS > PE > PP (McKeen, 2014). Polymers with unsaturated double bonds are more prone to degradation than polymers with saturated bonds (Gewert et al., 2015). However, the presence of impurities, such as traces of catalyst residues, additives, or metals from processing equipment can accelerate/initiate degradation of polymers with saturated bonds, i.e. PE, PP and PVC (Gijsman et al., 1999, Grassie and Scott, 1988, Scott, 2002, Vasile, 2005, cited in Gewert et al., 2015). The degree of unsaturation (DoU) gives information on the unsaturated (double, triple and rings) bonds present in the monomer. The fluidity of the polymer is directly proportional to the degree of unsaturation, increasing the saturation level the fluidity decreases. DoU of a polymer can be calculated from its repeating unit (Equation 2.1), which does not consider the O and S due to their neutrality in saturation (McKeen, 2014).

Equation 2.1 Formula of polymer degree of unsaturation.

$$\boldsymbol{DoU = \frac{2C + 2 + N - X - H}{2}}$$

where C, number of carbon atoms; N, number of nitrogen atoms; X, number of halogen atoms (F, Cl, Br, I); H, number of hydrogen atoms.

Degradation of plastics in the environment can occur either by photodegradation, auto-oxidative degradation, thermooxidative degradation, thermal degradation and biodegradation (Andrady, 2001). The degradation process is normally initiated by UV-light and heat followed by auto-oxidation of the polymers and scissions into smaller polymer fragments which can be degraded by microorganisms (Andrady, 2011). Degradation of plastic waste in landfills covers a period over 20 years and it is mainly related to thermooxidative degradation and anaerobic condition (Webb et al., 2013). The most common cause of degradation of polymers without heteroatoms, such as PP, PE and PS, in an aerobic environment, is the photodegradation followed by oxidation (Gijsman et al., 1999). Figure 2.1 shows the mechanism for a general polymer auto-oxidation process. Free radicals are initially formed from photo and thermal degradation. They react in the presence of oxygen to form peroxy radicals, which further react with organic material leading to hydroperoxides formation (ROOH) (Gijsman, 2008). New radicals are generated from the hydroperoxides, sustaining the process. Transition metals such as Fe, Cu, Ti and Cr can accelerate the degradation process (Gijsman, 2008). Transition metals such as Fe, Co, and Mn, can catalyse the formation of free radicals from hydroperoxides (Ammala et al., 2011). Photodegradation is more affected by iron, while thermal degradation is catalysed by cobalt and manganese (Ammala et al., 2011).

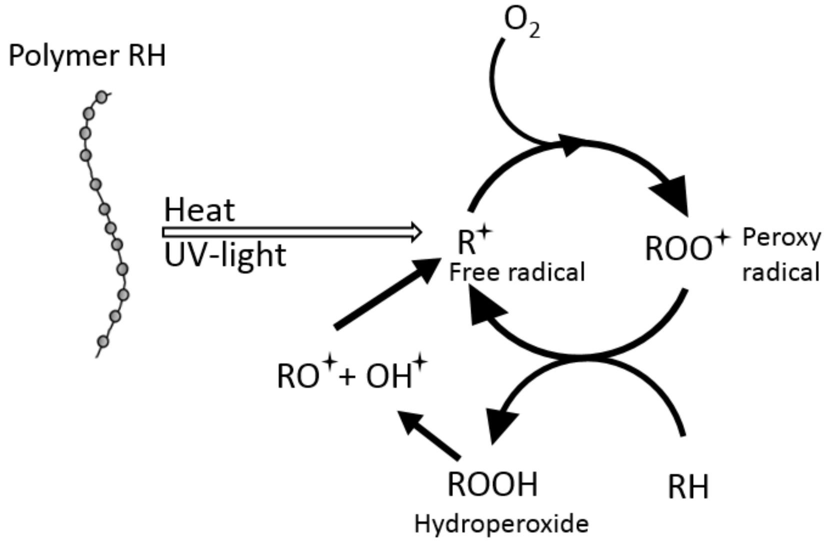
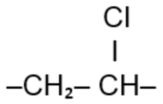
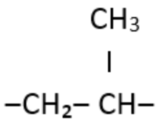
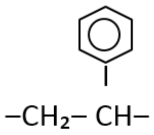
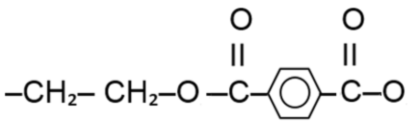


Figure 2.1 General polymer auto-oxidation process.

Thermooxidative degradation, which occurs at a moderate temperature (~70 °C), is one of the main oxidative degradation steps (Andrady, 2011; Gijsman, 2008). Several studies reported anaerobic biodegradation of plastics in landfills into water and methane (Gu et al., 2000 cited in Shah et al., 2008). The polymers are broken down into shorter chains by microorganism enzymes, until they reach a small size (M_n ~500 g/mol) and are able to penetrate the bacterial membranes (Andrady, 2011; Shah et al., 2008). Muenmee et al. (2016) also found that semi-aerobic condition in landfills enhanced the plastics biodegradation and decreased the methane emission. In aerobic conditions, biodegradation produces CO_2 and H_2O (Shah et al., 2008). Adamcová and Vaverková (2014) studied the degradation of HDPE with totally degradable plastic additives (TDPA) and 100 %-degradable PE samples placed in Štěpánovice landfill for a period of 12 months. The decomposition was considered as the breakdown of the polymer into carbon dioxide, methane, water, inorganic compounds or biomass via microbial activities. The degradation was associated with the disruption of plastic integrity. Neither decomposition nor degradation was found in the samples, and only a change in colour was reported (Adamcová and Vaverková, 2014). This observation is likely to be because the degradation of plastics is a long process and requires years to occur. Table 2.1 shows some degradation characteristics of most common plastics types.

Table 2.1 Degradation processes and degradation products for common plastics (adapted from Gewert et al., 2015; Venkatachalam, 2012).

Plastic type		**Chemical composition and repeating monomer**		**Typical degradation processes**	**Products from degradation**
PE	Polyethylene	Carbon-backbone Saturated bonds Chain of ethylene monomer	$–CH_2–CH_2–$	Inclined to photo-initiated oxidative degradation in aerobic condition.	Aliphatic carboxylic acids alcohols, aldehydes, and ketones
PVC	Polyvinyl chloride	Carbon-backbone Saturated bonds Heteroatoms - Cl	 $–CH_2–\overset{\overset{\displaystyle Cl}{\vert}}{CH}–$	Highly sensitive to photo-initiated oxidative degradation in aerobic condition. In aerobic condition, the presence of HCl and low molecular weight enhances the photo-initiated dechlorination rate. Dechlorination proceeds as an autocatalytic reaction after carboxylic end groups formation. Resistant to biodegradation. Semi-volatile organotin compounds are used as stabilisers.	Conjugated double bonds in a polyene polymer and hydrochloric acid

PP	Polypropylene	Carbon-backbone Saturated bonds Methyl groups bonded to the backbone carbons	 $-CH_2-\overset{CH_3}{\overset{\vert}{CH}}-$	Tending to photo-initiated oxidative degradation in aerobic condition. Tertiary carbon which is more susceptible to abiotic degradation and less to biodegradation.	Pentanes such as 2-methyl-1-pentene and 2,4-dimethyl-1-heptene
PS	Polystyrene	Carbon-backbone Benzene ring bonded to the backbone carbons		Sensitive to photo-initiated oxidative degradation in aerobic condition. Predominant end-chain scission. Most durable thermoplastic polymer towards biodegradation.	Ketones and olefins oligomers of styrene, such as dimer and trimer, benzene, ethylbenzene, a-methylstyrene, phenol, benzyl alcohol, benzaldehyde, ketones (acetophenone) and benzoic acid
PET or PETE	Polyethylene terephthalate	Heteroatoms – O		Inclined to photodegradation, photooxidative degradation, hydrolytic degradation and thermooxidative degradation in aerobic condition. Hydrolysis reaction proceeds as autocatalytic after carboxylic end groups formation.	Acetaldehyde, ethylene, benzene, biphenyl

	Resistant to biodegradation.

Plastic degradation affects the material physical properties leading to visible changes, such as discolouration and brittleness, and chemical changes, such as bond scissions and new functional groups formation (Pospisil and Nespurek, 1997; Shah et al., 2008). Microorganisms tend to attack the amorphous polymer structure while the crystalline component, characterised by slower degradation, is separated from the material structure (Shah et al., 2008). Moreover, the degradation of plastics releases pollutants into the air and leachate, such as benzene, toluene, xylenes, ethylbenzenes, trimethyl benzenes, bisphenol A (BPA) and nonylphenols (NP) (Teuten et al., 2009; Tsuchida et al., 2011; Urase et al., 2008; Webb et al., 2013; Xu et al., 2011). Further to this, several factors can influence plastic degradation in landfills such as presence of oxygen, leachate, corrosive chemicals, relatively elevated temperature, and acidic pH. Hydrogen sulphide (H_2S) is one of the chemicals that can cause corrosion of plastics (Table 2.2). H_2S formation occurs in landfills when sulphate-reducing bacteria (SRB) convert sulphate (SO_4^{2-}) to sulphite (SO_3^{2-}), and this into sulphide (S^{2-}) and H_2S at low pH (Ko et al, 2015; Tsuchida et al., 2011). Different types of waste have an opposite effect on H_2S production. Co-disposed landfill waste can influence H_2S production changing the pH in the landfill; for example, concrete increases the pH whereas wood waste decreases the pH under the optimum SRB pH range (Yang et al., 2006). New waste has a greater influence on the increase in the level of H_2S than aged waste due to the decrease of sulphur compounds with time (Ko et al, 2015). Tsuchida et al. (2011) remarked the use of some organic plastic additives such as phenols and organic phosphates as electron donors by SRB for H_2S production in inert waste landfills. In addition, SRB uses gypsum drywall, organic waste and sludge of wastewater treatment plants as a sulphur source in landfills in anaerobic condition (Ko et al, 2015). The activity of SRB is also affected by the presence of nitrate and ferric compounds which increase the propagation of nitrate and iron-reducing bacteria respectively (Eckford and Fedorak, 2002; Lovley, 1991).

Table 2.2 Plastic corrosion behaviour in the presence of H_2S (Pruett, 2000, Pruett, 1994, Schweitzer, 1995 cited in CCOHS, 2012).

Corrosion	No corrosion
Acetal	Chlorinated polyvinyl chloride (CPVC)
Nylon	Teflon
Polyurethane	Kynar (PVDF)
Viton A	Polyethylene
Hard rubber	Polypropylene
Chlorinated polyethylene	Polystyrene
Natural rubber	Polyvinyl chloride (PVC)
Soft rubber	Ethylene propylene
Isoprene	Ethylene propylene diene
Nitrile Buna-N (NBR)	Chloroprene
Styrene-butadiene (SBR)	Butyl rubber (isobutylene-isoprene)
Polyacrylate	Hypalon (chloro-sulfonyl-polyethylene (CSM))
Polyurethane	Neoprene
Silicone VMQ	Ethylene vinyl acetate

Plastic contains a variety of additives which during degradation can leach in the environment increasing the risk of pollution (Beißmann et al., 2013; Prudent et al, 1996; Quaghebeur et al., 2013; Teuten et al., 2009). Parameters such as the polymer pore size, the size and type of additive and temperature, influence the release mechanisms of additives from polymers in landfills (Teuten et al., 2009). Furthermore, leachates can exhibit different characteristics, such as pH and ionic strength, which result in different additive extraction potentials (Xu et al., 2011; Teuten et al., 2009). Additives are typically used to enhance the processing and the properties of plastic. Generally, additives with short alkyl chains tend to be more readily released in the leachate than those with longer alkyl chains (Teuten et al., 2009). Phthalates (alkyl/aryl esters of 1, 2-benzenedicarboxylic acid) are commonly used as plasticisers in PVC (Hahladakis et al. 2018). It has been reported that plasticisers with high solubility such as dimethyl phthalate (DMP) are released in landfills in greater amounts than hydrophobic plasticisers such as diethyl-hexyl phthalate (DEHP) (Teuten et al., 2009). Migration of plasticiser decreases when the polymer reaches its glass transition state (Ejlertsson et al. 2003). Alkylphenols are additives with plasticising and stabilising properties (Hahladakis et al. 2018; Teuten et al., 2009). Organotin compounds are highly used in rigid PVC as stabilisers and can be toxic to humans (Folarin and Sadiku, 2011). The release of phthalate esters and organotin compounds occurs in the neutral leachate of the methanogenic phase (Bauer and Herrmann 1998; Björn et al., 2007). BPA, which is used in building blocks of polycarbonate plastics, PVC and printer ink, has been reported to be released from the polymer in the acidogenic phase (Asakura et al., 2004). Different plastic types such as polycarbonates and epoxy resins can release BPA in the leachates, and for this reason, a larger quantity of plastic waste can lead to a major dispersion of this pollutant in the environment (Xu et al., 2011; Teuten et al., 2009). Leachate characteristics are variable (Table 2.3) along with its potential to degrade plastics and their additives (Teuten et al., 2009). Thus, the leachate from anaerobic landfills tends to be more acidic than that from semi-aerated landfills, due to the high amount of putrescible organic during the anaerobic degradation of MSW, and a higher concentration of BOD, COD and ammonia (Cossu et al., 2003). During the acetogenic phase, the leachate presents low pH level and high ionic strength which inhibit the release of plasticisers (Bauer and Herrmann, 1998). Some example of leachate chemicals which can affect plastics are given in Table 2.4. On the other hand, plastics have also a fundamental role as a sorbent organic matter for hydrophobic organic contaminants (HOCs) (Saquing et al., 2010). For this reason, plastics from landfill are likely to carry HOCs for instance toluene. Glassy or hard plastics which have high glass-transition temperature such as PVC (T_g 87 °C), are characterised by slower desorption of HOCs than rubbery or soft polymers such as PE (T_g -78 °C) (Saquing et al., 2010; ASM International, 2003; Yang et al., 2016).

Table 2.3 General characteristics of leachate at different age (adapted from Bhalla et al., 2012).

Parameter	Young	Intermediate	Old
Age (years)	<5	5-10	>10
pH	6.5	6.5-7.5	>7.5
COD (mg/l)	>10,000	4,000-10,000	<4,000
BOD_5/COD	>0.3	0.1-0.3	<0.1
Organic compounds	80 % volatile fat acids (VFA)	5-30 % VFA + humic and fluvic acids	Humic and fluvic acids
Heavy metals	Low-medium	Low	Low
Biodegradability	Important	Medium	Low

Table 2.4 Leachate chemicals and related plastics affected (adapted from El-Fadel et al., 2002; Ted Pella Inc., 2017).

Parameter	Concentration range (mg/l) in the leachate	Plastics affected
Benzene	0.1-0.6	LDPE, HDPE, PP, PS, PC
Ethylbenzene	0-4.9	LDPE, HDPE, PP, PS, PC
Phenol	0.17-6.6	LDPE, PS, PC
Toluene	0-3.2	LDPE, HDPE, PP, PS, PC

2.3 Landfill mining projects for recovering plastic waste

Although ~700 landfill mining projects have been carried out, project setup and parameters included are not always fully detailed making difficult to compare the results of different studies (Krook et al., 2012). Tielemans and Laevers (2010) investigated the “Closing the circle” project for the landfill site of Group Machiels in Belgium, studying the material distribution and energy valorization. The samples comprise of MSW waste and IW waste excavated from REMO landfill. The thermal valorisation was based on the process of RDF from the excavated waste through a Gasplasma^{TM} system. The excavated waste was classified in three fractions based on particle size, fine fraction <4 mm, fraction between 4-10 mm and fraction >10 mm. The fraction <10 mm, which comprises of fraction 4-10 mm and fraction <4 mm, represented the highest percentage, between 44±12 wt% for MSW and 64±16 wt% for IW (Tielemans and Laevers, 2010). Plastics suitable for material valorisation were detected in all the fractions >4 mm (Tielemans and Laevers, 2010). Gasplasma^{TM} was identified as an appropriate technology for landfill waste to energy valorisation using RDF as feedstock (Tielemans and Laevers, 2010). Quaghebeur et al. (2013) characterised the excavated waste for REMO landfill in Belgium, which maximum storage time was between 9-29 years. Chemical characteristics of the excavated plastic following years of storage are summarised in Table 2.5. The waste was manually sorted and not washed, for this reason plastic analyses were influenced by impurities such as soil particles (Quaghebeur et al., 2013). Plastic from IW presented a higher amount of metals than plastic from MSW (Table 2.5) (Quaghebeur et al., 2013). TOC of plastic from IW and MSW was similar, and plastic degradation was found to not have a significant effect on calorific value (Quaghebeur et al., 2013). The authors concluded that the thermochemical processing of recovered plastics to produce energy is a feasible alternative to recycling because they present a good level of calorific value (18-28 MJ/kg), and cannot produce high-quality recycled material due to high level of contamination (Quaghebeur et al., 2013). Zhou et al. (2014) analysed excavated plastics from Yingchun MSW landfill in China, which had maximum storage of 24 years (Table 2.5 and Table 2.6). The amount of plastics was larger in the layers between 1997 and 2004 than that from the period from 1989 to 1996. The total plastic samples were divided in white ‘PE bag’ (11.3 wt%), ‘coloured PE bag’ (29.8 wt%), ‘other plastic bag’ (28.0 wt%) and ‘other mixed plastics’ (30.9 wt%) (Zhou et al., 2014). The presence of soil and sand impurities in plastics were high (71.0 ± 6.3 wt%), especially in the older plastics stored for longer periods (Zhou et al., 2014). The major pressure present in the deepest layers could be a reason for resistance of impurities, embedded in plastics, even after washing them (Zhou et al., 2014). The calorific value is not affected by the years of storage (Quaghebeur et al., 2013; Zhou et al., 2014). According to Zhou et al. (2014) and Quaghebeur et al. (2013) alteration of ultimate analysis results, such as higher level of oxygen, silicon and aluminium content in excavated plastics compared to fresh plastic waste (this term refers to plastic waste that has not been in landfill), is probably related to the presence of impurities, such as soil and sand particles, which major constituents are SiO_2, Al_2O_3, oxynitride etc. The recycling potential of excavated plastics from the Nonthaburi dumpsite in Thailand has been analysed in two different studies (Prechthai et al., 2008; Chiemchaisri et al., 2010). The use of different technologies used for the separation of the waste influences the fraction size and the consequence material valorisation. The sorting methodology of Prechthai et al. (2008) and Tielemans and Laevers, (2010) led to the identification of different fine materials size <25 mm and <4 mm respectively. Indeed, the former used a pilot scale rotary trommel screen with size 25mm and 50 mm, while the latter used a combination of drum screen, screen, wind shifter, washer and dense medium barrel. Both did not characterize the fine fraction in waste streams, but the utilization of different technologies allowed Tielemans and Laevers, (2010) to identify potential upcycling of materials in the fraction between 4 mm and 25 mm which was directed to be recycled as compost in Prechthai et al. (2008) study. In Prechthai et al. (2008) study the excavated MSW (Table 2.6) samples were stored 3-5 years and were divided in particle size ranges <25 mm, between 25-50 mm and >50 mm. 90 wt% of the plastic was recovered from the coarse fraction (>50 mm) and 10 wt% from the medium particles fraction (25-50 mm) (Prechthai et al., 2008). In Chiemchaisri et al. (2010) recovered plastics were taken as well from Nonthaburi dumpsite in Thailand and the maximum storage time was 10 years (Table 2.6). They divided the excavated plastics into ‘carry bags’, ‘other bags’ and ‘other plastic’. Excavated plastics were found in both studies to have the potential to be recycled as RDF after further processing (Prechthai et al., 2008). Wolfsberger et al. (2015) chemically analysed the plastic fraction found in two different landfills in Austria. The maximum storage age was 20 and 30 for landfill site 1 (LF1) and landfill site 2 (LF2) respectively. The plastic fraction from LF2 showed a higher level of lead, cadmium, chromium, cobalt and mercury. The reason was attributed to the fact that the waste disposed of in LF2 was pre-treated in the MBT before disposal and was not related to longer storage time.

Bhatnagar et al. (2017) assessed the value of waste material excavated from the municipal landfill of Kudjape in Estonia, between 2012 and 2013. The analysed waste was stored for 4-8 years. The plastic waste fraction was comprised of different types of plastics and textile because it was not possible to distinguish synthetic textile from natural textile. The recovered PE represented the highest profit between all the excavated plastics. The authors stated that soft plastic (e.g. PE), which represented 20 wt% of the excavated materials, has potential for an income with a hypothetical market value of 35 €/t (Ventosa et al., 2014). Furthermore, SRF was considered as the most marketable materials after applying a pre-treatment to reduce the moisture content.

Table 2.5 Chemical characteristics of excavated plastics according to years of storage.

	Unit	**Plastic (MSW) from REMO landfill**[a]				**Plastic (IW) from REMO landfill**[a]		**Plastic (MSW) Yingchun landfill**[b]			
Years of storage	Year	24-29	19-23	14-18	9-13	19-24	9-14	21-24	17-20	13-16	9-12
Volatiles	wt%							86.31 (3.23)	87.44 (0.52)	87.50 (0.48)	87.09 (1.09)
Ash	wt%	25 (2)	32	38	20	23	35(2)	12.50 (0.93)	10.76 (0.48)	10.39 (0.26)	9.70 (0.75)
Total carbon	wt%	50 (2)	44	41	59	57	39 (7)				
TOC	wt%	57 (4)	51	53	67	58	37 (16)				
Fixed carbon	wt%							1.19 (2.36)	1.79 (0.76)	2.10 (0.40)	3.21 (1.84)
NCV	MJ/kg	24 (3)	21	18	27	26	21 (4)				
GCV	MJ/kg	25 (3)	23	19	28	28	22.1 (4)	41.29 (2.26)	42.79 (3.10)	43.91 (2.17)	44.75 (1.18)

H	wt%	6.7 (1)	7	6.0	8.1	6.9	5.4 (0.2)
N	wt%	0.7	1	0.59	0.2	0.7	0.75 (0.5)
S	wt%	0.2	0	0.27	0.2	0.47	0.42 (0.01)
Cl	wt%	7.3 (3)	0	1.8	5.5	3.9	1.6 (1)
F	wt%	0.01	0	0.006	0.0	0.056	0.061 (0.03)
Br	wt%	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Si	g/kg	68	110	100	41	72	74
Ca	g/kg	13	20	15	7.8	26	17.5
Fe	g/kg	18	26	13	10	23	38
As	mg/kg	33	6.9	6.2	7.6	9.9	12
Ba	mg/kg	430	540	600	110	2300	3600
Cd	mg/kg	51	18	19	18	47	41

Cr	mg/kg	490	320	280	270	780	530
Cu	mg/kg	1767	150	690	270	10,000	2405
Hg	mg/kg	0.6	0.36	0.46	0.1	2.0	1.1
Ni	mg/kg	327	86	73	740	640	275
Pb	mg/kg	550	280	230	160	1300	1900
Zn	mg/kg	1063	620	1700	470	5500	3800

[a] Quaghebeur et al., 2013
[b] Zhou et al., 2014
NCV: Net calorific value
GCV: Gross calorific value
(SD): Standard deviation

Table 2.6 Chemical characteristics of excavated plastics.

	Unit	**RDF processed from landfill waste** [a]	**White PE plastic bags**[b]	**Plastic from Nonthaburi dumpsite**[c]	**Carry bags Nonthaburi dumpsite**[d]	**Other bags Nonthaburi dumpsite**[d]	**Other plastic Nonthaburi dumpsite**[d]
Moisture content	wt%	14.4			3.46 (2.24)	1.49 (1.12)	0.85 (0.38)
Volatiles	wt%	80.4			72.99 (10.56)	83.48 (5.96)	91.77 (6.44)
Ash	wt%	27.1			27.01 (10.56)	16.54 (6.23)	8.23 (7.84)
NCV	MJ/kg	22.0					
GCV	MJ/kg				40.99 (1.19)	39.33 (3.36)	33.38 (3.35)
C	wt%	54.9	87.95 (1.23)				
H	wt%	7.38					
O	wt%		7.95 (0.71)				
N	wt%	2.03	1.04 (1.05)				
S	wt%	0.36	0.29 (0.07)		0.21 (0.04)	0.05 (0.04)	0.04 (0.01)
Cl	wt%		0.208-0.312[x]		2.51 (0.70)	1.23 (0.84)	3.95 (2.75)
Si	wt%		0.59 (0.07)				

Al	wt%	0.44 (0.07)	
Mn	mg/kg		107.2
Cr	mg/kg		43.4
Cd	mg/kg		1.6
Pb	mg/kg		42.5
Ni	mg/kg		21.1
Zn	mg/kg		313.3
Cu	mg/kg		150.5

[a] Bosmans et al., 2013
[b] Zhou et al. 2014
[c] Prechthai et al., 2008
[d] Chiemchaisri et al., 2010
[x] Range
NCV: Net calorific value
GCV: Gross calorific value
(SD): Standard deviation

2.4 Applicability and limitation of the current recycling technologies for energy recovery from excavated plastics

Fresh plastic waste is recovered in different ways, which can be summarised as reuse (primary), mechanical recycling (secondary), chemical or feedstock recycling (tertiary) and energy recovery (quaternary) (Al-Salem et al., 2009; Datta and Kopczyńska, 2016). Primary recycling involves the re-extrusion of semi-clean plastic scrap to produce similar material (Al-Salem et al., 2009). In the secondary or mechanical recycling, the plastic waste preferably characterised by single-polymer is processed by mechanical means to produce new products, for example the production of polyester fibres from PET bottles (Al-Salem et al., 2009). Tertiary recycling, or chemical and thermochemical recycling, involves the production of feedstock from plastic waste to be used as fuel or for the synthesis of petrochemicals and plastics (Al-Salem et al., 2009; Mastellone, 1999). Quaternary recycling, or energy recovery, involves the production of heat, steam and electricity from thermochemical processes, such as incineration (European Parliament. Council of the European Union, 2008; Korai et al., 2016). Both fresh plastic waste and excavated plastics need to meet certain requirements concerning the presence of chemical elements to be applicable for the recycling process (Johansson et al., 2017). REACH (European Parliament, 2009) established a series of restrictions on dangerous substances. For example, Cd limit in plastic products is 0.01 wt%, phthalates, used in plastics additives such as benzyl butyl phthalate, dibutyl phthalate, diisononyl phthalate and diisodecyl phthalate, must not exceed 0.1 wt% if the plastic is going to be used in toys and childcare articles (European Parliament, 2009). As it is summarised in Table 2.5, excavated plastics may content Cd and other heavy metals in concentrations that exceed the 0.01 wt% limit. This high level of impurities makes the reuse of excavated plastics more challenging than the reuse of fresh plastic waste, and creates uncertainties on the profitability of the products which should be conformed to industry standards (Bosmans et al., 2014; Breyer et al., 2017; Zhou et al., 2014).

2.4.1 Sorting

Sorting of plastics is an important step to enhance plastic recovery and recycling, and changes depending on the nature of feedstock, recycling method applied, and product required. Common sorting techniques of plastic waste are summarised in Table 2.7.

Table 2.7 Sorting techniques for plastic waste.

Sorting type	Comment	Reference
Manual sorting by operators	Used for large size plastic	Wienaah et al., 2007
	Labour intensive	Ruj et al., 2015
	Relative low cost, only if wages are low in the countries	
	Subjected to human error	
NIR (near infrared)	Effective sorting	Masoumi et al., 2012
	Fast identification	Ruj et al., 2015
	Difficult to detect dark plastic	Vrancken et al., 2017
X-Ray fluorescence		Masoumi et al., 2012
	Effective identification of PVC	Ruj et al., 2015
	Influenced by level of impurities and degradation	
Air sorting	Separates plastic based on its weight	VERC, 2001
Electrostatic	Separates plastic based on electrostatic charge difference	Ruj et al., 2015
	Able to separate polymers with similar density	
Sorting by melting	Based on differences in melting temperature	Ruj et al., 2015
	Only two resin types can be separated at the same time	

Sink-float sorting	Based on density difference Slow Difficult to control Presence of impurities can influence the separation Low grade of separation Separation of PET and PVC	Ruj et al., 2015 Zhou et al. 2014
Hydrocyclons	Based on density difference Presence of impurities can influence the separation Grade of purities depend on particle size (best <6 mm nominal size) and shape homogeneity	Ruj et al., 2015

Excavated waste can be separated into different sizes and streams using a series of processes such as screening, air separation, metal separation and wet separation (Vrancken et al., 2017). The different types of plastic waste can be further divided with sorting methods such as hydrophobicity method and optical technologies (Vrancken et al., 2017). The impurities present in the excavated plastics can modify their properties and thus interfere with the sorting process, especially with technique sensor based, such as NIR (near infrared). In addition, separation based on density differences will be difficult for excavated plastics as the presence of impurities can change their density (Zhou et al., 2014). Other techniques can be employed in the sorting excavated plastics, such as triboelectric separation, speed accelerator, X-ray fluorescence (XRF) spectroscopy but further research is needed to assess their applicability on excavated plastics (Al-Salem et al., 2009).

2.4.2 Mechanical recycling

Mechanical recycling of plastic waste involves a series of processes including pre-treatment: cutting/shredding, contaminant separation, sorting, milling, washing and drying, agglutination, extrusion and pelletization, and quenching (Al-Salem et al., 2009; Aznar et al, 2006; SubsTech, 2013). Prior to secondary recycling, the plastics need to be sorted and washed (Al-Salem et al., 2009). As in the case of fresh plastic waste, mechanically-treated excavated plastics can be used as construction materials. For example, different types of plastics such as PET, PC, PVC and PE could be mixed with concrete, improving their ductility and reducing the risk of concrete cracking (Saikia and de Brito, 2012; Sharma and Bansal, 2016). Nevertheless, they need to meet the limit criteria for leaching and exposure (Johansson et al., 2017), and the typical pollutants present in plastic waste, such as lead, cadmium, chromium and BPA, represent a leaching risk (Saikia and de Brito, 2012). Mechanical recycling of excavated plastics faces three main problems which are the uncertainties of chemical and physical condition of excavated plastics, regulatory framework and marketability. In fact, the variations on factors such as age and the environmental condition during storage do not allow to assume that sufficient cleaning of the treated waste can be always obtained. Furthermore, there are not univocal regulations, but they change in different countries. Moreover, for the moment there are no incentives to buy excavated material due to uncertainties in material quality and high cost derivate also from the treatment process which is needed to eliminate the impurities from the products.

2.4.3 Energy recovery via incineration

Plastic has a high calorific value that makes it feasible to be used as an energy source through incineration (Al-Salem et al., 2009). Nevertheless, incineration of synthetic polymers such as PVC, PET, PS and PE, leads to the production of air pollutants such as CO_2, NO_x, SO_x, volatile organic compounds (VOCs), particulate-bound heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs) and dioxins (Al-Salem et al., 2009). Therefore, high-performance cleaning units are required in-situ or downstream of the furnace to clean the flue gases at the required levels. Various technologies are applied, such as ammonia addition to the combustion chamber, flue gas cooling, acid neutralisation, activated carbon addition and filtration (Al-Salem et al., 2009; Yassin et al., 2005). Plastics excavated from landfill, along with other combustibles, will contain impurities (Zhou et al., 2014) and elevated levels of heavy metals (Rotheut and Quicker, 2017) (Table 2.5 and Table 2.6) due to contact with soil-like fines and leachate exposure respectively. Therefore, the use of excavated landfill materials as RDF requires consideration of the increased emissions and utilisation of pre-treatment. Although Rotheut and Quicker (2017) concluded that conventional flue gas systems can cope with the increased emissions, technical performance of the existing cleaning strategies needs to be properly addressed. Consideration of the management of air pollution control residues (APCr) is also needed. Thus, the extra cost for the already expensive management of these hazardous residues due to the use of RDF from landfill and the impact on the gate fees associated with such RDF must be assessed.

2.4.4 Chemical and thermochemical recycling

Tertiary recycling covers a series of chemical and thermochemical technologies which yield products that can be used as fuels or feedstock for synthesis of chemicals and new plastics (see Figure 2.2). During chemical recycling, the polymer chains are broken with the aid of decomposition agents such as diols, alcohols, and amines, at a relatively low temperature around 200 °C (Zia et al., 2007). On the other hand, the thermochemical recycling uses higher temperatures (300-1,000 °C) and reacting atmospheres such as H_2, H_2O or stoichiometric content of O_2 to produce monomers, fuels and industrial chemical precursors (Datta and Kopczyńska, 2016).

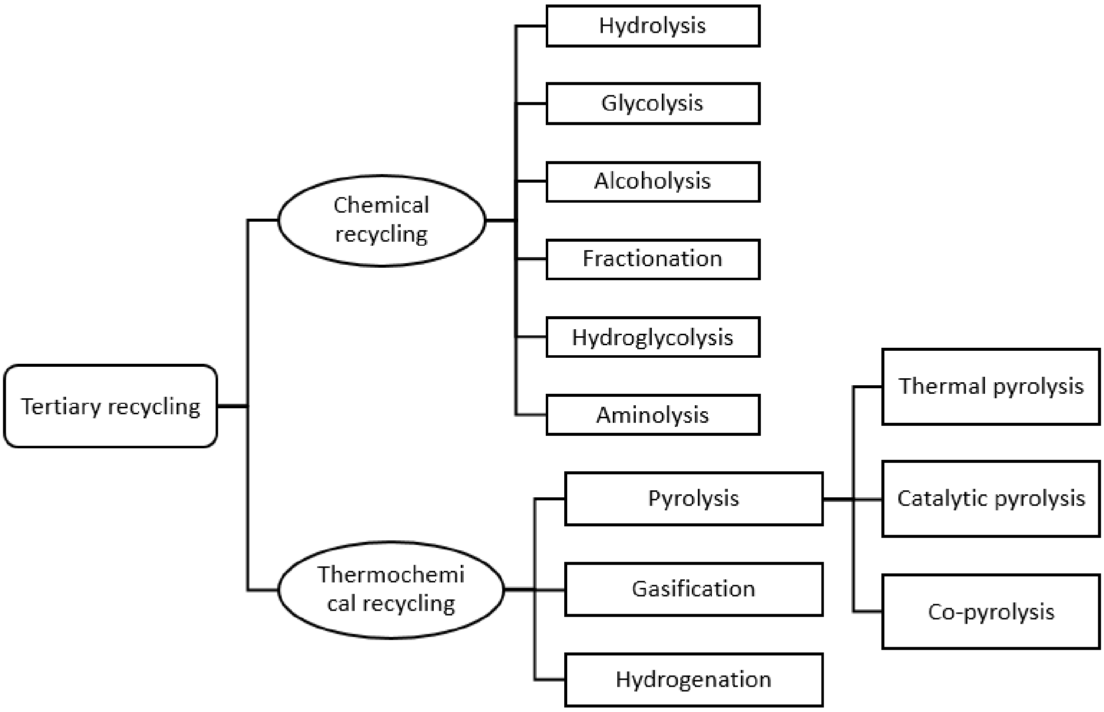


Figure 2.2 Tertiary recycling techniques (adapted from Zia et al., 2007; Al-Salem et al., 2009).

Zhou et al. (2014) concluded that incineration and RDF production was the most convenient treatment for excavated plastics based on input requirements, which in the case of pyrolysis were identified as particle size between 1-20 mm, moisture <0.5 wt% and ash <2 wt%. However, pyrolysis produces syngas and usable solid residue, with less NO_x and SO_x emissions than incineration (Younan et al., 2016). In addition, the capital costs for pyrolysis gas treatment is less expensive than the incineration gas treatment because it has a smaller volume (Bosmans et al., 2013). Datta and Kopczyńska (2016) recognised pyrolysis as an adequate technology to recover high yield of monomers from fresh plastic waste especially PS, PMMA and PTFE, when comparing tertiary recycling processes such as pyrolysis, catalytic cracking, hydrogenation and gasification. Bosmans et al. (2014) analysed the pyrolysis kinetics for excavated waste to identify the optimum parameters to maximise the product yield. They used a mixture of RDF obtained from excavated MSW and IW, with 29 and 24 years of maximum storage respectively. The results showed that the 'less stable plastics' (E = 99 kJ/mol) had lower activation energy than fresh waste, which may be related to changes of the excavated waste properties compared to fresh waste in composition, and the catalytic effect of impurities such as metals (Bosmans et al., 2014). Breyer et al. (2017) used excavated plastics from Mont-Saint-Guilbert landfill in Belgium in co-pyrolysis with lubrication oils. Most plastics were categorised as LDPE (85 wt%) while the rest (15 wt%) included PE, PP, PS and PET (Breyer et al., 2017). The plastics presented a variety of contaminants such as wood, textile, fines and metals. The degradation temperature increased with the mixture of plastics and oil, by maximum 20 °C, compared to the decomposition process of individual material (Breyer et al., 2017). The authors concluded that the co-pyrolysis of excavated plastics with oil was feasible even from an energy point of view; indeed, the combustion of the produced pyrolysis liquid yielded greater energy than that consumed during its production process (Breyer et al., 2017). Santaweesuk and Janyalertadun (2017) studied the production of fuel oil by slow thermal pyrolysis of excavated plastics (PP, LDPE, HDPE and mixed plastics) from the Warinchamrap municipal landfill, Thailand. The parameters used were temperature between 350 and 450 °C, atmospheric pressure, and retention time 4-6 hours. The gas was condensed at 25-30 °C. The yields of liquid fuel were 80 wt%, 73 wt%, 70 wt% and 46 wt% for PP, LDPE, HDPE and mixed plastics respectively. The pyrolysis liquid fuel was then distilled, and it was found to be a mixture of heavy naphtha (C_7-C_{10}), gasoline (C_8-C_{10}) and light gas oil (C_{10}-C_{20}). Higher operating temperature was found to increase the liquid and gas products. The authors concluded that quantity and quality of the produced pyrolysis liquid fuel are influenced by the plastics type. The pyrolysis of plastic waste has been largely studied (Anuar Sharuddin et al., 2016) compared with the pyrolysis of excavated plastics, which can benefit from the findings of the former. The properties of pyrolysis oil from plastic waste and excavated waste are similar to petroleum diesel oil (Miandad et al., 2016; Santaweesuk and Janyalertadun, 2017). In most of the studies on pyrolysis of plastic waste the heating rate was between 10 and 25 °C/min (Anuar Sharuddin et al., 2016). Various sweep gases have been used in pyrolysis of plastics; nitrogen is the most common one due to its relatively low reactivity, but also helium, argon, ethylene, propylene and hydrogen (Anuar Sharuddin et al., 2016). Typical reactors used for pyrolysis of plastics are fluidized bed reactors, batch reactors and screw kiln reactors (Kumar et al., 2011). Each type of reactor allows a different heating rate which affects the final product distribution. Thus, fluidized bed reactors allow a rapid heating and more uniform heat distribution within the unit (Kunwar et al., 2016), and are preferred for enhancing the production of the liquid fraction via fast pyrolysis. However, fluidization reactors require higher maintenance and capital cost compared to fixed bed reactors (Chen et al., 2015). Table 2.8 summarises the pyrolysis types according to the heating rate, final temperature and residence time employed. As explained above, pyrolysis product distribution depends on the temperature used during processing. In the case of plastics, temperatures >500 °C lead to more gas formation, while liquid yield is major at a lower temperature around 450 °C (Anuar Sharuddin et al., 2016; Miandad et al., 2017). Singh and Ruj (2016) stated that at higher heating rate the degradation is partially prevented due to shorter residence time of the volatile products at high temperature. Residence time is therefore particularly important, mainly when the process runs at temperatures <450 °C; at higher temperatures, its effect is less evident (Anuar Sharuddin et al., 2016). General problems related to the properties of plastic waste, such as the sticky behaviour of fused plastics, may compromise the reactor performance during pyrolysis (Lopez et al., 2017). Fast pyrolysis is normally the most appropriate operating mode to avoid this issue due to its high heat transfer rate (Lopez et al., 2017).

Table 2.8 Pyrolysis process categories (adapted from Bosmans et al., 2013).

Category	Characteristics	Main Product Fraction
Slow	Resident time 5-30 min Low heating rate (<1 °C/s) Maximum temperature 600 °C	Char Pyrolysis oil Gas
Fast	Resident time 0.5-5 s High heating rate (1-200 °C/s) Maximum temperature 650 °C	Pyrolysis oil

Flash	Resident time <1 s High heating rate (>1,000 °C/s) Maximum temperature >650 °C	Pyrolysis oil Gas

Pyrolysis of fresh plastic waste has been largely studied especially using thermogravimetric analyser (TGA) and laboratory scale reactors (Wong et al., 2016). Kunwar et al. (2016) studied the kinetics of pyrolysis of plastics using TGA. The activation energy was found to necessarily change according to the different number and type of bonds; for example, C–C has lower dissociation energy than C–H and C=C, i.e. 347, 414 and 611 kJ/mole respectively (Brydson, 1999; Kunwar et al., 2016). Sørum et al. (2001) used differential thermogravimetric (DTG) curves to identify the temperatures of the maximum degree of weight loss for PS, PP and LDPE, being 413, 456 and 472 °C respectively. Discrepancy of results obtained on the activation energy and degradation temperature values may be present in different studies due to the diverse methods of calculation and parameters used (Grammelis et al., 2009; Sørum et al., 2001). Grammelis et al. (2009) examined the thermal stability of some thermoplastics, classifying them from the most stable, that decomposes at high temperature, to the less stable: PC (maximum rate 510 °C) > HDPE (maximum rate 495 °C) > LDPE (maximum rate 495 °C) > PP (maximum rate ~460 °C) > PA (maximum rate ~455 °C) > PS (maximum rate ~450 °C) > PVC (maximum rate 320 °C and 470 °C). Furthermore, they identified the order of activation energy, i.e. the energy required to start the pyrolysis, as follow: E_{HDPE} (445.2 kJ/mol) > E_{LDPE} (437.1 kJ/mol) > E_{PS} (414.9 kJ/mol) > E_{PP} (373.4 kJ/mol) > E_{PC} (340.7 kJ/mol) > E_{PA} (256.6 kJ/mol) (Grammelis et al., 2009). Singh and Ruj (2016) studied the pyrolysis kinetics of fresh plastic waste through TGA analysis and found that individual fresh plastic waste type and a simulated mixture of them degrade between 350 and 520 °C while the mixed fresh plastic waste starts to degrade at lower temperature 300–550 °C. No explanation for the decrease in degradation temperature was provided by the authors. Caballero et al. (2016) studied the pyrolysis of plastic waste from landline and mobile phones, which comprises mostly of acrylonitrile–butadiene–styrene copolymer (ABS) and polycarbonate (PC). Aromatics were present in a very high percentage (>90 % area of GC-MS spectra) in the liquid product, likely due to the catalytic effect of metals such as Fe, Co, Ni, Zn, etc. (Caballero et al., 2016). Most of the Cl and Br contained in the plastic waste was transferred to the pyrolysis gas as HCl and HBr, which are corrosive and need to be removed before further gas utilisation (Caballero et al., 2016). The authors concluded that valuable chemicals can be extracted from the pyrolysis liquid of plastic waste such as styrene, toluene, ethyl-benzene and α-methylstyrene (Caballero et al., 2016). Catalytic pyrolysis is a possible modification to improve the quality of the product fractions in-situ and eliminate some pollutants. Some of the most common catalysts used in catalytic pyrolysis of plastic waste include NZ, ZSM-5, and HZSM-5 zeolites, fluid catalytic cracking (FCC) catalyst, Al_2O_3, and Red Mud (Miandad et al., 2016). Although catalytic pyrolysis can improve the product quality and reduce the required temperature, it has disadvantages such as high cost of catalysts and the limited possibility of catalysts reuse (Miandad et al., 2016). Studies have shown that some plastics are better feedstocks for pyrolysis processes. Among the most common plastic waste, PS and PP have appropriate properties to be processed through pyrolysis, such as lower thermal degradation temperature compared to other plastics and good fuel properties (Miandad et al., 2016). On the other hand, PVC and PET are considered not suitable for pyrolysis. PVC yields a high level of chlorine into the pyrolysis products. PET gives rise to low liquid yields with a high level of benzoic acid in composition (Anuar Sharuddin et al., 2016; Miandad et al., 2016). PE tends to convert into wax instead of oil due to its long chain structures, although the utilisation of relatively higher temperature (>500 °C) or catalysis can favour the wax cracking (Anuar Sharuddin et al., 2016; Miandad et al., 2016). In general, plastics with high volatile matter and low ash content are preferred to produce pyrolysis liquid (Abnisa and Wan Daud, 2014). The ash content in the excavated plastics has been found generally higher than that in fresh plastic waste, which may decrease the liquid yield (Zhou et al., 2014). Therefore, their use as pyrolysis feedstock requires comprehensive assessment.

2.5 Discussion on current trends and future developments

While excavated plastics from landfills present a great opportunity of resource recovery, presence of impurities and contamination with trace heavy metals or corrosive compounds (see Table 2.5 and Table 2.6) hampered their use in conventional energy recovery processes. Further to this, the heterogeneity of the plastic components found in landfill sites means that different environments characterised by the structure of the landfill or dumpsite, the climate in the area and type of waste collected can influence the chemical and physical changes of the plastic waste in landfill. Mechanical recycling of excavated waste can be a valuable recycling route if the degree of degradation is low and the sorting step allows the separation of different plastic types. These aspects significantly affect the quality of the products, therefore, their marketability. Assessing a time limit to plastic storage in landfill can increase the feasibility of this route. It is also important to consider that the excavated plastics derive from plastics potentially produced decades ago and under less restrictive legislation on plastics production, which differs from the current requirements, such as the new restrictions introduced with REACH in 2009. Incineration of excavated waste for energy recovery requires less pre-treatment and preparation than other processes such as pyrolysis (Zhou et al., 2014). However, the emissions released, with a feedstock in the form of RDF, have been reported as being higher than the emissions from non-landfilled wastes. Whilst these elevated emissions are not expected to cause problems for current flue gas cleaning technologies, this requires further consideration due to the impacts on air pollution control residues. Important barriers for incineration of excavated plastics are the ash content, which has been found to be higher than 20 % in different samples analysed, and the chlorine content, which should be less than 1.5 % (Johansson et al., 2017). Effective sorting and separation of PVC can reduce the level of chlorine. Upcycling of excavated plastics through pyrolysis has been highlighted as an alternative option to conventional recycling or combustion. This process requires a series of pre-treatments such as sorting, cleaning and drying. Understanding the heterogeneity of the excavated plastics and different changes in the chemical and physical characteristics of each type of excavated plastics due to the degree of degradation and variation in the levels of contamination is crucial to address their suitability as feedstock from thermochemical processing. The experiments on pyrolysis of excavated plastics have shown positive results but more studies are needed to identify the most suitable parameters in relation to the feedstock characteristics (Breyer et al., 2017; Santaweesuk and Janyalertadun, 2017). Recovered plastic value can increase with an effective separation of different plastics resins with low contamination level. Although there are some technical barriers associated with the technologies used for the waste separation that need to be overcome to guarantee efficient sorting, pyrolysis of excavated plastics offers a promising alternative that contributes to (i) the reduction of fossil fuels for energy production, (ii) increased production of liquid fuels and (iii) support the economic feasibility of ELFM. Furthermore, there is a lack of specific legislation regarding the recycling of excavated plastics. However, the introduction of the ELFM concept into the EU Landfill Directive is the first step for regulating and promoting the use of secondary raw materials from landfill.

2.6 Summary and conclusions

Landfills potentially contain large quantities of resources, including plastics, which have the potential to be recycled and reintroduced into a circular economy. Pyrolysis of fresh plastic waste has been studied previously for the potential to convert the plastic waste into valuable building blocks which can be further used as fuels and chemical precursors. This paper has highlighted different aspects related to the use of excavated plastics and the possible process encountered during the storage in landfills which can be summarised as follow:

- Plastics represent 5-25 wt% of the total waste in landfills. In 2014, 30 wt% of the total plastic waste produced in Europe was disposed of in landfills;
- 80 wt% of the generated plastics is represented by thermoplastics which include a series of resins that have different chemical and physical characteristics. These differences lead to diverse degradation processes in the landfill;

- Plastic waste degradation in landfills may be caused by biological activity (e.g. microorganisms) and chemical decomposition via compounds such as H_2S (in gas and solubilised forms) and organic acids found in leachate;
- Excavated plastics generally present a higher level of ash, impurities and heavy metals than fresh plastic waste. For this reason, pyrolysis is a more viable alternative than conventional recycling and combustion;
- Separation of single-polymer plastics can improve the value of products from the recycling of excavated plastics;
- Contamination level and degradation of excavated plastics need to be further studied to evaluate the production of valuable products through pyrolysis.

This review summarises key gaps in the scientific understanding of plastic degradation pathways in landfill environments. This impacts the viability of recycling plastics recovered from landfills using conventional methods, therefore further studies are required to enhance scientific evidence of the feasibility of managing excavated plastics through pyrolysis processes.

2.7 References

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3 EXCAVATED PLASTICS CHARACTERISATION

Degradation of excavated polyethylene and polypropylene waste from landfill

The findings in this chapter showed the degradation and contamination of excavated plastics compared with fresh plastic waste. It has been published in Science of the Total Environment (see Appendix E).

3.1 Introduction

In 2017 the MSW generated in Europe (EU-28) was 487 kg per capita (Eurostat, 2018). 23 % of this waste has been disposed of in landfill for a total of 58 million tonnes (Eurostat, 2018). The growing awareness about conscious waste management led to an absolute reduction of about 60 % (63 % per capita) from 1995 to 2017 of landfill waste in Europe (Eurostat, 2018). Europe is moving towards the concept of circular economy which promotes to “closing the loop” of product lifecycles (European Commission, 2018a). The EU targets include the recycling of 65 % of municipal waste and 75 % of packaging waste by 2030 (European Commission, 2018a). Plastic waste represents a large part of MSW. In 2016, plastic waste amounted to 27.1 million tonnes in Europe (EU-28) and 27.3 % was landfilled for a total of 7.4 million tonnes (Eurostat, 2018; PlasticsEurope, 2017). For this reason, the European Commission has included a strategy for plastics in the circular economy, which aims to reduce single use of plastic products and increases its reuse and recycling (European Commission, 2018b). In conjunction with the reduction of new waste, there is still a need to manage waste legacy contained in landfill. It has been estimated there are between 125,000 and 500,000 landfills in Europe (EURELCO, 2017), which contain potential secondary raw materials that can become part of the circular economy (Wagland et al., 2019). Although some concerns exist about the recovery of waste in landfill, in some cases landfill mining is an urgent necessity. Coastal landfills can be sources of marine and terrestrial plastic pollution affecting the ecosystems (Malizia and Monmany-Garzia, 2019). According to Brand et al. (2018) in only 6 years a great amount of waste from 79 UK coastal landfills will potentially increase sea pollution due to erosion. In order to avoid further environmental damage, it is important to investigate the most appropriate way to recover this waste. Besides the circular economy paradigm, the vision of dynamic landfill management (DLM) has been introduced during the Second enhanced landfill mining (ELFM) Seminar in the European Parliament in 2018. It involves a multidisciplinary approach for landfill management, pollution control, recovery of materials, energy and land in respect of European Policy and legislation (Jones at al., 2018). The ELFM concept focuses on maximising the valorisation of waste as material (WtM) and energy (WtE). The viability of ELFM is strictly related to the quality and quantity of buried waste material in the landfill (Bosmans et al., 2013). Plastic waste in landfill represents one of the major waste fractions that can potentially be recycled. However, due to contamination, such as trace heavy metals or corrosive compounds, and structural changes derived from the landfilling process, it might not meet the requirements for conventional recycling (Canopoli et al., 2018a). Polyethylene (PE) and polypropylene (PP) are the most demanded thermoplastics in Europe (PlasticsEurope, 2018) and the most common types in the MSW. Photodegradation and thermo-oxidative degradation are the most common causes of degradation for PE and PP in an aerobic and anaerobic environment (Webb et al., 2013, Andrady, 2011, Gijsman et al., 1999). In the case of photodegradation, the chromophores present in the plastic polymer absorb the sunlight initiating the process of auto-oxidation with the formation of polymer fragments (Andrady, 2011). In thermo-oxidative degradation, the auto-oxidation process can be thermally initiated in a combination of mechanical stress (Gijsman, 2008). Photo and thermal oxidation of PE and PP can be described in three steps, initiation, propagation and termination. The initiation step involves the formation of free radicals in the polymer chain caused by chromophoric or thermolabile group (Gardette et al., 2013). During propagation, the free radicals react with oxygen forming hydroperoxides which further decompose in alkoxy and hydroxyl radical. Then, the following reactions between alkoxy and hydroxyl radical, lead to the formation of different products through β scission, abstraction of hydrogen, or cage reaction (Gardette et al., 2013). The Norrish reactions I and II are only present during photodegradation (Gardette et al., 2013). The reaction terminates when the radicals recombine in a stable form. Some of the degradation effects are visible such as discolouration and brittleness while other chemical changes, such as bond scission and the formation of new functional groups can be detected only with specific analyses. Indeed, in order to identify the best approach for the recycling of excavated plastics, it is important to evaluate the condition of these plastics, such as the degradation level. Although several studies have investigated the degradation of plastics in soil and water under different experimental conditions, to the best of the knowledge of the authors none of them has specifically investigated plastic degradation under genuine conditions in landfill (Canopoli et al., 2018a.). The landfill environment is characterised by different stages and the waste is subject to mechanical stress, presence of leachate, decomposition of organic material, chemical reaction mostly in anaerobic condition (Kjeldsen et al., 2010). For these peculiarities, degradation of excavated plastics can easily be affected and need further investigation. Gaining such information is key to assess recycling and upcycling options of recovered plastics. Current recycling methods for fresh waste are reuse (primary), mechanical recycling (secondary), chemical and thermochemical recycling (tertiary) and energy recovery via incineration (quaternary) (Al-Salem et al., 2009). Recent studies on excavated plastics have identified tertiary and quaternary recycling as possible routes for this type of feedstock (Zhou et al., 2014; Breyer et al., 2017; Santaweesuk and Janyalertadun, 2017) but the information is still scarce. In the present study, the physicochemical characterisation of excavated PE and PP, from various waste layer depths and ages, from four landfill sites was carried out to shed light on the extent of degradation of buried plastic samples and its potential implications for recycling opportunities. This information is important to apply the most appropriate approach for the upcycling of recovered plastics leading to their introduction into the circular economy.

3.2 Materials and methods

3.2.1 Plastic samples collection and preparation

A total of 30 waste samples from 4 MSW landfills located in the UK were collected at depths between 5 and 55 m following the method used in previous studies (Frank et al., 2017, García et al., 2016, Gutiérrez-Gutiérrez et al., 2015). The samples from the drilled cores were taken randomly at different depth by a specialized private company hired by the operators of the landfill sites (Table 3.1**,** details in appendix Table A.1). The number of samples was not enough to characterize each landfill (Table A.1). For this reason, it was not possible to compare the wastes from different sites. The samples were grouped according to the age of the buried MSW as follows: less than 10 years (7 waste samples) and more than 10 years (23 waste samples). The plastic fraction was extracted by manual sorting of the waste samples. The samples used in the Scanning Electron Microscopy (SEM) were washed and left to dry at ambient temperature. The rest of the samples have been dried at 60 °C for 2 hours. Before the differential scanning calorimetry (DSC) analysis, the samples were ground in small particles ≤1 mm.

Table 3.1 Landfill samples information. Details are available in the appendix Table A.1.

	Samples n.	**Years**	**Depth**	**Waste sample**	**Plastic (wet)**		**Plastic (dry)**	**Impurities (wet)**	
			(m)	**(g)**	**(g)**	**(wt%)**	**(g)**	**(g)**	**(wt%)**
<10	**7**	**<10**	**5-18**	**12,335**	**1,407**	**11**	**302**	**1,105**	**79**
Average				1,762	201	13	43	158	78
SD				2,953	332	7	70	263	5
Min				390	31	5	9	22	70
Max				8,448	951	24	200	751	85

>10	**23**	**>10**	**3-55**	**141,603**	**9,276**	**7**	**5,084**	**4,192**	**45**
Average				6,157	403	7	221	182	45
SD				2,596	351	6	184	230	18
Min				1,891	21	0	12	9	11
Max				11,586	1,510	26	602	1,143	76
TOT	**30**			**153,938**	**10,683**	**7**	**5,386**	**5,297**	**50**
Average				5,131	356	9	180	177	52
SD				3,239	352	7	181	233	21
Min				390	21	0.3	9	9	11
Max				11,586	1,510	26	602	1,143	85

3.2.2 Surface morphology and chemical characterisation of the excavated plastic fraction

Environmental Scanning Electron Microscopy was used to characterise the surface morphology of the PE and PP fragments at a magnification of x500. Concomitantly the chemical elements present at the surface of a representative plastic sample for each plastic type were determined using Energy Dispersive spectroscopy (EDS) to evaluate the extent of degradation and contamination levels of the plastic fragments. The surfaces of the excavated samples were compared with the surface of fresh PE and PP waste. The excavated PE and PP analysed were the largest pieces, and for this reason the most representative, from each group (<10 years and >10 years).

3.2.3 Composition of the excavated plastic fraction

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used for the identification of different plastic polymers and calculation of the carbonyl index (Barbeş et al., 2014). The carbonyl index is often used to evaluate the oxidation level of polymers. It is defined as the ratio of the band area attributed to the carbonyl group -C=O and the band area attributed to methylene group -CH_2 (ter Halle et al., 2017; Barbeş et al., 2014). The carbonyl band was integrated between 1779 and 1680 cm^{-1} and the methylene between 1490-1420 cm^{-1} for PE, 2700-2750 cm^{-1} for PP (ter Halle et al., 2017; Moldovan et al., 2012; Longxiang et al., 2005). According to Rouillon et al. (2016) study, the oxidation of PP leads to the formation of volatile products that carry CH_3 moieties such as acetic acid and acetone. Therefore, it is expected that CH_3 decreases during oxidation. Carbonyl index, CH_3 for PP and CH_2 for PE, taken between 1490-1420 cm^{-1}, have been analysed. FTIR was applied on the fresh and excavated plastic samples using a Bruker vertex 70 instrument equipped with an attenuated total reflection (ATR) device Bruker Platinum ATR. Background and sample spectra were acquired using 16 scans at a spectral resolution of 4 cm^{-1} in the wavenumber range of 4000 to 400 cm^{-1} (ter Halle et al., 2017). A minimum of 3 replicates of infrared spectra were recorded for fresh PE and PP and excavated PE and PP samples.

3.2.4 Differential Scanning Calorimetry analysis

To understand the amorphous and crystalline behaviour of the excavated plastic residues, DSC analysis was conducted on 3 replicates of each sample (weight between 4 and 10 mg) using a DSC Q-200 (TA Instruments, UK). The temperature ranges were from 20 to 150 °C for PE, and from 20 to 180 °C for PP. A heating rate of 10 °C/min was used in a nitrogen atmosphere for first and second cooling and heating cycles. The degree of crystallisation of the samples was calculated from the first heating experiment, which gives information on thermal history, using Equation 3.1:

Equation 3.1 Formula of degree of crystallisation**.**

$$\% \, \boldsymbol{Crystallinity} = \frac{\boldsymbol{\Delta H_m}}{\boldsymbol{\Delta H_m^{ref}}} \times 100$$

Where ΔH_m is the melting enthalpy of the sample and ΔH_m^{ref} is the melting enthalpy of 100 % crystalline polymer. The ΔH_m^{ref} was taken as 293 J/g for PE and 207 J/g for PP (Blaine). The peaks were measured using sigmoidal baseline (ISO 11357-1:2016).

3.2.5 Statistics

T-test is normally applied to compare the means of two groups and check if there is a statistically significant difference between them. Two-tailed t-test has been applied to analyse the results from FTIR, such as carbonyl index, CH_2 and CH_3, and DSC, crystallinity and melting. The significant difference was considered $p < 0.05$. It was used to evaluate the difference between excavated (>10 years and <10 years) and fresh samples for each plastic type, PE and PP.

3.3 Results and discussion

3.3.1 Percentage of excavated plastics from landfill

The average percentage of excavated plastics with more than 10 years of disposal is 8 wt%, ranging from 0.3 wt% to 26 wt%. The average percentage of excavated plastics with a disposal period of less than 10 years is 12 wt% ranging from 5 wt% to 24 wt%. This result is in accordance with other studies where the mean values of plastic percentage were between 10 and 26 wt% (García et al., 2016; Sel et al., 2016; Quaghebeur et al., 2013; Jones et al., 2013; Van Passel et al., 2013). The excavated plastics were divided into different plastic types with FTIR spectroscopy. Thermoplastic such as PE and PP are the most demanded polymer types; about 36 wt% of the total plastic demand in Europe which amounts to 50 million tonnes (PlasticsEurope, 2018; PlasticsEurope, 2017). According to this, the PE and PP represent also the major fractions found after sorting in both groups (Table 3.2). The percentages of PE and PP in the MSW samples with <10 years were 50 wt% and 13 wt%, respectively. The PE and PP percentages in the MSW samples with >10 years were 48 wt% and 19 wt%, respectively. Rubber properties are different from conventional plastic and need a specific recycling route. For this reason, rubber is not considered in the main plastic types of this study.

Table 3.2 Percentages of different plastic types. Details are available in the appendix Table A.2, A.3, A.4.

	Sample n.	PE	PP	PVC	PS	PET	PE/PP Blend	PA	Rubber	Rest
							(wt%)			
<10	**7**	**55**	**12**	**2**	**2**	**1**	**1**	**0**	**0**	**26**
Average		50	13	4	5	4	7	1		31
SD		14	10	1	2	3	7			11
Min		32	2	3	3	1	0	1		18
Max		70	32	5	6	6	15	1		43
>10	**23**	**45**	**19**	**11**	**4**	**3**	**0**	**0**	**14**	**4**
Average		48	19	16	5	20	6	1	34	8
SD		27	21	17	4	26	7		40	11
Min		2	1	0	1	2	1	1	0	0
Max		92	85	50	16	39	11	1	97	41
TOT	**30**	**45**	**19**	**10**	**3**	**3**	**0**	**0**	**13**	**6**
Average		48	17	14	5	11	6	1	34	14
SD		24	18	16	4	16	6	0	40	15
Min		2	1	0	1	1	0	1	0	0

Max	92	85	50	16	39	15	1	97	43

3.3.2 Surface degradation of the excavated plastics

Comparison of fresh and excavated PE and PP surfaces showed a general major surface alteration in the excavated samples (Figure 3.1). The first visual sign of surface degradation that can be detected is the loss of gloss which is characteristic of fresh PE and PP (Rouillon et al., 2016; Gijsman, 2008). Table 3.3 summarises the main characteristics of the analysed surfaces and elements detected from the EDS. Oxygen was in the main elements in all samples except for fresh PP. Presence of oxygen in PE and PP is a sign of degradation. This can be seen also in the surfaces imagines. In fact, fresh PP has visible smooth surface compared to the other samples (Figure 3.1), showing a lower degree of degradation. Cracks are present in PE <10 years (Figure 3.1B) and PP >10 years (Figure 3.1F) which are signs of ageing (Elanmugilan et al., 2013). General roughness increase can be detected in the surfaces of excavated PE and PP compared to the fresh samples (Figure 3.1). The figures 3.1 shows one sample images for each category. Across the effectuated SEM images was not detectable a clear trend between <10 years and >10 years samples that can be related to the increase of storage age in landfill. The elements identified in the majority of the samples are calcium (Ca), Titanium (Ti), Silicon (Si), Magnesium (Mg) and Aluminium (Al) (Table 3.3). Ca can be linked to the commonly used filler calcium carbonate ($CaCO_3$) (Tolinski, 2015; Brydson, 1999). Ti and Al are used in Ziegler-Natta catalysts for PP and PE production (Shamiri et al., 2014). Si and Al present in the excavated samples can be related to the SiO_2 and Al_2O_3 contained in the soil. The identified elements can also be associated to the use of additives in plastics, such as quartz (SiO_2), wollastonite ($CaSiO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$), fire retardant $Mg(OH)_2$, magnetite (Fe_3O_4), titanium carbide (TiC), and pigment (TiO_2) (Turku et al., 2017; Brydson, 1999).

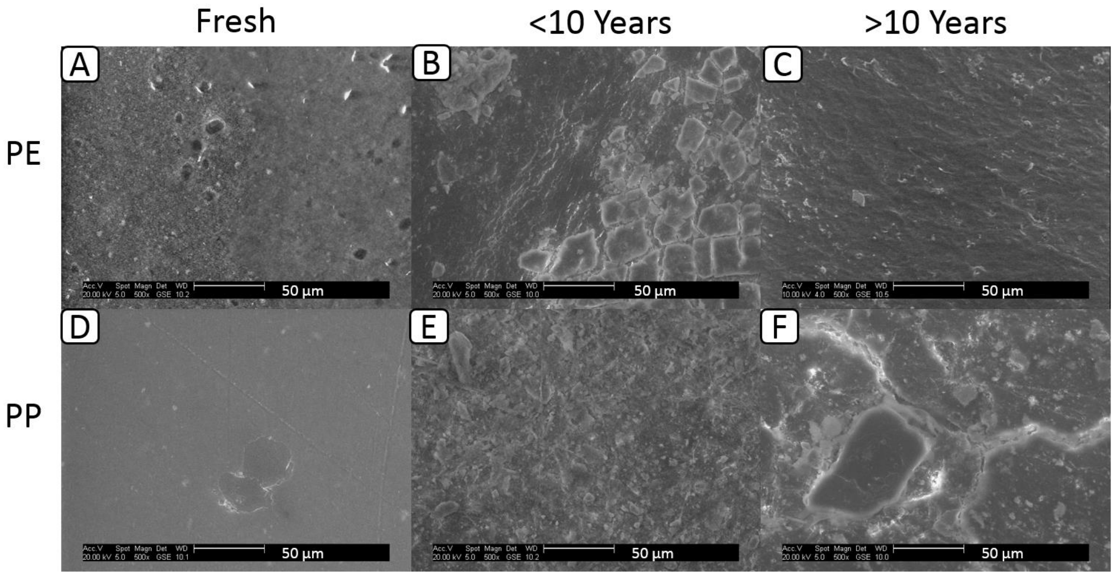

Figure 3.1 Scanning electron microscope (SEM) images of fresh plastic waste (A and D) and excavated plastics (B, C, E, F) under 500x magnification. Fresh PE coloured packaging; B: Excavated PE <10 years; C: Excavated PE >10 years; D: fresh PP; E: Excavated PE <10 years; F: Excavated PE >10 years. Adapted from Canopoli et al., 2018b**.**

Table 3.3 Surface characteristics and chemical elements detected by SEM-EDS (minimum concentration detected 0.08 wt%) of fresh and excavated PE and PP. Adapted from Canopoli et al., 2018b.

Sample	Figure	Surface texture	Main elements	Minor elements (<5 wt%)	Trace elements (<0.5 wt%)
PE	1A	P	C, O, Ti	Al, Cl, Ba	Si, P, S, Cu
PE <10 Years	1B	F, AP, Gr	C, O	Mg, Si, Ca	Al, P, S, Cl, Ti, Fe, Cu, Mo
PE >10 Years	1C	Fl, AP	C, O, Ca	Al, Si, Cl, K, Ti, Fe	Na, Mg, P, S, Cu, Zn
PP	1D	S	C,	Ca, Ti, Fe	Mg, Al, Si, Cl
PP <10 Years	1E	Fl, AP, Gr	C, O, Si, Ba	Al, S, K, Ca, Fe, Zn	Mg, P

PP >10 Years	1F	F, AP, Gr	C, O	Si, Ca, Ti, Fe	Mg, Al, S, Cl, K, Zn

F = fractures; AP = adhering parts; P = pits; Fl = flakes; Gr = granulates; S = smooth.

3.3.3 Carbonyl index of the excavated plastic materials

The carbonyl index (CI) is presented as the average value of different infrared spectra for each sample. The CI average of fresh PE is 0.53, higher than the excavated PE which seems to decrease over time, 0.46 and 0.41 for PE <10 years and PE >10 years respectively (Figure 3.2). However, the CI results of PE do not present a statistically significant difference. The slight decrease of carbonyl index in the PE samples with >10 years disposal could indicate an advanced degradation. Indeed, after initial degradation the samples may proceed the degradation with chain scission, crosslinking and CO release (Moldovan et al., 2012). In this case, the carbonyl group is depleted and the CI decreases consequently. The difference between fresh and excavated PE can be related to the presence of TiO_2 additive. Indeed, Ti is found as a major element only in fresh PE (Table 3.3). Conversely, PP presents an opposite trend which suggests that the CI average increases with storage years 0.76, 1.34 and 1.78 for fresh PP, PP <10 years and PP >10 years respectively. CI results of PP, fresh and excavated, are statistically different (Figure 3.2).

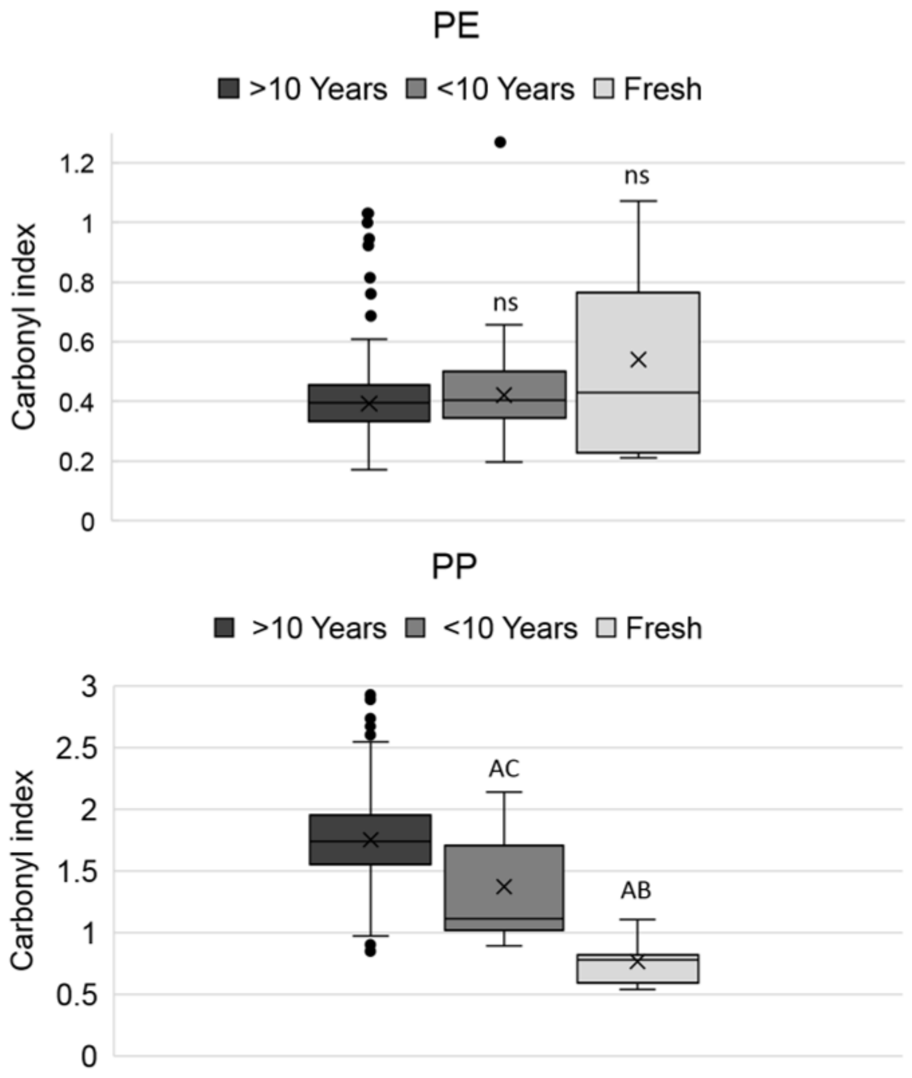

Figure 3.2 Carbonyl indices of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Number of samples: PE >10 (184), PE <10 (18), PE fresh (14), PP >10 (153), PP <10 (12), PP fresh (9). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples (ns: not significant). The outliers were identified as any value greater than 1.5 multiplied by the interquartile ranges (IQR) below the first quartile and above the third quartile. Outliers are plotted individually (points).

The CH_2 absorbance of excavated PE >10 years is significantly lower compared with fresh and <10 years PE (Figure 3.3). PP showed similar results (Figure 3.3). In fact, the difference between excavated PP >10 years and the other two samples, fresh and <10 years, is statistically significant. CH_3 band of PP samples

>10 years storage is lower than newer samples and this can be related to the loss of volatile products as suggested by Rouillon et al. (2016).

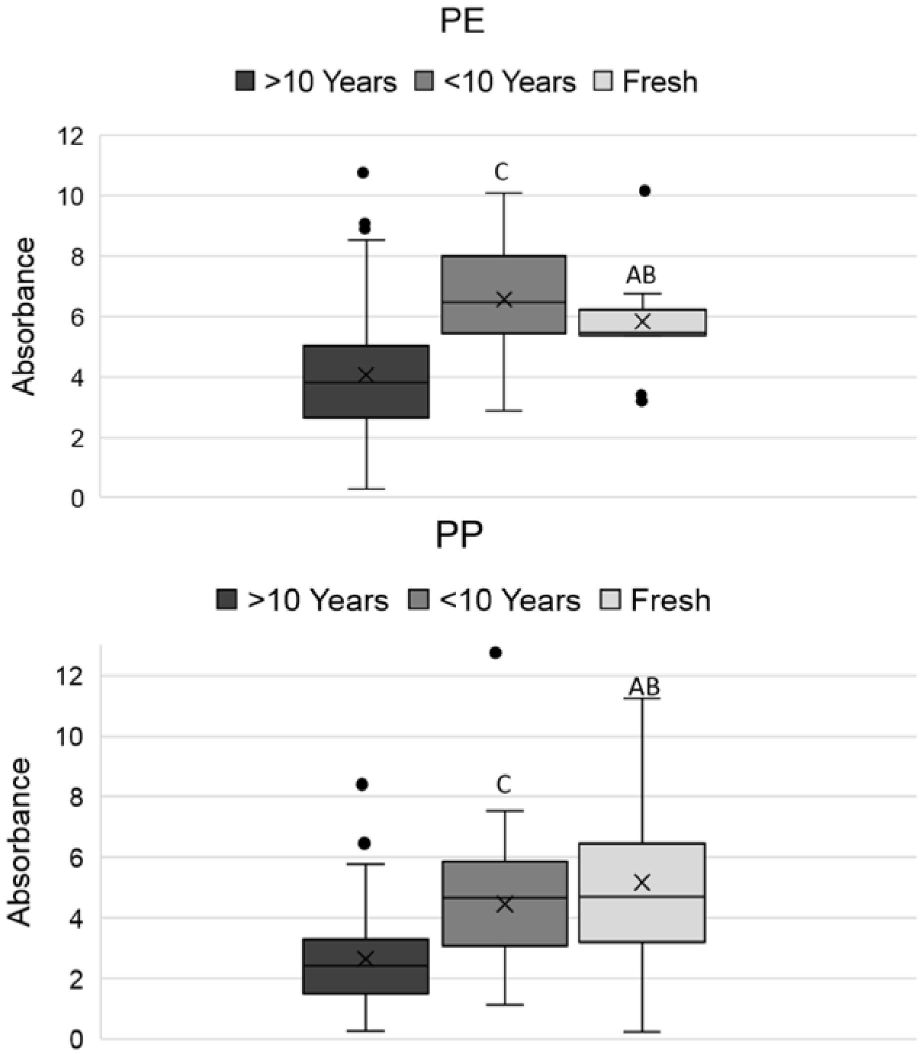

Figure 3.3 Absorbance of CH_2 and CH_3 vibration of ~1456 cm^{-1} of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Number of samples: PE >10 (184), PE <10 (18), PE fresh (14), PP >10 (153), PP <10 (12), PP fresh (9). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples. The outliers were identified as any value greater than 1.5 multiplied by the interquartile ranges (IQR) below the first quartile and above the third quartile. Outliers are plotted individually (points).

Hydroxyl group (-OH 3650-3200 cm^{-1}) is another degradation product together with carbonyl group (Moldovan et al., 2012). The degradation products showed in this band are alcohols and hydro-peroxides (Gardette et al., 2013). Presence of a board peak can be distinguished in the excavated samples compared to the fresh samples in both PE and PP (Figure 3.4).

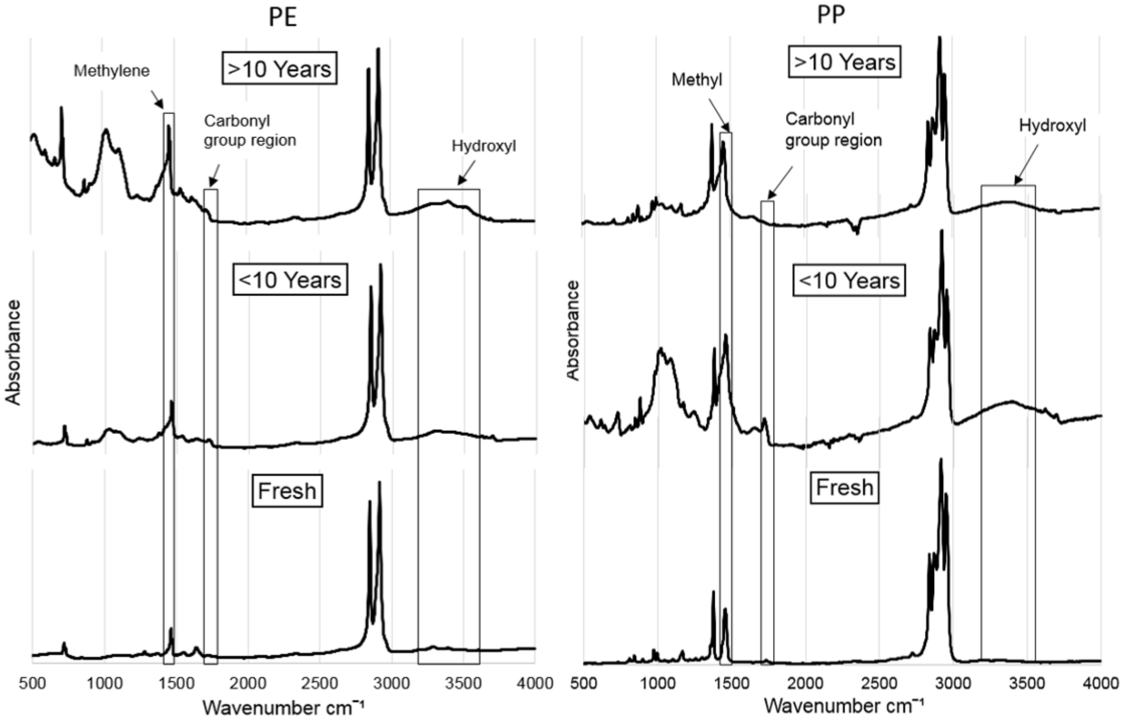

Figure 3.4 FTIR spectra of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years).

3.4 Differential Scanning Calorimetry (DSC).

The crystallinity in PE increases during ageing (Figure 3.5). Higher crystallinity for the older samples can be related to the different degradation rate of the crystalline and amorphous phase of plastic (Andrady, 2017). In fact, the amorphous fraction is the first part that is affected by mechanical stress, biodegradation and weathering (Andrady, 2017; Yang, 2014, Shah, 2008). The crystallinity average is 39 %, 45 % and 51 % for fresh PE, PE <10 years and PE >10 years, respectively. However, only fresh PE and PE >10 years present a significant difference. Figure 3.6 presents the thermograms of fresh and excavated PE. The presence of a double peak, such as in the excavated PE, characterises plastic samples with different lengths of molecular chains and degraded samples (Stangenberg et al., 2004). In fact, fresh plastic polymer presents a single peak (Figure 3.6). The melting point average of fresh PE, PE

<10 years and PE >10 years was 116.6 °C, 130.5 °C and 127.5 °C respectively. These results are not statically different from each other. The crystallinity percentage average of fresh PP, PP <10 years and >10 years is 38 %, 35 % and 41 %, respectively (Figure 3.5). There is not a clear trend and only PP >10 years and PP <10 years present a statistically significant difference. The melting average is 163.5 °C, 155.4 °C and 164.5 °C for fresh PP, PP <10 years and PP >10 years respectively. These results are not statistically different.

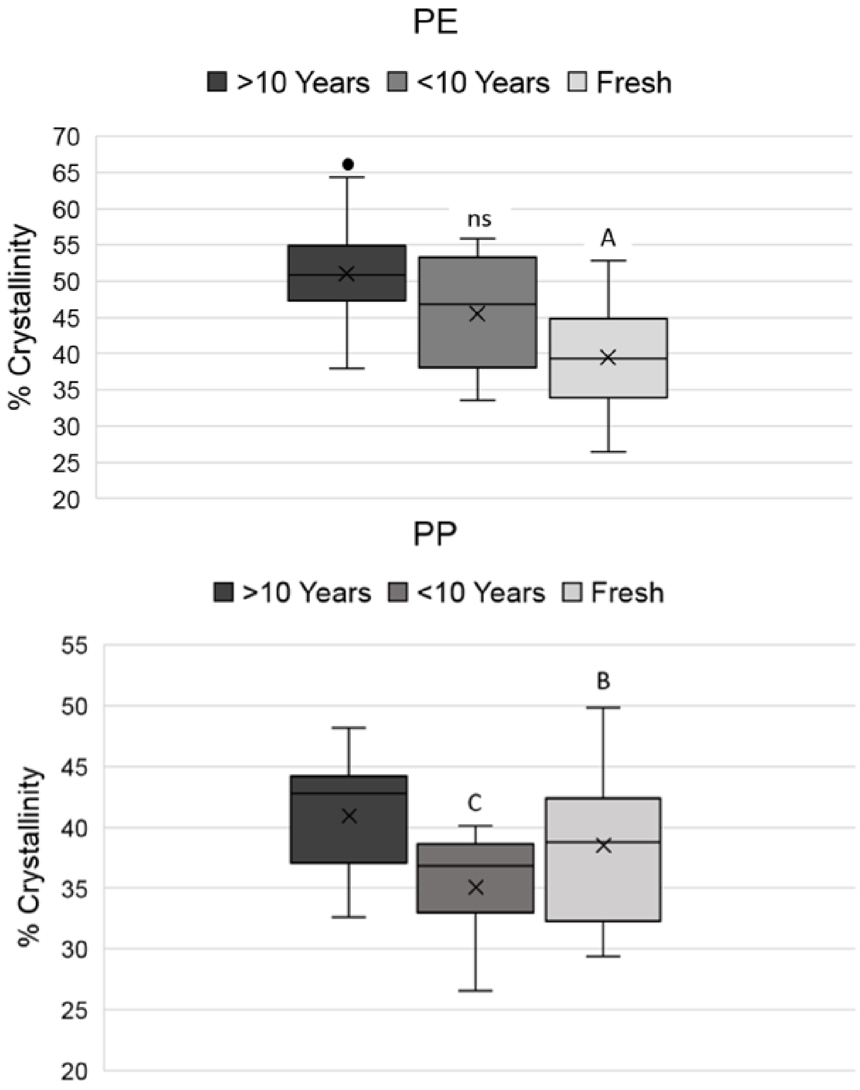

Figure 3.5 Crystallinity percentage of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Number of samples: PE >10 (24), PE <10 (9), PE fresh (8), PP >10 (16), PP <10 (6), PP fresh (8). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples (ns: not significant). The outliers were identified as any value greater than 1.5 multiplied by

the interquartile ranges (IQR) below the first quartile and above the third quartile. Outliers are plotted individually (points).

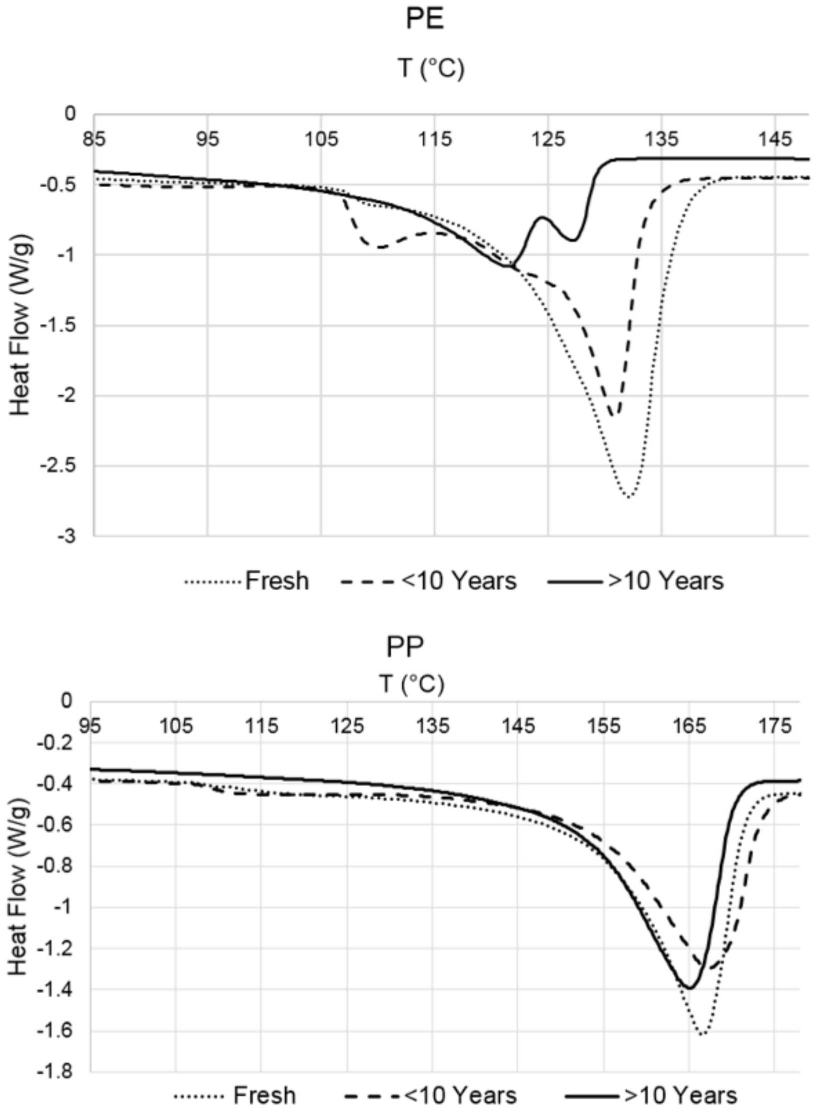

Figure 3.6 DSC thermograms of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years).

3.5 Recycling implication

These results need to be considered for the evaluation of the introduction of excavated plastics into the circular economy. Not all recycling routes of fresh plastic waste are feasible for excavated plastics. Due to the physico-chemical characteristics of excavated plastics, thermochemical recycling might be the best option compared to mechanical recycling and energy recovery via incineration.

Mechanical recycling requires higher quality sorting for the identification of polymer types and feedstock material with appropriated physico-chemical properties (Butler et al., 2011). Plastic degradation comprises of contaminants such as oxygenated groups and organic matter which can affect the product quality (Ragaert et al., 2017). Indeed, changes in crystallinity and CI affect the mechanical properties of plastic. Increasing the degree of crystallinity and CI, the plastic material becomes more brittle and more susceptible to future thermo and photo-degradation (Wypych, 2013, Fotopoulou, K.N., Karapanagioti, 2019). Mechanical recycling of plastics is known to decrease the mechanical properties of plastics after a certain number of extrusion cycles (Oblak et al., 2016). Energy recovery via incineration cannot be considered practicable in the circular economy view. In contrast, pyrolysis can process contaminated plastics and heterogeneous feedstock, and represents a valuable opportunity for the excavated plastics recycling (Fox and Stacey, 2019; Ragaert et al., 2017; Butler et al., 2011). However, the use of plastic polymers such as PVC and PET should be avoided during pyrolysis (Lopez at al., 2017). The presence of carbonyl groups in the feedstock could lead to the production of oxygenated compounds in the pyrolysis oil. Oxygenated compounds are undesirable products that cause corrosion problems and negatively affect the pyrolysis oil quality decreasing the calorific value and stability (Czajczyńska et al., 2017; Lu et al., 2009). These compounds such as hydroxyl groups are present in the pyrolysis of plastic and can be attributed to the additives (Hakeem et al., 2018). To the author's knowledge, the effect of degradation of excavated plastics on pyrolysis products has not been verified. On the other side, limited information is available about the contamination effect from elements such as Al and Fe. Presence of Al_2O_3 and Fe_2O_3 can catalyse the decomposition of plastics during pyrolysis (Bosman et al., 2014; Liu and Meuzelaar, 1996). Chemical compounds such as ethene, propene and benzene, could be recovered through the pyrolysis of excavated plastics and reintroduced in the circular economy. A recent study (Fox and Stacey, 2019) has investigated the potential profit of fresh plastic waste pyrolysis and selling of alkene products. The potential value of fresh plastic waste is evaluated between \$80-\$160 per tonne (Fox and Stacey, 2019). Table 3.4 shows the potential monetary value associated with the recovery through pyrolysis of the plastics disposed of in landfill in 2016 in Europe (~7.4 million tonnes) (PlasticsEurope, 2017). The plastic types amounts have been calculated from the percentages of excavated plastics found in this study (Table 3.2). It is assumed that the identified percentages for each recovered plastic type can be applied to European plastic waste disposed of in landfill in 2016. The plastic types considered for the pyrolysis are PE, PP, PS, PE/PP blend. The potential monetary value is between $402 million and $805 million. Further studies are needed to investigate the production of chemical compounds from the excavated plastics pyrolysis and their marketability.

Table 3.4 The potential monetary value associated with the plastic waste disposed of in landfill in 2016 in Europe (PlasticsEurope, 2017). Price per tonne from Fox and Stacey 2019.

Landfilled plastic 2016	Weight (%)	Tonnes	Price per tonne $80	Price per tonne $160
PE	45	3,330,000	266,400,000	532,800,000
PP	19	1,406,000	112,480,000	224,960,000
PS	3	222,000	17,760,000	35,520,000
PE/PP Blend	1	74,000	5,920,000	11,840,000
PVC	10	740,000	-	-
PET	3	222,000	-	-
Rubber	13	962,000	-	-
Rest	6	444,000	-	-
Tot		7,400,000	402,560,000	805,120,000

3.6 Conclusion

PE and PP are the most common polymer type found in excavated waste from landfill. Fresh PP presents a smooth surface compared to the other samples and no oxygen has been detected from the EDS. The CI excavated PP samples >10 years was almost 2 times higher than <10 years and fresh PP, respectively, confirming the increase of degradation over time. CH_2 and CH_3 of excavated PP and PE >10 years were statistically lower (almost twice) than the newer samples. The degree of crystallinity of PP and PE samples >10 years was also 1.3 times higher than fresh materials. Overall, the PE and PP which have been buried for more than 10 years had a greater extent of degradation than samples with fewer years of storage, which suggests that chemical and thermochemical recycling such as pyrolysis with the production of chemical base compounds would be the preferred route for excavated plastics. It would also contribute to the circular economy and the development of ELFM projects. Future studies should evaluate if the increase of CI in the feedstock lowers the pyrolysis oil quality due to the presence of a major quantity of oxygenated compounds. The presence of oxygenated compounds is known to lower the heating value which is an important parameter for transportation fuels (Lopez et al., 2017). In addition, the catalyst effect of elements such as Al and Fe should be further investigated. Indeed, these elements found in the excavated plastic samples, are known to act as catalysts during the pyrolysis of plastic waste (Bosman et al., 2014; Liu and Meuzelaar, 1996).

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4 PYROLYSIS SIMULATION MODEL

Pyrolysis simulation of recovered plastics from landfill using ASPEN Plus

This chapter presents a pyrolysis simulation model in ASPEN Plus for the prediction of products from excavated plastics pyrolysis.

4.1 Introduction

Plastic production in the world increased from 230 to 359 million tonnes between 2005 and 2018 (PlasticsEurope, 2019). A large fraction of this plastic is produced for the packaging sector which uses mainly polyethylene (PE) and polypropylene (PP) (PlasticsEurope, 2019). From 2006 and 2018 the landfilled plastic in Europe (EU28 + Norway and Switzerland) decreased by 44 % (PlasticsEurope, 2019). However, in Europe in 2018 it was estimated that 7.2 million tonnes of plastic waste were disposed of in landfill. Its continuous accumulation in landfill and environment needs to be addressed finding effective recycling route for this discarded material. The development of new strategies for the management of plastic waste is one of the main projects towards the circular economy (PACE, 2020). In 2018, the World Resources Institute, International Resource Panel, Ellen MacArthur Foundation, Accenture Strategy, World Economic Forum and Circle Economy launched the Platform Accelerating The Circular Economy (PACE) which aim to accelerate the conversion from a linear to a circular economy. Following the circular economy concept, this material should be upgraded to be reintroduced into the market and become part of a closed-loop. The buried plastics present some peculiarities such as soil and fine fractions attached to their surface and variable degradation level related to the history of the samples and years of storage in landfill (Zhou et al, 2014; Canopoli et al., 2020). Another important aspect, which can influence the identification of optimum recycling route, is the level of heavy metals. Common recycling routes of fresh plastic waste are mechanical recycling, energy recovery via incineration and chemical recycling (Al-Salem et al., 2009). The plastics incineration for energy recovery does not reflect the principles of the circular economy concept because it has more affinity for the linear economy. Besides, mechanical recycling of excavated plastics seems inappropriate due to the restrictions related to the quality of the material before and after recycling (Canopoli et al., 2018). In contrast, chemical recycling appears to represent the balance between the upgrading of excavated plastics and the feedstock requirements for this technology. Indeed, recovered plastics from landfill can potentially be recycled through tertiary recycling, such as pyrolysis, to produce energy and chemical compounds (Canopoli et al., 2020). Olefins and benzene, toluene and xylene (BTX) are valuable pyrolysis products which are widely used in the petrochemical industries (Thunman et al., 2019). Olefins are commonly utilised as co-monomers in the production of PE and PP, precursors for detergents, lubricants, plasticisers and as copolymers. BTX are important building blocks for the production of polymers such as polystyrene and polyethylene terephthalate, solvents and dyes. Virgin fossil resources are the principle feedstocks of these products. In order to mitigate climate change and the overconsumption of finite resources, new sustainable sources are needed. The global BTX consumption is expected to grow in the next 3 years, with an average annual growth rate of 2.9 % for benzene (IHS Markit, 2019a, 2019b, 2019c). Chemical compounds such as olefins and BTX from pyrolysis of recovered plastics could play an important role in the upgrading of this material which will return in the market as a valuable resource. For these reasons, pyrolysis of recovered plastics needs to be investigated. The degradation of plastic during pyrolysis is characterised by three steps such as initiation, propagation and termination. The reactions involved are mainly random scission, β-scission, hydrogen transfer, and finally the termination by recombination, cyclization and aromatization (Singh et al., 2019; Mohanraj et al., 2017; Bockhorn et al., 1999). ASPEN (Advanced System for Process Engineering) Plus was used for the simulation of pyrolysis of different feedstocks such as biomass, tyre and plastic (Ismail et al., 2017; Peters et al., 2017; Sahu et al., 2014). A thermodynamic equilibrium simulation model was used to determine the pyrolysis compounds and lumped yields pyrolysis products such as gas, oil and char (Moses et al., 2018; Sahu et al., 2014). Its limitations are related to the simplification of the models which not include information on residence time, reaction rate and for this reasons cannot be used for reactor design (Ismail et al., 2017). The kinetic model gives detailed information on the products at different operating conditions. Modelling plastic pyrolysis products can be complex due to the different compounds formed from different feedstocks. Approximations need to be used during the simulation. Pyrolysis plants are often designed for the pyrolysis of both plastics and tires. In both cases, the long polymer molecules are broken into shorter chains. The pyrolysis of tires produces generally more char yield and less oil yield than plastic pyrolysis (William, 2013; Anuar Sharuddin et al., 2016). The major gases and many oil compounds produced during plastic pyrolysis can be found also in the products of pyrolysis of tires. The oil compounds comprise of aliphatic hydrocarbons and aromatic such as BTX and styrene (William, 2013; Anuar Sharuddin et al., 2016). A recent study used the reaction kinetics from Ismail et al. (2017) to model the pyrolysis of plastic simulating a real pyrolysis plant in New York (Garrido Rodriguez et al., 2018). The results fairly approximate the results reported from the real pyrolysis plant. For these reasons, the reactions kinetic from Ismail et al. (2017)'s study were applied to the simulation model of excavated plastics pyrolysis. This paper presents a kinetic model of plastic pyrolysis simulated in ASPEN Plus software for the identification of potential recyclable products which can upgrade the excavated plastics to valuable chemicals. Although the presented model is inspired by other pyrolysis models, the novelty is related to the simulation of excavated plastics pyrolysis. The aim of this paper was to create a simulation model to predict the gas, oil and char yields from the pyrolysis of recovered plastics in order to evaluate the introduction of this discarded material into the circular economy. In addition, the possible olefins and BTX yields were evaluated to give information on potential monetary value.

4.2 Model development and description

Pyrolysis of plastic produces three main products such as gas, oil and char. The components considered in the simulation were selected from previous studies and experimental results (Anuar Sharuddin et al., 2016). The feedstock proximate and ultimate analyses used for the model validation are summarised in Table 4.1 (Singh et al., 2019).

Table 4.1 Feedstock parameters used for the validation of the simulation model (Singh et al., 2019).

	PE	**PP**
Proximate analysis		
Moisture (wt%)	0.32	0.44
Fixed Carbon (wt%)	3.9	2.04
Volatiles (wt%)	91.88	93.84
Ash (wt%)	3.9	3.68
Ultimate analysis (wt%)		
Carbon	83.4	83.28
Hydrogen	12.71	13.81
Nitrogen	1.08	1.01
Sulphur	0.002	0.001
Oxygen	2.8	1.9

After validation, the model was used to simulate the pyrolysis of recovered PE and PP, single polymer and mixed together in equal quantity, from different storage age (<10 and >10 years). The information related to the recovered plastics inserted in the model is shown in Table 4.2.

Table 4.2 The proximate and ultimate analysis used for the simulation of pyrolysis of excavated PE and PP from different storage age (<10 and >10 years) (adapted from Table 5.3, Chapter 5).

	PE<10	**PE>10**	**PP<10**	**PP>10**
Proximate analysis				
Moisture (wt%)	0.47	05	0.2	0.3
Fixed Carbon (wt%)	0	1.6	1.8	0
Volatiles (wt%)	94.5	93.6	90.9	88.5
Ash (wt%)	7.0	4.5	7.3	18.9
Ultimate analysis (wt%)				
Carbon	82.6	79.6	70.9	81.7
Hydrogen	13.6	13.1	11.1	13.3
Nitrogen	0.3	0.5	0.1	0.2
Chlorine	0.3	1.7	0	0
Sulphur	0.4	0.4	0.63	0.3
Oxygen	0	1.9	9.97	0

Figure 4.1 shows the ASPEN Plus flowsheet of plastic pyrolysis and the different steps involved in the simulation such as drying, decomposition, reaction and condensation. The process of plastic pyrolysis can be described as follow. The feedstock is pre-treated with a drying step in order to reduce the moisture content (DRIER, SEP). Then, it is fed into the pyrolysis reactor (DECOMP, RCSTR). Here the plastic thermally degrades in absence of oxygen. In the pyrolysis reactor

gases and char are formed. The gases pass through the cyclone system where the char is separated from the gases and collected in a char collector (SEP2). Then the gases pass through the condensing system which can comprise of different condensers, where the condensable and non-condensable gases are separated (COOLER, SEP3). The oil is collected in a tank for future distillation. The non-condensable gases can be cleaned and sent to a gas burner to be reused to support the process.

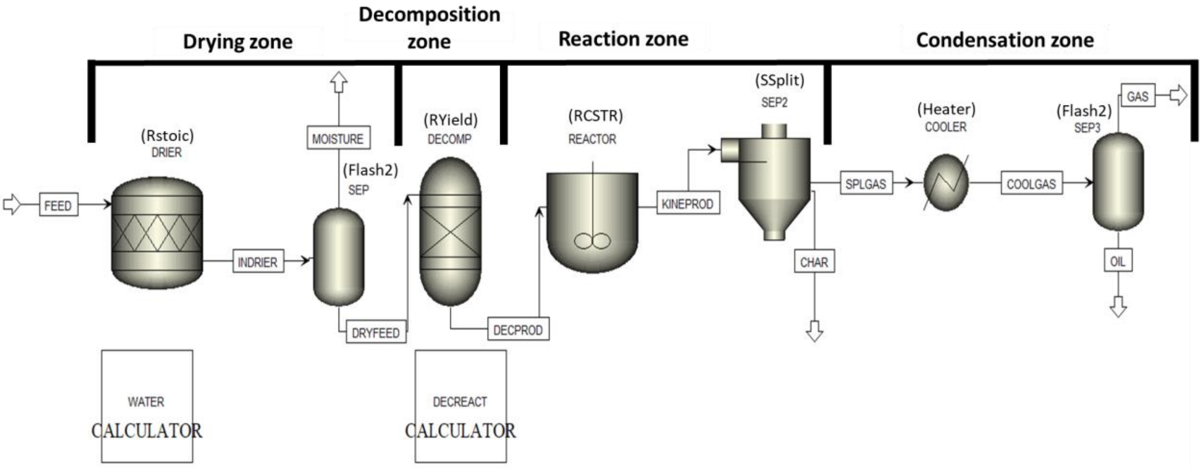

Figure 4.1 Flowsheet of ASPEN Plus simulation model.

The property method used to estimate the physical properties of conventional components in the simulation was the Peng-Robinson equation of state with Boston-Mathias modification (PR-BM) (Kabir et al., 2015). The Boston-Mathias modification helps to better simulate the behaviour of components above critical temperature. HCOALGEN and DCOALIGT models were used for the calculation of enthalpy and the density of non-conventional compounds. During the simulation, 100 kg/hr of plastic feedstock (FEED) were pyrolyzed at different temperatures (between 300-1,000 °C) and at a pressure of 1 atm. The plastic feedstock was dried at 105 °C in the DRIER (RStoic). The moisture was separated from the feedstock in the SEP (Flash2). The plastic feedstock was defined as a nonconventional solid in the model with composition presented in Table 4.1 and Table 4.2. The RYield and RCSTR were used together to simulate the pyrolysis of nonconventional solid, which were transformed firstly in conventional elemental compounds and then pyrolyzed. The dry feedstock was converted to C, H, O, N, S and ash in the DECOMP (RYield). This reaction step is required by the reaction model but does not reflect the real pyrolysis reaction mechanism. Indeed, nonconventional solid needs to be transformed at first into their conventional elemental compounds for simulating the pyrolysis products formation. After the decomposition step, it reacted in RCSTR to produce gas and char. The reactions kinetic were imported from a similar pyrolysis process (see appendix Table B.21) (Ismail et al., 2017). Most of the product compounds identified from different studies on the pyrolysis of plastic are within carbon chain C24 (Singh et al., 2019; Anuar Sharuddin et al., 2016). For this reason, the reactions cover until carbon chain C24. The reactions follow power-law kinetics with first order dependence on H_2. The pyrolysis products char and gas were separated in the SEP2 (SSplit). The char was assumed to contain only ash and unreacted carbon. The gases were cooled down at 0 °C. Finally, the liquid fraction and non-condensable gases were separated in a Flash2 block. Two external FORTRAN subroutines were used for calculating the water content during drying (RStoic) and determining the product yields during decomposition (RYield) (Figure 4.2). The assumed total conversion of 100 % is in line with the studies on plastic pyrolysis (Wong et al., 2016; Anuar Sharuddin et al., 2016). Indeed, the gas percentage is mostly calculated as oil and char weight percentages subtracted from 100 %.

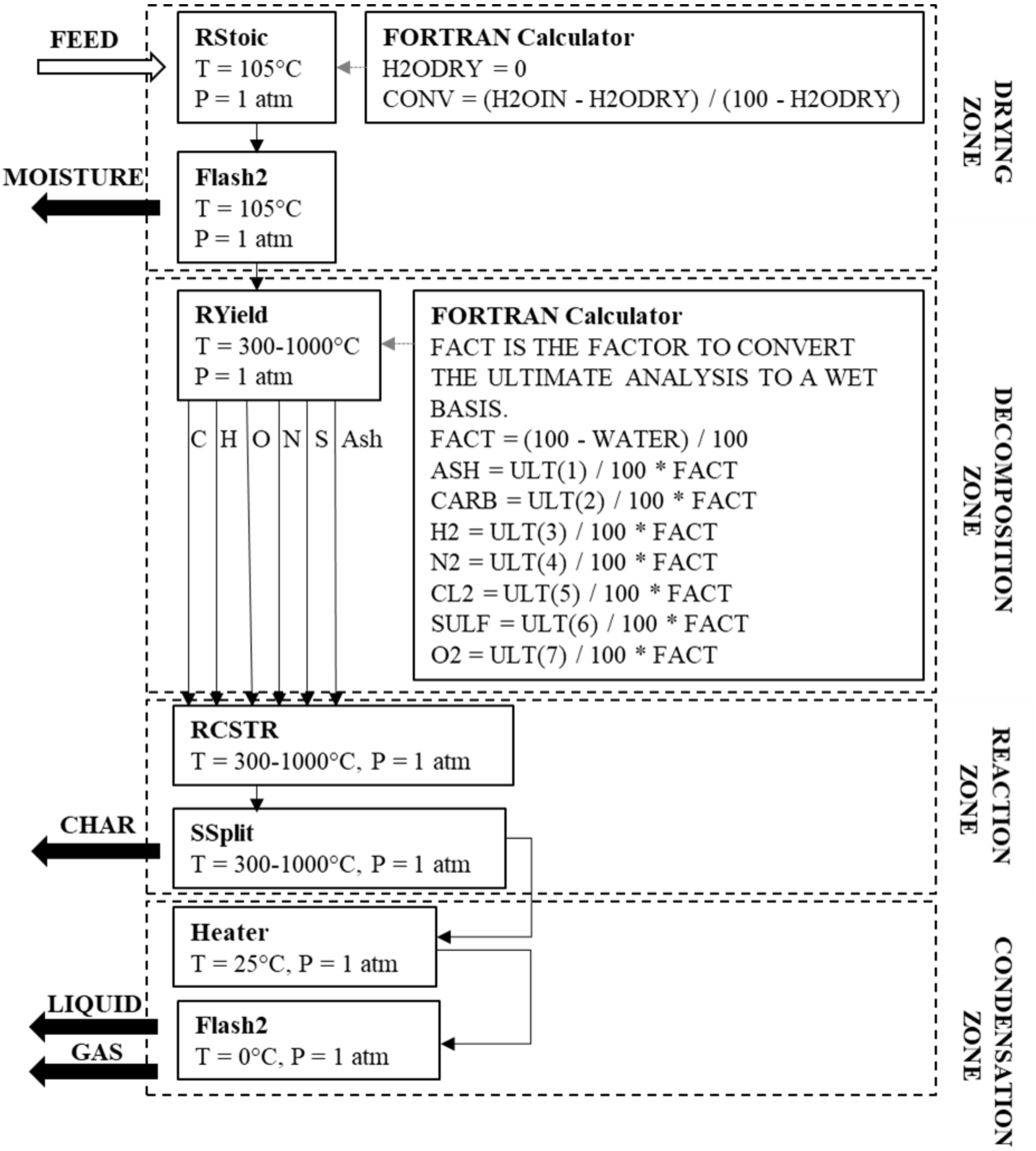

Figure 4.2 Schematic diagram of pyrolysis process.

4.3 Results and discussion

4.3.1 Plastic pyrolysis simulation model validation

The model was validated comparing the results with the experimental data from Singh et al. (2019) on PE and PP pyrolysis (Table 4.3 and Figure 4.3). The relative error (RE) percentage was calculated for each product at different temperatures. It indicates the simulation precision related to the size of data.

Table 4.3 Experimental (Exp.) (Singh et al., 2019) and simulation (Sim.) data used for validation and relative error percentage.

	Gas (wt%)		**RE (%)**	**Oil (wt%)**		**RE (%)**	**Char (wt%)**		**RE (%)**
PE	**Exp.**	**Sim.**		**Exp.**	**Sim.**		**Exp.**	**Sim.**	
450°C	8.5	9.1	7.2	87.5	87.1	0.4	4	3.8	5.9
500°C	9.0	9.8	8.5	89.0	86.5	2.8	2	3.8	88.2
550°C	9.0	10.4	15.4	89.5	85.9	4.1	1.5	3.8	150.8
600°C	10.5	10.9	4.1	88.0	85.3	3.1	1.5	3.8	150.9
PP	**Exp.**	**Sim.**		**Exp.**	**Sim.**		**Exp.**	**Sim.**	
450°C	9.5	9.2	2.8	82.5	85.3	3.5	8.0	5.4	32.2
500°C	8.5	9.9	16.4	86.5	84.7	2.1	8.5	5.4	8.4
550°C	12.5	10.5	15.9	83.5	84.1	0.7	4.0	5.4	35.5
600°C	13.5	11.1	18.0	82.5	23.5	1.2	4.0	5.4	35.5

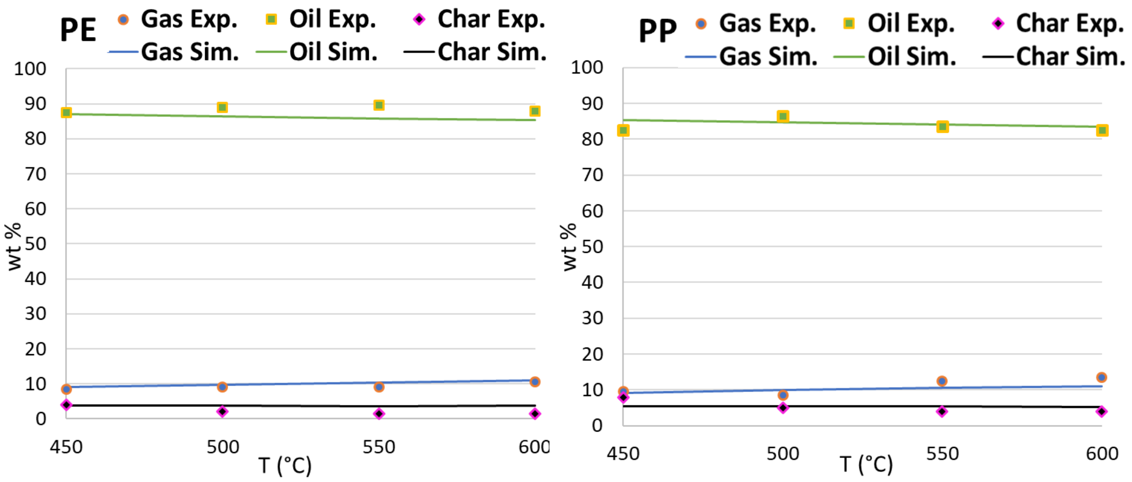

Figure 4.3 Experimental (Exp.) (Singh et al., 2019) and simulation (Sim.) data comparison of product yields at different temperatures using PE and PP feedstocks.

The simulation model was able to accurately predict the PE and PP oil yields within ~4 % error. The gas yields predicted from the model fitted the experimental data with an average maximum error of 11 %. Only the char showed a weaker prediction probably related to the assumption of its composition. However, the decreasing of chars was present in the results from both sources, but it was much lower in the simulation (~0.03 %) than in the experimental data. The similarity between simulated and experimental data can be seen in Figure 4.3. The olefins and BTX yields present in the liquid fraction were calculated and compared with literature data. The olefins and BTX simulation results exhibited the same trend showed in the literature data from Jung et al. (2010). Rising the temperature, the olefins tended to decrease while the BTX yield increased (Figure 4.4). However, BTX yield from experimental results grew at a much higher rate than BTX from the simulation model. This might be related to the reaction kinetic used for BTX in the simulation which underestimates the transformation rate.

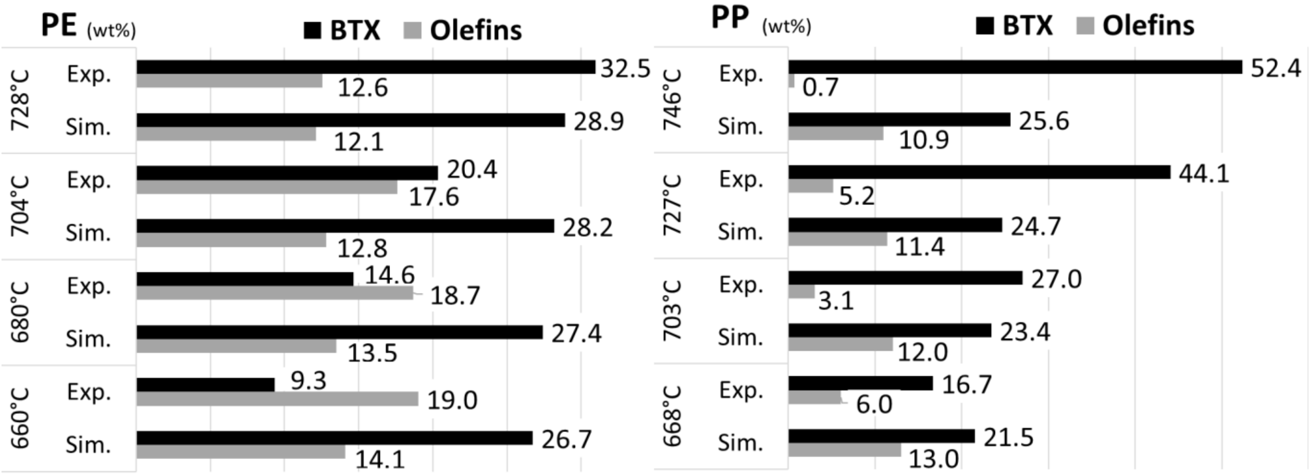

Figure 4.4 Comparison between simulation model (Sim.) and literature results (Exp.) (Jung et al., 2010) of produced BTX and olefins from the pyrolysis of PE (right) and PP (left).

4.3.2 Simulation for the prediction of recovered plastic pyrolysis outputs

The validated model was used to simulate the pyrolysis of recovered plastics from landfill and evaluate the possible outputs. Figure 4.5 shows the results from pyrolysis simulation of recovered PE and PP, single polymer and mixed together, from landfill with different storage age.

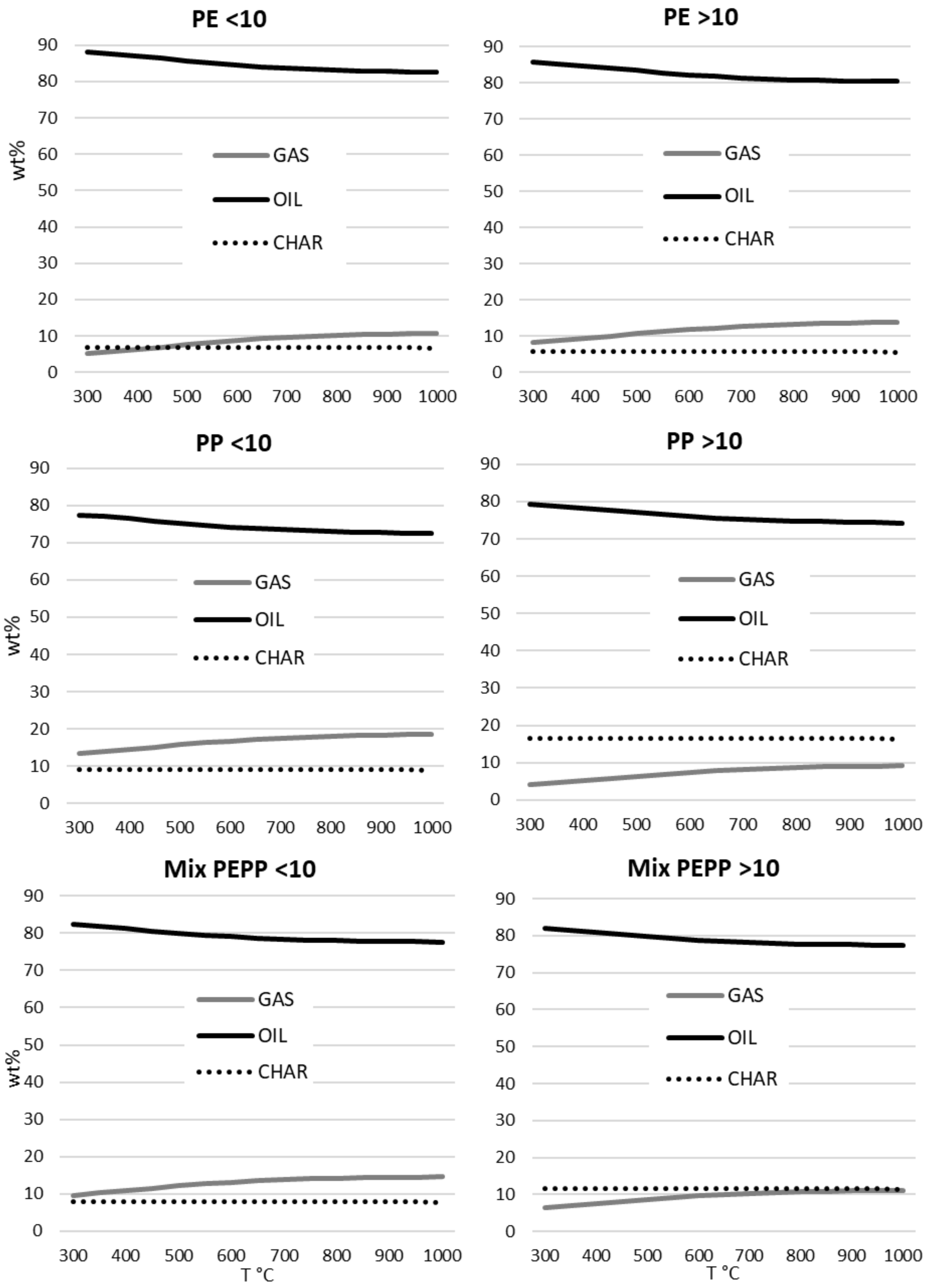

Figure 4.5 Product yields of recovered plastic pyrolysis simulation from different storage age (<10 and >10 years).

The oil yields decreased while the temperature rose to produce more gas fraction. PP presented higher char and lower oil yields compared to PE as observed in other studies (Jung et al., 2010; Singh et al., 2019). This can be related to major ash content present in PP than in PE. The olefins and BTX present in the oil fraction did not show a significant difference between samples (Table 4.4).

Table 4.4 Olefins and BTX yields from simulated pyrolysis of recovered plastics.

T (°C)	**PE<10 (wt%)**		**PE>10 (wt%)**		**PP<10 (wt%)**		**PP>10 (wt%)**		**PEPP<10 (wt%)**		**PEPP>10 (wt%)**	
	Olefin	**BTX**	**Olefin**	**BTX**	**Olefin**	**BTX**	**Olefin**	**BTX**	**Olefin**	**BTX**	**Olefin**	**BTX**
300	22.4	2.3	22.3	2.3	22.3	2.3	22.4	2.3	25.2	2.6	23.1	2.4
350	21.6	3.9	21.6	3.9	21.5	3.9	21.7	3.9	23.7	4.3	21.7	3.9
400	20.6	6.0	20.6	6.0	20.5	6.0	20.6	6.0	21.9	6.4	20.1	5.9
450	19.4	8.6	19.3	8.5	19.3	8.5	19.4	8.6	19.9	8.8	18.2	8.0
500	18.0	11.4	17.9	11.4	17.9	11.4	18.0	11.4	17.8	11.3	16.2	10.3
550	16.4	14.4	16.4	14.4	16.4	14.4	16.5	14.5	15.7	13.8	14.3	12.6
600	14.9	17.5	14.9	17.5	14.9	17.4	15.0	17.5	13.8	16.1	12.6	14.5
650	13.4	20.4	13.4	20.4	13.4	20.4	13.5	20.5	12.0	18.3	11.0	16.7
700	12.1	23.2	12.0	23.1	12.0	23.1	12.1	23.2	10.5	20.2	9.6	18.4

750	10.8	25.7	10.8	25.6	10.5	25.6	10.8	25.7	9.2	21.8	8.4	20.0
800	9.6	27.9	9.6	27.9	9.6	27.8	9.7	28.0	8.0	23.3	7.4	21.3
850	8.6	29.9	8.6	29.8	8.6	29.8	8.6	29.9	7.1	24.5	6.5	22.4
900	7.7	31.6	7.7	31.6	7.7	31.5	7.8	31.7	6.3	25.6	5.7	23.4
950	6.7	33.1	6.9	33.1	6.9	33.0	6.7	33.2	5.6	26.5	5.1	24.2
1,000	6.3	34.4	6.3	34.4	6.2	34.3	6.3	34.5	5.0	27.3	4.5	24.9

Olefins and BTX had an opposite trend increasing the temperature from 300 to 1,000 °C. The former decreased from ~22 wt% to ~6 wt% while the latter rose from ~2 wt% to ~34 wt%, in PE and PP. The simulated pyrolysis of mixed PEPP sample presented slightly higher olefins and BTX levels in the sample with storage of <10 years than >10 years. The average percentage decrease of olefins was ~8 % and ~11 % for single polymers and mixed samples, respectively. The BTX average increase was ~22 % and ~19 % for single polymers and mixed samples, respectively. Due to the underestimated transformation rate, it can be supposed that olefins and BTX reach the results presented at 1,000 °C at a lower temperature. The present simulation model can be useful to give an idea of possible outputs from pyrolysis of recovered PE and PP with different chemical characteristics. An estimated 4.9 billion tonnes of plastic were disposed of in the past 70 years (Geyer et al., 2017). PE (36 wt%) and PP (21 wt%) represent together about 57 % of the produced plastic (Geyer et al., 2017) so it can be assumed that 2.7 billion tonnes of PE (1.7 billion tonnes) and PP (1 billion tonnes) were disposed of since 1950. In 2018, 7.2 million tonnes of plastics were disposed of in landfill in Europe and the percentages of produced PE and PP were 31.5 wt% and 19.3 wt%, respectively (PlasticsEurope, 2019).

Table **4.5** shows the potential monetary value of recovering olefins and BTX from all these wasted PE and PP. These data are highly speculative but can be useful for reflecting on the lost value besides the environmental impact of this disposed of plastics. The oil tonnes for the single polymers were calculated from the average percentage of excavated PE and PP pyrolysis oil results, 83.5 wt% and 75 wt% respectively. The mixed PEPP oil tonnes were estimated from 79.2 wt%, which was the simulated oil average percentage of mixed PEPP. The olefins (13.4 wt% PE and PP; 11.5 wt% mixed PEPP) and BTX (20.4 wt% PE and PP; 17.5 wt% mixed PEPP) average percentage results at 650 °C, from both storage time, were used for determining the tonnes of chemical compounds. Indeed, temperatures over 600 °C were identified as most favourable for BTX production (Jung et al., 2010). The prices of BTX and olefins were set at 770 USD/tonne and 1,000 USD/tonne, respectively (ICIS, 2019; Industry ARC, 2019). The cost associated with a pyrolysis plant for the treatment of plastic waste varies based on different factors such as plant equipment, size and operating costs. Fivga and Dimitriou, (2018) estimated the cost of pyrolysis plant for plastic waste with a capacity of 1,000 kg per hour, summarising it in USD ~3.7 million of capital investment and USD 1.5 million of annual operating costs. Further costs are associated with the utilisation of excavated plastics which involves the recovering of this material through an ELFM project.

Table 4.5 Potential monetary value of olefins and BTX recovering from pyrolysis of disposed PE and PP between 1950 and 2018.

1950-2017 World	**PE**	**PP**	**Total**	**Mixed PEPP**
Feedstock billion tonnes	1.7	1	2.7	2.7
Average Oil billion tonnes	1.4	0.8	2.2	2.1
BTX billion tonnes[a]	0.3	0.2	0.4	0.4
Olefins billion tonnes[b]	0.2	0.1	0.3	0.2
Price BTX USD billion (770 USD/tonne)	223	118	341	283
Price Olefins USD billion (1,000 USD/tonne)	190	101	291	242
Total BTX and Olefins USD billion	413	219	632	524
2018 Europe	**PE**	**PP**	**Total**	**Mixed PEPP**
Feedstock million tonnes	2.3	1.4	3.7	3.7
Average Oil million tonnes	1.7	1.1	2.8	2.9
BTX million tonnes[a]	0.4	0.2	0.6	0.5
Olefins million tonnes[b]	0.2	0.1	0.4	0.3

Price BTX USD million (770 USD/tonne)	270	165	435	391
Price Olefins USD million (1,000 USD/tonne)	230	141	371	334
Total BTX and Olefins USD million	500	306	806	724

[a] calculated from: 20.4 wt% for PE and PP; 17.5 wt% for mixed PEPP.
[b] calculated from: 13.4 wt% for PE and PP; 11.5 wt% for mixed PEPP.

These results showed the potential value of recovered plastic materials, which is often underestimated. PE presented a higher monetary value than PP because of its higher average liquid yield. The pyrolysis of single polymers seems to be more beneficial than the mixed PEPP sample for the olefins and BTX production. Indeed, the estimated monetary value from the total selling of products from separate polymer pyrolysis was USD ~140 million higher than products from mixed PEPP. The market size of aromatics in 2015 was USD 5.41 billion (Market Watch, 2019). The potential monetary value of BTX from 2018 landfilled PE and PP in Europe represents 8 % of the 2015 global aromatic market size. These data can improve awareness about the potential value of wasted resources. The difference between the pyrolysis of single polymer and mixed should be considered to evaluate the best approach to pyrolyze this material. The sorting techniques applied for plastic waste involve near infrared (NIR), X-Ray fluorescence, air or flotation separation, triboelectrostatic separator, and manual sorting. However, excavated plastics can present more impurities attached to the surface, such as soil and fine fraction, and a higher level of degradation (Canopoli et al., 2020). For these reasons, the application of these sorting techniques for the recovered plastics might be expensive, time consuming and not efficient. All these data should be evaluated in order to identify the most convenient method to undertake for the upcycling of this material. Further studies should evaluate the separation rate of excavated plastics in different polymers applying the current technologies used for plastic waste sorting. The enhanced landfill mining (ELFM) concept highlights the importance of recovering valuable waste materials from landfills (Jones et al., 2013). The plastic represents an important percentage of landfill waste and this paper showed the potential value of upcycling it through pyrolysis.

4.4 Conclusion

It is fundamental to point out the limit of current plastic waste management which focuses on what is more visible forgetting the buried materials. Indeed, this plastic keeps increasing and not much attention is given to their recovery. The circular plastic economy should consider both fresh plastic waste and excavated plastic waste as potential resources. The combination of ELFM and the plastic economy could help to introduce the excavated plastics into the circular economy. This study showed the possibility of simulating the pyrolysis of recovered PE and PP from landfill using ASPEN Plus. The findings can help to evaluate the feasibility of pyrolysis of recovered plastics providing reasonable results on products quality and quantity. Further model improvement can lead to the identification of a variety of valuable chemical compounds that can be sold. A reaction model is a useful tool for estimating the value of potential resources such as landfilled plastics. Further studies are needed on detailed cost and benefit and a life cycle analysis on pyrolysis of recovered plastics to globally evaluate the pros and cons of this process.

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5 PYROLYSIS OF RECOVERED PLASTICS WITH PY-GC-MS

Evaluation of high-value chemicals production from recovered plastics from excavated municipal solid waste

This chapter presents the chemical compounds identified from the pyrolysis of excavated PE, PP and mixed plastics.

5.1 Introduction

The yearly global production of plastic has grown from 1.5 million tonnes in 1950 to 350 million tonnes in 2017 at a compound annual growth rate (CAGR) of about 8.5 % (PlasticsEurope, 2018a; PlasticsEurope, 2016). In total, half of all plastics produced are designed to be used only once. It has been estimated that more than 8.3 billion tonnes of plastics have been produced since the early ‘50s and about 60 % of that plastics has ended up either in landfill or in the natural environment (Geyer et al., 2017). More than 99 % of plastics is produced from chemicals derived from fossil fuels (Nielsen et al., 2019). In Europe, over 400,000 municipal solid waste (MSW) landfill sites have been reported (EURELCO, 2018) and the average percentage of plastic ranged between 9 and 25 wt% (Quaghebeur et al, 2013; Zhou et al., 2014; Jones et al., 2013; Wagland et al., 2019; Canopoli et al., 2020). This amount of plastic can potentially be recycled through enhanced landfill mining (ELFM) and can be reintroduced into the market sector, therefore, embracing the circular economy concept. The Global Commitment launched in 2018 by the Ellen MacArthur Foundation in collaboration with UN Environment Programme, deals with the new circular plastics economy covering the production, consumption and reuse or recycling of plastic products which never become waste (Ellen MacArthur Foundation and UN Environment Programme, 2019). The new circular plastics economy aims to reduce the need for virgin plastics and finite resources. This view can be expanded to the recycling of disposed plastics which can become sustainable feedstock contributing to climate change mitigation. However, some challenges need to be addressed in order to upgrade this material as a sustainable resource. Indeed, plastics buried for several years in landfill sites are likely to have experienced weathering processes which have affected their chemical and mechanical properties (Canopoli et al., 2018a). Excavated plastics were found to have a major quantity of impurities such as soil, surface alteration, higher oxidation level, silicon and aluminium content and a higher degree of crystallinity (Quaghebeur et al, 2013; Zhou et al., 2014; Canopoli et al., 2020). Considering these characteristics, pyrolysis technologies was identified as a potential treatment for the upgrading of recovered plastics from landfill (Canopoli et al., 2020). Valuable chemicals and transportation fuel can be produced through pyrolysis (Achilias et al. 2007; Jung et al., 2010; Cho et al., 2010; Wang et al., 2019; Anuar Sharuddin et al., 2016). However, only a few studies used recovered plastics from landfill, while the majority investigated the pyrolysis of plastic waste and virgin plastics (Bosmans et al., 2014; Breyer et al. 2017; Santaweesuk and Janyalertadun, 2017; Anuar Sharuddin et al., 2016; Singh and Ruj, 2016). In addition, the studies on recovered plastics focussed more on the fuel production without giving information on the chemical compounds, such as styrene, toluene and benzene, that can potentially be introduced in a closed-loop recycling process (Breyer et al. 2017; Santaweesuk and Janyalertadun, 2017; Butler et al., 2011; Ragaert et al., 2017; Canopoli et al., 2020). In order to evaluate the best approach to apply in the management of excavated plastics, it is fundamental to state the possible advantages associated with its recycling. It can be clarified by investigating the pyrolysis products and their eventual applications. The peculiarities related to physicochemical characteristics of excavated plastics might have an impact on the pyrolysis product quality and quantity. The focus of this study is to analyse the outputs of the pyrolysis of excavated plastics with a view to considering the products from the new circular plastics economy perspective. The objectives of this study comprise of estimating the thermal behaviour of recovered plastics compared to the fresh plastic waste; examining the pyrolysis products of recovered plastics and fresh plastic waste at different temperatures; evaluating the difference of the pyrolysis products between diverse polymer types commonly found in the landfills; identifying the products with potential marketability. Pyrolysis gas chromatography mass spectrometry (Py-GC-MS) is a valid technique for the identification of quality and quantity of decomposition products (Kumar et al., 2011). It was applied in different studies on plastics, biomass, metal-alignate, printed circuit boards (Gu et al., 2013; Maruyama et al., 2015; Evangelopoulos et al., 2015; Sight et al., 2019). Azeez et al (2010) compared the results from Py-GC-MS and a fluidized bed pyrolysis unit, which were found in good agreement and specifically no significant difference was found on the quality of the products. The challenges related to the pyrolysis at industrial scale are related to the different types of reactors, parameters and plastic types used as feedstock. However limited information is available on plastic pyrolysis at a large scale to compare the process with small-scale pyrolysis.

5.2 Materials and methods

5.2.1 MSW samples, plastic materials reference and characteristics determination

A total of 154 kg of waste, in 30 samples, were excavated from four MSW landfills at depths of between 5 and 55 m (Table 5.1). The samples from landfills appeared generally wet with much of the soil and fine fraction attached to the plastic samples. The plastic samples were pre-dried in an oven, at 60 °C for 2 h, before the identification of plastic types and in order to easily separate the soil and fine fraction from their surface. Seven plastic material types were identified using an attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and the main fractions with the highest percentages are shown in Table 5.1. The FTIR spectra were recorded over 16 scans at a spectral resolution of 4 cm^{-1} in a wavenumber range of 4,000 to 400 cm^{-1}. After the identification, the plastic materials were manually washed with cold water and air-dried at room temperature. The ash content was determined using a furnace set at a temperature of 250 °C for 60 min and then 550 °C for 120 minutes (British Standards Institute 2011a). The gross calorific value (GCV) was determined by the combustion of ~1 g of the sample in a bomb calorimeter. About 1 g of sample was placed in inside a crucible with a lid and this was placed in a furnace at 600 °C for 7 min to measure the volatile matter (Zhou et al., 2014). Ultimate and metals analyses were carried out following the British Standards methods (2011b, 2011c, 2011d). The samples of fresh and excavated polyethylene (PE) and polypropylene (PP) were analysed in triplicate.

Table 5.1 Average amount of plastics and percentages of main plastic types recovered from the excavated MSW samples across the 4 landfill sites (adapted from Canopoli et al., 2020).

		Total	Min	Average	Max
MSW samples (<10 years) n = 7	Mass (g)	12,335	390	1,762 ± 2,953	8,448
	% plastic (wet basis)	11	5	13 ± 7	24
MSW samples (>10 years) n = 23	Mass (g)	141,603	1,891	6,157 ± 2,596	11,586
	% plastic (wet basis)	7	0.3	7 ± 6	26
Total n = 30	Mass (g)	153,938	390	5,131 ± 3,239	11,586
	% plastic (wet basis)	7	0.3	9 ± 7	26
PE (wt%)	<10 years	55	32	50 ± 14	70
	>10 years	45	2	48 ± 27	92
PP (wt%)	<10 years	12	2	13 ± 10	32
	>10 years	19	1	19 ± 21	85
PS (wt%)	<10 years	2	3	5 ± 2	6
	> 10 years	4	1	5 ± 4	16

PET (wt%)	<10 years	1	1	4 ± 3	6
	>10 years	3	2	20 ± 26	39
PVC (wt%)	<10 years	2	3	4 ± 1	5
	>10 years	11	0	16 ± 17	50

These are the same samples analysed in chapter 3.

5.2.2 Plastic materials stability using thermogravimetric analysis

As shown in chapter 3, the recovered plastic with more than 10 years of storage presented a generally higher degree of degradation that can affect their thermal decomposition. Thermogravimetric analysis (TGA) was used to quantitatively identify differences in the thermal decomposition of plastic samples of the same type but with different storage ages. This analysis helped to evaluate if the characteristics of excavated plastics affect their thermal behaviour, which could have a consequence on the pyrolysis products. PE and PP, fresh and excavated, <10 years and >10 years, were thermally characterised in duplicate using TGA. PE samples were mainly represented by soft plastic, such as plastic bags, while PP was, for the majority, hard pieces of plastics. Due to this difference in density, the PE and PP samples studied were ~5 mg and ~10 mg, respectively, so as to maintain a similar bulk volume. A sample mass range of between 5 and 10 mg is commonly used for TGA of plastic samples (Sørum et al. 2001; Klein-Bendavid et al., 2014; Gallo and Severini, 2017). The samples were placed in a ceramic crucible, heated at 10 °C/min from 50 °C to 600 °C and held for 5 min in a nitrogen atmosphere with a flow rate of 40 mL/min (Breyer et al. 2017). The first derivative of the weight loss was calculated from the TGA results to identify the temperature of greatest weight loss. The data reproduced in this paper are the mean values of duplicate runs per each sample.

5.2.3 The identification of pyrolysis compounds from excavated plastics by Pyrolysis-gas chromatography-mass spectrometry

The fresh and excavated plastic waste were pyrolyzed using a Pyrola 2000 (Pyrol AB) connected to a quadrupole gas chromatograph-mass spectrometer (GC-MS) (Agilent Technologies 7890A GC - 5975c inert xl EI/CI MSD). A sample, between ~150 and 200 µg for a single plastic and between ~300 and 550 µg of mixed plastics, was used for each analysis. In the Pyrola, a sample is placed on a resistively heated platinum filament, where the sample takes place. The filament is surrounded by a glass cell. The Pyrola 2000 measures the temperature in two different ways, increasing the accuracy and reproducibility. The exact temperature the sample has reached during pyrolysis is recorded as a temperature-time profile (TTP). Above 600 °C measurement is taken by a photodiode which is very accurate, and the resistance of the filament is used for temperatures below 600 °C. Calibration was performed for six temperatures on the filament used for the sample analysis to determine the current required to reach and hold the pyrolysis temperatures that would be used for the sample analysis. The platinum filament and glass cell were cleaned after each sample by heating them with a micro-torch. Helium was used as a carrier gas with a flow rate of 26 mL/min through the glass cell when pyrolysis was taking place. Temperature is recognised as one of the main parameters during plastic pyrolysis because it highly affects the kinetics of the reactions taking place and therefore the final product composition (Anuar Sharuddin et al., 2016). In order to inspect the variance in product composition at different temperatures, fractionated pyrolysis was performed for 2 seconds at each temperature, with a sequential temperature rise time of 8 milliseconds, at each temperature: 350, 500, 650 and 800 °C (Westphal et al., 2001; Evangelopoulos et al., 2015). The Pyrola 2000 chamber temperature was set isothermally at 200 °C. The GC inlet was a standard Agilent split/splitless injector, installed with a 2 mm internal diameter empty liner. The transfer line temperature, between the pyrolyzer and the GC injector, was held isothermally at 290 °C (Jin et al., 2016). The GC separation column was an Agilent HP5-MSUI (30 m × 0.25 mm × 0.25 µm) (Aguado et al., 2007; Jin et al., 2016). A GC inlet split ratio of 20:1 was used. The GC oven was programmed from 30 °C (held for 0.5 min) to 350 °C (held for 1.5 min) at 10 °C/min. The running time for the GC was 34 min (Jin et al., 2016; Sophonrat et al., 2017). The MS operated under electron ionisation (EI) of 70 eV with a mass spectral range of between 33 and 500 m/z. The National Institute of Standards and Technology (NIST) library was used for the identification of products. Fresh and excavated PE and PP (<10 years and >10 years) were pyrolyzed in triplicate. In addition to the single polymer runs, two mixes of excavated plastic samples were pyrolyzed. Polystyrene (PS), PE and PP nominated as sample A, polyethylene terephthalate (PET), polyvinyl chloride (PVC), PE and PP nominated as sample B (more details are given in Table 5.2). The mentioned plastic types were the most commonly identified in the landfill samples. The pyrolysis of PVC and PET produces undesirable products such as hydrogen chloride and benzoic acid (Anuar Sharuddin et al., 2016). In addition, pyrolysis of PET and PVC produce lower oil yield than the other mentioned plastic type (Singh et al. 2019, Anuar Sharuddin et al., 2016). However, some pyrolysis plants accept a low level of PVC and PET. For these reasons, the pyrolyzed mixed samples were firstly divided in the mix with and without excavated PVC and PET in order to evaluate their effects in the produced compounds. Then, the different percentage were tested to identify the possible impact on the products from the excavated plastics pyrolysis. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was used for the relative quantification of the products from recovered plastics from landfill. The signals considered in the results appeared in the mass spectrum at a signal-to-noise ratio of 5:1. The repeatability was calculated from the relative abundance of compounds identified (more details available in the appendix Table C.38 and C.39). The average relative standard deviation is 9 (±6) % which is in the acceptance range (Hermabessiere et al., 2018). The pyrolysis experiment can be summarised as follow. The shredded sample was placed on the filament in the pyrolysis chamber. The temperature in the pyrolysis chamber reached progressively 350 °C, 500 °C, 650 °C and 800 °C. The produced volatiles at each temperature were injected into the GC. Then, the separated components were ionized by the mass spectrometer. Finally, the components were identified using the NIST library. The results were further analysed to give the relative quantity of identified compounds.

Table 5.2 Information of mixed samples A mix and B mix <10 years and >10 years storage time.

Name (run number)	Feedstock ratio (%)	Content
A <10 and >10 (1)	33/33/33	PS = PP = PE
A <10 and >10 (2)	25/75	PS < PE PP
A <10 and >10 (3)	70/30	PS > PE PP
B <10 and >10 (1)	20/20/20/20/20	PET = PVC = PP = PE = PS
B <10 and >10 (2)	30/70	PET PVC < PE PP PS
B <10 and >10 (3)	75/25	PET PVC > PE PP PS

5.3 Results and discussion

Detailed analyses were performed for PE and PP, fresh and excavated (Table 5.3). In general PE and PP, fresh and excavated, presented a high calorific value (average value 39 MJ/kg). PP <10 years of storage time showed the lowest calorific value with 28 MJ/kg and the highest oxygen content (10 wt%). The oldest samples, PE >10 and PP >10 years of storage, had lower volatile matter than the rest of the samples. The metals analysis (Table 3.3) revealed a lower content when compared to the results for mixed excavated plastics analysis from other studies (Quaghebeur et al., 2013; Prechthai et al., 2008). In the other studies, the high metals content is likely to be related to the soil attached to the plastics.

Table 5.3 Proximate, ultimate and metals analyses of fresh and excavated PE and PP samples.

		PE	**PE <10**	**PE >10**	**PP**	**PP <10**	**PP >10**
Proximate analysis	Ash (wt%)	7.6* (0.4)	7.0* (4.4)	4.5* (0.5)	2.2* (0.5)	7.3 (8.5)	18.9 (1.2)
	VM (wt%)	98.7 (0.1)	94.5 (0.4)	93.6 (0.2)	98 (0.2)	90.9 (1.0)	88.5 (2.2)
	GCV (MJ/kg)	40.4 (0.3)	42.3 (1.5)	42.1 (1.1)	45.7 (0.6)	42.3 (4.7)	36.3 (0.8)
Ultimate analysis	C (wt%)	72.9*	82.6*	79.6*	84.2*	70.9	81.7
	N (wt%)	0.3*	0.3*	0.5*	0.2*	0.1	0.2
	H (wt%)	11.9*	13.6*	13.1*	13.6*	11.1	13.3
	O (wt%) [a]	7.3	0	1.9	0	10	0
	S (wt%)	0.006	0.12	0.13	0.024	0.210	0.094
Element analysis	Cl (wt%)	0.024	0.26	1.72	0.004	0.016	0.025
	Br (wt%)	0	0.022	0	0	0	0
	F (wt%)	0	0.004	0.002	0.001	0.001	0.001
	As (mg/kg)	<1*	<1*	<1*	<1*	1.8	2.3
	Cd (mg/kg)	<1*	<1*	<1*	<1*	<1	<1
	Co (mg/kg)	<1*	<1*	<1*	<1*	<1	<1
	Cr (mg/kg)	<1*	<1*	2.2*	1.6*	2.8	2.6

	Cu (mg/kg)	11*	8.1*	5.9*	4.8*	30	21
	Hg (mg/kg)	<1*	<1*	<1*	<1*	<1	<1
	Mn (mg/kg)	4.9*	3*	1.3*	2.7*	2.5	<1
	Ni (mg/kg)	<1*	<1*	<1*	<1*	2.9	4.2
	Pb (mg/kg)	1.1*	3.2*	6.7*	5.1*	11	8.8
	Sb (mg/kg)	<1*	<1*	<1*	<1*	<1	<1
	Sn (mg/kg)	<1*	<1*	<1*	<1*	2.6	1.6
	Tl (mg/kg)	<1*	<1*	<1*	<1*	<1	<1
	V (mg/kg)	<1*	<1*	<1*	<1*	<1	<1

[a] Calculated by difference
*Adapted from Canopoli et al., 2018b
These are the same samples analysed in chapter 3.

5.3.1 Thermal degradation stability of PE and PP

TG analysis was performed to compare the degradation temperature ranges of fresh and excavated PE and PP from different years of storage. The average maximum weight loss for fresh PE, PE <10, PE >10 were at 491 °C, 494 °C and 493 °C, respectively (Figure 5.1). The maximum weight loss for fresh PP, PP <10, PP >10 were at 481 °C, 477 °C and 475 °C, respectively. The maximum mass loss rate is exhibited by PE <10 and fresh PP. PP fresh and excavated degraded at a lower temperature than PE. Degradation of fresh and excavated PE samples did not show significant differences. All temperature results were in the ranges identified for PE and PP waste degradation in Yan et al. (2015) study. The landfill environment and storage time did not seem to have a critical effect on the thermal behaviour of excavated plastic.

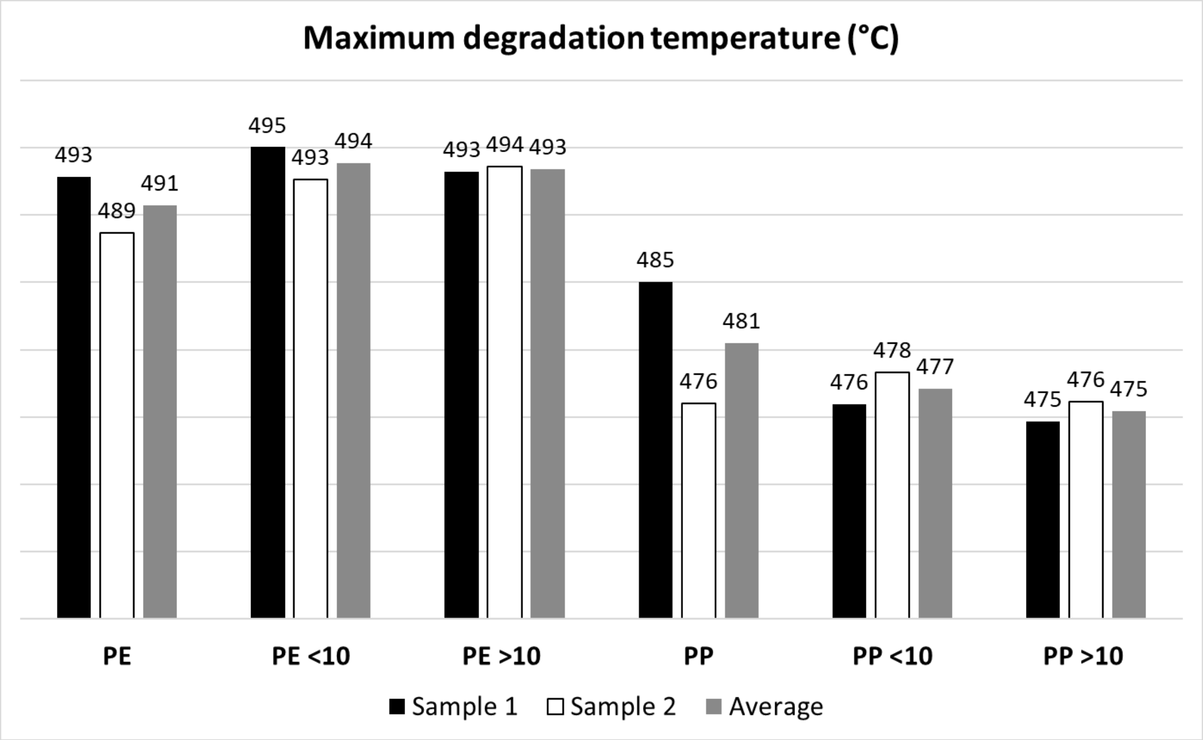

Figure 5.1 Maximum degradation temperature (duplicate and average of each sample) of fresh and excavated polyethylene (PE) and polypropylene (PP) with different storage time (<10 years and >10 years).

5.3.2 Identification of chemical compounds produced by pyrolysis of recovered plastics from landfill

The relative abundance of produced compounds at different temperatures are shown in Table 5.4**,** Figure 5.2 and Figure 5.3. The main products, as revealed from the Py-GC-MS analyses, are aliphatic hydrocarbons, followed by aromatics and fluorine containing compounds (Table 5.4). Plastics such as PE and PP are often fluorinated to improve and preserve their characteristics, especially when they are intended as chemicals and solvent containers (Kharitonov and Kharitonova, 2009). In addition, fluorine containing compounds are also used in plastic food containers or wrappers. Bromine is commonly used as a flame retardant (AccuStandard, 2018). Siloxane and organosulfur are also common additives in plastics (Ryan et al., 2000; AccuStandard, 2018). Oxygenated compounds (esters, ketones, alcohols, fatty acids, carboxylic acids, aldehydes and heterocyclic aromatic compounds) were present in all samples and not only in sample B, where PET mix was present. Similarly, the formation of oxygenated compounds from plastic waste pyrolysis was found also in a previous study (Toraman et al., 2014).

Table 5.4 Relative abundance (%) products at the different pyrolysis temperatures for each sample.

	Relative abundance (%)									
350 °C	**PE fresh**	**PE <10**	**PE >10**	**PP fresh**	**PP <10**	**PP >10**	**A <10**	**A >10**	**B <10**	**B >10**
Aliphatic hydrocarbons	31	13	10	45	24	62	39	26	57	59
Aromatic hydrocarbons	0	0.23	0	0	0	0	4	11	0.17	1
Other aromatics	0	0.17	0	0	0	0.32	8	5	9	16
Fluorine containing compounds	0	20	90	47	65	24	24	28	13	14
Bromine containing compounds	0	0	0	7	8	8	6	9	9	8
Esters	6	56	0	0	0	0	16	10	10	0.08
Siloxane compounds	54	0	0	0	4	6	0	3	0	3
Alcohols	0	8	0	0	0	0	0.1	0.5	0.46	0.05
Amines	0	2	0	0	0	0	0	4	0	0
Organosulfur compounds	0	0	0	0	0	0	2	2	0	0.01

Fatty acids	0	0	0	0	0	0	0	0	1	0.04
Gas (CO_2)	9	0	0	0	0	0	0	0	1	0
Total	100	100	100	100	100	100	100	100	100	100

500 °C	**PE fresh**	**PE <10**	**PE >10**	**PP fresh**	**PP <10**	**PP >10**	**A <10**	**A >10**	**B <10**	**B >10**
Aliphatic hydrocarbons	64	8	18	68	68	53	23	10	16	38
Aromatic hydrocarbon	0	25	0	0	1	0.1	43	51	35	16
Other aromatics	8	0	0	0	0.31	6	0.5	0.2	6	28
Fluorine containing compounds	1	25	77	14	5	0	6	10	3	2
Bromine containing compounds	0	0	0	4	0	15	4	5	2	2
Esters	5	1	1	1	1	8	1	0.4	1	2
Siloxane compounds	8	0	0	0	0	7	0	2	0	3
Alcohols	6	0.1	4	13	23	8	4	1	1	2
Organosulfur compounds	0	0	0	0	2	0	18	20	11	3
Fatty acids	0	0.2	0	0	0	0	0	0	4	3
Hydrogen halides	0	40	0	0	0	0	0	0	16	4

Aldehydes	2	0	1	0	0	0	0	0	0	0
Chlorinated hydrocarbons	0	0	0	0	0	0	0	0	3	0
Gas (CO_2 and N_2O)	6	0.33	1	0	0	4	0	0	0	0
Total	100	100	100	100	100	100	100	100	100	100

650 °C	**PE fresh**	**PE <10**	**PE >10**	**PP fresh**	**PP <10**	**PP >10**	**A <10**	**A >10**	**B <10**	**B >10**
Aliphatic hydrocarbons	64	41	49	68	65	38	54	34	28	35
Aromatic hydrocarbon	0	18	0	0	0	2	27	28	33	16
Other aromatics	0	0.06	0	0	0	39	1	9	18	29
Fluorine containing compounds	0.04	3	30	1	0.5	0.23	0	1	0	1
Bromine containing compounds	0	0	0	0	0	1	0	0	0	0
Esters	2	3	0.02	5	3	4	2	1	3	3
Siloxane compounds	0	7	0	0	0	0	0	0	0	0
Alcohols	30	17	16	24	29	11	12	16	10	12
Organosulfur compounds	0	0	0	3	1	3	2	9	7	4
Aldehydes	4	2	1	0.06	0.21	0.05	1	2	1	1

Ketones	0.01	3	0.01	0	0	2	0.1	0	0	0
Gas (CO_2)	0	7	4	0	0	1	0	0.32	0.49	0
Total	100	100	100	100	100	100	100	100	100	100

	PE	**PE**	**PE**	**PP**	**PP**	**PP**	**A**	**A**	**B**	**B**
800 °C	**fresh**	**<10**	**>10**	**fresh**	**<10**	**>10**	**<10**	**>10**	**<10**	**>10**
Aliphatic hydrocarbons	7	0	7	0	5	3	32	36	26	44
Aromatic hydrocarbon	0	8	0	0	0.02	8	0	3	12	9
Other aromatics	0.3	0	0	0	0.03	22	0.06	0.4	20	11
Fluorine containing compounds	68	38	57	64	80	61	42	45	12	21
Bromine containing compounds	0	0	0	2	13	6	9	0	2	8
Esters	0	12	0	0	0	0	0	0	0	0
Siloxane compounds	0	26	18	0	0	0	0	2	0	0
Alcohols	4	0	3	31	0	0	13	13	24	3
Amines	0	0	0	0	0	0	1	1	1	0.37
Gas (CO_2)	21	16	15	3	2	0	4	1	3	5
Total	100	100	100	100	100	100	100	100	100	100

Details on compounds included in each group can be found in the appendix Table C.22 - C.37.

The aliphatic hydrocarbons (Figure 5.2) reached their highest relative abundant for PE <10, PE >10, A <10 at 650 °C, and were almost equivalent at 500 and 650 °C for PE, PP, PP <10. In the other samples, PP >10, B <10, B >10, they were most abundant at 350 °C, whilst at 800 °C they were only the most abundant in A >10.

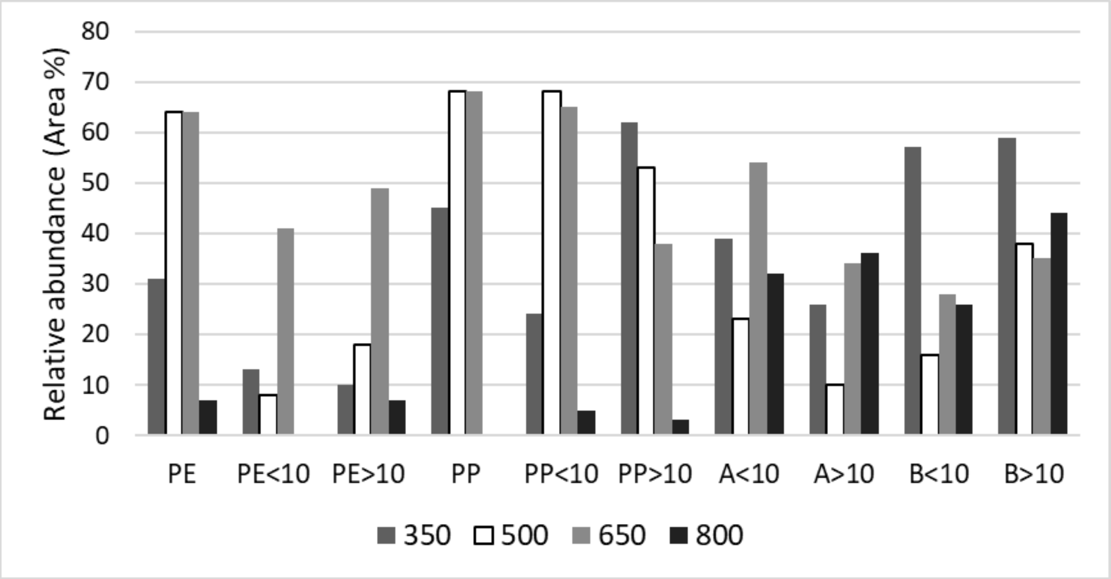

Figure 5.2 Relative abundance (%) of aliphatic hydrocarbons in each sample at different temperatures.

The aromatic hydrocarbons (Figure 5.3) were most abundant at 500 °C for PE, PE <10, PP <10, A <10 and >10, while for PP >10, B <10 and >10 it was at 650 °C. Styrene is the main aromatic hydrocarbon produced in the pyrolysis of A <10 and >10, B <10 and >10 at 500 °C (Table 5.5). A high percentage of styrene was also reported in other studies on plastic pyrolysis (Anuar Sharuddin et al., 2016; Miandad et al., 2017; Miandad et al., 2019).

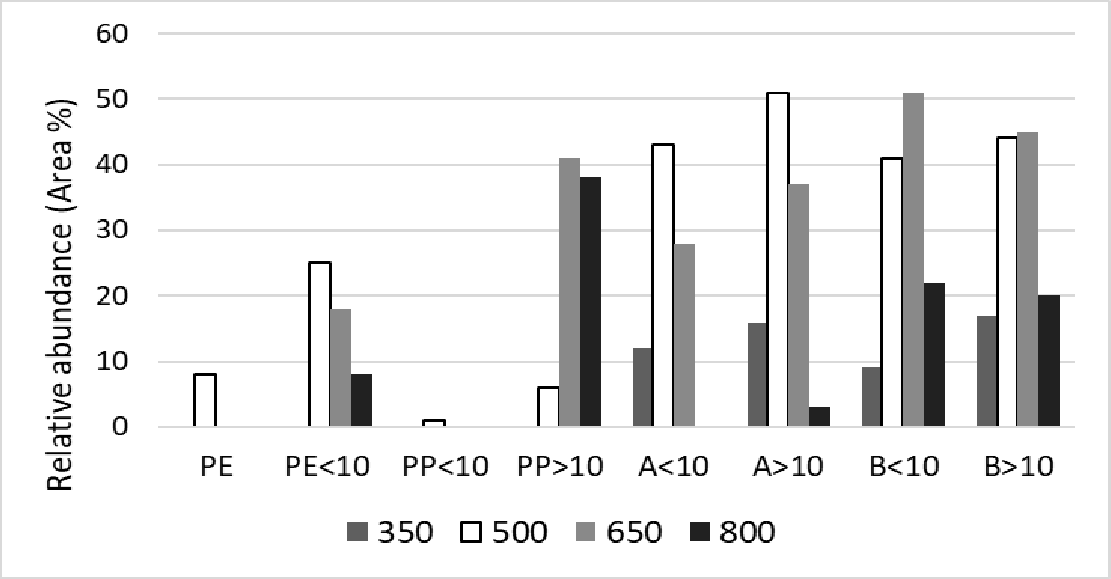

Figure 5.3 Relative abundance (≥1 %) of aromatic compounds in each sample at different temperatures.

Table 5.5 shows the compounds that have been identified and are likely to be found in the pyrolysis oil. Some of the main compounds are diethyl phthalate (which is used to improve the plastic flexibility) 13-Docosen-1-ol, benzene, benzoic acid, styrene, and vinyl benzoate, all are commonly used in the plastic industry. The presence of PET and PVC is known to facilitate the production of oxygenated and chlorinated compounds. Comparing mixed samples, A (without PET and PVC) and sample B (with PVC and PET), the difference in the percentage of the oxygenated compound was evident only at 650 °C, presenting a higher level in the B samples. The averages of the oxygenated compounds at 500 °C were 33 % for both A >10 and B >10, whilst they were 29 % and 27 % for A <10 and B <10, respectively. In B >10 at 650 °C, oxygenated compounds were 47 %, 10 % higher than A >10 (36 %), while in A <10 and B <10 the former was 20 % lower than the latter with 17 % and 37 %, respectively. Most chlorinated compounds, such as hydrogen chloride and chlorinated aromatics, were detected in sample B, mainly at 500 °C. The average abundance of chlorinated compounds in sample A was ~1 %, while B <10 had 22 % and B >10 10 %. Hydrogen chloride was the main halogenated compound in B <10, with an average value of 16 %. B >10 chlorinated compounds were mainly represented by aromatics with 7 %.

Table 5.5 Relative abundance (≥3 %) of main compounds that can be found in the pyrolysis oil of different samples at 500 and 650 °C.

	PE fresh (%)		PE <10 (%)		PE >10 (%)		PP fresh (%)		PP <10 (%)		PP >10 (%)		A <10 (%)		A >10 (%)		B <10 (%)		B >10 (%)	
Temperature (°C)	**500**	**650**	**500**	**650**	**500**	**650**	**500**	**650**	**500**	**650**	**500**	**650**	**500**	**650**	**500**	**650**	**500**	**650**	**500**	**650**
(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	0	0	0	0	0	0	0	0	0	0	0	0	17	2	20	9	11	6	2	3
1,13-Tetradecadiene	0	3	0	1	0	3	0	0	0	0	0	0	0	0.4	0	1	0	0.2	0	0
1,19-Eicosadiene	0	5	0	5	0	9	0	0	0	0.1	0	0	0	1	0	1	0	0	0	0
1,2-Ethanediol, dibenzoate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	3	0	2
13-Docosen-1-ol -	0	7	0	0	0	0	0	0	0	0.04	0	0	0	1	0	3	0	1	0	1
17-Pentatriacontene	0	1	2	0.03	0	0	0	0	0	0	0	0	0	1	2	2	6	2	3	4
1-Decene	4	3	0.4	2	2	2	0	0.2	0.1	0.3	0	0	0.2	1	0.2	1	0.1	1	0.05	1
1-Decene, 2,4-dimethyl-	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0

1-Heptacosanol	0	6	0	2	1	2	0	0	0	1	0	0	0	1	0	2	0	1	0	0
1-Heptene	0	3	0.2	1	1	2	0	0	0	0	0	0	0	1	0.05	1	0	0	0	0
1-Hexadecanol, 3,7,11,15-tetramethyl-	0	0	0	0	0	0	0	2	0	3	0	1	0	0	0	0	0	0	0	0
1-Hexene	0	5	1	3	1	3	0	0	0	0	0	0	0	1	0	1	0	0	0	0.2
1-Nonadecene	0	2	0.4	3	1	5	0	5	1	3	0	1	0	1	0	1	0	0.4	0	0.2
1-Nonene, 4,6,8-trimethyl-	0	0	0	0	0	0	6	0.2	0	0.2	2	0.4	0.2	0.03	0	0	0	0	0	0
1-Pentadecene	3	3	0.2	1	1	2	0	0.1	0	0.1	0	0	0	1	0.1	1	0	1	0	1
1-Pentene, 2-methyl-	0	0	0	0	0	0	6	4	6	4	3	2	1	2	0.3	1	1	2	1	1
1-Tetradecene	3	3	0.3	0	1	2	1	1	2	1	0	0	0.2	1	0.1	1	0.3	0	0	0
1-Undecene	3	3	0.3	1	2	2	0	0.1	0	0.2	0	0.02	0	1	0.1	1	0	1	0	1
2,4-Dimethyl-1-heptene	0	0	0.1	0.2	0	0.01	30	14	29	14	18	10	8	6	4	3	6	6	13	7

2-Isopropyl-5-methyl-1-heptanol	0	0	0	0	0	0	0.5	11	16	11	8	6	3	1	0	1	0	0	0	3
3-Octene, 2,2-dimethyl-	0	0	0	0	0	0	0	2	0	3	0	2	0	0	0	0	0	0	0	0
9-Eicosene	1	0	0	0	0	0	0	0.2	0.3	0.3	4	0	0	1	0	0.4	0	0	10	0
Benzene	0	0	14	1	0	0	0	0	0	0	0	0.5	0	0.2	0	0.3	3	2	5	1
Benzeneethanamine, 3-fluoro-.beta.,5-dihydroxy-N-methyl-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.004	0	0.2	0	9	0.2
Benzoic acid	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	2	1	1	0.4	3
Benzoic acid, 2-(1-oxopropyl)-	0	0	0	0	0	0	0	0	0	0	0	11	0	0	0	1	2	4	3	7
Benzoic acid, 4-(2-bromoethyl)-, 4-formylphenyl ester	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0
Bicyclo[4.2.0]octa-1,3,5-triene	0	0	0	0	0	0	0	0	0	0	0	0.03	0	16	0	6	0	19	0	7
Butane, 1-chloro-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0

Cyclopentanone	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cyclopropylmethanol	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Decanoic acid, octyl ester	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Diethyl Phthalate	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hydrogen chloride	0	0	40	0	0	0	0	0	0	0	0	0	0	0	0	0	16	0	4.	0
Heptacosane	0	0	0	0	0	0	0	0	0	0	0.3	0	3	0	0.3	0.3	0	0	4	0
Heptane	3	1	0.2	1	1	1	0	0	0	0	0	0	0	0.3	0.1	0.3	0	0.3	0	0.1
Hexanedioic acid, dioctyl ester	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Isophthalic acid	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	3	0
Methyl 2,6-dihydroxybenzoate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	6
Naphthalene, 2-methyl-	0	0	0.3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

n-Heptadecanol-1	1	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
n-Tridecan-1-ol	0	0	0	0	0	0	8	2	2	2	0	1	1	0	0	0	1	0	0	0
Octacosanol	0	10	0	12	0	6	0	0.2	0	2	0	0	0	4	0	5	0	3	0	3
Octadecane, 1,1'-[1,3-propanediylbis(oxy)]bis-	0	0	0	0	0	0	0	0	0	0	8	0	0	0	0	0	0	0	0	0
Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	8	0	0	7	0	0	0	0	0	0	7	0	0	0	2	0	0	0	0	0
Octatriacontyl pentafluoropropionate	0	0	25	3	77	30	14	1	4	0.2	0	0	6	0	10	0	3	0	2	0
Quinoline, 6-methoxy-, 1-oxide	0	0	0	0	0	0	0	0	0	0	3	7	0	0	0	0	0	1	1	0
Styrene	0	0	0.3	1	0	0	0	0	0	0	0.1	0.2	39	0	45	5	27	0	7	1
Terephthalic acid, di(2-chloroethyl) ester	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	6	0
Tetrapentacontane, 1,54-dibromo-	0	0	0	0	0	0	4	0	0	0	15	0	4	0	5	0	2	0	2	0

Toluene	0	0	2	4	0	0	0	0	0	0	0	0.2	2	3	2	3	2	2	0.3	1
Vinyl benzoate	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	1	0	3	0	3

From these results, 500 and 650 °C were identified as the principle temperatures for the production of hydrocarbons. The total fraction of hydrocarbon products, formed at 500 and 650 °C, as a function of the number of carbon atoms in a molecule are presented in Table 5.6. The carbon range C5-C9 had the highest percentage in most of the samples such as PP, fresh and excavated, PE <10 and the mixed plastic A and B. For PE and PE >10 the most abundant fraction was C10-C15. The aromatic hydrocarbons were mostly produced in PE <10 and in the mixed plastic samples A and B.

Table 5.6 Relative abundance (%) of hydrocarbons fractions from the pyrolysis of plastic materials at 500 °C and 650 °C.

500 °C		**PE**	**PE <10**	**PE >10**	**PP**	**PP <10**	**PP >10**	**A <10**	**A >10**	**B <10**	**B >10**
<C5	Aliphatic	1	0	0	6	8	2	2	0	0	0
	Aromatic	0	0	0	0	0	0	0	0	0	0
C5-C9	Aliphatic	11	2	4	50	50	27	11	7	8	15
	Aromatic	0	19	0	0	0	0.1	42	48	34	13
C10-C15	Aliphatic	30	2	9	12	8	5	2	1	1	1
	Aromatic	0	6	0	0	0	0	1	1	1	3
C16-C20	Aliphatic	14	1	3	0	1	4	0	0.1	1	12
	Aromatic	0	0	0	0	0	0	0.3	2	0.2	0.1
>C20	Aliphatic	9	2	3	0	0	15	8	3	7	11
	Aromatic	0	0	0	0	0	0	0.1	1	0.5	0

650 °C		**PE**	**PE <10**	**PE >10**	**PP**	**PP <10**	**PP >10**	**A <10**	**A >10**	**B <10**	**B >10**
<C5	Aliphatic	2	1	1	6	6	4	3	1	3	3
	Aromatic	0	0	0	0	0	0	0	0	0	0
C5-C9	Aliphatic	19	15	10	39	39	24	31	13	13	14
	Aromatic	0	10	0	0	0	1	9	13	26	12
C10-C15	Aliphatic	28	11	18	15	15	8	11	10	6	8
	Aromatic	0	8	0	0	0	1	8	7	4	4
C16-C20	Aliphatic	13	12	17	6	4	1	5	5	3	2
	Aromatic	0	0	0	0	0	0.2	9	8	2	1
>C20	Aliphatic	3	1	4	1	1	2	5	4	3	6
	Aromatic	0	0	0	0	0	0	0.1	0	0	0

5.3.3 Potential recycling of pyrolysis products from recovered plastics

The pyrolysis oil from excavated plastics is considered as a resource, due to its high calorific value if used as a fuel, and the production of feedstock for chemical synthesis and plastics production (Khan et al., 2016; Canopoli et al., 2018a; Fox and Stacey, 2019). The area percentage of condensable pyrolysis products at ambient temperature was more than 80 % in most of the samples (Table 5.7). The majority is represented by aliphatic and aromatic hydrocarbons. A high percentage of aliphatic hydrocarbons compounds have commonly been found in pyrolysis of PE and PP (Al-Salem, 2019; Jung et al., 2010; Achilias et al., 2007).

Table 5.7 Relative abundance (%) of condensable products at ambient temperature.

T	PE	PE <10	PE >10	PP	PP <10	PP >10	A <10	A >10	B <10	B >10
°C	Area %									
350	91	100	100	100	100	100	100	100	99	100
500	93	60	99	94	92	93	96	100	99	98
650	97	92	95	88	90	93	97	98	97	96
800	79	84	85	97	98	100	96	99	97	95

The pyrolysis liquid needs to be upgraded to be used, for example as fuels. Indeed, the pyrolysis oil from plastics may present ash and heteroatoms such as sulphur and nitrogen, which lower the quality of the fuels (Thahir et al., 2019; Miskolczi et al., 2004). Fractionation is a crucial stage for the separation of fuel fractions as presented in Table 5.8 (Costa and Santos, 2019). Some of the upgrades involved in the refining process are hydrogenation and cracking steam reforming (Bezergianni et al., 2017; Remón et al., 2014). Table 5.8 shows the relative abundance for different possible uses of the hydrocarbons produced in this study at 500 and 650 °C. The major percentage of compounds for PP, fresh and excavated, PE <10, and mixed A and B, fits in the naphtha range. Pyrolysis products of fresh PE and PE >10 at 500 °C are mostly represented by kerosene range, while PE >10 at 650 °C presented more compounds for the diesel range.

Table 5.8 Relative abundance (%) of hydrocarbons fractions obtained at pyrolysis temperature of 500 °C and 650 °C.

500 °C		**PE**	**PE <10**	**PE >10**	**PP**	**PP <10**	**PP >10**	**A <10**	**A >10**	**B <10**	**B >10**
LGP, Fuel gas, Refinery gas <C5	Aliphatic	1	0	0	6	8	2	2	0	0	0
	Aromatic	0	0	0	0	0	0	0	0	0	0
Gasoline C5-C8	Aliphatic	7	2	3	19	21	8	3	3	8	15
	Aromatic	0	17	0	0	0	0.1	42	48	32	12
Naphtha C6-C10	Aliphatic	16	2	7	41	44	24	11	7	8	15
	Aromatic	0	22	0	0	0	0	42	48	34	15
Kerosene (Paraffin) C10-C16	Aliphatic	34	2	9	12	8	5	2	1	1	1
	Aromatic	0	6	0	0	0	0	1	3	0.2	0.1
Diesel oil	Aliphatic	24	2	5	1	4	4	0.2	0.4	1	12

C14-C20	Aromatic	0	0	0	0	0	0	1	3	0.2	0.1
Lubricating oil C18-C25	Aliphatic	16	1	4	0	1	4	0	0.1	2	11
	Aromatic	0	0	0	0	0	0	0	1	0.5	0
Fuel oil C20-C27	Aliphatic	11	0.4	3	0	0.3	5	5	0.5	2	15
	Aromatic	0	0	0	0	0	0	0.1	1	0	0
Wax and greases C25-C35	Aliphatic	2	2	0.4	0	0	11	11	3	7	9
	Aromatic	0	0	0	0	0	0	0.1	0	0	0
Bitumen >C35	Aliphatic	1	0	0	0	0	5	1	0	0.2	2
	Aromatic	0	0	0	0	0	0	0	0	0	0
650 °C		**PE**	**PE <10**	**PE >10**	**PP**	**PP <10**	**PP >10**	**A <10**	**A >10**	**B <10**	**B >10**
	Aliphatic	2	1	1	6	6	4	3	1	3	3

LGP, Fuel gas, Refinery gas <C5	Aromatic	0	0	0	0	0	0	0	0	0	0
Gasoline **C5-C8**	Aliphatic	15	13	8	20	20	10	23	10	6	6
	Aromatic	0	5	0	0	0	1	4	9	23	11
Naphtha **C6-C10**	Aliphatic	22	17	13	41	42	27	34	15	15	18
	Aromatic	0	15	0	0	0	1	11	14	27	12
Kerosene (Paraffin) **C10-C16**	Aliphatic	28	11	18	15	16	8	12	11	7	8
	Aromatic	0	8	0	0	0	1	14	12	5	4
Diesel oil **C14-C20**	Aliphatic	24	15	24	9	7	2	8	8	4	4
	Aromatic	0	0	0	0	0	0.2	14	13	5	2
Lubricating oil **C18-C25**	Aliphatic	12	12	19	7	4	3	7	5	3	5
	Aromatic	0	0	0	0	0	0	3	3	1	0.4

Fuel oil C20-C27	Aliphatic	8	7	13	1	2	2	5	4	2	4
	Aromatic	0	0	0	0	0	0	0	0	0	0
Wax and greases C25-C35	Aliphatic	0	0	0	1	1	2	4	3	3	5
	Aromatic	0	0	0	0	0	0	0.2	0	0	0
Bitumen >C35	Aliphatic	1	0.03	0	0	0	0	0.1	0	0	0
	Aromatic	0	0	0	0	0	0	0	0	0	0

Figure 5.4 shows the comparison between the percentages of hydrocarbons, divided in carbon ranges, present in the oil fraction from the ASPEN Plus model (Chapter 4) and the Py-GC-MS at 500 °C and 650 °C. The ranges C5-C9 and C10-C15 were higher than C16-C20 and >C20 in the majority of the simulated and experimental runs. In addition, most of the pyrolysis products from the simulation and experiment were in the naphtha (C6-C10) and kerosene (C10-C16) ranges. However, the simulation model generally showed a higher level of hydrocarbons within the C10 and C15 range than the experimental results.

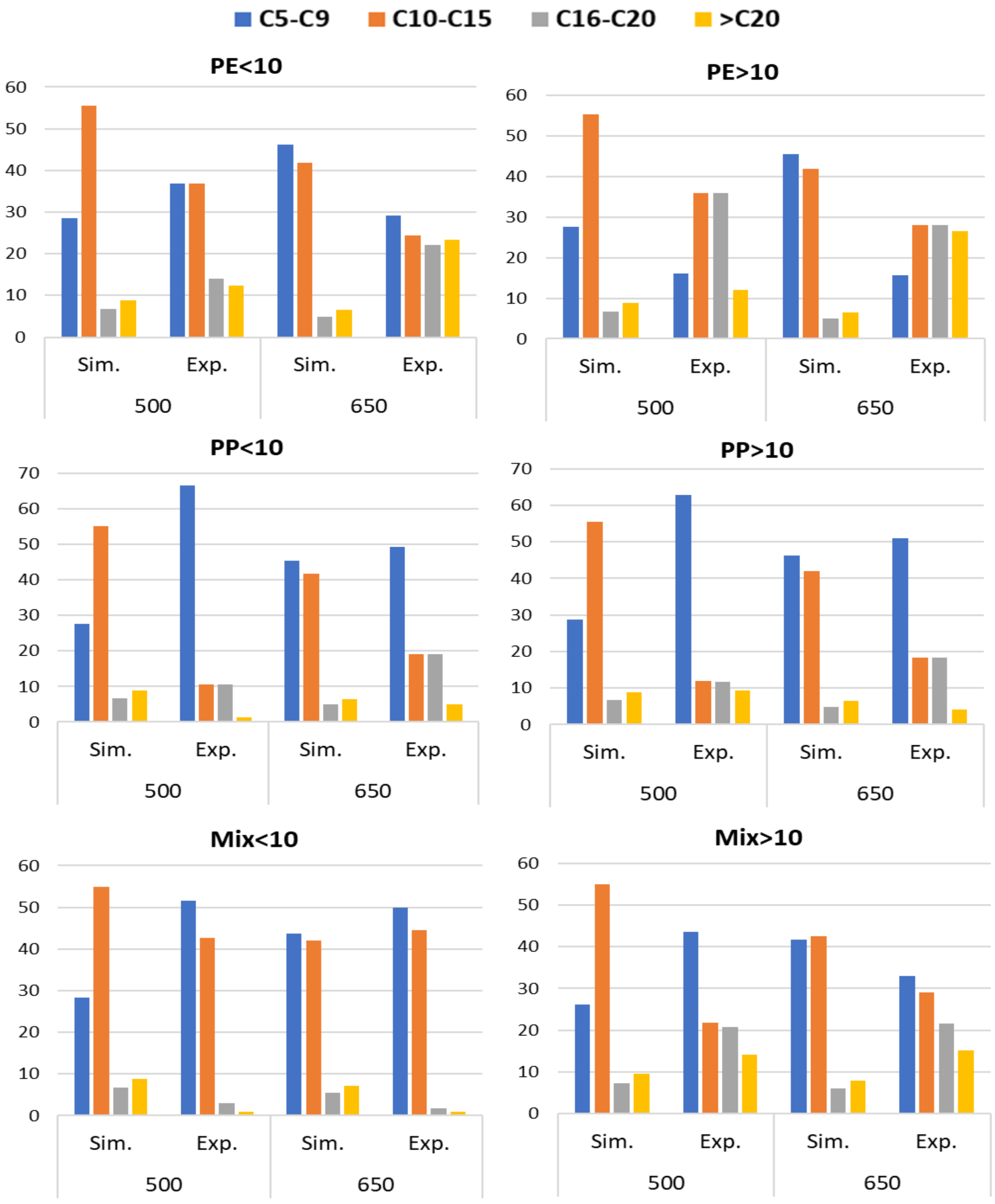

Figure 5.4 Comparison of produced hydrocarbons fractions percentages from Py-GC-MS experimental (Exp.) and ASPEN Plus simulation (Sim.) at 500 °C and 650 °C. The Mix sample includes the results of PEPP pyrolysis for the simulation and of PEPPPS pyrolysis for the experiment.

In 2018, the world produced about 360 million tonnes of plastics (PlasticsEurope, 2019). In Europe, within 51.2 million tonnes of plastics the most in demand polymers were PE (~30 wt%), PP (~19 wt%) and PVC (~10 wt%) (PlasticsEurope, 2019). These plastics are produced mostly from virgin fossil resources and in minimal part from mechanical recycling of fresh plastic waste. However, this recycling of fresh plastic waste generally leads to a downcycling where the outputs are of lower value than the feedstock (Nielsen et al., 2019). The use of HVCs from recovered plastics pyrolysis could reduce the needs of virgin fossil resources.The recovered plastics pyrolysis products such as naphtha could be used in petrochemicals cluster. The naphtha cracking produces around 55 wt% high-value chemicals (HVCs) such as ethylene, propylene, butadiene, aromatics and >C5 (Ren et al., 2006). The unsaturated hydrocarbons and aromatics such as benzene, toluene and styrene, can be sold to produce new plastic and other products (Fox and Stacey, 2019; Miandad et al., 2019). The aliphatic compounds can be used to produce ethylene and propylene. Benzene can be recycled to produce plastic, detergents, dyes and pesticides. Toluene can be employed as solvent and starting material for the synthesis of organic compounds such as benzoic acid, benzaldehyde. The recovered styrene can be reused to make synthetic rubber, polystyrene and expanded polystyrene (PlasticsEurope, 2018b). Benzoic acid could be recycled for the synthesis of dyes and other organic compounds. This would lead to the upcycling of recovered plastic which has been disposed and unused, sometimes for decades. Table 5.9 shows the potential monetary value from selling the naphtha produced from the pyrolysis of PE, PP and PS wasted in the landfill and environment in the last 70 years and for European landfilled plastics in 2018. The assumptions are:

- price of naphtha in January 2020 was 565.43 USD/tonnes (Trading Economy, 2020);
- 68 wt% was the average amount of mixed plastics (PE 50 wt%, PP 15 wt%, 3 PS wt%) identified in recovered plastics (Table 5.1);

- the produced naphtha percentage was taken from data of mixed sample A (PE, PP and PS) in Table 5.8;
- HVCs recovery from naphtha was 55 wt% (Ren et al., 2006);
- 7.2 million tonnes of plastics were disposed of in landfill in 2018 in Europe (PlasticsEurope, 2019);

- costs of recovering and processing the plastics are not considered. The cost of a landfill mining project can be variable according to different aspects such as the quantity of waste in the landfill, technologies applied and geographical location of the landfill. The estimated cost for an ELFM project of a landfill in Belgium with a surface area of 2,000 hectares was USD ~11 billion and comprised of excavation, sorting, pre-treatment, incineration and contingency (Van Passel et al., 2013). The incineration of waste counted about USD 6 billion, and it was considered a worthy process for the recovery of energy which was estimated to be USD ~9 billion. In contrast, a similar project in China for a smaller landfill of 11.3 hectares was estimated to cost about USD 6 million covering the prices for excavation, screening and sorting, construction of material handling facility, transportation of materials and final waste disposal (Zhou et al., 2015). In this study, the first three potential benefits were obtained from the electricity generated by combustible incineration, reclamation of the land, and recycling of soil-like materials. In addition, the capital investment for the valorisation of the plastic fraction through pyrolysis was estimated to be USD ~3.7 million for a pyrolysis plant with a capacity of 1,000 kg of plastic waste per hour (Fivga and Dimitriou, 2018). The estimated annual operating costs for this type of plant were USD 1.5 million (Fivga and Dimitriou, 2018). The introduction of recovered plastics in the new circular plastics economy, could lower the environmental impact related to the mismanagement of this material and offers a variety of HVCs. These products can be sold gaining revenue from current unused materials.

Table 5.9 Potential monetary value of naphtha produced from plastics disposed of in landfills and natural environment in the last 70 years and European landfilled plastics in 2018.

	Billion tonnes	**Price (USD billion)**	**HVCs (billion tonnes)**
Wasted plastics (last 70 years)	4.9		
PE, PP and PS	3.3		
Naphtha (average value)	1.5	856	0.8
Naphtha (Min value)	1.0	545	0.5
Naphtha (Max value)	1.8	1034	1.0
	Million tonnes	**Price (USD billion)**	**HVCs (Million tonnes)**
Plastics landfilled (2018)	7.2		
PE, PP and PS	4.9		
Naphtha (average value)	2.2	1.3	1.2
Naphtha (Min value)	1.4	0.8	0.8
Naphtha (Max value)	2.7	1.5	1.5

5.4 Conclusion

The increasing demand of the plastics and the environmental concern related to their short service life need to be addressed. The estimated mass of plastics present in landfills and natural environment is 4.9 billion tonnes. This study gave an insight into the compounds that can be produced from the pyrolysis of different types of recovered plastics from landfills and the influence of storage age on their relative abundance. The products of mixed excavated plastics pyrolysis presented a high level of hydrocarbons in the naphtha range (C6-C10) which is commonly used for plastic production. A remarkable level of aromatic compounds that can be sold to produce plastics and other products was also identified. Excavated plastics have the potential to be upcycled and become part of a closed-loop recycling mechanism that makes full use of previously disposed of plastics. In this way, it is possible to decrease the dependency of raw materials and reduce the waste in landfills. The thermal behaviour of excavated plastics did not show crucial differences from the fresh plastic waste. This finding could facilitate the evaluation on treating also excavated plastics in designed pyrolysis plants for fresh plastic waste. Further studies should explore the actual costs and benefits of this closed-loop methodology for the production of new plastics from recovered plastics from landfills and identify the potential reduction in environmental emissions with a life cycle analysis.

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6 CONCLUSION AND RECOMMENDATION FOR FUTURE WORKS

This PhD study provided a comprehensive detailed characterisation of recovered plastics, identifying the plastic types and examining the physico-chemical properties through a series of analyses. Then, the potential valuable products from the pyrolysis were investigated using a combination of modelling prediction and pyrolyzing using Pyrola 2000 system connected to a gas chromatography-mass spectrometry (Py-GC-MS).

6.1 Key findings and novelty

The novelty and key findings for each objective are discussed in this section.

The key focus of this research was to identify the uncertainties related to the quantity and quality of plastics we can expect in landfill (1), and the possibility of producing high value products from pyrolysis of excavated plastics (2).

(1) Novelty. The former required the identification of different plastic types which in the past studies were often evaluated all together as “plastic”, limited groups such as “soft PE” and “other plastics”, or less than a quarter was classified from the total plastics (Chapter 2). In this study, every plastics piece present in the plastic fraction passed through the identification step with the Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The average value of unrecognised plastics was 6 wt%. This process is highly time-consuming but was fundamental to give specific information not found in previous studies. The different steps followed to answer the question “What type of plastic and quality can we expect in landfill?” were:

  - collection of genuine landfill waste samples (Chapter 3);
  - manual sorting of different waste fractions (Chapter 3);
  - plastic types identification by ATR-FTIR (Chapter 3);

    - degradation analyses of main plastic types PE and PP such as surface analysis with scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS), crystallinity and melting point identification with differential scanning calorimetry (DSC), carbonyl index, CH_2 and CH_3 with ART-FTIR (Chapter 3);
    - chemical analysis of main plastic types PE and PP such as proximate, ultimate and metals analyses (Chapter 4).

(2) Novelty. The pyrolysis of recovered plastics was investigated focusing on recovering of chemical compounds. Few studies investigated the pyrolysis of excavated waste and the main driver was the production of transportation fuels (Chapter 2). However, transportation fuels from plastics release greenhouse gases such as CO_2, CH_4 and N_2O, making it environmental unsustainable such as common fossil fuels. The steps involved to answer the question “Is it possible to produce high value products from pyrolysis of excavated plastics?” were:

    - model simulation for the prediction of pyrolysis products yields (Chapter 4);
    - pyrolysis using Py-GC-MS for the identification of compounds likely to be found during pyrolysis of recovered polyethylene (PE), polypropylene (PP) and mixed plastics (Chapter 5).

1. *Critically review the literature on plastics from MSW landfills and the possibility of recovery through pyrolysis.*

The literature review presented in chapter 2 described the most common produced plastic types and their typical degradation process. It explored the current limitation of enhanced landfill mining (ELFM) feasibility related to the lack of knowledge on recovered material condition and how to upcycle it. After overviewing the different recycling strategy, the potential upcycling of recovered plastics was identified in the chemical and thermochemical recycling (tertiary recycling) of this material. Few studies have investigated the application of tertiary recycling to recovered plastics from landfill. The analysis of genuine plastics from MSW landfills is very limited in the literature and most of the studies conducted to date only evaluated the plastics as a whole stream without identifying the different polymers for energy recovery (Chapter 2). Chapter 2 enlarges the circular economy concept including the recovered plastics from landfill.

2. *Characterise the extent of degradation of recovered plastics from MSW landfills according to the age of the buried waste and landfill conditions.*

30 waste samples for a total of 154 kg of waste from 4 different landfills were manually sorted to identify the waste fractions percentage. ATR-FTIR was used for the identification of different plastics types. Further analyses investigated the extent of degradation (Chapter 3) and chemical composition (Chapter 3 and Chapter 4) of main plastic types such as PE and PP which represented 64 wt% of total recovered plastics. Overall, PE and PP with storage of more than 10 years in landfill showed a greater extent of degradation compared to newer samples with fewer years of storage and fresh plastic waste samples.

3. *Develop a pyrolysis model for recovered plastics from MSW landfills to predict valuable product outputs from the pyrolysis.*

The recovered plastics pyrolysis was simulated with a model built in ASPEN Plus software for predicting the pyrolysis products yields (Chapter 4). The model was validated using data from literature and the oil yields were predicted within ~4 % error. The PE produced higher oil yield compared to PP probably due to higher ash content. Commodity chemicals such as olefins and BTX were further analysed in order to give information on related potential monetary value. The pyrolysis of single polymers seems to be more beneficial than the mixed PEPP sample for the olefins and BTX production. Assuming the possibility to recover and process the estimated amount of PE and PP disposed of in the past 70 years (~2.7 billion tonnes), the value of selling the olefins and BTX fractions is estimated to be USD 632 billion. In addition, the recovery of these materials could help to mitigate the utilisation of virgin fossil resources.

4. *Perform and assess the effects of thermochemical conversion operating conditions on recovered plastics and product outputs.*

The pyrolysis of recovered plastics was performed using Pyrola 2000 connected to GC-MS at a temperature between 350 °C and 800 °C (Chapter 5). Detailed information of potential recyclable chemicals compounds was given suggesting the inclusion of recovered plastics into the new circular plastic economy point of view. The pyrolyzed samples were single polymer PE and PP, and two mixture nominated sample A (PS, PE and PP) and sample B (PET, PVC, PE and PP). Hydrocarbons production reached the highest level at 500 °C and 650 °C. Aromatics are more abundant in mixed samples than PE and PP pyrolysis due to PS presence which led to the production of a high level of styrene. Most compounds were identified in the products fitted within the naphtha range (C6-C10) which has a high potential to be used in the petrochemical cluster. In general, sample B presented a higher level of chlorinated compounds than sample A due to the presence of PVC, which should be avoided because it causes reactor corrosion (Al-Salem et al., 2017).

5. *Evaluate the quality of the pyrolysis products in relation to feedstock characteristics.*

The main effects related to landfill environment on plastics feedstock are:

- separation of plastics from other materials. The manual sorting showed that an average of 50 wt% of the separated plastics comprised of wet soil (Chapter 3). A drying step and sieving before pyrolysis could help to effectively decrease the soil quantity;
- volatile matter of PE and PP showed a decrease from newer to older samples (Chapter 5). Lower volatile matter is one of the factors that can reduce the pyrolysis oil yield (Abnisa and Wan Daud, 2014);

- non-excavated PE and PP presented a generally higher level of aliphatic hydrocarbons and lower aromatics than the recovered samples (Chapter 5);
- the average higher amount of ash in PP compared to PE can decrease the oil yields (Chapter 4);
- the compounds in the gasoline (C5-C8) and naphtha (C6-C10) ranges were generally higher in the samples with <10 years of storage than >10 years (Table 5.8).

6.2 Research implications

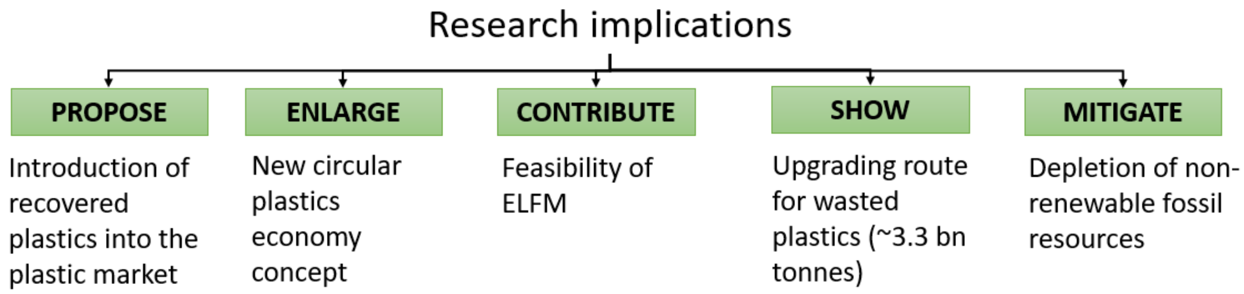

Figure 6.1 Schematic diagram of research implications.

Figure 6.1 shows a summary of implications related to this research. Plastic production has increased from 230 to 359 between 2005 and 2018 and is expected to grow at a CAGR of ~4 % in the next five years (Grand view research, 2019; PlasticsEurope, 2019). The recovered plastics could play a role in the growing plastic market participating in the production of new plastics. Indeed, the use of excavated plastics would mitigate the depletion of non-renewable fossil resources which are the main sources for plastics production. This is in line with the new plastic economy global commitment launched in 2018 by Ellen MacArthur Foundation in collaboration with UN Environment Programme, which aims to reduce the need for virgin plastics and finite resources (Ellen MacArthur Foundation and UN Environment Programme, 2019). However, for the moment the new plastic economy focuses on production, consumption and reuse or recycling of plastic products without considering the existing plastics waste. In Europe, there are over 400,000 landfills and plastics represents between 9 wt% and 25 wt%. In 2018, 7.2 million tonnes of plastic were disposed of in landfill in Europe. The plastics disposed of in the landfills and environment from 1950 were estimated to be 4.9 billion tonnes (Geyer et al., 2017). This research highlights the urgency of considering the new management of disposed plastics important as the management of new plastics waste. For example, 79 UK costal landfills have been identified as a potential source of sea pollution due to erosion by 2024 (Brand et al., 2018). The material present in landfills can be valorised through ELFM. Due to the high percentage of plastics in landfills, the feasibility of ELFM depends also to the valorisation of this material. Based on the research data PE, PP and PS can be supposed to represent 3.3 billion tonnes of disposed plastics (Chapter 3, 4 and 5). The potential monetary value associated with the hypothetical pyrolysis of all wasted plastics was defined as USD 856 billion for naphtha produced from PE, PP, PS, and USD 632 billion for BTX and Olefins from PE and PP (Chapter 4 and 5). However, the pyrolysis of excavated plastics involves costs related to the ELFM and pyrolysis treatment which need to be evaluated. The amount of waste in the landfill, technologies applied, and geographical location of the landfill are some of the factors that influence the cost of a landfill mining project. Two different studies estimated the cost-benefit of an ELFM project in Belgium and China. The former evaluated a cost of USD ~11 billion for a landfill of 2,000 hectares with total revenue of USD ~2 billion, while the latter assessed a cost of USD ~9 billion for a landfill of 11.3 hectares with a total benefit of USD ~26 million(Van Passel et al., 2013; Zhou et al., 2015). The cost associated with a plastic pyrolysis plant of a 1,000 kg per hour in the UK, was estimated USD ~3.7 million of capital investment and USD 1.5 million of annual operating costs (Fivga and Dimitriou, 2018). The data on chemical compounds derived from pyrolysis of recovered plastics can help to evaluate the feasibility of ELFM projects, introduce the recovered plastics into the circular economy and reduce the use of virgin fossil resources.

6.3 Limitation of the research

The limitations related to this study are listed in this section.

- Some of the waste samples from landfills did not have complete information such as specific storage age for each sample. This datum could have been used in association with the depth of excavated samples in order to evaluate the effect of both variables on plastics degradation (Chapter 3).
- The weight and number of the samples provided were not consistent for each landfill and sample. For this reason, it was not possible to compare the quantity and quality of plastics between landfills. Samples from different landfills of the same number, size and storage age could be analysed giving more emphasis on landfill characterises such as other types of waste, meters of depth, leachate composition etc.
- The amount of waste sample was relatively small compared to the amount of waste present in the landfills. However, hand sorting of waste material is not feasible for a much greater quantity. A high level of sorting efficiency was reached with this method at the expense of quantity.
- Due to their peculiarities, plastics analyses often required specific equipment. Especially the melting behaviour has caused concerns which needed time to be overcome. This fact limited the possibility to use pyrolysis reactor commonly used for biomass. For this reason, Pyrola 2000 connected to GC-MS was utilised for the pyrolysis of excavated plastics (Chapter 5).
- The compounds prediction from ASPEN Plus simulation model could be improved with specific information on the kinetics of compounds from excavated PE and PP pyrolysis. Some of the main components identified in chapter 5, and not present in the current reaction kinetics, should be included in the simulation model. Data from a real industrial scale pyrolysis plant could be used to modify the simulation model and gives more realistic results for a large scale excavated plastic pyrolysis. Although the assumed

total conversion of 100% is in line with the studies on plastic pyrolysis, it could be different from an industrial scale scenario which needs to be further evaluated.

- The chemical analysis (proximate, ultimate and metals analyses) were not extended for all plastic types identified due to the relatively small amount of some plastics types such as PS and PET.
- The data given from the analyses of excavated plastics could be improved performing more replicates. Indeed, this material presents different characteristics related to the production, use and storage in landfills.

6.4 Further research recommendations

The need for finding sustainable ways to manage new plastics waste and old wasted plastics is spreading in different sectors. This research highlighted some uncovered aspects that could help to upgrade unused materials such as buried plastics. Further studies should analyse excavated plastics samples from different countries. The difference in habits and legislation on waste disposal can affect the quality and quantity of the waste. Many countries have dumpsites with poor sorting before disposal. In addition, the plastic waste ended up in the natural environment increases the global pollution creating a cascade that affects the ecosystem. The different environmental condition such as temperature, solar radiation, rain, decomposition of surrounding waste can alter the plastic waste physico-chemical characteristics. It would be interesting to compare the characteristics of recovered plastics from different environments such as landfill, dumpsite, ocean and coastal environment. This study analysed the excavated plastics from regulated landfills, but it is worth it to investigate how harsher environments affect this material. A larger overview would give more information for the creation of a protocol about the recycling of recovered plastics. Indeed, the aim of ELFM and circular economy should be to turn most of the old waste in resources, adapting the approach to all different scenarios. An effective sorting of recovered plastic polymers is important for their treatments. In the case of pyrolysis treatment, PVC and PET can produce undesirable products. For this reason, it should be assessed the sorting efficiency of technologies such as NIR scanner applied to recovered plastics from different environments. The pyrolysis of recovered plastics from landfill and natural environment should be further tested focusing on the production of high value chemicals. The pyrolysis chemical products should be inspected comparing the peculiarities associated with the different environments. Absolute quantitative data on produced chemicals are necessary for their introduction into the markets. The reaction kinetics of chemicals compounds that are produced during pyrolysis need to be investigated. This will facilitate their modelling and the prediction of the best approach to be applied for the different characteristics linked to the material history. The recovered plastic pyrolysis should be explored on a large scale. Many companies are investing in pyrolysis plants for the treatment of plastic waste that cannot be mechanically recycled due to degradation and contamination. The utilization of these plants for both fresh and recovered plastic waste should be evaluated. The effects on the products and equipment of mixing recovered plastics from different environments and fresh plastic waste need to be carefully investigated. This would facilitate the introduction of recovered plastics into the circular economy. Finally, the cost-benefit analysis and life cycle analysis should be applied to the whole process from recovering to pyrolysis treatment and introduction of the products into the market. The different sources of recovered plastics need to be considered separately in order to give specific information on economic and environmental advantages and disadvantages of different scenarios. The investigation of all these aspects could enable an economically and environmentally feasible upcycling of recovered plastics.

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APPENDICES

Appendices A-C present the appendices data of chapters 3-5.

Appendices D-G present the articles published during this PhD:

Journal papers

Appendix D - (2018) Physico-chemical properties of excavated plastic from landfill mining and current recycling routes. Waste Management, 76, 55-67.

Appendix E - (2020) Degradation of excavated polyethylene and polypropylene waste from landfill Science of the Total Environment, 698 (134125), 1-8.

Appendix F - (2019) Developing the case for enhanced landfill mining in the UK, Detritus Journal, 5, 105-110. DOI 10.31025/2611-4135/2019.13772

Peer-reviewed Conference Publication

Appendix G - (2018) Characterisation of excavated plastics for thermochemical upcycling to platform chemicals and liquid fuels. Proceedings of the 4th International Symposium on Enhanced Landfill Mining, 5-6th February 2018, Mechelen, Belgium.

Appendix A Chapter 3

Landfill samples detailed data

Table A.1 Landfill samples information. The 30 waste samples were collected from 4 landfills which are coded as A, B, C and D respectively.

Sample n. (landfill code)	Years	Depth	Waste sample	Plastic (wet)		Plastic (dry)	Impurities (wet)	
		(m)	(g)	(g)	(wt%)	(g)	(g)	(wt%)

1 (A)	4-6 months	5	8,448	951	11	200	751	79
2 (B)	7	6.5	553	91	17	22	69	76
3 (B)	7	18.5	870	66	8	10	56	85
4 (B)	7	8	390	77	20	14	64	82
5 (B)	7	18	603	31	5	9	22	70
6 (B)	7	6	595	140	24	36	104	74
7 (B)	7	18	876	51	6	11	40	79
8 (C)	17-19	39	5,838	1,510	26	368	1,143	76
9 (D)	>10	3-7	5,054	792	16	602	190	24
10 (D)	>10	7-9	7,689	390	5	238	152	39
11 (D)	>10	9-11	4,019	632	16	297	335	53
12 (D)	>10	11-13.5	7,523	475	6	251	224	47
13 (D)	>10	13.5-17	3,328	150	5	61	90	60
14 (D)	>10	17-20	3,010	198	7	169	29	14
15 (D)	>10	20-23	3,111	211	7	147	65	31
16 (D)	>10	22.5	6,850	21	0	12	9	44
17 (D)	>10	23-25	3,874	243	6	215	28	11

18 (D)	>10	25-27	4,051	710	18	525	185	26
19 (D)	>10	29.30.5	5,836	46	1	20	26	57
20 (D)	>10	32.5-35	10,307	126	1	74	52	42
21 (D)	>10	35-36.5	11,586	561	5	381	180	32
22 (D)	>10	36-37.5	9,176	870	10	572	298	34
23 (D)	>10	37.5-39	9,519	244	3	131	113	46
24 (D)	>10	40-41.5	6,651	175	3	50	126	72
25 (D)	>10	41-43	8,213	320	4	90	230	72
26 (D)	>10	44.5-46	8,234	180	2	121	59	33
27 (D)	>10	46-48	3,591	67	2	27	40	59
28 (D)	>10	48-50.5	6,016	378	6	198	181	48
29 (D)	>10	50-51	1,891	208	11	62	146	70
30 (D)	>10	53-55	6,236	769	12	475	294	38
TOT			**153,938**	**10,683**	**7**	**5,403**	**5,280**	**49**
Average			**5,131**	**356**	**9**	**180**	**177**	**52**
SD			**3,239**	**352**	**7**	**181**	**233**	**21**

Table A.2 Percentages of different plastic types.

Sample n.	**Years**	**PE**	**PP**	**PVC**	**PS**	**PET**	**PE/PP Blend**	**PA**	**Rubber**	**Rest**
							(wt%)			
1	4-6 months	61	11.5	3	3	1	0			22
2	7	32	32					1		36
3	7	56	15	5	5					18
4	7	70	11							19
5	7	44	6			6	15			37
6	7	47	2	5	6		5			43
7	7	37	14	5		5				40
Average	**<10**	**50**	**13**	**4**	**5**	**4**	**7**	**1**		**31**
SD		**14**	**10**	**1**	**2**	**3**	**7**			**11**
8	17-19	50	3	1	1	39				6
9	>10	25	13	1	1	2			59	
10	>10	36	3	50	1					10
11	>10	54	22	8	16					
12	>10	41	14	2	2					41

13	>10	78	12						10
14	>10	92	1		3			4	0
15	>10	87	1	6	2				4
16	>10	27	44	2					27
17	>10	2	1					97	0
18	>10	14	85	0			1		
19	>10	50	42		7				2
20	>10	27	27	35	1				10
21	>10	60	20	14	4			1	
22	>10	55	16	18	8				3
23	>10	19	30	47	3				1
24	>10	32	36			11		6	15
25	>10	49	32	3	9				7
26	>10	81	2	17					1
27	>10	88			12				
28	>10	7	5	15				69	5
29	>10	52	3	42	4				0
30	>10	75	3	13	6	1		0	2

Average	**>10**	**48**	**19**	**16**	**5**	**20**	**6**	**1**	**34**	**8**
SD		**27**	**21**	**17**	**4**	**26**	**7**		**40**	**11**
TOT Average		**48**	**17**	**14**	**5**	**11**	**6**	**1**	**34**	**14**
SD		**24**	**18**	**16**	**4**	**16**	**6**	**0**	**40**	**15**

Table A.3 Different plastic types with storage time <10 years.

Sample n.	**Years**	**PE**	**PP**	**PVC**	**PS**	**PET**	**PE/PP Blend**	**PA**	**Rubber**	**Rest**
						(g)				
1	4-6 months	121.5	23	5.5	5	1.5	0.67	0	0	43
2	7	7	7	0	0	0	0	0.2	0	7.8
3	7	5.5	1.5	0.5	0.5	0	0	0	0	1.8
4	7	9.5	1.5	0	0	0	0	0	0	2.5
5	7	3.5	0.5	0	0	0.5	1.4	0	0	3.5
6	7	16	0.5	0.5	2	0	1.8	0	0	15.5
7	7	4	1.5	0.5	0	0.5	0	0	0	4.3
TOT		**167**	**36**	**7**	**8**	**3**	**4**	**0**	**0**	**78**
Average		**24**	**5**	**1**	**1**	**0**	**1**	**0**	**0**	**11**

SD		**43**	**8**	**2**	**2**	**1**	**1**	**0**	**0**	**15**

Table A.4 Different plastic types with storage time >10 years.

Sample n.	**Years**	**PE**	**PP**	**PVC**	**PS**	**PET**	**PE/PP Blend**	**PA**	**Rubber**	**Rest**
						(g)				
8	17-19	184	11.5	3.5	2	143	0	0	0	23.5
9	>10	149.9	78.9	5.9	2.9	11.9	0	0	352.8	0
10	>10	85.8	7.9	119.9	1.2	0	0	0	0	23.2
11	>10	158.9	65.9	23.9	47.9	0	0	0	0	0
12	>10	102.9	34.9	4.2	5.2	0	0	0	0	103.9
13	>10	47	7.2	0	0	0	0	0	0	6.3
14	>10	155.9	1.9	0	4.2	0	0	0	7.2	0.2
15	>10	126.7	1.2	9.2	3.2	0	0	0	0	6.2
16	>10	3.2	5.2	0.2	0	0	0	0	0	3.2
17	>10	4.9	1.5	0	0	0	0	0	207.9	0.8
18	>10	72.5	447.5	1	0	0	0	4.2	0	0
19	>10	9.9	8.3	0	1.3	0	0	0	0	0.4
20	>10	19.9	19.9	25.9	0.7	0	0	0	0	7.2

21	>10	229.5	76.9	53.9	16.9	0	0.9	0	3.2	0
22	>10	315.5	89.9	103.9	46.9	0	0	0	0	16
23	>10	24.9	38.9	61.9	4.2	0	0	0	0	1.2
24	>10	15.9	17.9	0	0	0	5.2	0	3.2	7.3
25	>10	43.9	28.9	2.9	8.2	0	0	0	0	6.1
26	>10	97.9	1.9	19.9	0	0	0	0	0	1.2
27	>10	24.2	0	0	3.2	0	0	0	0	0
28	>10	12.9	8.9	29.9	0	0	0	0	136.1	9.7
29	>10	31.9	1.9	25.9	2.2	0	0	0	0	0.1
30	>10	357.5	11.9	63.1	28.9	0	3.9	0	0.2	9.2
TOT		**2276**	**969**	**555**	**179**	**155**	**10**	**4**	**711**	**226**
Average		**99**	**42**	**24**	**8**	**7**	**0**	**0**	**31**	**10**
SD		**99**	**93**	**34**	**14**	**30**	**1**	**1**	**86**	**22**

Carbonyl indices

Table A.5 Carbonyl indices average of PE.

Sample PE	N	Median	Average (Outliers)	Standard deviation	Standard error
Fresh	14	0.43	0.53	0.32	0.08

<10 Years	18	0.40	0.46	0.24	0.06
>10 Years	184	0.40	0.41	0.14	0.01

Table A.6 Carbonyl indices average of PP.

Sample PP	**N**	**Median**	**Average (Outliers)**	**Standard deviation**	**Standard error**
Fresh	10	0.78	0.76	0.19	0.06
<10 Years	12	1.11	1.34	0.46	0.13
>10 Years	153	1.74	1.78	0.38	0.03

Table A.7 Carbonyl indices - T-test results p value PE.

PE	**<10 Years**	**>10 Years**
Fresh	0.72	0.31
<10 Years		0.37

Table A.8 Carbonyl indices - T-test results p value PP.

PP	**<10 Years**	**>10 Years**
Fresh	1.2E-03	5.5E-10
<10 Years		6.8E-03

Absorbance CH_2 and CH_3 (1490-1420)

Table A.9 Absorbance CH_2 average of PE.

Sample PE	N	Median	Average (Outliers)	Standard deviation	Standard error
Fresh	14	5.46	6.14	2.90	0.78
<10 Years	18	6.45	6.65	1.88	0.44
>10 Years	184	3.80	3.93	1.89	0.14

Table A.10 CH_2 - T-test results p value PE.

PE	<10 Years	>10 Years
Fresh	0.29	0.01
<10 Years		9.1E-06

Table A.11 Absorbance CH_3 average of PP.

Sample PP	N	Median	Average (Outliers)	Standard deviation	Standard error
Fresh	15	4.67	4.90	2.60	0.67
<10 Years	12	4.65	5.03	3.01	0.87
>10 Years	153	2.43	2.54	1.27	0.10

Table A.12 CH_3-T-test results p value PP.

PP	**<10 Years**	**>10 Years**
Fresh	0.45	3.5E-3
<10 Years		0.02

Differential Scanning Calorimetry

Table A.13 % Crystallinity average of PE.

Sample PE	**N**	**Median (%)**	**Average (Outliers) (%)**	**Standard deviation (%)**	**Standard error (%)**
Fresh	8	39.35	39.45	8.35	2.95
<10 Years	9	46.79	45.20	8.24	2.75
>10 Years	24	50.81	51.16	7.72	1.58

Table A.14 %Crystallinity - T-test results p value PE.

PE	**<10 Years**	**>10 Years**
Fresh	0.17	4.8E-3
<10 Years		0.08

Table A.15 Melting temperature of PE.

Sample PE	N	Median (°C)	Average (Outliers) (°C)	Standard deviation (°C)	Standard error (°C)
Fresh	8	113.73	116.62	21.60	7.63
<10 Years	9	131.98	130.52	8.07	2.69
>10 Years	21	127.23	127.48	7.27	1.59

Table A.16 Melting - T-test results p value PE.

PE	<10 Years	>10 Years
Fresh	0.12	0.20
<10 Years		0.35

Table A.17 % Crystallinity average of PP.

Sample PP	N	Median (%)	Average (Outliers) (%)	Standard deviation (%)	Standard error (%)
Fresh	8	38.76	38.26	6.82	2.41
<10 Years	6	36.85	35.34	5.01	2.04
>10 Years	16	42.76	40.97	4.54	1.14

Table A.18 %Crystallinity - T-test results p value PP.

PP	<10 Years	>10 Years
Fresh	0.37	0.33
<10 Years		0.04

Table A.19 Melting temperature of PP.

Sample PP	N	Median (°C)	Average (Outliers) (°C)	Standard deviation (°C)	Standard error (°C)
Fresh	8	165.5	163.46	3.90	1.38
<10 Years	9	165.86	155.38	8.03	3.28
>10 Years	21	165.18	164.49	1.22	0.30

Table A.20 Melting - T-test results p value PP.

PP	<10 Years	>10 Years
Fresh	0.87	0.35
<10 Years		0.57

Appendix B Chapter 4

Table B.21 Reactions used for modelling the plastic pyrolysis process in ASPEN Plus (adapted from Ismail et al., 2017).

N.	Reaction	Products	A (s-1)	E (kJ/mol)	n (Temperature coefficient)
1	$C + 2H_2 \rightarrow CH_4$	Methane	4.877	23.01	0
2	$C + 0.5O_2 \rightarrow CO$	Carbon monoxide	0.096	23.01	0
3	$C + O_2 \rightarrow CO_2$	Carbon dioxide	0.226	23.01	0
4	$6C + 3H_2 \rightarrow C_6H_6$	Benzene	1.654	33.89	0
5	$6C + 6H_2 \rightarrow C_6H_{12}$	Methylpentene	0.009	1.59	0
6	$7C + 3H_2 + O_2 \rightarrow C_7H_6O_2$	Benzoic acid	0.549	33.89	0
7	$7C + 4H_2 \rightarrow C_7H_8$	Toluene	7.305	33.89	0
8	$8C + 4H_2 \rightarrow C_8H_8$	Styrene	4.049	33.89	0
9	$8C + 5H_2 \rightarrow C_8H_{10}$	Xylene	4.476	33.89	0
10	$8C + 5H_2 \rightarrow C_8H_{10}$	Ethylbenzene	4.708	33.89	0
11	$8C + 8H_2 \rightarrow C_8H_{16}$	Octene	0.007	1.59	0
12	$9C + 4H_2 \rightarrow C_9H_8$	Indene	1.278	33.89	0
13	$9C + 6H_2 \rightarrow C_9H_{12}$	Propylbenzene	1.808	33.89	0
14	$9C + 6H_2 \rightarrow C_9H_{12}$	Methylethylbenzene	0.392	33.89	0

15	$9C + 9H_2 \rightarrow C_9H_{18}$	Nonene	0.017	1.59	0
16	$10C + 4H_2 \rightarrow C_{10}H_8$	Naphthalene	0.979	33.89	0
17	$11C + 12H_2 \rightarrow C_{11}H_{24}$	Undecane	35.684	6.3	-1.089
18	$11C + 5H_2 \rightarrow C_{11}H_{10}$	Methylnaphthalene	125.001	6.3	-1.089
19	$12C + 5H_2 \rightarrow C_{12}H_{10}$	Diphenyl	142.201	6.3	-1.089
20	$12C + 6H_2 \rightarrow C_{12}H_{12}$	Dimethylnaphthalene	85.169	6.3	-1.089
21	$13C + 5H_2 \rightarrow C_{13}H_{10}$	Fluorene	47.77	6.3	-1.089
22	$14C + 5H_2 \rightarrow C_{14}H_{10}$	Anthracene	38.059	6.3	-1.089
23	$14C + 14H_2 \rightarrow C_{14}H_{28}$	Tetradecene	118.294	6.3	-1.089
24	$15C + 15H_2 \rightarrow C_{15}H_{30}$	Pentadecene	17.88	6.3	-1.089
25	$15C + 16H_2 \rightarrow C_{15}H_{32}$	Pentadecane	56.974	6.3	-1.089
26	$16C + 17H_2 \rightarrow C_{16}H_{34}$	Hexadecane	46.822	6.3	-1.089
27	$19C + 20H_2 \rightarrow C_{19}H_{40}$	Nonadecane	12.247	6.3	-1.089
28	$20C + 21H_2 \rightarrow C_{20}H_{42}$	Eicosane	13.594	6.3	-1.089
29	$21C + 22H_2 \rightarrow C_{21}H_{44}$	Heneicosane	15.524	6.3	-1.089
30	$22C + 23H_2 \rightarrow C_{22}H_{46}$	Docosane	12.028	6.3	-1.089
31	$23C + 24H_2 \rightarrow C_{23}H_{48}$	Tricosane	15.641	6.3	-1.089
32	$24C + 25H_2 \rightarrow C_{24}H_{50}$	Tetracosane	3.029	6.3	-1.089

Appendix C Chapter 5

Table C.22 Aliphatic hydrocarbons found from the pyrolysis of plastic at different temperatures.

Aliphatic hydrocarbons			
350°C	**500°C**	**650°C**	**800°C**
(1R)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene	17-Pentatriacontene	(Z),(Z)-2,4-Hexadiene	17-Pentatriacontene
17-Pentatriacontene	1-Decene	1,10-Undecadiene	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-
1-Heptadecene	1-Decene, 2,4-dimethyl-	1,11-Dodecadiene	
3-Carene	1-Docosene	1,12-Tridecadiene	
D-Limonene	1-Dodecene	1,13-Tetradecadiene	
Docosane	1-Eicosene	1,15-Hexadecadiene	
Eicosane	1-Heptene	1,19-Eicosadiene	
Heneicosane	1-Heptene, 2-methyl-	1,3,5-Hexatriene	
Heptacosane	1-Heptene, 4-methyl-	1,3-Butadiene, 2-ethyl-	
Heptane, 2,2,4,6,6-pentamethyl-	1-Hexene	1,3-Cyclopentadiene, 5-methyl-	

Hexacosane	1-Hexene, 4,5-dimethyl-	1,3-Hexadiene, 3-ethyl-2-methyl-
Limonene	1-Nonadecene	1,3-Octadiene
Nonacosane	1-Nonene	1,3-Pentadiene
Nonadecane	1-Nonene, 4,6,8-trimethyl-	1,3-Pentadiene, 2,3-dimethyl-
Octacosane	1-Octadecene	1,3-Pentadiene, 2,4-dimethyl-
Pentacosane	1-Octene	1,3-Pentadiene, 3-methyl-, (E)-
Tetracosane	1-Pentadecene	1,4-Dihydro-1,4-ethanoanthracene
Tetradecane	1-Pentene, 2,4-dimethyl-	1,4-Hexadiene, 2,3-dimethyl-
Tetradecane, 2,6,10-trimethyl-	1-Pentene, 2-methyl-	1,4-Hexadiene, 2-methyl-
	1-Tetradecene	1,5-Hexadiene
	1-Tridecene	1,5-Hexadiene, 2,5-dimethyl-
	1-Undecene	1,5-Hexadiene, 2-methyl-
	2,4-Dimethyl-1-heptene	1,5-Hexene, 2-methyl-
	2,4-Dimethyl-1-hexene	1,6-Heptadiene

	2-Decene, 7-methyl-, (Z)-	1,6-Heptadiene, 2,5-dimethyl-
	2-Heptene, 4-methyl-, (E)-	1,6-Octadiene, 2,6-dimethyl-, (Z)-
	2-Octene, (Z)-	1,7-Octadiene
	2-Undecene, (E)-	1,8-Nonadiene
	2-Undecene, (Z)-	1,9-Decadiene
	3-Heptadecene, (Z)-	1,9-Tetradecadiene
	3-Heptene, 2,6-dimethyl-	17-Pentatriacontene
	4-Decene, 2-methyl-, (Z)-	18-Nonadecen-1-ol
	4-Decene, 9-methyl-, (E)-	1-Decene
	5-Ethyl-1-nonene	1-Decene, 4-methyl-
	9-Eicosene, (E)-	1-Decene, 5-methyl-
	9-Hexacosene	1-Docosene
	9-Nonadecene	1-Dodecene

	9-Tricosene, (Z)-	1-Eicosene
	Cetene	1-Ethyl-2,2,6-trimethylcyclohexane
	Cyclohexane, 1,2,4-triethenyl-	1-Heptadecene
	Cyclohexane, 1,3,5-trimethyl-	1-Heptene
	Cyclohexene, 4-ethenyl-	1-Heptene, 2,6-dimethyl-
	Cyclooctane, 1,4-dimethyl-, cis-	1-Heptene, 2-methyl-
	Cyclooctane, 1,4-dimethyl-, trans-	1-Heptene, 5-methyl-
	Cyclooctene, 5,6-diethenyl-, cis-	1-Hexacosene
	Cyclopropane	1-Hexene
	Cyclopropane, 1-methyl-2-pentyl-	1-Hexene, 2,5-dimethyl-
	Cyclopropane, pentyl-	1-Hexene, 2-methyl-

	Cycloundecane, 1,1,2-trimethyl-	1-Hexene, 3,3,5-trimethyl-
	Decane	1-Isopropyl-1,4,5-trimethylcyclohexane
	Decane, 4-methyl-	1-Methyl-2-methylenecyclohexane
	Dispiro[2.0.2.5]undecane, 8-methylene-	1-Nonadecene
	Docosane	1-Nonene
	Dodecane	1-Nonene, 4,6,8-trimethyl-
	Dotriacontane	1-Nonylcycloheptane
	Eicosane	1-Octadecene
	Ethylidenecyclobutane	1-Octene
	Heneicosane	1-Octene, 2,6-dimethyl-
	Henicos-1-ene	1-Octene, 2-methyl-
	Heptacosane	1-Octene, 3-methyl-
	Heptadecane	1-Pentadecene
	Heptane	1-Pentene, 2,4-dimethyl-
	Heptane, 2,4-dimethyl-	1-Pentene, 2-methyl-

	Heptane, 3-methylene-	1-Pentene, 4-methyl-
	Heptane, 4-methyl-	1-Tetradecene
	Hexadecane	1-Tricosene
	Hexane, 2,4-dimethyl-	1-Tridecene
	Hexane, 3-methyl-	1-Undecene
	Hexatriacontane	1-Undecene, 7-methyl-
	Methylenecyclopropane	2,3-Dimethyl-3-heptene, (Z)-
	Nonacosane	2,3-Dimethyldecane
	Nonadecane	2,4,6-Trimethyl-3-heptene
	Nonane	2,4-Dimethyl 1,4-pentadiene
	Nonane, 2,6-dimethyl-	2,4-Dimethyl-1-heptene
	Nonane, 2-methyl-3-methylene-	2,4-Dimethyl-1-hexene
	Nonane, 4-methyl-	2,4-Hexadiene, 2,5-dimethyl-

	Octacosane	2,6-Octadiene, 2,4-dimethyl-
	Octadecane	2-Butene
	Octane	2-Butyl-1-decene
	Octane, 3,3-dimethyl-	2-Decene, (Z)-
	Pentacosane	2-Decene, 7-methyl-, (Z)-
	Pentadecane	2-Heptene
	Pentane	2-Heptene, 4-methyl-, (E)-
	Pentane, 2-methyl-	2-Hexene, 2,3-dimethyl-
	Propane	2-Hexene, 3,5-dimethyl-
	Propene	2-Hexene, 3-methyl-, (Z)-
	Tetracosane	2-Methyl-1-nonene
	Tetradecane	2-Methyl-E-7-hexadecene
	Tetratetracontane	2-Nonene, (E)-
	Triacontane	2-Nonene, 2-methyl-
	Tricosane	2-Octene
	Tridecane	2-Octene, (Z)-

Undecane	2-Octene, 2,6-dimethyl-
	2-Octene, 2,7-dimethyl-
	2-Octene, 3,7-dimethyl-, (Z)-
	2-Pentene, 3-methyl-, (E)-
	2-Pentene, 3-methyl-, (Z)-
	2-Undecene, (Z)-
	2-Undecene, 9-methyl-, (E)-
	3-Dodecene, (E)-
	3-Dodecene, (Z)-
	3-Ethyl-4-methyl-2-pentene
	3-Heptadecene, (Z)-
	3-Heptene
	3-Heptene, 2,6-dimethyl-
	3-Heptene, 4-methyl-
	3-Heptene, 4-propyl-
	3-Hexadecyne
	3-Hexene, 2,3-dimethyl-

	3-Octadecyne
	3-Octene, (Z)-
	3-Octene, 2,2-dimethyl-
	3-Tetradecene, (E)-
	3-Tridecene
	3-Tridecene, (E)-
	3-Undecene, (Z)-
	4,5-Nonadiene, 2-methyl-
	4-Decene
	4-Nonene
	4-Octene, (E)-
	4-Tridecene, (Z)-
	5-Decene, (E)-
	5-Eicosene, (E)-
	5-Tetradecene, (Z)-
	5-Undecene
	6-Dodecene, (Z)-
	7-Octadecyne, 2-methyl-

	7-Tetradecene
	9-Eicosene, (E)-
	9-Methylbicyclo[3.3.1]nonane
	9-Tricosene, (Z)-
	Bicyclo[3.1.0]hexane
	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-
	Bicyclo[4.2.0]octa-1,3,5-triene
	Bicyclo[5.1.0]octane
	Cetene
	cis-1,4-Dimethyl-2-methylenecyclohexane
	cis-2-Nonene
	cis-4-Nonene
	Cis-bicyclo[4.2.0]octane
	Cyclobutane, methylene-
	Cyclodecene, (Z)-
	Cyclododecane, ethyl-

	Cyclohexane
	Cyclohexane, 1,1,3-trimethyl-2-(3-methylpentyl)-
	Cyclohexane, 1,3,5-trimethyl-
	Cyclohexane, 1,3-dimethyl-2-methylene-, trans-
	Cyclohexane, 1,4-bis(methylene)-
	Cyclohexane, 1,4-dimethyl-
	Cyclohexane, 1,4-dimethyl-, cis-
	Cyclohexane, 1-methyl-2-propyl-
	Cyclohexane, 1-propenyl-
	Cyclohexane, 2-propenyl-
	Cyclohexane, butyl-
	Cyclohexane, ethyl-
	Cyclohexane, methyl-
	Cyclohexene

	Cyclohexene, 1,4-dimethyl-
	Cyclohexene, 1-methyl-
	Cyclohexene, 3,3,5-trimethyl-
	Cyclohexene, 3,5-dimethyl-
	Cyclohexene, 3-methyl-
	Cyclohexene, 4-methyl-
	Cyclooctane, 1,4-dimethyl-, cis-
	Cyclooctane, 1,4-dimethyl-, trans-
	Cyclooctane, ethenyl-
	Cyclooctene
	Cyclooctene, 1,2-dimethyl-
	Cyclopentane, 1,2,3,4,5-pentamethyl-
	Cyclopentane, 1,2-dimethyl-, cis-
	Cyclopentane, 1-methyl-2-(2-propenyl)-, trans-

	Cyclopentane, 1-methyl-2-(4-methylpentyl)-, trans-
	Cyclopentane, 1-methyl-2-methylene-
	Cyclopentane, 1-methyl-3-(2-methyl-2-propenyl)-
	Cyclopentane, ethyl-
	Cyclopentane, methyl-
	Cyclopentene
	Cyclopentene, 1,2,3-trimethyl-
	Cyclopentene, 3-methyl-
	Cyclopentene, 4,4-dimethyl-
	Cyclopropane
	Cyclopropane, (1-methylethylidene)-
	Cyclopropane, (2,2-dimethylpropylidene)-
	Cyclopropane, 1,1-dimethyl-
	Cyclopropane, 1-methyl-2-(1-methylethyl)-3-(1-methylethylidene)-, cis-

	Cyclopropane, ethyl-
	Cyclopropane, ethylidene-
	Cyclopropane, pentyl-
	Decane
	Decane, 4-methyl-
	Deltacyclene
	Docosane
	Dodecane
	Eicosane
	Ethylidenecyclobutane
	Ethylidenecyclooctane
	Heneicosane
	Henicos-1-ene
	Henicosanal
	Heptacos-1-ene
	Heptadecane
	Heptadecane, 2,6,10,15-tetramethyl-

	Heptane
	Heptane, 2,4,6-trimethyl-
	Heptane, 2,4-dimethyl-
	Heptane, 4-methyl-
	Hexadecane
	Hexane, 2,4-dimethyl-
	Hexane, 3-ethyl-
	Neophytadiene
	Nonacos-1-ene
	Nonadecane
	Nonane
	Nonane, 2,6-dimethyl-
	Nonane, 2,8-dimethyl-4-methylene-
	Nonane, 2-methyl-3-methylene-
	Nonane, 3-methylene-
	Nonane, 4-methyl-
	Nonane, 5-methylene-

	Octadecane
	Octane
	Octane, 3,3-dimethyl-
	Pentacos-1-ene
	Pentadecane
	Pentane
	Propane
	Propene
	Tetracosane
	Tetradecane
	Tetradecane, 2,6,10-trimethyl-
	Toluene
	trans-7-Methyl-3-octene
	Tricosane
	Tridecane
	Tridecane, 3-methylene-
	Undecane

Z-5-Nonadecene

Table C.23 Aromatic hydrocarbons found from the pyrolysis of plastic at different temperatures.

Aromatic hydrocarbons			
350°C	**500°C**	**650°C**	**800°C**
1,3-di-iso-propylnaphthalene	1,1'-Biphenyl, 2-methyl-	1,1'-Biphenyl, 3-methyl-	1,1'-Biphenyl, 3-methyl-
1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	1H-Indene, 2,3-dihydro-4-methyl-	1,1'-Biphenyl, 4-methyl-	1,1'-Biphenyl, 4-methyl-
2,6-Diisopropylnaphthalene	1-Phenyl-1-butene	1,5-Diphenyl-1,5-hexadiene	1H-Benz[f]indene, 2-phenyl-
9H-Fluorene, 9-methylene-	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	1H-Indene, 1-ethyl-2,3-dihydro-	9H-Fluorene, 9-methylene-
Benzene	2,5-Diphenyl-1,5-hexadiene	1H-Indene, 1-methyl-	Anthracene
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	Anthracene	1H-Indene, 2,3-dihydro-1,2-dimethyl-	Benz[a]anthracene
Benzene, 1-ethynyl-4-methyl-	Benzaldehyde, 2,5-dimethyl-	1H-Indene, 3-methyl-	Benzene

Biphenyl	Benzene	1-Phenylbicyclo[2.1.1]hexane	Benzene, 1-ethynyl-4-methyl-
Naphthalene	Benzene, (2-methyl-1-propenyl)-	2,5-Diphenyl-1,5-hexadiene	Biphenyl
Naphthalene, 1-phenyl-	Benzene, 1,1'-(1,3-propanediyl)bis-	Benzene	Diphenylmethane
Styrene	Benzene, 1,1'-(1-butene-1,4-diyl)bis-, (Z)-	Benzene, (1-methyl-2-propynyl)-	Fluorene
	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	Benzene, (1-methylenebutyl)-	Methyl 2,6-dihydroxybenzoate
	Benzene, 1,3-dimethyl-	Benzene, (1-methylenepentyl)-	Naphthalene
	Benzene, 1-ethenyl-2-methyl-	Benzene, (1-methylenepropyl)-	Naphthalene, 2-phenyl-
	Benzene, 1-ethyl-2-methyl-	Benzene, (1-methylethyl)-	Phenanthrene
	Benzene, 1-ethynyl-4-methyl-	Benzene, (2-methyl-3-butenyl)-	p-Terphenyl
	Benzene, 1-methyl-2-(2-propenyl)-	Benzene, (3-methyl-3-butenyl)-	Stilbene
	Benzene, 1-methyl-4-propyl-	Benzene, 1,1'-(1,3-butadienylidene)bis-	Styrene
	Benzene, 1-propynyl-	Benzene, 1,1'-(1,3-propanediyl)bis-	Toluene

	Benzene, 2-propenyl-	Benzene, 1,1'-(1-butene-1,4-diyl)bis-, (Z)-	Triphenylene
	Benzene, 3-cyclohexen-1-yl-	Benzene, 1,1'-(1-methyl-1,2-ethanediyl)bis-	
	Benzene, n-butyl-	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	
	Benzene, propyl-	Benzene, 1,2,3-trimethyl-	
	Biphenyl	Benzene, 1,3-dimethyl-	
	Cholesta-3,5-diene	Benzene, 1-ethenyl-2-methyl-	
	Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-	Benzene, 1-ethyl-2-methyl-	
	Ethylbenzene	Benzene, 1-ethyl-3-methyl-	
	Fluorene	Benzene, 1-ethynyl-4-methyl-	
	Indane	Benzene, 1-methyl-4-(1-propynyl)-	
	Indene	Benzene, 2-propenyl-	
	Naphthalene	Benzene, 3-butenyl-	

	Naphthalene, 1,2,3,4-tetrahydro-	Benzene, 4-ethenyl-1,2-dimethyl-
	Naphthalene, 1,2,3,4-tetrahydro-1-phenyl-	Benzene, propyl-
	Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	Bibenzyl
	Naphthalene, 1,2-dihydro-	Bicyclo[4.2.0]octa-1,3,5-triene
	Naphthalene, 1,2-dihydro-4-methyl-	Biphenyl
	Naphthalene, 1-methyl-	Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-
	Naphthalene, 2-methyl-	Diphenylmethane
	p-Xylene	Ethylbenzene
	Stilbene	Indane
	Styrene	Indene
	Toluene	Naphthalene
	α-Methylstyrene	Naphthalene, 1,2-dihydro-4-methyl-
		Naphthalene, 1,7-dimethyl-

		Naphthalene, 1-methyl-	
		Naphthalene, 2-methyl-	
		o-Xylene	
		p-Terphenyl	
		p-Xylene	
		Stilbene	
		Styrene	
		Toluene	
		α-Methylstyrene	

Table C.24 Other aromatics found from the pyrolysis of plastic at different temperatures.

Other aromatics			
350°C	**500°C**	**650°C**	**800°C**
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	1H-Indene, 1-chloro-2,3-dihydro-	1,2-Benzenedicarbonitrile	1H-Indene, 1-ethylidene-
2-Chloroethyl benzoate	2,4-Di-tert-butylphenol	1,2-Ethanediol, dibenzoate	2-Chloroethyl benzoate

2-Sulfamyl-4-nitro-4'-acetamidodiphenyl sulfide	2,4-Di-tert-butylphenol	1,2-Ethanediol, monobenzoate	2-Sulfamyl-4-nitro-4'-acetamidodiphenyl sulfide
7-Acetyl-6-ethyl-1,1,4,4-tetramethyltetralin	2-Chloroethyl benzoate	2,3-Diazabicyclo[2.2.1]hept-2-ene, 1,4-diphenyl-	9H-Fluoren-9-one
Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-	4-Ethylbenzoic acid, 2-chloroethyl ester	2,5-Pyrrolidinedione, 1-[(4-methylbenzoyl)oxy]-	Acetophenone
Benzene, 1-methyl-3-(1-methylethyl)-	Aniline	2-Chloroethyl benzoate	Anthrone
Benzeneethanamine, 3-fluoro-.beta.,5-dihydroxy-N-methyl-	Azetidine, 3-methyl-3-phenyl-	4-(Trifluoroacetyl)benzoic acid	Azetidine, 3-methyl-3-phenyl-
Benzeneethanamine, N-[(4-hydroxy)hydrocinnamoyl]-	Benzaldehyde, 2,5-dimethyl-	4-Ethylbenzoic acid	Benzaldehyde
Benzenesulfonamide, N-ethyl-2-methyl-	Benzenamine, 2,4-dimethyl-	4-Ethylbenzoic acid, phenyl ester	Benzeneethanamine, 3-fluoro-.beta.,5-dihydroxy-N-methyl-
Benzenesulfonamide, N-ethyl-4-methyl-	Benzeneethanamine, 3-fluoro-.beta.,5-dihydroxy-N-methyl-	4-Phenylbenzhydrazide	Benzeneethanamine, N-[(4-hydroxy)hydrocinnamoyl]-
Benzoic acid, 2-(1-oxopropyl)-	Benzoic acid	4-Vinylbenzoic acid	Benzo[h]cinnoline

Benzophenone	Benzoic acid, 2-(1-oxopropyl)-	9H-Fluoren-9-one	Benzocycloheptatriene
Benzoyl isothiocyanate	benzoic acid, 4-(2-bromoethyl)-, 4-formylphenyl ester	Acetophenone	Benzoic acid
Dibutyl phthalate	Benzoyl bromide	Benzaldehyde	Benzophenone
Diethyl Phthalate	Benzoyl isothiocyanate	Benzeneacetaldehyde	Benzoyl bromide
Diisooctyl phthalate	Diethyl Phthalate	Benzeneacetic acid, .alpha.-oxo-, methyl ester	Cannabinol
	Ethanedione, diphenyl-	Benzeneethanamine, 3-fluoro-.beta.,5-dihydroxy-N-methyl-	Ethanedione, diphenyl-
	Isophthalic acid	Benzenepropanal	Heptanediamide, N,N'-di-benzoyloxy-
	Isophthalic acid, 2-chloroethyl ethyl ester	Benzoic acid	Methyl 2,6-dihydroxybenzoate
	Phthalic anhydride	Benzoic acid, 2-(1-oxopropyl)-	Phthalic anhydride
	Quinoline, 6-methoxy-, 1-oxide	Benzoic acid, 4-ethyl-, 4-cyanophenyl ester	
	Terephthalic acid, di(2-chloroethyl) ester	Benzoic acid, 4-methyl-	

	Benzoic acid, 4-propyl-, 4-cyanophenyl ester
	Benzoic acid, ethyl ester
	Benzoic acid, hydrazide
	Benzophenone
	Benzoyl isothiocyanate
	Biphenyl-4-carboxylic acid
	Diethylene glycol dibenzoate
	Ethanedione, diphenyl-
	Ethanone, 1,1'-(1,4-phenylene)bis-
	Ethanone, 1-[1,1'-biphenyl]-4-yl-2-bromo-
	Heptanediamide, N,N'-di-benzoyloxy-
	Methyl 2,6-dihydroxybenzoate

		Phenol	
		Phthalic acid, cyclobutyl ethyl ester	
		Quinoline, 6-methoxy-, 1-oxide	
		Terephthalic acid	
		Terephthalic acid, methyl vinyl ester	
		Terephthalic monohydroxamic acid	
		Vinyl benzoate	
		Vinyl trans-cinnamate	

Table C.25 Fluorine containing compounds found from the pyrolysis of plastic at different temperatures.

Fluorine containing compounds			
350°C	**500°C**	**650°C**	**800°C**
Octatriacontyl pentafluoropropionate	Heptacosyl pentafluoropropionate	4-(Trifluoroacetyl)benzoic acid	Dotriacontyl heptafluorobutyrate

	4-Trifluoroacetoxytridecane	4-Trifluoroacetoxyhexadecane	17-Pentatriacontene
	Nonadecyl pentafluoropropionate	Docosyl pentafluoropropionate	Dodecane, 1-cyclopentyl-4-(3-cyclopentylpropyl)-
	Octatriacontyl pentafluoropropionate	Nonadecyl pentafluoropropionate	Octatriacontyl pentafluoropropionate
		Octatriacontyl pentafluoropropionate	Octatriacontyl trifluoroacetate
		Oleyl alcohol, trifluoroacetate	Tetratriacontyl heptafluorobutyrate
		Tetracosyl heptafluorobutyrate	
		Tetratriacontyl heptafluorobutyrate	
		Heptacosyl pentafluoropropionate	

Table C.26 Bromine containing compounds found from the pyrolysis of plastic at different temperatures.

Bromine containing compounds			
350°C	**500°C**	**650°C**	**800°C**

Tetrapentacontane, 1,54-dibromo-	Tetrapentacontane, 1,54-dibromo-	4-(1-Bromoethyl)benzoic acid	Tetrapentacontane, 1,54-dibromo-
		Pentane, 2-bromo-	

Table C.27 Esters found from the pyrolysis of plastic at different temperatures.

Esters			
350°C	**500°C**	**650°C**	**800°C**
Butyl 9,12-octadecadienoate	Decanoic acid, octyl ester	(Z)-14-Tricosenyl formate	Octadecane, 1,1'-[1,3-propanediylbis(oxy)]bis-
Butyl 9-octadecenoate	1-Heneicosyl formate	1-Heneicosyl formate	
Decanoic acid, decyl ester	Cyclohexanol, 1-methyl-4-(1-methylethenyl)-, acetate	6-Octen-1-ol, 3,7-dimethyl-, formate	
Elaidic acid, isopropyl ester	Hexanedioic acid, bis(2-ethylhexyl) ester	Acetic acid, 3,7,11,15-tetramethyl-hexadecyl ester	
Ethyl 9.cis.,11.trans.-octadecadienoate	Methyl methacrylate	Carbonic acid, eicosyl vinyl ester	
Ethyl 9-hexadecenoate	Octadecane, 1,1'-[1,3-propanediylbis(oxy)]bis-	Dichloroacetic acid, 4-hexadecyl ester	
Ethyl Oleate	Oleic acid, eicosyl ester	Ethanol, 2-(9-octadecenyloxy)-, (Z)-	

Hexadecanoic acid, 2-methylpropyl ester	Trichloroacetic acid, hexadecyl ester	Hexanedioic acid, dioctyl ester
Hexadecanoic acid, butyl ester	Trichloroacetic acid, pentadecyl ester	Methyl methacrylate
Hexadecanoic acid, ethyl ester		m-Toluic acid, 4-cyanophenyl ester
Hexadecanoic acid, hexyl ester		m-Toluic acid, 4-nitrophenyl ester
Hexadecanoic acid, propyl ester		Tetrahydroionyl acetate
Hexanedioic acid, bis(2-ethylhexyl) ester		Trichloroacetic acid, hexadecyl ester
Hexanedioic acid, mono(2-ethylhexyl)ester		Trichloroacetic acid, pentadecyl ester
Hexanoic acid, butyl ester		Trichloroacetic acid, tridecyl ester
Hexanoic acid, dodecyl ester		Tricosyl pentafluoropropionate
i-Propyl 14-methylpentadecanoate		
i-Propyl 9-octadecenoate		
Linoleic acid ethyl ester		

n-Butyl laurate
n-Butyric acid 2-ethylhexyl ester
n-Propyl 9,12-octadecadienoate
n-Propyl 9-octadecenoate
Octadecanoic acid, butyl ester
Octadecanoic acid, ethyl ester
Octadecanoic acid, propyl ester
Oleic acid, butyl ester
Trichloroacetic acid, hexadecyl ester

Table C.28 Siloxane compounds found from the pyrolysis of plastic at different temperatures.

Siloxane compounds			
350°C	**500°C**	**650°C**	**800°C**
Octasiloxane, 1,1,3,3,5,5,7,7,9,9,	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,

11,11,13,13,15,15-hexadecamethyl-	11,11,13,13,15,15-hexadecamethyl-	11,11,13,13,15,15-hexadecamethyl-	11,11,13,13,15,15-hexadecamethyl-

Table C.29 Alcohols found from the pyrolysis of plastic at different temperatures.

Alcohols			
350°C	**500°C**	**650°C**	**800°C**
(R)-(-)-2-Amino-1-propanol	Cyclopropylmethanol	(2,4,6-Trimethylcyclohexyl)methanol	Octacosanol
1-Hexanol, 2-ethyl-	1-Decanol, 2-hexyl-	(R)-(-)-(Z)-14-Methyl-8-hexadecen-1-ol	
2-Isopropyl-5-methyl-1-heptanol	1-Decanol, 2-octyl-	11-Hexadecen-1-ol, (Z)-	
Cyclohexanol, 1-methyl-4-(1-methylethenyl)-, acetate	1-Dodecanol, 2-hexyl-	13-Docosen-1-ol, (Z)-	
	1-Dodecanol, 2-methyl-, (S)-	18-Nonadecen-1-ol	
	1-Hexadecanol	18-Nonadecen-1-ol	
	1-Hexanol, 2-ethyl-	1-Butanol, 2,3-dimethyl-	
	1-Undecanol	1-Decanol, 2-hexyl-	
	2-Isopropyl-5-methyl-1-heptanol	1-Decanol, 2-octyl-	
	Behenic alcohol	1-Dodecanol	

	n-Heptadecanol-1	1-Dodecanol, 2-hexyl-
	n-Tetracosanol-1	1-Dodecanol, 2-octyl-
	n-Tridecan-1-ol	1-Dodecanol, 3,7,11-trimethyl-
		1-Eicosanol
		1-Heneicosanol
		1-Heptacosanol
		1-Hexacosanol
		1-Hexadecanol, 3,7,11,15-tetramethyl-
		1-Octadecanol
		1-Octanol, 2-butyl-
		1-Octyn-3-ol, 4-ethyl-
		1-Pentanol, 2-methyl-
		1-Tricosanol
		2-Hexyl-1-octanol
		2-Isopropyl-5-methyl-1-heptanol
		2-Nonen-1-ol, (Z)-
		3-Decen-1-ol, (E)-

	3-Decen-1-ol, (Z)-
	6-Hepten-1-ol, 3-methyl-
	9-Octadecen-1-ol, (Z)-
	9-Tetradecen-1-ol, (E)-
	Behenic alcohol
	cis-9-Tetradecen-1-ol
	Cyclopentadecanol
	Cyclopropyl carbinol
	E-10-Pentadecenol
	E-2-Hexadecacen-1-ol
	E-2-Octadecadecen-1-ol
	E-7-Tetradecenol
	Eicosen-1-ol, cis-9-
	n-Heptadecanol-1
	n-Nonadecanol-1
	n-Pentadecanol

	n-Tetracosanol-1
	n-Tridecan-1-ol
	Octacosanol
	Oleyl alcohol, trifluoroacetate
	Phytol
	Z-10-Pentadecen-1-ol

Table C.30 Amines found from the pyrolysis of plastic at different temperatures.

Amines			
350°C	**500°C**	**650°C**	**800°C**
(2-Aziridinylethyl)amine	-	-	(2-Aziridinylethyl)amine
Butanamide, N-methyl-4-(methylthio)-2-(2,2-dimethylpropylidene)amino-			

Table C.31 Organosulfur compounds found from the pyrolysis of plastic at different temperatures.

Organosulfur compounds			
350°C	**500°C**	**650°C**	**800°C**

(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	-
2-Undecanethiol, 2-methyl-	2-Undecanethiol, 2-methyl-	2-Undecanethiol, 2-methyl-	

Table C.32 Fatty acids found from the pyrolysis of plastic at different temperatures.

Fatty acids			
350°C	**500°C**	**650°C**	**800°C**
n-Hexadecanoic acid	n-Hexadecanoic acid	-	-
Octadecanoic acid	Octadecanoic acid		
	Oleic Acid		
	Tetradecanoic acid		

Table C.33 Aldehydes found from the pyrolysis of plastic at different temperatures.

Aldehydes			
350°C	**500°C**	**650°C**	**800°C**
-	E-14-Hexadecenal	2-Decenal, (E)-	-
	E-15-Heptadecenal	2-Nonenal, (E)-	
		E-14-Hexadecenal	

		E-15-Heptadecenal	
		Heptacosanal	
		Hexacosanal	
		Octadecanal	

Table C.34 Hydrogen halides found from the pyrolysis of plastic at different temperatures.

Hydrogen halides			
350°C	**500°C**	**650°C**	**800°C**
-	Hydrogen chloride	-	-

Table C.35 Carboxylic acids found from the pyrolysis of plastic at different temperatures.

Carboxylic acids			
350°C	**500°C**	**650°C**	**800°C**
-	Decanoic acid, octyl ester	-	-

Table C.36 Chlorinated hydrocarbons found from the pyrolysis of plastic at different temperatures.

Chlorinated hydrocarbons

350°C	500°C	650°C	800°C
-	Butane, 1-chloro-	-	-
	Butane, 2-chloro-		

Table C.37 Ketones found from the pyrolysis of plastic at different temperatures.

Ketones			
350°C	**500°C**	**650°C**	**800°C**
-	-	2-Nonadecanone	-
		3-Methyl-4-propenyl-oxetan-2-one	
		Bicyclo[3.1.0]hexan-2-one, 5-(1-methylethyl)-	
		Cyclopentanone	
		Ethanedione, diphenyl-	

Table C.38 Py-GC-MS repeatability RSD of relative abundance of all samples.

Sample	T (°C)	Run 1 (area %)	Run 2 (area %)	Run 3 (area %)	Mean	SD	%RDS
PE	350	12	52	52	39	19	49
	500	28	62	65	52	17	32
	650	35	94	93	74	28	37

	800	90	94	90	91	2	2
Average		**41**	**76**	**75**	**64**	**16**	**25**
PE <10	350	90	93	87	90	2	3
	500	75	91	85	83	7	8
	650	45	33	90	56	24	43
	800	79	23	95	66	31	47
Average		**72**	**60**	**89**	**74**	**12**	**16**
PE >10	350	80	87	67	78	8	11
	500	60	60	59	59	0	1
	650	77	62	91	77	12	15
	800	55	94	89	79	17	22
Average		**68**	**76**	**76**	**73**	**4**	**5**
PP	350	21	31	70	41	21	52
	500	66	68	68	67	1	2
	650	50	50	51	50	1	1
	800	72	81	68	74	5	7
Average		**52**	**58**	**65**	**58**	**5**	**9**
PP <10	350	11	64	26	34	22	66

	500	70	60	70	67	5	8
	650	59	51	60	57	4	7
	800	76	68	69	71	4	5
Average		**54**	**61**	**56**	**57**	**3**	**5**
PP >10	350	84	86	92	87	3	4
	500	63	61	78	67	8	11
	650	47	43	67	52	10	20
	800	61	86	75	74	10	14
Average		**64**	**69**	**78**	**70**	**6**	**8**
A <10	350	63	46	70	59	10	17
	500	65	61	67	64	2	4
	650	62	62	59	61	1	2
	800	69	66	82	72	7	9
Average		**65**	**59**	**69**	**64**	**4**	**7**
A >10	350	67	65	82	71	7	10
	500	67	74	71	71	3	4
	650	64	79	70	71	6	8
	800	73	80	80	78	3	4

Average		**68**	**75**	**76**	**73**	**3**	**5**
B <10	350	46	43	51	47	3	7
	500	66	62	66	65	2	3
	650	56	54	58	56	1	3
	800	64	59	61	62	2	3
Average		**58**	**55**	**59**	**57**	**2**	**3**
B >10	350	71	69	52	64	9	14
	500	32	72	60	54	17	31
	650	48	53	54	52	3	5
	800	68	70	67	68	1	2
Average		**55**	**66**	**58**	**60**	**5**	**8**

Table C.39 Py-GC-MS repeatability RSD average of relative abundance of all samples.

Sample	**RDS%**
PE	25
PE <10	16
PE >10	5
PP	9

PP <10	5
PP >10	8
A <10	7
A >10	5
B <10	3
B >10	8
Average	9
SD	6

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Physico-chemical properties of excavated plastic from landfill mining and current recycling routes

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ABSTRACT

In Europe over 5.25 billion tonnes of waste has been landfilled between 1995 and 2015. Among this large amount of waste, plastic represents typically 5–25 wt% which is significant and has the potential to be recycled and reintroduced into the circular economy. To date there is still however little information available of the opportunities and challenges in recovering plastics from landfill sites. In this review, the impacts of landfill chemistry on the degradation and/or contamination of excavated plastic waste are analysed. The feasibility of using excavated plastic waste as feedstock for upcycling to valuable chemicals or liquid fuels through thermochemical conversion is also critically discussed. The limited degradation that is experienced by many plastics in landfills (>20 years) which guarantee that large amount is still available is largely due to thermooxidative degradation and the anaerobic conditions. However, excavated plastic waste cannot be conventionally recycled due to high level of ash, impurities and heavy metals. Recent studies demonstrated that pyrolysis offers a cost effective alternative option to conventional recycling. The produced pyrolysis oil is expected to have similar characteristics to petroleum diesel oil. The production of valuable product from excavated plastic waste will also increase the feasibility of enhanced landfill mining projects. However, further studies are needed to investigate the uncertainties about the contamination level and degradation of excavated plastic waste and address their viability for being processed through pyrolysis.

Contents

Abbreviations: ABS, acrylonitrile–butadiene–styrene; APCr, air pollution control residues; BOD, biological oxygen demand; BPA, bisphenol A; COD, chemical oxygen demand; DEHP, diethyl-hexyl phthalate; DMP, dimethyl phthalate; DoU, degree of unsaturation; DTG, differential thermogravimetric; E_a, activation energy; ELFM, enhanced landfill mining; FCC, fluid catalytic cracking; GC-MS, gas chromatography-mass spectrometry; GCV, gross calorific value; HDPE, high-density polyethylene; HOCs, hydrophobic organic contaminants; IW, industrial waste; LDPE, low-density polyethylene; M_n, number average of molecular weight; MBT, mechanical biological treatment; MSW, municipal solid waste; NCV, net calorific value; NP, nonylphenols; PA, polyamide; PAHs, polycyclic aromatic hydrocarbons; PC, polycarbonate; PCDFs, polychlorinated dibenzofurans; PE, polyethylene; PET, polyethylene terephthalate; PMMA, polymethyl methacrylate; PP, polypropylene; PS, polystyrene; PTFE, polytetrafluoroethylene; PU, polyurethane; PVC, polyvinyl chloride; RDF, refused derived fuel; SD, standard deviation; SEM, scanning electron microscopy; SRB, sulphate-reducing bacteria; TDPA, totally degradable plastic additives; TGA, thermogravimetric analyser; TOC, total organic carbon; VOCs, volatile organic compounds; WtE, waste to energy; WtM, waste to material; XRF, X-ray fluorescence.

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1. Introduction

Over the last two decades, the amount of waste being managed by landfill disposal each year has decreased across Europe and the UK. According to the Eurostat (2016) waste estimation, 473 kg per capita of MSW was generated in 1995 in EU-27, of which 64 wt% were disposed in landfill and 11 wt% were recycled. In 2015, the EU-27 reported 477 kg of MSW per capita of which 28 wt% were recycled, 26 wt% incinerated (including energy recovery), 25 wt% landfilled, and 16 wt% were processed by composting and digestion (Eurostat, 2016). New legislation, such as Council Directive 1999/31/EC (European Parliament. Council of the European Union, 1999) and Waste Framework Directive 2008/98/EC (European Parliament. Council of the European Union, 2008), has driven the changes in the management of landfill, encouraged sustainable waste management and resulted in the closure of many landfills (Hogland et al., 2011). The waste management hierarchy included in Framework Directive 2008/98/EC has become part of the European waste management, defining different aspects of this topic such as waste, recycling, recovery, secondary raw materials and by-products (European Commission, 2016).

Recently, Europe has moved towards the 'new' concept of a Circular Economy, aiming to recycle 65 wt% of MSW and reduce the amount of MSW disposed in landfill by 10 wt% before 2030 (European Parliament. Council of the European Union, 2015). However, there are between 125,000 and 500,000 landfills (EURELCO, 2017) in Europe, many of which are now closed; waste in landfills represents an important legacy that needs to be addressed. It is estimated that over 5.25 billion tonnes of waste were deposited in landfills between 1995 and 2015 across the EU-27 countries (Eurostat, 2016). The first landfill mining (LFM) project was carried out in Israel in 1953 (Savage et al., 1993), but only until the late 1980s, interest began to increase, especially in USA and Europe (Hogland et al., 2004). The concept of enhanced landfill mining (ELFM), which started to develop in 2008 (Jones et al., 2013), focuses on maximising the valorisation of waste found in landfills and dump-sites as material (WtM) and energy (WtE) (Jones et al., 2012). Landfills can be considered as temporary storage for waste while the technologies for their valorisation are improved and achieve large-scale deployment (Bosmans et al., 2013). Landfills operating between the 1950s to the mid-1990 s have been identified as the most suitable for ELFM, because they were not affected by the directives that lead to a minimization and pre-treatment of waste disposed in landfills and have higher content of valuable and combustible materials (Hogland et al., 2011; Van Passel et al. 2013).

A key challenge exists in the recovery of value from materials excavated from landfills, which has been partially addressed in previous academic publications, however this review specifically focuses on plastics. Here there is an opportunity to explore alternative methods of recovering value from plastics as conventional recycling/recovery methods will not be viable. Similarly, recovery of energy from waste and advanced conversion processes require further research and development due to the pollution and the unknown effects of landfill contamination on the chemical transformation pathways.

A variety of the landfilled materials can theoretically be recycled or used for energy recovery, which can contribute to the security of energy supply and substitute raw materials (Greedy, 2016). For example, recovery of secondary raw materials available within landfills such as valuable metals (Gutiérrez-Gutiérrez et al., 2015) can mitigate the increasing concern about the availability and security of critical raw materials (European Commission, 2017). Opportunities also exist in the recovery of plastics, which represent between 5–25 wt% of the total waste deposited; the proportion increases in landfills during time due to the degradation of organic matter and its consequent weight loss (García et al., 2016; Sel et al., 2016; Münnich et al., 2015; Quaghebeur et al., 2013; Jones et al., 2013; Van Passel et al., 2013; Van Vossen and Prent, 2011).

The annual worldwide plastic production has increased from 1.5 Mt in the 1950 s to 322 Mt in 2015 (PlasticsEurope, 2016). In 2014 59 Mt and 311 Mt of plastics were generated in Europe and in the world respectively (PlasticsEurope, 2016). In the same year, of 25.8 Mt of plastic waste produced, 29.7 wt% were recycled, 39.5 wt% used for energy recovery and 30 wt% were landfilled (PlasticsEurope, 2016). Over the years, the inadequate plastic waste management has led to the accumulation of plastics in the environment, causing pollution and consequent health risks (Singh and Ruj, 2016; Thompson et al., 2009). The conjunction of increasing energy demand and scarce resources such as fossil fuel has resulted in a need for sustainable secondary fuels and chemical resources (Sharma et al., 2014; Singh and Ruj, 2016). Plastics from landfills can potentially be reprocessed to other plastic products, used as part of a waste-derived fuel for energy or used as a feedstock to produce valuable base petrochemicals (Al-Salem et al., 2009; Mastellone, 1999). Because 90% of the plastic are produced from petroleum, pyrolysis of plastic waste is considered a feasible process to recover chemical building blocks and a valuable alternative to the ordinary plastics disposal routes, such as landfill (Al-Salem et al., 2009; Al-Salem and Lettieri, 2010).

Critical reviews and studies on technical and economic aspects of LFM and ELFM has been previously published (Krook et al., 2012; Jones et al., 2013; Bosmans et al., 2013; Van Passel et al.; 2013). However, these do not focus on the excavated plastic waste fraction and therefore do not consider its chemical characteristics. This paper reviews the research focusing on excavated plastics and the physico-chemical properties of this fraction along with the gaps in scientific knowledge that need to be filled to consolidate and enable development of upcycling technologies. The aim of the work is to critically review the likely impacts of landfill chemistry on the degradation and/or contamination of plastic waste and its properties, and assess the viability of using excavated plastic waste as feedstock for upcycling to valuable chemicals or liquid fuels via thermochemical conversion.

2. Plastic components of landfill waste and factors affecting their degradation

2.1. Plastic components of landfill waste

Plastics can be thermoplastic, which are capable of melting and flowing at a certain temperature without undergoing chemical changes, and thermoset such as bakelite, which are characterised by irreversible cross-linked polymer chains formed at high-temperature treatments (Jasso-Gastinel et al., 2017). The molecular structure is characterised either by a random arrangement of polymer chains forming an amorphous structure such as PS and PVC, or by an alternation of random and regular orders forming semi-crystalline structure such as PE and PP (Gilbert, 2017).

Thermoplastics have secondary bonding between molecules while thermosets cross-linking often have primary covalent bonds and occasionally hydrogen bonds (Lampman, 2003). Chemical reactivity and thermal stability are related to the primary bonds while the solubility of the polymers is associated with the secondary bonds (Brydson, 1999).

Thermoplastics include polyethylene (PE), which can be subdivided into low-density (LDPE) and high-density polyethylene (HDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). Thermoplastics represent approximately 80 wt% of the consumed plastics and constitute most of the plastic fraction of municipal plastic waste (Dewil et al., 2006; Andrady and Neal, 2009; Lettieri and Al-Salem, 2011).

2.2. Factors affecting plastic waste degradation

Their chemical composition and structure influence their degradation behaviour (Brydson, 1999). Thus, polymers with heteroatoms such as PET, are more susceptible to degradation than polymers with pure carbon backbones (Zheng et al., 2005; Müller et al., 2001). The water permeability of plastics is directly proportional to their polarity; hence nonpolar polymers are less affected by water permeability (McKeen, 2014).

Most common plastics can be classified from the most polar to the less polar as follows: PET > PU > PC > PS > PE > PP (McKeen, 2014). Polymers with unsaturated double bonds are more prone to degradation than polymers with saturated bonds (Gewert et al., 2015). However, the presence of impurities, such as traces of catalyst residues, additives, or metals from processing equipment can accelerate/initiate degradation of polymers with saturated bonds, i.e. PE, PP and PVC (Gijsman et al., 1999; Grassie and Scott, 1988; Scott, 2002; Vasile, 2005, cited in Gewert et al., 2015).

The degree of unsaturation (DoU) gives information on the unsaturated (double, triple and rings) bonds present in the monomer. The fluidity of the polymer is directly proportional to the degree of unsaturation, increasing the saturation level the fluidity decreases. DoU of a polymer can be calculated from its repeating unit (Eq. (1)), which does not consider the O and S due to their neutrality in saturation (McKeen, 2014).

Formula of polymer degree of unsaturation.

$$DoU = \frac{2C + 2 + N - X - H}{2} \tag{1}$$

where C, number of carbon; N, number of nitrogen; X, number of halogen (F, Cl, Br, I); H, number of hydrogen.

Degradation of plastics in the environment can occurs either by photodegradation, auto-oxidative degradation, thermooxidative degradation, thermal degradation and biodegradation (Andrady, 2011). The degradation process is normally initiated by UV-light and heat followed by auto-oxidation of the polymers and scissions into smaller polymer fragments which can be degraded by microorganisms (Andrady, 2011).

Degradation of plastic waste in landfills covers a period over 20 years and it is mainly related to thermooxidative degradation and anaerobic condition (Webb et al., 2013). The most common cause of degradation of polymers without heteroatoms, such as PP, PE and PS, in an aerobic environment, is the photodegradation followed by oxidation (Gijsman et al., 1999). Fig. 1 shows the mechanism for a general polymer auto-oxidation process. Free radicals are initially formed from photo and thermal degradation. They react in the presence of oxygen to form peroxy radicals, which further react with organic material leading to hydroperoxides formation (ROOH) (Gijsman, 2008). New radicals are generated from the hydroperoxides, sustaining the process. Transition metals such as Fe, Cu, Ti and Cr can accelerate the degradation process (Gijsman, 2008). Transition metals such as Fe, Co, and Mn, can catalyse the formation of free radicals from hydroperoxides (Ammala et al., 2011). Photodegradation is more affected by iron, while thermal degradation is catalysed by cobalt and manganese (Ammala et al., 2011).Thermooxidative degradation, which occurs at moderate temperature (~70 °C), is one of the main oxidative degradation steps (Andrady, 2011; Gijsman, 2008).

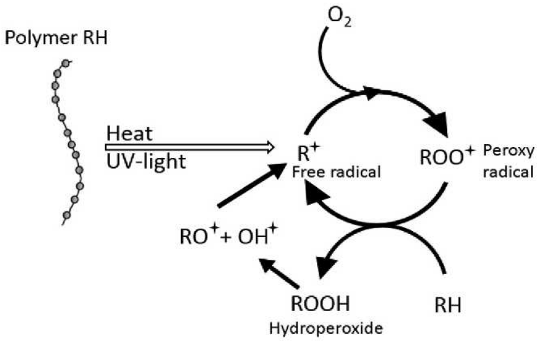


Fig. 1. General polymer auto-oxidation process.

Several studies reported anaerobic biodegradation of plastics in landfills into water and methane (Gu et al., 2000 cited in Shah et al., 2008). The polymers are broken down into shorter chains by microorganism enzymes, until they reach a small size (M_n ~500 g/mol) and are able to penetrate the bacterial membranes (Andrady, 2011; Shah et al., 2008). Muenmee et al. (2016) also found that semi-aerobic condition in landfills enhanced the plastics biodegradation and decreased the methane emission. In aerobic conditions, biodegradation produces CO_2 and H_2O (Shah et al., 2008). Adamcová and Vaverková (2014) studied the degradation of HDPE with totally degradable plastic additives (TDPA) and 100%-degradable PE samples placed in Štěpánovice landfill for a period of 12 months. Neither decomposition nor degradation was found in the samples, and only a change in colour was reported (Adamcová and Vaverková, 2014). This observation is likely to be because degradation of plastics is a long process and requires years to occur. Table 1 shows some degradation characteristics of most common plastics types.

Plastic degradation affects the material physical properties leading to visible changes, such as discoloration and brittleness, and chemical changes, such as bond scissions and new functional groups formation (Pospisil and Nespurek, 1997; Shah et al., 2008). Microorganisms tend to attack the amorphous polymer structure while the crystalline component, characterised by slower degradation, is separated from the material structure (Shah et al., 2008). Moreover, the degradation of plastics releases pollutants into the air and leachate, such as benzene, toluene, xylenes, ethylbenzenes, trimethyl benzenes, bisphenol A (BPA) and nonylphenols (NP) (Teuten et al., 2009; Tsuchida et al., 2011; Urase et al., 2008; Webb et al., 2013; Xu et al., 2011).

Further to this, several factors can influence plastic degradation in landfills such as presence of oxygen, leachate, corrosive chemicals, relatively elevated temperature, and acidic pH. Hydrogen sulphide (H_2S) is one of the chemicals that can cause corrosion of plastics (Table 2). H_2S formation occurs in landfills when sulphate-reducing bacteria (SRB) convert sulphate (SO_4^{2-}) to sul-

Table 1
Degradation processes and degradation products for common plastics (adapted from Gewert et al., 2015; Venkatachalam et al., 2012).

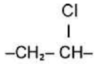
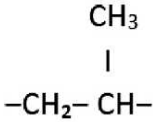
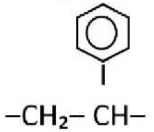
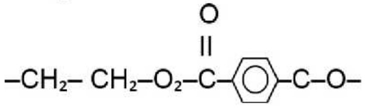
Plastic type		Chemical composition and repeating monomer		Typical degradation processes	Products from degradation
PE	Polyethylene	Carbon-backbone Saturated bonds Chain of ethylene monomer	$-CH_2-CH_2-$	Inclined to photo-initiated oxidative degradation in aerobic condition	Aliphatic carboxylic acids alcohols, aldehydes, and ketones
PVC	Polyvinyl chloride	Carbon-backbone Saturated bonds Heteroatoms – Cl	 $-CH_2-\overset{\overset{Cl}{\vert}}{CH}-$	Highly sensitive to photo-initiated oxidative degradation in aerobic condition In aerobic condition, the presence of HCl and low molecular weight enhances the photo-initiated dechlorination rate. Dechlorination proceeds as an autocatalytic reaction after carboxylic end groups formation Resistant to biodegradation Semi-volatile organotin compounds are used as stabiliser	Conjugated double bonds in a polyene polymer and hydrochloric acid
PP	Polypropylene	Carbon-backbone Saturated bonds Methyl groups bonded to the backbone carbons	 $-CH_2-\overset{\overset{CH_3}{\vert}}{CH}-$	Tending to photo-initiated oxidative degradation in aerobic condition Tertiary carbon which is more susceptible to abiotic degradation and less to biodegradation	Pentanes such as 2-methyl-1-pentene and 2,4-dimethyl-1-heptene
PS	Polystyrene	Carbon-backbone Benzene ring bonded to the backbone carbons		Sensitive to photo-initiated oxidative degradation in aerobic condition Predominant end-chain scission Most durable thermoplastic polymer towards biodegradation	Ketones and olefins oligomers of styrene, such as dimer and trimer, benzene, ethylbenzene, a-methylstyrene, phenol, benzyl alcohol, benzaldehyde, ketones (acetophenone) and benzoic acid
PET or PETE	Polyethylene terephthalate	Heteroatoms – O		Inclined to photodegradation, photooxidative degradation, hydrolytic degradation and thermooxidative degradation in aerobic condition Hydrolysis reaction proceeds as autocatalytic after carboxylic end groups formation Resistant to biodegradation	Acetaldehyde, ethylene, benzene, biphenyl

Table 2
Plastic corrosion behaviour in the presence of H_2S (Pruett, 2000, Pruett, 1994, Schweitzer, 1995 cited in CCOHS, 2012).

Corrosion	No corrosion
Acetal	Chlorinated polyvinyl chloride (CPVC)
Nylon	Teflon
Polyurethane	Kynar (PVDF)
Viton A	Polyethylene
Hard rubber	Polypropylene
Chlorinated polyethylene	Polystyrene
Natural rubber	Polyvinyl chloride (PVC)
Soft rubber	Ethylene propylene
Isoprene	Ethylene propylene diene
Nitrile Buna-N (NBR)	Chloroprene
Styrene-butadiene (SBR)	Butyl rubber (isobutylene-isoprene)
Polyacrylate	Hypalon (chloro-sulfonyl-polyethylene (CSM))
Polyurethane	
Silicone VMQ	Neoprene
	Ethylene vinyl acetate

Table 3
General characteristics of leachate at different age (adapted from Bhalla et al., 2012).

Parameter	Young	Intermediate	Old
Age (years)	<5	5–10	>10
pH	6.5	6.5–7.5	>7.5
COD (mg/l)	>10,000	4000–10,000	<4000
BOD_5/COD	>0.3	0.1–0.3	<0.1
Organic compounds	80% volatile fat acids (VFA)	5–30% VFA + humic and fluvic acids	Humic and fluvic acids
Heavy metals	Low-medium	Low	Low
Biodegradability	Important	Medium	Low

Table 4
Leachate chemicals and related plastics affected (adapted from El-Fadel et al., 2002; Ted Pella Inc, 2017).

Parameter	Concentration range (mg/l) in the leachate	Plastics affected
Benzene	0.1–0.6	LDPE, HDPE, PP, PS, PC
Ethylbenzene	0–4.9	LDPE, HDPE, PP, PS, PC
Phenol	0.17–6.6	LDPE, PS, PC
Toluene	0–3.2	LDPE, HDPE, PP, PS, PC

phite (SO_3^{2-}), and this into sulphide (S^{2-}) and H_2S at low pH (Ko et al., 2015; Tsuchida et al., 2011). Different types of waste have an opposite effect on H_2S production. Co-disposed landfill waste can influence H_2S production changing the pH in the landfill; for example concrete increases the pH whereas wood waste decreases the pH under the optimum SRB pH range (Yang et al., 2006). New waste has greater influence on the increase in the level of H_2S than aged waste due to the decrease of sulphur compounds with time (Ko et al., 2015). Tsuchida et al. (2011) remarked the use of some organic plastic additives such as phenols and organic phosphates as electron donors by SRB for H_2S production in inert waste landfills. In addition, SRB uses gypsum drywall, organic waste and sludge of wastewater treatment plants as a sulphur source in landfills in anaerobic condition (Ko et al., 2015). The activity of SRB is also affected by the presence of nitrate and ferric compounds which increase the propagation of nitrate and iron reducing bacteria respectively (Eckford and Fedorak, 2002; Lovley, 1991).

Plastic contains a variety of additives which during degradation can leach in the environment increasing the risk of pollution (Beiβmann et al., 2013; Prudent et al., 1996; Quaghebeur et al., 2013; Teuten et al., 2009). Parameters such as the polymer pore size, the size and type of additive and temperature, influence the release mechanisms of additives from polymers in landfills (Teuten et al., 2009). Furthermore, leachates can exhibit different characteristics, such as pH and ionic strength, which result in different additive extraction potentials (Xu et al., 2011; Teuten et al., 2009). Additives are typically used to enhance the processing and the properties of plastic. Generally, additives with short alkyl chains tend to be more readily released in the leachate than those with longer alkyl chains (Teuten et al., 2009).

Phthalates (alkyl/aryl esters of 1,2-benze-nedicarboxylic acid) are commonly used as plasticisers in PVC (Hahladakis et al. 2018). It has been reported that plasticisers with high solubility such as dimethyl phthalate (DMP) are released in landfills in greater amounts than hydrophobic plasticisers such as diethylhexyl phthalate (DEHP) (Teuten et al., 2009). Migration of plasticiser decreases when the polymer reaches its glass transition state (Ejlertsson et al. 2003). Alkylphenols are additives with plasticising and stabilising properties (Hahladakis et al. 2018; Teuten et al., 2009). Organotin compounds are highly used in rigid PVC as stabilisers and can be toxic for humans (Folarin and Sadiku, 2011). The release of phthalate esters and organotin compounds occurs in the neutral leachate of the methanogenic phase (Bauer and Herrmann 1998; Björn et al., 2007). BPA, which is used in building blocks of polycarbonate plastics, PVC and printer ink, has been reported to be released from the polymer in the acidogenic phase (Asakura et al., 2004). Different plastic types such as polycarbonates and epoxy resins can release BPA in the leachates, and for this reason larger quantity of plastic waste can lead to a major dispersion of this pollutant in the environment (Xu et al., 2011; Teuten et al., 2009).

Leachate characteristics are variable (Table 3) along with its potential to degrade plastics and their additives (Teuten et al., 2009). Thus, the leachate from anaerobic landfills tends to be more acidic than that from semi-aerated landfills, due to the high amount of putrescible organic during the anaerobic degradation of MSW, and a higher concentration of BOD, COD and ammonia (Cossu et al., 2003). During the acetogenic phase, the leachate presents low pH level and high ionic strength which inhibit the release of plasticisers (Bauer and Herrmann, 1998). Some example of leachate chemicals which can affect plastics are given in Table 4.

On the other hand, plastics have also a fundamental role as a sorbent organic matter for hydrophobic organic contaminants (HOCs) (Saquing et al., 2010). For this reason, plastics from landfill are likely to carry HOCs for instance toluene. Glassy or hard plastics which have high glass-transition temperature such as PVC (T_g 87 °C), are characterised by slower desorption of HOCs than rubbery or soft polymers such as PE (T_g −78 °C) (Saquing et al., 2010; ASM International, 2003; Yang et al., 2016).

3. Landfill mining projects for recovering plastic waste

Although ~700 landfill mining projects have been carried out, project setup and parameters included are not always fully detailed making difficult to compare the results of different studies (Krook et al., 2012).

Tielemans and Laevers (2010) investigated the "Closing the circle" project for the landfill site of Group Machiels in Belgium, studying the material distribution and energy valorization. The samples comprise of MSW waste and IW waste excavated from REMO landfill. The thermal valorisation was based on the process of RDF from the excavated waste through a Gasplasma™ system. The excavated waste was classified in three fractions based on particle size, fine fraction <4 mm, fraction between 4–10 mm and fraction >10 mm; the fraction <10 mm represented the highest percentage, between 44–56 wt% for MSW and 64–80 wt% for IW (Tielemans and Laevers, 2010). Plastics suitable for material valorisation were identified in the fraction > 4 mm (Tielemans and Laevers, 2010). Gasplasma™ was identified as an appropriate technology for landfill waste to energy valorisation using RDF as feedstock (Tielemans and Laevers, 2010).

Quaghebeur et al. (2013) characterised the excavated waste for REMO landfill in Belgium, which maximum storage time was between 9–29 years. Chemical characteristics of the excavated plastic following years of storage are summarised in Table 5. The waste was manually sorted and not washed, for this reason plastic analyses were influenced by impurities such as soil particles (Quaghebeur et al., 2013). Plastic from IW presented a higher amount of metals than plastic from MSW (Table 5) (Quaghebeur et al., 2013). TOC of plastic from IW and MSW was similar, and plastic degradation was found to not have a significant effect on calorific value (Quaghebeur et al., 2013). The authors concluded that the thermochemical processing of recovered plastic to produce energy is a feasible alternative to recycling because they present a good level of calorific value (18–28 MJ/kg), and cannot produce high-quality recycled material due to high level of contamination (Quaghebeur et al., 2013).

Zhou et al. (2014) analysed excavated plastics from Yingchun MSW landfill in China, which had a maximum storage of 24 years (Tables 5 and 6). The amount of plastics was larger in the layers between 1997 and 2004 than that from the period from 1989 to 1996. The total plastic samples were divided in white 'PE bag' (11.3 wt%), 'coloured PE bag' (29.8 wt%), 'other plastic bag' (28.0 wt%) and 'other mixed plastics' (30.9 wt%) (Zhou et al., 2014). The presence of soil and sand impurities in plastics were high (71.0 ± 6.3 wt%), especially in the older plastics stored for longer periods (Zhou et al., 2014). The major pressure present in the deepest layers could be a reason for resistance of impurities, embedded in plastics, even after washing them (Zhou et al., 2014). The calorific value is not affected by the years of storage (Quaghebeur et al., 2013; Zhou et al., 2014).

According to Zhou et al. (2014) and Quaghebeur et al. (2013) alteration of ultimate analysis results, such as higher level of oxygen, silicon and aluminium content in excavated plastic waste compared to fresh plastic waste (this term refers to plastic waste that has not been in landfill), is probably related to the presence of impurities, such as soil and sand particles, which major constituents are SiO_2, Al_2O_3, oxynitride, etc.

The recycling potential of excavated plastic waste from the Nonthaburi dumpsite in Thailand has been analysed in two different studies (Prechthai et al., 2008; Chiemchaisri et al., 2010). In Prechthai et al. (2008) study the excavated MSW (Table 6) samples were stored 3–5 years and were divided in particle size ranges <25 mm, between 25–50 mm and >50 mm. 90 wt% of the plastics were recovered from the coarse fraction (>50 mm) and 10 wt% from the medium particles fraction (25–50 mm) (Prechthai et al., 2008). In Chiemchaisri et al. (2010) plastic waste was taken as well from Nonthaburi dumpsite in Thailand and the maximum storage time was 10 years (Table 6). They divided the excavated plastics into 'carry bags', 'other bags' and 'other plastic'. Excavated plastic was found in both studies to have the potential to be recycled as RDF after further processing (Prechthai et al., 2008).

Wolfsberger et al. (2015) chemically analysed the plastic fraction found in two different landfills in Austria. The maximum storage age was 20 and 30 for landfill site 1 (LF1) and landfill site 2 (LF2) respectively. The plastic fraction from LF2 showed a higher level of lead, cadmium, chromium, cobalt and mercury. The reason was attributed to the fact that the waste disposed in LF2 was pretreated in the MBT before disposal and was not related to a longer storage time.

Bhatnagar et al. (2017) assessed the value of waste material excavated from the municipal landfill of Kudjape in Estonia, between 2012 and 2013. The analysed waste was stored 4–8 years. The plastic waste fraction was comprised of different types of plastics and textile because it was not possible to distinguish the synthetic textile from the natural textile. The waste PE represented the

Table 5
Chemical characteristics of excavated plastic according to years of storage.

		Plastic (MSW) from REMO landfill[a]				Plastic (IW) from REMO landfill[a]		Plastic (MSW) Yingchun landfill[b]			
Years of storage	Unit	24–29	19–23	14–18	9–13	19–24	9–14	21–24	17–20	13–16	9–12
Volatiles	wt%							86.31 (3.23)	87.44 (0.52)	87.50 (0.48)	87.09 (1.09)
Ash	wt%	25 (2)	32	38	20	23	35 (2)	12.50 (0.93)	10.76 (0.48)	10.39 (0.26)	9.70 (0.75)
Total carbon	wt%	50 (2)	44	41	59	57	39 (7)				
TOC	wt%	57 (4)	51	53	67	58	37 (16)				
Fixed carbon	wt%							1.19 (2.36)	1.79 (0.76)	2.10 (0.40)	3.21 (1.84)
NCV	MJ/kg	24 (3)	21	18	27	26	21 (4)				
GCV	MJ/kg	25 (3)	23	19	28	28	22.1 (4)	41.29 (2.26)	42.79 (3.10)	43.91 (2.17)	44.75 (1.18)
H	wt%	6.7 (1)	7	6.0	8.1	6.9	5.4 (0.2)				
N	wt%	0.7	1	0.59	0.2	0.7	0.75 (0.5)				
S	wt%	0.2	0	0.27	0.2	0.47	0.42 (0.01)				
Cl	wt%	7.3 (3)	0	1.8	5.5	3.9	1.6 (1)				
F	wt%	0.01	0	0.006	0.0	0.056	0.061 (0.03)				
Br	wt%	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025				
Si	g/kg	68	110	100	41	72	74				
Ca	g/kg	13	20	15	7.8	26	17.5				
Fe	g/kg	18	26	13	10	23	38				
As	mg/kg	33	6.9	6.2	7.6	9.9	12				
Ba	mg/kg	430	540	600	110	2300	3600				
Cd	mg/kg	51	18	19	18	47	41				
Cr	mg/kg	490	320	280	270	780	530				
Cu	mg/kg	1767	150	690	270	10,000	2405				
Hg	mg/kg	0.6	0.36	0.46	0.1	2.0	1.1				
Ni	mg/kg	327	86	73	740	640	275				
Pb	mg/kg	550	280	230	160	1300	1900				
Zn	mg/kg	1063	620	1700	470	5500	3800				

NCV: Net calorific value.
GCV: Gross calorific value.
(SD): Standard deviation.
[a] Quaghebeur et al. (2013).
[b] Zhou et al. (2014).

Table 6
Chemical characteristics of excavated plastics.

	Unit	RDF processed from landfill waste [a]	White PE plastic bags[b]	Plastic from Nonthaburi dumpsite[c]	Carry bags Nonthaburi dumpsite[d]	Other bags Nonthaburi dumpsite[d]	Other plastic Nonthaburi dumpsite[d]
Moisture content	wt%	14.4			3.46 (2.24)	1.49 (1.12)	0.85 (0.38)
Volatiles	wt%	80.4			72.99 (10.56)	83.48 (5.96)	91.77 (6.44)
Ash	wt%	27.1			27.01 (10.56)	16.54 (6.23)	8.23 (7.84)
NCV	MJ/kg	22.0					
GCV	MJ/kg				40.99 (1.19)	39.33 (3.36)	33.38 (3.35)
C	wt%	54.9	87.95 (1.23)				
H	wt%	7.38					
O	wt%		7.95 (0.71)				
N	wt%	2.03	1.04 (1.05)				
S	wt%	0.36	0.29 (0.07)		0.21 (0.04)	0.05 (0.04)	0.04 (0.01)
Cl	wt%		0.208–0.312[x]		2.51 (0.70)	1.23 (0.84)	3.95 (2.75)
Si	wt%		0.59 (0.07)				
Al	wt%		0.44 (0.07)				
Mn	mg/kg			107.2			
Cr	mg/kg			43.4			
Cd	mg/kg			1.6			
Pb	mg/kg			42.5			
Ni	mg/kg			21.1			
Zn	mg/kg			313.3			
Cu	mg/kg			150.5			

NCV: Net calorific value.
GCV: Gross calorific value.
(SD): Standard deviation.
[a] Bosmans et al. (2013).
[b] Zhou et al. (2014).
[c] Prechthai et al. (2008).
[d] Chiemchaisri et al. (2010).
[x] Range.

highest profit between all the plastic waste. The authors stated that soft plastic (e.g. PE), which represented 20 wt% of the excavated materials, has potential for an income with a hypothetical market value of 35 €/t (Ventosa et al., 2014). Furthermore, SRF was considered as the most marketable materials after applying a pretreatment to reduce the moisture content.

4. Applicability and limitation of the current recycling technologies for energy recovery from excavated plastics

Fresh plastic waste is recovered in different ways, which can be summarised as reuse (primary), mechanical recycling (secondary), chemical or feedstock recycling (tertiary) and energy recovery (quaternary) (Al-Salem et al., 2009; Datta and Kopczyńska, 2016). Primary recycling involves the re-extrusion of semi-clean plastic scrap to produce similar material (Al-Salem et al., 2009). In the secondary or mechanical recycling, the plastic waste preferably characterised by single-polymer is processed by mechanical means to produce new products, for example the production of polyester fibers from PET bottles (Al-Salem et al., 2009). Tertiary recycling, or chemical and thermochemical recycling, involves the production of feedstock from plastic waste to be used as fuel or for synthesis of petrochemicals and plastics but for the moment there are no large-scale industrial applications (Al-Salem et al., 2009; Mastellone, 1999). Quaternary recycling, or energy recovery, involves the production of heat, steam and electricity from thermochemical processes, such as incineration (European Parliament. Council of the European Union, 2008; Korai et al., 2016).

Both fresh plastic waste and excavated plastic waste need to meet certain requirements concerning the presence of chemical elements to be applicable for recycling process (Johansson et al., 2017). REACH (European Parliament, 2009) established a series of restrictions on dangerous substances. For example, Cd limit in plastic products is 0.01 wt%, phthalates, used in plastics additives such as benzyl butyl phthalate, dibutyl phthalate, diisononyl phthalate and diisodecyl phthalate, must not exceed 0.1 wt% if plastic is going to be used in toys and childcare articles (European Parliament, 2009). As it is summarised in Table 5, excavated plastic waste may content Cd and other heavy metals in concentrations that exceed the 0.01 wt% limit. This high level of impurities makes the reuse of excavated plastics more challenging than the reuse of fresh plastic waste, and creates uncertainties on the profitability of the products which should conformed to industry standards (Bosmans et al., 2014; Breyer et al., 2017; Zhou et al., 2014).

4.1. Sorting

Sorting of plastics is an important step to enhance plastic recovery and recycling, and changes depending on the nature of feedstock, recycling method applied and product required. Common sorting techniques of plastic waste are summarised in Table 7.

Excavated waste can be separated into different sizes and streams using a series of processes such as screening, air separation, metal separation and wet separation (Vrancken et al., 2017). The different types of plastic waste can be further divided with sorting methods such as hydrophobicity method and optical technologies (Vrancken et al., 2017). The impurities present in the excavated plastic waste can modify their properties and thus interfere with the sorting process, especially with technique sensor based, such as NIR (near infrared). In addition, separation based on density differences will be difficult for excavated plastics as the presence of impurities can change their density (Zhou et al., 2014). Other techniques can be employed in the sorting excavated plastics, such as triboelectric separation, speed accelerator, X-ray fluorescent (XRF) spectroscopy but further research is needed to

Table 7
Sorting techniques for plastic waste.

Sorting type	Comment	Reference
Manual sorting by operators	Used for large size plastic	Wienaah (2007)
	Labour intensive	Ruj et al. (2015)
	Relative low cost, only if wages are low in the countries	
	Subjected to human error	
NIR (near-infrared)	Effective sorting	Masoumi et al. (2012)
X-ray fluorescence	Fast identification	Ruj et al. (2015)
	Difficult to detect dark plastic	Vrancken et al. (2017)
	Effective identification of PVC	Masoumi et al. (2012)
	Influenced by level of impurities and degradation	Ruj et al. (2015)
Air sorting	Separates plastic based on its weight	VERC (2001)
Electrostatic	Separates plastic based on electrostatic charge difference	Ruj et al. (2015)
	Able to separate polymers with similar density	
Sorting by melting	Based on differences of melting temperature	Ruj et al. (2015)
	Only two resin types can be separated at the same time	
Sink-float sorting	Based on density difference	Ruj et al. (2015)
	Slow	Zhou et al. (2014)
	Difficult to control	
	Presence of impurities can influence the separation	
	Low grade of separation	
	Separation of PET and PVC	
Hydrocyclones	Based on density difference	Ruj et al. (2015)
	Presence of impurities can influence the separation	
	Grade of purities depend on particle size (best <6 mm nominal size) and shape homogeneity	

assess their applicability on excavated plastic waste (Al-Salem et al., 2009).

4.2. Mechanical recycling

Mechanical recycling of plastic waste involves a series of processes including pretreatment: cutting/shredding, contaminant separation, sorting, milling, washing and drying, agglutination, extrusion and pelletization, and quenching (Al-Salem et al., 2009; Aznar et al., 2006; SubsTech, 2013). Prior to secondary recycling, the plastics need to be sorted and washed (Al-Salem et al., 2009).

As in the case of fresh plastic waste, mechanically-treated excavated plastic can be used as construction materials. For example, different types of plastics such as PET, PC, PVC and PE could be mixed with concrete, improving its ductility and reducing the risk of concrete cracking (Saikia and de Brito, 2012; Sharma and Bansal, 2016). Nevertheless, they need to meet the limit criteria for leaching and exposure (Johansson et al., 2017), and the typical pollutants present in plastic waste, such as lead, cadmium, chromium and BPA, represent a leaching risk (Saikia and de Brito, 2012). Mechanical recycling of excavated plastic waste faces three main problems which are the uncertainties of chemical and physical condition of excavated plastic waste, regulatory framework and marketability. In fact, the variations on factors such as age and the environmental condition during storage do not allow to assume that sufficient cleaning of the treated waste can be always obtained. Furthermore, there are not univocal regulations, but they change in different countries. Moreover, for the moment there are no incentives to buy excavated material due to uncertainties in material quality and high cost derivate also from the treatment process which is needed to eliminate the impurities from the products.

4.3. Energy recovery via incineration

Plastic has a high calorific value that makes it feasible to be used as an energy source through incineration (Al-Salem et al., 2009). Nevertheless, incineration of synthetic polymers such as PVC, PET, PS and PE, leads to the production of air pollutants such as CO_2, NO_x, SO_x, volatile organic compounds (VOCs), particulate-bound heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans (PCDFs) and dioxins (Al-Salem et al., 2009). Therefore, high-performance cleaning units are required in-situ or downstream of the furnace to clean the flue gases at the required levels. Various technologies are applied, such as ammonia addition to the combustion chamber, flue gas cooling, acid neutralisation, activated carbon addition and filtration (Al-Salem et al., 2009; Yassin et al., 2005).

Plastics excavated from landfill, along with other combustibles, will contain impurities (Zhou et al., 2014) and elevated levels of heavy metals (Rotheut and Quicker, 2017) (Tables 5 and 6) due to contact with soil-like fines and leachate exposure respectively. Therefore, the use of excavated landfill materials as RDF requires consideration of the increased emissions and utilisation of pretreatment. Although Rotheut and Quicker (2017) concluded that conventional flue gas systems can cope with the increased emissions, technical performance of the existing cleaning strategies needs to be properly addressed. Consideration on the management of air pollution control residues (APCr) is also needed. Thus, the extra cost for the already expensive management of these hazardous residues due to the use of RDF from landfill and the impact on the gate fees associated with such RDF must be assessed.

4.4. Chemical and thermochemical recycling

Tertiary recycling covers a series of chemical and thermochemical technologies which yield products that can be used as fuels or feedstock for synthesis of chemicals and new plastics (see Fig. 2). During chemical recycling, the polymer chains are broken with the aid of decomposition agents such as diols, alcohols, and amines, at a relatively low temperature around 200 °C (Zia et al., 2007). On the other hand, the thermochemical recycling uses higher temperatures (300–1000 °C) and reacting atmospheres such as H_2, H_2O or stoichiometric content of O_2 to produce monomers, fuels and industrial chemical precursors (Datta and Kopczyńska, 2016).

Zhou et al. (2014) concluded that incineration and RDF production was the most convenient treatment for excavated plastics based on input requirements, which in the case of pyrolysis were identified as particle size between 1–20 mm, moisture <0.5 wt%

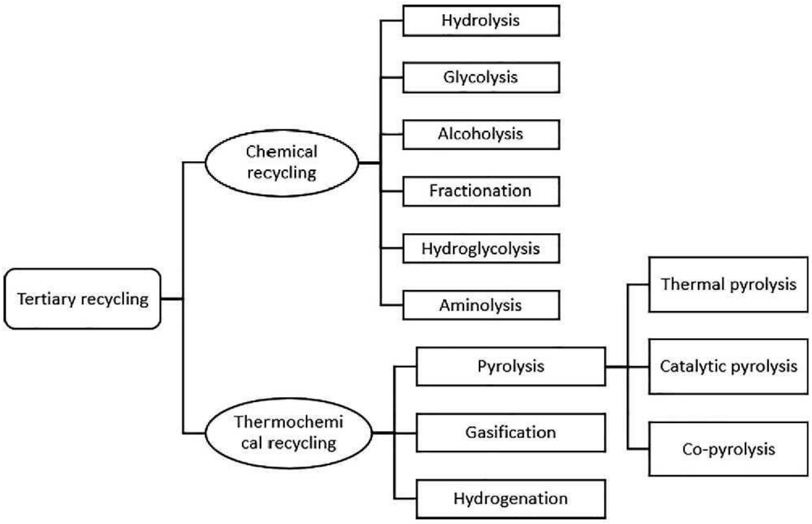


Fig. 2. Tertiary recycling techniques (adapted from Zia et al., 2007; Al-Salem et al., 2009).

and ash <2 wt%. However, pyrolysis produces syngas and usable solid residue, with less NO_x and SO_x emissions than incineration (Younan et al., 2016). In addition, the capital costs for pyrolysis gas treatment is less expensive than the incineration gas treatment because it has a smaller volume (Bosmans et al., 2013). Datta and Kopczyńska (2016) recognised pyrolysis as an adequate technology to recover high yield of monomers from fresh plastic waste especially PS, PMMA and PTFE, when comparing tertiary recycling processes such as pyrolysis, catalytic cracking, hydrogenation and gasification.

Bosmans et al. (2014) analysed the pyrolysis kinetics for excavated waste to identify the optimum parameters to maximise the product yield. They used a mixture of RDF obtained from excavated MSW and IW, with 29 and 24 years of maximum storage respectively. The results showed that the 'less stable plastics' (E = 99 kJ/mol) had lower activation energy than fresh waste, which may be related to changes of the excavated waste properties compared to fresh waste in composition, and the catalytic effect of impurities such as metals (Bosmans et al., 2014). Breyer et al. (2017) used excavated plastics from Mont-Saint-Guilbert landfill in Belgium in co-pyrolysis with lubrication oils. Most plastics were categorised as LDPE (85 wt%) while the rest (15 wt%) included PE, PP, PS and PET (Breyer et al., 2017). The plastics presented a variety of contaminants such as wood, textile, fines and metals. The degradation temperature increased with the mixture of plastics and oil, by maximum 20 °C, compared to the decomposition process of individual material (Breyer et al., 2017). The authors concluded that the co-pyrolysis of excavated plastic with oil was feasible even from an energy point of view; indeed, the combustion of the produced pyrolysis liquid yielded greater energy than that consumed during its production process (Breyer et al., 2017).

Santaweesuk and Janyalertadun (2017) studied the production of fuel oil by slow thermal pyrolysis of excavated plastic waste (PP, LDPE, HDPE and mixed plastics) from the Warinchamrap municipal landfill, Thailand. The parameters used were temperature between 350 and 450 °C, atmospheric pressure, and retention time 4–6 h. The gas was condensed at 25–30 °C. The yields of liquid fuel were 80 wt%, 73 wt%, 70 wt% and 46 wt% for PP, LDPE, HDPE and mixed plastics respectively. The pyrolysis liquid fuel was then distilled, and it was found to be a mixture of heavy naphtha (C_7-C_{10}), gasoline (C_8-C_{10}) and light gas oil (C_{10}-C_{20}). Higher operating temperature was found to increase the liquid and gas products. The authors concluded that quantity and quality of the produced pyrolysis liquid fuel is influenced by the plastics type.

The pyrolysis of plastic waste has been largely studied (Anuar Sharuddin et al., 2016) compared with the pyrolysis of excavated plastic waste, which can benefit from the findings of the former. The properties of pyrolysis oil from plastic waste and excavated waste are similar to petroleum diesel oil (Miandad et al., 2016; Santaweesuk and Janyalertadun, 2017). In most of the studies on pyrolysis of plastic waste the heating rate was between 10 and 25 °C/min (Anuar Sharuddin et al., 2016). Various sweep gases have been used in pyrolysis of plastics; nitrogen is the most common one due to its relatively low reactivity, but also helium, argon, ethylene, propylene and hydrogen (Anuar Sharuddin et al., 2016). Typical reactors used for pyrolysis of plastics are fluidized bed reactors, batch reactors and screw kiln reactors (Kumar et al., 2011). Each type of reactor allows a different heating rate which affects the final product distribution. Thus, fluidized bed reactors allow a rapid heating and more uniform heat distribution within the unit (Kunwar et al., 2016), and are preferred for enhancing the production of the liquid fraction via fast pyrolysis. However, fluidization reactors require higher maintenance and capital cost compared to fixed bed reactors (Chen et al., 2015). Table 8 summarises the pyrolysis types according to the heating rate, final temperature and residence time employed. As explained above, pyrolysis product distribution depends on the temperature used during processing. In the case of plastics, temperatures > 500 °C lead to more gas formation, while liquid yield is major at a lower

Table 8
Pyrolysis process categories (adapted from Bosmans et al., 2013).

Category	Characteristics	Main Product Fraction
Slow	Resident time 5–30 min Low heating rate (<1 °C/s) Maximum temperature 600 °C	Char Pyrolysis oil Gas
Fast	Resident time 0.5–5 s High heating rate (1–200 °C/s) Maximum temperature 650 °C	Pyrolysis oil
Flash	Resident time <1 s High heating rate (>1000 °C/s) Maximum temperature >650 °C	Pyrolysis oil Gas

temperature around 450 °C (Anuar Sharuddin et al., 2016; Miandad et al., 2017). Singh and Ruj (2016) stated that at higher heating rate the degradation is partially prevented due to shorter residence time of the volatile products at high temperature. Residence time is therefore particularly important, mainly when the process runs at temperatures <450 °C; at higher temperatures, its effect is less evident (Anuar Sharuddin et al., 2016). General problems related to the properties of plastic waste, such as the sticky behaviour of fused plastics, may compromise the reactor performance during pyrolysis (Lopez et al., 2017). Fast pyrolysis is normally the most appropriate operating mode to avoid this issue due to its high heat transfer rate (Lopez et al., 2017).

Pyrolysis of fresh plastic waste has been largely studied especially using thermogravimetric analyser (TGA) and laboratory scale reactors (Wong et al., 2016). Kunwar et al. (2016) studied the kinetics of pyrolysis of plastics using TGA. The activation energy was found to necessarily change according to the different number and type of bonds; for example, C—C has lower dissociation energy than C—H and C = C, i.e. 347, 414 and 611 kJ/mole respectively (Brydson, 1999; Kunwar et al., 2016). Sørum et al. (2001) used differential thermogravimetric (DTG) curves to identify the temperatures of the maximum degree of weight loss for PS, PP and LDPE, being 413, 456 and 472 °C respectively. Discrepancy of results obtained on the activation energy and degradation temperature values may be present in different studies due to the diverse methods of calculation and parameters used (Grammelis et al., 2009; Sørum et al., 2001).

Grammelis et al. (2009) examined the thermal stability of some thermoplastics, classifying them from the most stable, that decomposes at high temperature, to the less stable: PC (maximum rate 510 °C) > HDPE (maximum rate 495 °C) > LDPE (maximum rate 495 °C) > PP (maximum rate ~ 460 °C) > PA (maximum rate ~ 455 °C) > PS (maximum rate ~ 450 °C) > PVC (maximum rate 320 °C and 470 °C). Furthermore, they identified the order of activation energy, i.e. the energy required to start the pyrolysis, as follow: E_{HDPE} (445.2 kJ/mol) > E_{LDPE} (437.1 kJ/mol) > E_{PS} (414.9 kJ/mol) > E_{PP} (373.4 kJ/mol) > E_{PC} (340.7 kJ/mol) > E_{PA} (256.6 kJ/mol) (Grammelis et al., 2009).

Singh and Ruj (2016) studied the pyrolysis kinetics of fresh plastic waste through TGA analysis and found that individual fresh plastic waste type and a simulated mixture of them degrade between 350 and 520 °C while the mixed fresh plastic waste starts to degrade at lower temperature 300–550 °C. No explanation for the decrease of degradation temperature was provided by the authors.

Caballero et al. (2016) studied the pyrolysis of plastic waste from landline and mobile phones, which comprises mostly of acrylonitrile–butadiene–styrene copolymer (ABS) and polycarbonate (PC). Aromatics were present in very high percentage (>90% area of GC-MS spectra) in the liquid product, likely due to the catalytic effect of metals such as Fe, Co, Ni, Zn, etc. (Caballero et al., 2016). Most of the Cl and Br contained in the plastic waste was transferred to the pyrolysis gas as HCl and HBr, which are corrosive and need to be removed before further gas utilisation (Caballero et al., 2016). The authors concluded that valuable chemicals can be extracted from the pyrolysis liquid of plastic waste such as styrene, toluene, ethyl-benzene and α-methylstyrene (Caballero et al., 2016).

Catalytic pyrolysis is a possible modification to improve the quality of the product fractions in-situ and eliminate some pollutants. Some of the most common catalysts used in catalytic pyrolysis of plastic waste include NZ, ZSM-5, and HZSM-5 zeolites, fluid catalytic cracking (FCC) catalyst, Al_2O_3, and Red Mud (Miandad et al., 2016). Although catalytic pyrolysis can improve the product quality and reduce the required temperature, it has disadvantages such as high cost of catalysts and the limited possibility of catalysts reuse (Miandad et al., 2016).

Studies have shown that some plastics are better feedstocks for pyrolysis processes. Among the most common plastic waste, PS and PP have appropriate properties to be processed through pyrolysis, such as lower thermal degradation temperature compared to other plastics and good fuel properties (Miandad et al., 2016). On the other hand, PVC and PET are considered not suitable for pyrolysis. PVC yields a high level of chlorine into the pyrolysis products. PET gives rise to low liquid yields with a high level of benzoic acid in composition (Anuar Sharuddin et al., 2016; Miandad et al., 2016). PE tends to convert into wax instead of oil due to its long chain structures, although the utilisation of relatively higher temperature (>500 °C) or catalysis can favour the wax cracking (Anuar Sharuddin et al., 2016; Miandad et al., 2016). In general, plastics with high volatile matter and low ash content are preferred to produce pyrolysis liquid (Abnisa and Wan Daud, 2014). The ash content in the excavated plastics has been found generally higher than that in fresh plastic waste, which may decrease the liquid yield (Zhou et al., 2014). Therefore, their use as pyrolysis feedstock requires comprehensive assessment.

5. Discussion on current trends and future developments

While excavated plastic waste from landfills present a great opportunity of resource recovery, presence of impurities and contamination with trace heavy metals or corrosive compounds (see Tables 5 and 6) hampered their use in conventional energy recovery processes. Further to this the heterogeneity of the plastic components found in landfill sites means that different environments characterised by the structure of the landfill or dumpsite, the climate in the area and type of waste collected can influence the chemical and physical changes of the plastic waste in landfill. Mechanical recycling of excavated waste can be a valuable recycling route if the degree of degradation is low and the sorting step allows the separation of different plastic types. These aspects significantly affect the quality of the products therefore their marketability. Assessing a time limit to plastic storage in landfill can increase the feasibility of this route. It is also important to consider that the excavated plastic waste derives from plastics potentially produced decades ago and under less restrictive legislation on plastics production, which differs from the current requirements, such as the new restrictions introduced with REACH in 2009.

Incineration of excavated waste for energy recovery requires less pre-treatment and preparation than other process such as pyrolysis (Zhou et al., 2014). However, the emissions released, with a feedstock in the form of RDF, have been reported as being higher than the emissions from non-landfilled wastes. Whilst these elevated emissions are not expected to cause problems for current flue gas cleaning technologies, this requires further consideration due to the impacts on air pollution control residues. Important barriers for incineration of excavated plastic waste are the ash content, which has been found to be higher than 20% in different samples analysed, and the chlorine content, which should be less than 1.5% (Johansson et al., 2017). Effective sorting and separation of PVC can reduce the level of chlorine.

Upcycling of excavated plastic waste through pyrolysis has been highlighted as an alternative option to conventional recycling or combustion. This process requires a series of pre-treatments such as sorting, cleaning and drying. Understanding the heterogeneity of the excavated plastic waste and different changes in the chemical and physical characteristics of each type of excavated plastic due to the degree of degradation and variation in the levels of contamination is crucial to address their suitability as feedstock from thermochemical processing. The experiments on pyrolysis of excavated plastic have shown positive results but more studies are needed to identify the most suitable parameters in relation to the feedstock characteristics (Breyer et al., 2017; Santaweesuk and Janyalertadun, 2017).

Excavated plastic waste value can increase with an effective separation of different plastics resins with low contamination level. Although there are some technical barriers associated with the technologies used for the waste separation that need to be overcome to guarantee efficient sorting, pyrolysis of excavated plastic waste offers a promising alternative that contributes to (i) the reduction of fossil fuels for energy production, (ii) increased production of liquid fuels and (iii) support the economic feasibility of ELFM.

. Furthermore, there is a lack of specific legislation regarding the recycling of excavated plastic waste. However, the introduction of the ELFM concept into the EU Landfill Directive is the first step for regulating and promoting the use of secondary raw materials from landfill.

6. Summary and conclusions

Landfills potentially contain large quantities of resources, including plastics, which have the potential to be recycled and reintroduced into a circular economy. Pyrolysis of fresh plastic waste has been studied previously for the potential to convert the plastic waste into valuable building blocks which can be further used as fuels and chemical precursors. This paper has highlighted different aspects related to the use of excavated plastic waste and the possible process encountered during the storage in landfills which can be summarised as follow:

- Plastics represent 5–25 wt% of the total waste in landfills. In 2014, 30 wt% of the total plastic waste produced in Europe was disposed of in landfills;
- 80 wt% of the generated plastics is represented by thermoplastics which include a series of resins that have different chemical and physical characteristics. These differences lead to diverse degradation processes in the landfill;
- Plastic waste degradation in landfills may be caused by biological activity (e.g. microorganisms) and chemical decomposition via compounds such as H_2S (in gas and solubilised forms) and organic acids found in leachate;
- Excavated plastic waste generally presents higher level of ash, impurities and heavy metals than fresh plastic waste. For this reason, pyrolysis is a more viable alternative than conventional recycling and combustion;
- Separation of single-polymer plastics can improve the value of products from recycling of excavated plastic waste;
- Contamination level and degradation of excavated plastics need to be further studied to evaluate the production of valuable products through pyrolysis.

This review summarises key gaps in the scientific understanding of plastic degradation pathways in landfill environments. This impacts the viability of recycling plastics recovered from landfills using conventional methods, therefore further studies are required to enhance scientific evidence of the feasibility of managing excavated plastics through pyrolysis processes.

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Degradation of excavated polyethylene and polypropylene waste from landfill

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HIGHLIGHTS

- CI excavated PP samples >10 years was almost 2 times higher than newer PP.
- CH_2 and CH_3 of samples >10 years were statistically lower than the newer samples.
- Crystallinity of PP and PE >10 years was 1.3 times higher than fresh materials.
- Production of chemical base compounds through excavated plastics pyrolysis
- Chemical base compounds potential revenue is $402–805 million.

GRAPHICAL ABSTRACT

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ABSTRACT

In 2016, it was estimated that 7.4 million tonnes of plastic waste have been disposed in landfill in Europe. This waste represents an important opportunity for resource recovery through enhanced landfill mining consistent with recent Circular Economy initiatives. However, a recent review found a lack of data describing the degradation of excavated plastic waste and the potential impact on recycling products such as pyrolysis oil. In this study, the physicochemical characteristics of the main plastic types found in landfills and their implications for recovery and recycling were investigated using a combination of scanning electron microscopy energy dispersive spectroscopy (SEM-EDS), attenuated total reflectance Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). Loss of gloss was visually detected for the buried plastic waste samples (polyethylene (PE) and polypropylene (PP)) compared to fresh plastic samples. The SEM-EDS analysis further showed that oxygen was the main element related to the plastic surface alteration. The carbonyl index (CI) of plastic samples buried for >10 years was between 1.5 and 2 times higher than <10 years and fresh materials. Similarly, the degree crystallinity of the old samples (>10 years) was 2 times higher than the fresh and < 10 years samples. Based on these findings, tertiary recycling, such as pyrolysis, seems to be a convenient route for upcycling of recovered plastics from municipal solid waste landfills.

1. Introduction

In 2017 the MSW generated in Europe (EU-28) was 487 kg per capita (Eurostat, 2018). 23% of this waste has been disposed in landfill for a total of 58 million tonnes (Eurostat, 2018). The growing awareness

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about conscious waste management led to an absolute reduction of about 60% (63% per capita) from 1995 to 2017 of landfill waste in Europe (Eurostat, 2018). Europe is moving towards the concept of Circular Economy which promotes to "closing the loop" of product lifecycles (European Commission, 2018a). The EU targets include the recycling of 65% of municipal waste and 75% of packaging waste by 2030 (European Commission, 2018a). Plastic waste represents a large part of MSW. In 2016, plastic waste amounted to 27.1 million tonnes in Europe (EU-28) and 27.3% was landfilled for a total of 7.4 million tonnes (Eurostat, 2018; Plastics Europe, 2017). For this reason, the European Commission has included a strategy for plastics in the Circular Economy, which aims to reduce single use of plastic products and increases its reuse and recycling (European Commission, 2018b). In conjunction with the reduction of new waste, there is still a need to manage waste legacy contained in landfill. It has been estimated there are between 125,000 and 500,000 landfills in Europe (EURELCO, 2017), which contain potential secondary raw materials that can become part of the Circular Economy (Wagland et al., 2019). Although some concerns exist about the recovery of waste in landfill, in some cases landfill mining is an urgent necessity. Coastal landfills can be sources of marine and terrestrial plastic pollution affecting the ecosystems (Malizia and Monmany-Garzia, 2019). According to Brand et al. (2018) in only 6 years a great amount of waste from 79 UK coastal landfills will potentially increase sea pollution due to erosion. In order to avoid further environmental damage, it is important to investigate the most appropriate way to recover this waste. Besides the circular economy paradigm, the vision of dynamic landfill management (DLM) has been introduced during the Second enhanced landfill mining (ELFM) Seminar in the European Parliament in 2018. It involves a multidisciplinary approach for landfill management, pollution control, recovery of materials, energy and land in respect of European Policy and legislation (Jones et al., 2018). The ELFM concept focuses on maximising the valorisation of waste as material (WtM) and energy (WtE). The viability of ELFM is strictly related to the quality and quantity of buried waste material in the landfill (Bosmans et al., 2013). Plastic waste in landfill represents one of the major waste fractions that can potentially be recycled. However, due to contamination, such as trace heavy metals or corrosive compounds, and structural changes derived from the landfilling process, it might not meet the requirements for conventional recycling (Canopoli et al., 2018a). Polyethylene (PE) and polypropylene (PP) are the most demanded thermoplastics in Europe (Plastics Europe, 2018) and the most common types in the MSW.

Photodegradation and thermo-oxidative degradation are the most common causes of degradation for PE and PP in an aerobic and anaerobic environment (Webb et al., 2013; Andrady, 2011; Gijsman et al., 1999). In the case of photodegradation, the chromophores present in the plastic polymer absorb the sunlight initiating the process of autooxidation whit the formation of polymer fragments (Andrady, 2011). In thermo-oxidative degradation, the auto-oxidation process can be thermally initiated in a combination of mechanical stress (Gijsman, 2008).

Photo and thermal oxidation of PE and PP can be described in three steps, initiation, propagation and termination. The initiation step involves the formation of free radicals in the polymer chain caused by chromophoric or thermolabile group (Gardette et al., 2013). During propagation, the free radicals react with oxygen forming hydroperoxides which further decompose in alkoxy and hydroxyl radical. Then, the following reactions between alkoxy and hydroxyl radical, lead to the formation of different products through β scission, abstraction of hydrogen, or cage reaction (Gardette et al., 2013). The Norrish reactions I and II are only present during photodegradation (Gardette et al., 2013). The reaction terminates when the radicals recombine in a stable form.

Some of the degradation effects are visible such as discolouration and brittleness while other chemical changes, such as bond scission and the formation of new functional groups can be detected only with specific analyses. Indeed, in order to identify the best approach for the recycling of excavated plastics, it is important to evaluate the condition of these plastics, such as the degradation level. Although several studies have investigated the degradation of plastics in soil and water under different experimental conditions, to the best of the knowledge of the authors none of them has specifically investigated plastic degradation under genuine conditions in landfill (Canopoli et al., 2018a.). The landfill environment is characterised by different stages and the waste is subject to mechanical stress, presence of leachate, decomposition of organic material, chemical reaction mostly in anaerobic condition (Kjeldsen et al., 2010). For these peculiarities, degradation of excavated plastics can easily be affected and need further investigation. Gaining such information is key to assess recycling and upcycling options of recovered plastics. Current recycling methods for fresh waste are reuse (primary), mechanical recycling (secondary), chemical and thermochemical recycling (tertiary) and energy recovery via incineration (quaternary) (Al-Salem et al., 2009). Recent studies on excavated plastics have identified tertiary and quaternary recycling as possible routes for this type of feedstock (Zhou et al., 2014; Breyer et al., 2017; Santaweesuk and Janyalertadun, 2017) but the information is still scarce. In the present study, the physicochemical characterisation of excavated PE and PP, from various waste layer depths and ages, from four landfill sites was carried out to shed light on the extent of degradation of buried plastic samples and its potential implications for recycling opportunities.

2. Materials and methods

2.1. Plastic samples collection and preparation

A total of 30 waste samples from 4 MSW landfills located in the UK were collected at depths between 5 and 55 m following the method used in previous studies (Frank et al., 2017; García et al., 2016; Gutiérrez-Gutiérrez et al., 2015). The cores were drilled at different depths and years of waste storage were given by the landfill site operators (Table 1, details in supplementary data Table S1). The samples were grouped according to the age of the buried MSW as follows: <10 years (7 waste samples) and >10 years (23 waste samples). The plastic fraction was extracted by manual sorting of the waste samples. The sample used in the SEM were washed and left to dry at ambient temperature. The rest of the samples have been dried at 60 °C for 2 h. Before the DSC analysis, the samples were ground in small particles ≤1 mm.

Table 1
Landfill samples information. Details are available in the supplementary data.

	Samples n.	Years	Depth	Waste sample	Plastic (wet)		Plastic (dry)	Impurities (wet)	
			(m)	(g)	(g)	(wt %)	(g)	(g)	(wt %)
<10	**7**	**<10**	**5–18**	**12,335**	**1407**	**11**	**302**	**1105**	**79**
Average				1762	201	13	43	158	78
SD				2953	332	7	70	263	5
Min				390	31	5	9	22	70
Max				8448	951	24	200	751	85
>10	**23**	**>10**	**3–55**	**141,603**	**9276**	**7**	**5084**	**4192**	**45**
Average				6157	403	7	221	182	45
SD				2596	351	6	184	230	18
Min				1891	21	0	12	9	11
Max				11,586	1510	26	602	1143	76
TOT	**30**			**153,938**	**10,683**	**7**	**5386**	**5297**	**50**
Average				5131	356	9	180	177	52
SD				3239	352	7	181	233	21
Min				390	21	0.3	9	9	11
Max				11,586	1510	26	602	1143	85

2.2. Surface morphology and chemical characterisation of the excavated plastic fraction

Environmental Scanning Electron Microscopy was used to characterise the surface morphology of the PE and PP fragments at a magnification of x500. Concomitantly the chemical elements present at the surface of a representative plastic sample for each plastic type was determined using Energy Dispersive spectroscopy to evaluate the extent of degradation and contamination levels of the plastic fragments. The surfaces of the excavated samples were compared with the surface of fresh PE and PP waste. The excavated PE and PP analysed were the largest pieces, and for this reason the most representative, from each group (<10 years and >10 years).

2.3. Composition of the excavated plastic fraction

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used for the identification of different plastic polymers and calculation of the carbonyl index (Barbeş et al., 2014). The carbonyl index is often used to evaluate the oxidation level of polymers. It is defined as the ratio of the band area attributed to the carbonyl group -C=O and the band area attributed to methylene group -CH$_2$ (ter Halle et al., 2017; Barbeş et al., 2014). The carbonyl band was integrated between 1779 and 1680 cm^{-1} and the methylene between 1490 and 1420 cm^{-1}for PE, 2700–2750 cm^{-1} for PP (ter Halle et al., 2017; Moldovan et al., 2012; Longxiang et al., 2005). According to Rouillon et al. (2016) study, the oxidation of PP leads to the formation of volatile products that carry CH$_3$ moieties such as acetic acid and acetone. Therefore, it is expected that CH$_3$ decreases during oxidation. Carbonyl index, CH$_3$ for PP and CH$_2$ for PE, taken between 1490 and 1420 cm^{-1} have been analysed.

FTIR was applied on the fresh and excavated plastic waste samples using a Bruker vertex 70 instrument equipped with an attenuated total reflection (ATR) device Bruker Platinum ATR. Background and sample spectra were acquired using 16 scans at a spectral resolution of 4 cm^{-1} in the wavenumber range of 4000 to 400 cm^{-1} (ter Halle et al., 2017). A minimum of 3 replicates of infrared spectra were recorded for fresh PE and PP and excavated PE and PP samples.

2.4. Differential scanning calorimetry analysis

To understand the amorphous and crystalline behaviour of the excavated plastic residues, differential scanning calorimetry (DSC) analysis was conducted on 3 replicates of each sample (weight between 4 and 10 mg) using a DSC Q-200 (TA Instruments, UK). The temperature ranges were from 20 to 150 °C for PE, and from 20 to 180 °C for PP. A heating rate of 10 °C/min was used in a nitrogen atmosphere for first and second cooling and heating cycles. The degree of crystallisation of the samples was calculated from the first heating experiment, which gives information on thermal history, using **formula (1)**:

$$\%Crystallinity = \frac{\Delta H_m}{\Delta H_m^{ref}} \times 100 \tag{1}$$

where ΔH_m is the melting enthalpy of the sample and ΔH_m^{ref} is the melting enthalpy of 100% crystalline polymer. The ΔH_m^{ref} was taken as 293 J/g for PE and 207 J/g for PP (Blaine).

The peaks were measured using sigmoidal baseline (ISO 11357-1, 2016).

2.5. Statistics

t-Test is normally applied to compare the means of two groups and check if there is a statistically significant difference between them. Two-tailed t-test has been applied to analyse the results from FTIR, such as carbonyl index, CH$_2$ and CH$_3$, and DSC, crystallinity and melting. The significant difference was considered $p < 0.05$. It was used to evaluate the difference between excavated (>10 years and <10 years) and fresh samples for each plastic type, PE and PP.

3. Results and discussion

3.1. Percentage of excavated plastics from landfill

The average percentage of excavated plastics with >10 years of disposal is 8 wt%, ranging from 0.3 wt% to 26 wt%. The average percentage of excavated plastics with a disposal period of <10 years is 12 wt% ranging from 5 wt% to 24 wt%. This result is in accordance with other studies where the mean values of plastic percentage were between 10 and 26 wt% (García et al., 2016; Sel et al., 2016; Quaghebeur et al., 2013; Jones et al., 2013; Van Passel et al., 2013).

The excavated plastics were divided into different plastic types with FTIR spectroscopy. Thermoplastic such as PE and PP are the most demanded polymer types; about 36 wt% of the total plastic demand in Europe which amounts to 50 million tons (Plastics Europe, 2018; Plastics Europe, 2017). According to this, the PE and PP represent also the major fractions found after sorting in both groups (Table 2). The percentages of PE and PP in the MSW samples with <10 years were 50 wt% and 13 wt%, respectively. The PE and PP percentages in the MSW samples with >10 years were 48 wt% and 19 wt%, respectively. Rubber properties are different from conventional plastic and need a specific recycling route. For this reason, rubber is not considered in the main plastic types of this study.

3.2. Surface degradation of the excavated plastics

Comparison of fresh and excavated PE and PP surfaces showed a general major surface alteration in the excavated samples (Fig. 1). The first visual sign of surface degradation that can be detected is the loss of gloss which is characteristic of fresh PE and PP (Rouillon et al., 2016; Gijsman, 2008). Table 3 summarises the main characteristics of the analysed surfaces and elements detected from the EDS. Oxygen was in the main elements in all samples except for fresh PP. Presence of oxygen in PE and PP is a sign of degradation. This can be seen also in the surfaces imagines. In fact, fresh PP has visible smooth surface compared to the other samples (Fig. 1), showing a lower degree of degradation. Cracks are present in PE <10 years (Fig. 1B) and PP >10 years (Fig. 1F) which are signs of ageing (Elanmugilan et al., 2013). General roughness increase can be detected in the surfaces of excavated PE and PP compared to the fresh samples (Fig. 1). The SEM images do not show a clear difference in surface degradation between <10 years and >10 years samples.

Table 2
Percentages of different plastic types. Details are available in the supplementary data.

	Sample n.	PE	PP	PVC	PS	PET	PE/PP Blend	PA	Rubber	Rest
		(wt%)								
<10	**7**	**55**	**12**	**2**	**2**	**1**	**1**	**0**	**0**	**26**
Average		50	13	4	5	4	7	1		31
SD		14	10	1	2	3	7			11
Min		32	2	3	3	1	0	1		18
Max		70	32	5	6	6	15	1		43
>10	**23**	**45**	**19**	**11**	**4**	**3**	**0**	**0**	**14**	**4**
Average		48	19	16	5	20	6	1	34	8
SD		27	21	17	4	26	7		40	11
Min		2	1	0	1	2	1	1	0	0
Max		92	85	50	16	39	11	1	97	41
TOT	**30**	**45**	**19**	**10**	**3**	**3**	**0**	**0**	**13**	**6**
Average		48	17	14	5	11	6	1	34	14
SD		24	18	16	4	16	6	0	40	15
Min		2	1	0	1	1	0	1	0	0
Max		92	85	50	16	39	15	1	97	43

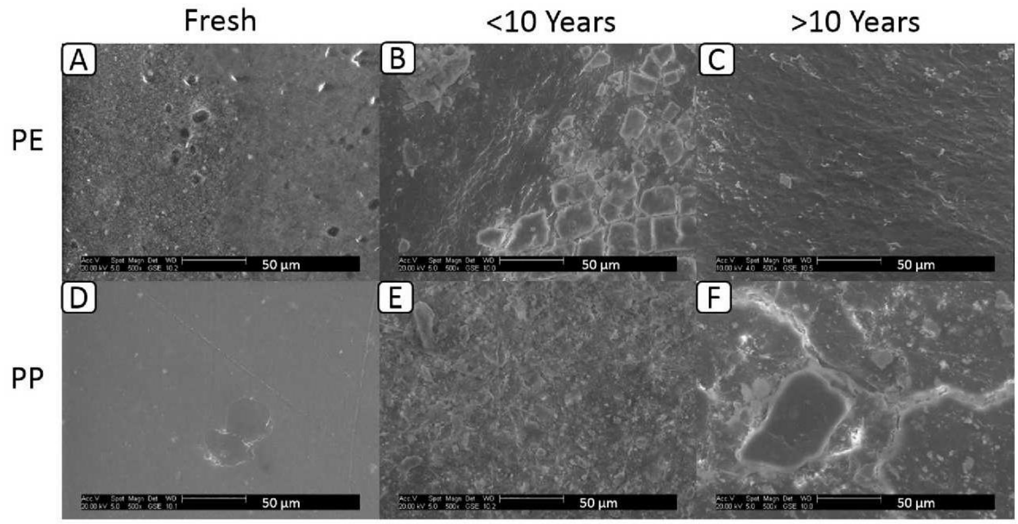

Fig. 1. Scanning electron microscope (SEM) images of fresh plastic waste (A and D) and excavated plastic (B, C, E, F) under 500× magnification. Fresh PE coloured packaging; B: Excavated PE <10 years; C: Excavated PE >10 years; D: fresh PP; E: Excavated PE <10 years; F: Excavated PE >10 years. Adapted from Canopoli et al., 2018b.

The elements identified in the majority of the samples are calcium (Ca), Titanium (Ti), Silicon (Si), Magnesium (Mg) and Aluminium (Al) (Table 3). Ca can be linked to the commonly used filler calcium carbonate ($CaCO_3$) (Tolinski, 2015; Brydson, 1999). Ti and Al are used in Ziegler-Natta catalysts for PP and PE production (Shamiri et al., 2014). Si and Al present in the excavated samples can be related to the SiO_2 and Al_2O_3 contained in the soil. The identified elements can also be associated to the use of additives in plastics, such as quartz (SiO_2), wollastonite ($CaSiO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$), fire retardant $Mg(OH)_2$, magnetite (Fe_3O_4), titanium carbide (TiC), and pigment (TiO_2) (Turku et al., 2017; Brydson, 1999).

3.3. Carbonyl index of the excavated plastic materials

The carbonyl index (CI) is presented as the average value of different infrared spectra for each sample. The CI average of fresh PE is 0.53, higher than the excavated PE which seems to decrease over time, 0.46 and 0.41 for PE <10 years and PE >10 years respectively (Fig. 2). However, the CI results of PE do not present a statistically significant difference. The slight decrease of carbonyl index in the PE samples with >10 years disposal could indicate an advanced degradation. Indeed, after initial degradation the samples may proceed the degradation with chain scission, crosslinking and CO release (Moldovan et al., 2012). In this case, the carbonyl group is depleted and the CI decreases consequently. The difference between fresh and excavated PE can be related to the presence of TiO_2 additive. Indeed, Ti is found as a major element only in fresh PE (Table 3).

Conversely, PP presents an opposite trend which suggests that the CI average increases with storage years 0.76, 1.34 and 1.78 for fresh PP, PP <10 years and PP >10 years respectively. CI results of PP, fresh and excavated, are statistically different (Fig. 2).

The CH_2 absorbance of excavated PE >10 years is significantly lower compared with fresh and <10 years PE (Fig. 3).

PP showed similar results (Fig. 3). In fact, the difference between excavated PP >10 years and the other two samples, fresh and <10 years, is statistically significant. CH_3 band of PP samples >10 years storage is lower than newer samples and this can be related to the loss of volatile products as suggested by Rouillon et al. (2016).

Hydroxyl group (-OH 3650–3200 cm^{-1}) is another degradation product together with carbonyl group (Moldovan et al., 2012). The degradation products showed in this band are alcohols and hydroperoxides (Gardette et al., 2013). Presence of a board peak can be distinguished in the excavated samples compared to the fresh samples in both PE and PP (Fig. 4).

3.4. Differential scanning calorimetry (DSC)

The crystallinity in PE increases during ageing (Fig. 5). Higher crystallinity for the older samples can be related to the different degradation rate of the crystalline and amorphous phase of plastic (Andrady, 2017). In fact, the amorphous fraction is the first part that is affected by mechanical stress, biodegradation and weathering (Andrady, 2017; Yang et al., 2014; Shah et al., 2008). The crystallinity average is 39%, 45% and 51% for fresh PE, PE <10 years and PE >10 years, respectively. However, only fresh PE and PE >10 years present a significant difference. Fig. 5 presents the thermograms of fresh and excavated PE. The presence of a double peak, such as in the excavated PE, characterises plastic samples with different lengths of molecular chains and degraded

Table 3
Surface characteristics and chemical elements detected by SEM-EDS (minimum concentration detected 0.08 wt%) of fresh and excavated PE and PP. Adapted from Canopoli et al., 2018b.

Sample	Figure	Surface texture	Main elements	Minor elements (<5 wt%)	Trace elements (<0.5 wt%)
PE	1A	P	C, O, Ti	Al, Cl, Ba	Si, P, S, Cu
PE < 10 years	1B	F, AP, Gr	C, O	Mg, Si, Ca	Al, P, S, Cl, Ti, Fe, Cu, Mo
PE > 10 years	1C	Fl, AP	C, O, Ca	Al, Si, Cl, K, Ti, Fe	Na, Mg, P, S, Cu, Zn
PP	1D	S	C,	Ca, Ti, Fe	Mg, Al, Si, Cl
PP < 10 years	1E	Fl, AP, Gr	C, O, Si, Ba	Al, S, K, Ca, Fe, Zn	Mg, P
PP > 10 years	1F	F, AP, Gr	C, O	Si, Ca, Ti, Fe	Mg, Al, S, Cl, K, Zn

F = fractures; AP = adhering parts; P = pits; Fl = flakes; Gr = granulates; S = smooth.

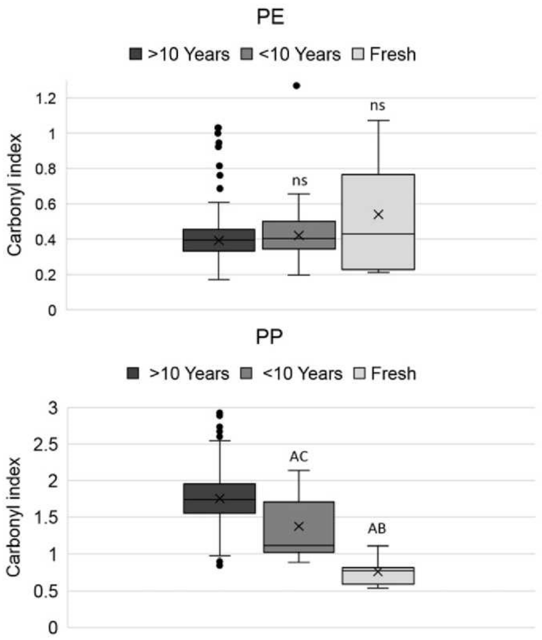

Fig. 2. Carbonyl indices of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples (ns: not significant). Outliers are plotted individually (points).

samples (Stangenberg et al., 2004). In fact, fresh plastic polymer presents a single peak (Fig. 6). The melting point average of fresh PE, PE <10 years and PE >10 years was 116.6 °C, 130.5 °C and 127.5 °C respectively. These results are not statically different from each other.

The crystallinity percentage average of fresh PP, PP <10 years and > 10 years is 38%, 35% and 41%, respectively (Fig. 5). There is not a clear trend and only PP >10 years and PP <10 years present a statistically significant difference. The melting average is 163.5 °C, 155.4 °C and 164.5 °C for fresh PP, PP <10 years and PP >10 years respectively. These results are not statistically different.

3.5. Recycling implication

These results need to be considered for the evaluation of the introduction of excavated plastics into the circular economy. Not all recycling routes of fresh plastic waste are feasible for excavated plastics. Due to the physico-chemical characteristics of excavated plastics, thermo-chemical recycling might be the best option compared to mechanical recycling and energy recovery via incineration. Mechanical recycling requires higher quality sorting for the identification of polymer types and feedstock material with appropriated physico-chemical properties (Butler et al., 2011). Plastic degradation comprises of contaminants such as oxygenated groups and organic matter which can affect the product quality (Ragaert et al., 2017). Indeed, changes in crystallinity and CI affect the mechanical properties of plastic. Increasing the degree of crystallinity and CI, the plastic material becomes more brittle and more susceptible to future thermo and photo-degradation (Wypych, 2013; Fotopoulou and Karapanagioti, 2019). Mechanical recycling of plastics is known to decrease the mechanical properties of plastics after a certain number of extrusion cycles (Oblak et al., 2016). Energy recovery via incineration cannot be considered practicable in the circular economy view. In contrast, pyrolysis can process contaminated plastics and heterogeneous feedstock, and represents a valuable opportunity for the excavated plastics recycling (Fox and Stacey, 2019; Ragaert et al., 2017; Butler et al., 2011). However, the use of plastic polymers such as PVC and PET should be avoided during pyrolysis (Lopez et al., 2017). The presence of carbonyl groups in the feedstock could lead to the production of oxygenated compounds in the pyrolysis oil. Oxygenated compounds are undesirable products that cause corrosion problems and negatively affect the pyrolysis oil quality decreasing the calorific value and stability (Czajczyńska et al., 2017; Lu et al., 2009). These compounds such as hydroxyl groups are present in the pyrolysis of plastic and can be attributed to the additives (Hakeem et al., 2018). To the author's knowledge, the effect of degradation of excavated plastics on pyrolysis products has not been verified. On the other side, limited information is available about the contamination effect from elements such as Al and Fe. Presence of Al_2O_3 and Fe_2O_3 can catalyse the decomposition of plastics during pyrolysis (Bosman et al., 2014; Liu and Meuzelaar, 1996). Chemical compounds such as ethene, propene and benzene, could be recovered through the pyrolysis of excavated plastic waste and reintroduced in the circular economy. A recent study (Fox and Stacey, 2019) has investigated the potential profit of fresh plastic waste pyrolysis and selling of alkene products. The potential value of fresh plastic waste is evaluated between $80–$160 per tonne (Fox and Stacey, 2019). Table 4 shows the potential revenue of excavated plastics disposed in landfill in 2016. The plastic types amounts have been calculated from the percentages found in this study. The plastic types considered for the pyrolysis are PE, PP, PS, PE/PP blend. The potential revenue is between $402 million and $805 million. Further studies are needed to investigate the production of chemical compounds from the excavated plastics pyrolysis and their marketability.

4. Conclusion

PE and PP are the most common polymer type found in excavated waste from landfill. Fresh PP presents a smooth surface compared to the other samples and no oxygen has been detected from the EDS. The

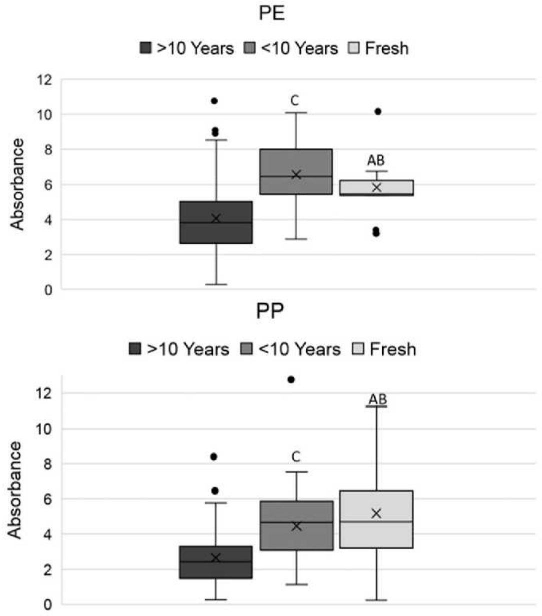

Fig. 3. Absorbance of CH_2 and CH_3 vibration of ~1456 cm^{-1} of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples Outliers are plotted individually (points).

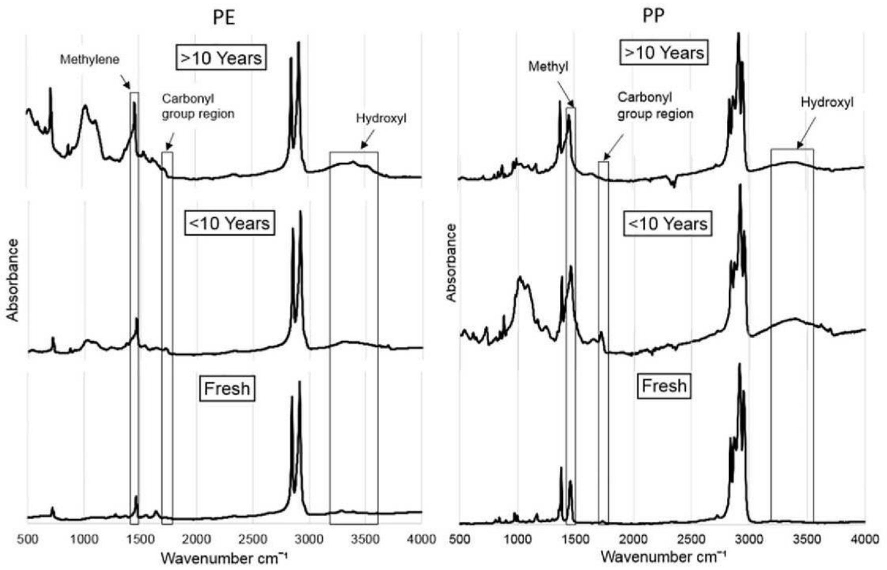

Fig. 4. FTIR spectra of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years).

CI excavated PP samples >10 years was almost 2 times higher than <10 years and fresh PP, respectively, confirming the increase of degradation over time. CH_2 and CH_3 of excavated PP and PE >10 years were statistically lower (almost twice) than the newer samples. The degree of crystallinity of PP and PE samples >10 years was also 1.3 times higher than fresh materials. Overall, the PE and PP which have been buried for >10 years had a greater extent of degradation than samples with

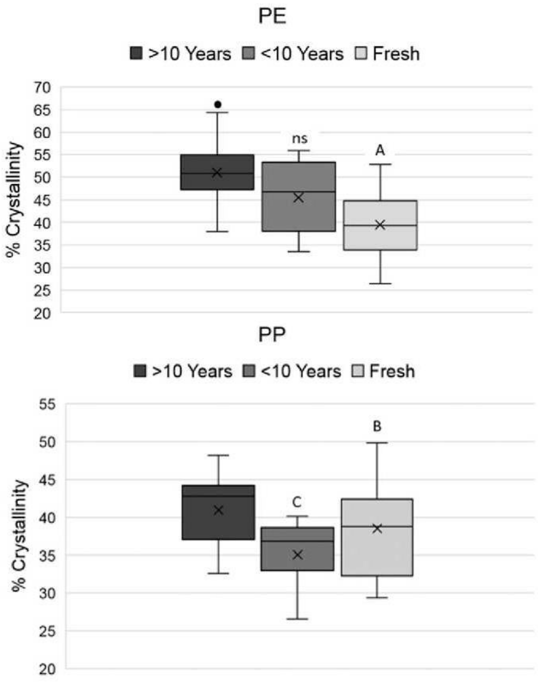

Fig. 5. Crystallinity percentage of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years). Letters (ABC) represent the statistically significant differences ($p < 0.05$) between samples (ns: not significant). Outliers are plotted individually (points).

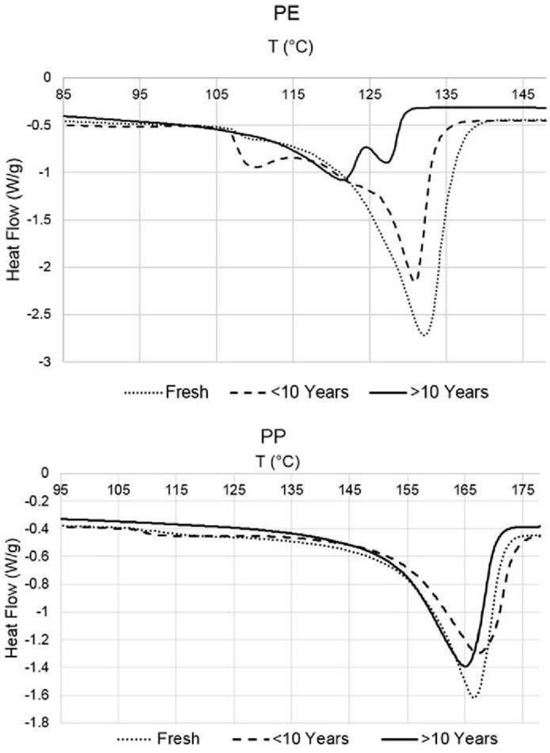

Fig. 6. DSC thermograms of fresh and excavated polyethylene and polypropylene with different storage time (>10 years and <10 years).

Table 4
Potential revenue from plastic waste disposed in landfill in 2016. Price per tonne from Fox and Stacey, 2019.

Landfilled plastic 2016	Weight (%)	Tonnes	Price per ton $80	Price per ton $160
PE	45	3,330,000	266,400,000	532,800,000
PP	19	1,406,000	112,480,000	224,960,000
PS	3	2,22,000	17,760,000	35,520,000
PE/PP blend	1	74,000	5,920,000	11,840,000
PVC	10	740,000	–	–
PET	3	222,000	–	–
Rubber	13	962,000	–	–
Rest	6	444,000	–	–
Tot		7,400,000	402,560,000	805,120,000

fewer years of storage, which suggests that chemical and thermochemical recycling such as pyrolysis with the production of chemical base compounds would be the preferred route for excavated plastics. It would also contribute to the circular economy and the development of ELFM projects. Future studies should evaluate if the increase of Cl in the feedstock lowers the pyrolysis oil quality due to the presence of a major quantity of oxygenated compounds. The presence of oxygenated compounds is known to lower the heating value which is an important parameter for transportation fuels (Lopez et al., 2017). In addition, the catalyst effect of elements such as Al and Fe should be further investigated. Indeed, these elements found in the excavated plastic samples, are known to act as catalysts during the pyrolysis of plastic waste (Bosmans et al., 2014; Liu and Meuzelaar, 1996).

CRediT authorship contribution statement

Luisa Canopoli: Conceptualization, Investigation, Writing - original draft.**Frederic Coulon:** Supervision, Conceptualization, Writing - review & editing.**Stuart T. Wagland:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.134125.

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Supplementary data

Degradation of excavated polyethylene and polypropylene waste from landfill

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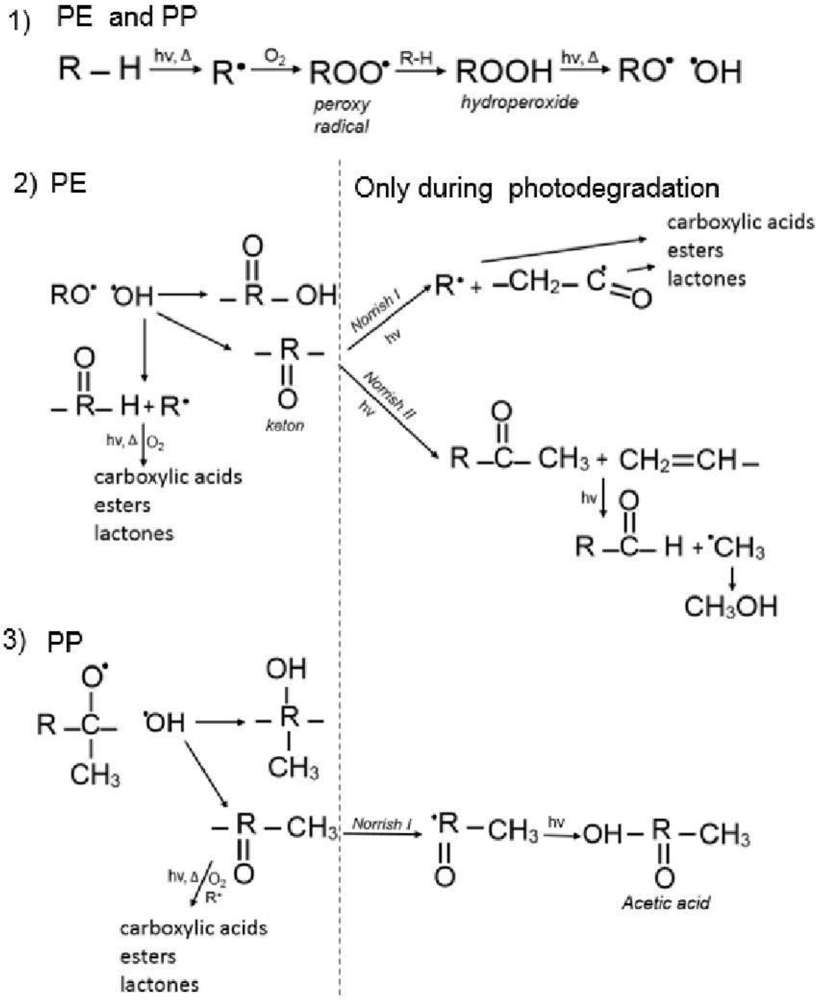

Fig. S1. Simplified photo and thermo oxidation of PP and PE based on Rouillon et al. (2016), Gardette et al. (2013), Fernando et al. (2007) and Delprat et al. (1995).

Landfill samples detailed data

Table S1. Landfill samples information.

Sample n.	**Years**	**Depth**	**Waste sample**	**Plastic (wet)**		**Plastic (dry)**	**Impurities (wet)**	
		(m)	**(g)**	**(g)**	**(wt%)**	**(g)**	**(g)**	**(wt%)**
1	4-6 months	5	8,448	951	11	200	751	79
2	7	6.5	553	91	17	22	69	76
3	7	18.5	870	66	8	10	56	85
4	7	8	390	77	20	14	64	82
5	7	18	603	31	5	9	22	70
6	7	6	595	140	24	36	104	74
7	7	18	876	51	6	11	40	79
8	17-19	39	5,838	1,510	26	368	1,143	76
9	>10	3-7	5,054	792	16	602	190	24
10	>10	7-9	7,689	390	5	238	152	39
11	>10	9-11	4,019	632	16	297	335	53
12	>10	11-13.5	7,523	475	6	251	224	47
13	>10	13.5-17	3,328	150	5	61	90	60
14	>10	17-20	3,010	198	7	169	29	14
15	>10	20-23	3,111	211	7	147	65	31
16	>10	22.5	6,850	21	0	12	9	44
17	>10	23-25	3,874	243	6	215	28	11
18	>10	25-27	4,051	710	18	525	185	26
19	>10	29.30.5	5,836	46	1	20	26	57
20	>10	32.5-35	10,307	126	1	74	52	42
21	>10	35-36.5	11,586	561	5	381	180	32
22	>10	36-37.5	9,176	870	10	572	298	34
23	>10	37.5-39	9,519	244	3	131	113	46
24	>10	40-41.5	6,651	175	3	50	126	72
25	>10	41-43	8,213	320	4	90	230	72
26	>10	44.5-46	8,234	180	2	121	59	33
27	>10	46-48	3,591	67	2	27	40	59
28	>10	48-50.5	6,016	378	6	198	181	48
29	>10	50-51	1,891	208	11	62	146	70
30	>10	53-55	6,236	769	12	475	294	38
TOT			**153,938**	**10,683**	**7**	**5,403**	**5,280**	**49**
Average			**5,131**	**356**	**9**	**180**	**177**	**52**
SD			**3,239**	**352**	**7**	**181**	**233**	**21**

Table S2. Percentages of different plastic types.

Sample n.	Years	PE	PP	PVC	PS	PET	PE/PP Blend	PA	Rubber	Rest
							(wt%)			
1	4-6 months	61	11.5	3	3	1	0			22
2	7	32	32					1		36
3	7	56	15	5	5					18
4	7	70	11							19
5	7	44	6			6	15			37
6	7	47	2	5	6		5			43
7	7	37	14	5		5				40
Average	**<10**	**50**	**13**	**4**	**5**	**4**	**7**	**1**		**31**
SD		**14**	**10**	**1**	**2**	**3**	**7**			**11**
8	17-19	50	3	1	1	39				6
9	>10	25	13	1	1	2			59	
10	>10	36	3	50	1					10
11	>10	54	22	8	16					
12	>10	41	14	2	2					41
13	>10	78	12							10
14	>10	92	1		3				4	0
15	>10	87	1	6	2					4
16	>10	27	44	2						27
17	>10	2	1						97	0
18	>10	14	85	0				1		
19	>10	50	42		7					2
20	>10	27	27	35	1					10
21	>10	60	20	14	4				1	
22	>10	55	16	18	8					3
23	>10	19	30	47	3					1
24	>10	32	36				11		6	15
25	>10	49	32	3	9					7
26	>10	81	2	17						1
27	>10	88			12					
28	>10	7	5	15					69	5
29	>10	52	3	42	4					0
30	>10	75	3	13	6		1		0	2
Average	**>10**	**48**	**19**	**16**	**5**	**20**	**6**	**1**	**34**	**8**
SD		**27**	**21**	**17**	**4**	**26**	**7**		**40**	**11**
TOT Average		**48**	**17**	**14**	**5**	**11**	**6**	**1**	**34**	**14**
SD		**24**	**18**	**16**	**4**	**16**	**6**	**0**	**40**	**15**

Table S3. Different plastic types with storage time <10 years.

Sample n.	Years	PE	PP	PVC	PS	PET	PE/PP Blend	PA	Rubber	Rest
						(g)				
1	4-6 months	121.5	23	5.5	5	1.5	0.67	0	0	43
2	7	7	7	0	0	0	0	0.2	0	7.8
3	7	5.5	1.5	0.5	0.5	0	0	0	0	1.8
4	7	9.5	1.5	0	0	0	0	0	0	2.5
5	7	3.5	0.5	0	0	0.5	1.4	0	0	3.5
6	7	16	0.5	0.5	2	0	1.8	0	0	15.5
7	7	4	1.5	0.5	0	0.5	0	0	0	4.3
TOT		**167**	**36**	**7**	**8**	**3**	**4**	**0**	**0**	**78**
Average		**24**	**5**	**1**	**1**	**0**	**1**	**0**	**0**	**11**
SD		**43**	**8**	**2**	**2**	**1**	**1**	**0**	**0**	**15**

Table S4. Different plastic types with storage time >10 years.

Sample n.	Years	PE	PP	PVC	PS	PET	PE/PP Blend	PA	Rubber	Rest
						(g)				
8	17-19	184	11.5	3.5	2	143	0	0	0	23.5
9	>10	149.9	78.9	5.9	2.9	11.9	0	0	352.8	0
10	>10	85.8	7.9	119.9	1.2	0	0	0	0	23.2
11	>10	158.9	65.9	23.9	47.9	0	0	0	0	0
12	>10	102.9	34.9	4.2	5.2	0	0	0	0	103.9
13	>10	47	7.2	0	0	0	0	0	0	6.3
14	>10	155.9	1.9	0	4.2	0	0	0	7.2	0.2
15	>10	126.7	1.2	9.2	3.2	0	0	0	0	6.2
16	>10	3.2	5.2	0.2	0	0	0	0	0	3.2
17	>10	4.9	1.5	0	0	0	0	0	207.9	0.8
18	>10	72.5	447.5	1	0	0	0	4.2	0	0
19	>10	9.9	8.3	0	1.3	0	0	0	0	0.4
20	>10	19.9	19.9	25.9	0.7	0	0	0	0	7.2
21	>10	229.5	76.9	53.9	16.9	0	0.9	0	3.2	0
22	>10	315.5	89.9	103.9	46.9	0	0	0	0	16
23	>10	24.9	38.9	61.9	4.2	0	0	0	0	1.2
24	>10	15.9	17.9	0	0	0	5.2	0	3.2	7.3
25	>10	43.9	28.9	2.9	8.2	0	0	0	0	6.1
26	>10	97.9	1.9	19.9	0	0	0	0	0	1.2
27	>10	24.2	0	0	3.2	0	0	0	0	0

28	>10	12.9	8.9	29.9	0	0	0	0	136.1	9.7
29	>10	31.9	1.9	25.9	2.2	0	0	0	0	0.1
30	>10	357.5	11.9	63.1	28.9	0	3.9	0	0.2	9.2
TOT		**2276**	**969**	**555**	**179**	**155**	**10**	**4**	**711**	**226**
Average		**99**	**42**	**24**	**8**	**7**	**0**	**0**	**31**	**10**
SD		**99**	**93**	**34**	**14**	**30**	**1**	**1**	**86**	**22**

Carbonyl indices

Table S5. Carbonyl indices average PE.

Sample PE	N	Median	Average (Outliers)	Standard deviation	Standard error
Fresh	14	0.43	0.53	0.32	0.08
<10 Years	18	0.40	0.46	0.24	0.06
>10 Years	184	0.40	0.41	0.14	0.01

Table S6. Carbonyl indices average PP.

Sample PP	N	Median	Average (Outliers)	Standard deviation	Standard error
Fresh	10	0.78	0.76	0.19	0.06
<10 Years	12	1.11	1.34	0.46	0.13
>10 Years	153	1.74	1.78	0.38	0.03

Table S7. Carbonyl indices - T-test results p value PE.

PE	<10 Years	>10 Years
Fresh	0.72	0.31
<10 Years		0.37

Table S8. Carbonyl indices - T-test results p value PP.

PP	<10 Years	>10 Years
Fresh	1.2E-03	5.5E-10
<10 Years		6.8E-03

Absorbance CH_2 and CH_3 (1490-1420)

Table S9. Absorbance CH_2 average of PE.

Sample PE	N	Median	Average (Outliers)	Standard deviation	Standard error
Fresh	14	5.46	6.14	2.90	0.78
<10 Years	18	6.45	6.65	1.88	0.44
>10 Years	184	3.80	3.93	1.89	0.14

Table S10. CH_2 - T-test results p value PE.

PE	**<10 Years**	**>10 Years**
Fresh	0.29	0.01
<10 Years		9.1E-06

Table S11. CH_3 average of PP.

Sample PP	**N**	**Median**	**Average (Outliers)**	**Standard deviation**	**Standard error**
Fresh	15	4.67	4.90	2.60	0.67
<10 Years	12	4.65	5.03	3.01	0.87
>10 Years	153	2.43	2.54	1.27	0.10

Table S12. CH_3 -T-test results p value PP.

PP	**<10 Years**	**>10 Years**
Fresh	0.45	3.5E-3
<10 Years		0.02

Differential Scanning Calorimetry

Table S13. % Crystallinity average PE.

Sample PE	**N**	**Median (%)**	**Average (Outliers) (%)**	**Standard deviation (%)**	**Standard error (%)**
Fresh	8	39.35	39.45	8.35	2.95
<10 Years	9	46.79	45.20	8.24	2.75
>10 Years	24	50.81	51.16	7.72	1.58

Table S14. %Crystallinity - T-test results p value PE.

PE	**<10 Years**	**>10 Years**
Fresh	0.17	4.8E-3
<10 Years		0.08

Table S15. Melting PE.

Sample PE	**N**	**Median (°C)**	**Average (Outliers) (°C)**	**Standard deviation (°C)**	**Standard error (°C)**
Fresh	8	113.73	116.62	21.60	7.63
<10 Years	9	131.98	130.52	8.07	2.69
>10 Years	21	127.23	127.48	7.27	1.59

Table S16. Melting - T-test results p value PE.

PE	<10 Years	>10 Years
Fresh	0.12	0.20
<10 Years		0.35

Table S17. % Crystallinity average PP.

Sample PP	N	Median (%)	Average (Outliers) (%)	Standard deviation (%)	Standard error (%)
Fresh	8	38.76	38.26	6.82	2.41
<10 Years	6	36.85	35.34	5.01	2.04
>10 Years	16	42.76	40.97	4.54	1.14

Table S18. DSC - T-test results p value PP.

PP	<10 Years	>10 Years
Fresh	0.37	0.33
<10 Years		0.04

Table S19. Melting PP.

Sample PP	N	Median (°C)	Average (Outliers) (°C)	Standard deviation (°C)	Standard error (°C)
Fresh	8	165.5	163.46	3.90	1.38
<10 Years	9	165.86	155.38	8.03	3.28
>10 Years	21	165.18	164.49	1.22	0.30

Table S20. Melting - T-test results p value PP.

PP	<10 Years	>10 Years
Fresh	0.87	0.35
<10 Years		0.57

Reference

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DEVELOPING THE CASE FOR ENHANCED LANDFILL MINING IN THE UK

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ABSTRACT

Across the UK there are around 22,000 landfills sites, suggesting a significant opportunity for recovering value from previously discarded materials. Enhanced landfill mining (ELFM) has been identified as a concept to recover value from landfills through optimized valorization of the resources extracted. This approach, including waste-to-energy (WtE), waste-to-material (WtM) and waste-to-land (WtL) options can also assist in addressing critical and secondary raw material demands and scarcity. However, to date, there is still limited evidence on this potential. In this paper, the results of 9 UK landfill sites characterization and feasibility studies for ELFM are presented. Waste characterisation from 9 landfill sites located in the UK was carried out. Overall 36 core drills and 118 unique waste samples were analysed. High volumes of fines (soil-like) organic material were observed across all samples and significant levels of valuable metals were observed in this fraction. Previous work had determined significant aluminium and copper are contained in the soil-like fines fraction, which does not include the separate metals fraction (i.e. aluminium cans, copper wires etc). At one site the combustible fraction was assessed as a potential refuse-derived fuel [RDF]. Typically, 10-40% by weight of the samples at this site were 'combustible', with an average gross calorific value of 12.9 MJ/kg. Plastics extracted from the sites are contaminated and degraded, therefore further work is required to understand the extent of degradation and to assess available options upcycle these materials.

1. INTRODUCTION

Steady raw materials supply is essential for the UK and EU economy and increasingly under pressure to sustain the businesses and industries demand (Rockström et al., 2009). The supply of raw materials is not only a matter of availability of primary but also secondary raw materials (SRM) (Dino et al., 2016; European Commission, 2017). As such, we need to consider both the scarcity and raising prices of raw materials and the waste management policies aiming at reducing the environmental and health impacts of waste. Recent research has demonstrated that landfill sites can offer a high potential of primary and secondary raw materials [SRM] (Dino et al., 2016) rather than just representing contaminated land that needs remediation (Ortner et al., 2014). Across Europe there are around 500,000 landfill sites (EURELCO, 2016) and around 22,000 historic landfill sites in the UK, of which 90% have been closed before 1996 (EA, 2015).

Mining landfill solely for SRM or critical raw materials [CRM] is not expected to be financially viable given the extent of the recovery operations involved (Gutiérrez-Gutiérrez et al., 2015). However, concepts such as 'enhanced landfill mining' (Jones et al., 2013) which provides an integrated valorization of landfilled waste streams as materials (Waste-to-Material) and energy (Waste-to-Energy), using innovative transformation technologies and respecting the most stringent social and ecological criteria has the potential to minimize costs through the recovery of multiple commodities and allowing the recovery of valuable land.

While traditional landfill mining has a long history, enhanced landfill mining (ELFM) has come into focus only recently (Jones et al., 2013). ELFM aims at providing optimized valorization of different types of materials extracted from landfill sites and increased energy recovery from waste, aiming to reduce the amount of re-buried waste to almost zero. Furthermore, ELFM projects aim to mitigate greenhouse emissions from landfill sites and landfill mining activities to the atmosphere. To achieve this, various technologies are developed to make waste streams usable for different valorization techniques.

Different options exist for recovery including Waste-to-Material (WtM), Waste-to-Energy (WtE) and Waste-to-Land (WtL) (Jones et al., 2013; OVAM, 2013; Van Passel et al., 2013). Besides WtM and WtE, (Van Passel et al., 2013) also considers WtL, the creation of space at the

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location of the landfill site, as well as allocation of new land use to the remediated landfill site. Furthermore, in ELFM concept, resource management which is defined as “the temporary storage of waste with a view to a later valorization and use of this waste” is taken into account (OVAM, 2013). In most cases of traditional landfill mining, recycling and recovery of materials are only of secondary importance as the main drivers being landfill capacity increase or land clearance for urban development (Ford et al., 2013). This has resulted in a standstill development of specialized mining technologies for ELFM (Ford et al., 2013).

It has been previously reported that recovered materials from landfill sites could provide high economic revenues – the value will depend on the amount and quality of the recovered fractions and the market (Jones et al., 2013; Van Passel et al., 2013). However, the amount of waste that could potentially be recovered depends mainly on the physical and chemical conditions of the landfill site and the efficiency of equipment and technology used (Rosendal, 2009). According to the World Resource Foundation (Strange, 1998), purity of the excavated waste fractions can vary between 70% and 90%. In this context, purity refers to the level of contamination and the level of target material (i.e. non-target material would make up 10-30% of a specific recovered stream). A high amount of plastics can be found in landfills. Joseph et al. (2007) concluded that it is not viable to recycle plastics due to highly diminished quality. Quaghebeur et al. (2013) reaches the same conclusion. The authors state that excavated plastic, textile, paper/cardboard and wood do not have the required quality for recycling and reintegration in the production market. Therefore, the best valorization route for these types of waste is widely considered to be WtE in the absence of other viable means of recovering value from these materials.

As the concept of ELFM gains traction, it is critical to further our understanding of the wastes contained within the landfills across Europe in order to develop robust plans for undertaking large-scale operations and to identify the technology, and technology development, needs.

This paper compiles the data from 9 landfill sites sampled across the UK, investigating the physical composition of each site, determining metal content and the potential of using landfill-derived materials as refuse-derived fuels [RDF].

2. MATERIALS AND METHODS

2.1 Sample collection

Samples were taken from landfill sites across the UK, predominantly handling municipal waste and general waste from commercial premises. 36 core samples were extracted from 9 landfill sites located across the United Kingdom, which were then divided into 118 samples based on the depths, for example the 22 samples from Site 8 is 1x core drill divided into 1 metre increments (up to 22 metres). The core samples were taken from drilling activities using a 450 mm diameter auger (drill barrel). The samples used in this work are summarized in Table 1; the age and status of the sites is shown, however the specific age of each core and sample is not possible to specify accurately. Two separate test sites were investigated at Site 4 which were wet and dry areas of the site and are referred to as 4a and 4b, respectively. The depths of the samples typically ranged from 0-22 metres, with many samples being in the range of 6-18 metres.

2.2 Composition analysis and characterisation

The samples were collected from the landfill sites, sealed in double-layered bags and stored at 4°C until analysis. The samples were hand-sorted Waste was screened and separated by hand into plastics, paper and fines as defined by Quaghebeur et al. (2013) (degraded garden and food materials), textiles, glass and metal. Waste composition was reported as a percentage contribution of total weight. Dry matter (DM) or Total solids (TS) and Volatile Solids (VS) of the paper and fines were determined in triplicate following the procedure British Standard methods (British Standards Institute, 2011a, 2011b, 2011c).

In addition to the DM, TS and VS content, the calorific values of the combustible fractions were determined in accordance with the standard method (British Standards Institute, 2011d) using a Parr 6400 Isoperibol bomb calorimeter.

The composition was determined for all sites. The calorific values were measured for all samples (combustibles

TABLE 1: Overview of sites and samples used.

Site n°.	Site status	Age of site (as of 2018)	Total sample count	No. cores	Maximum sample depth (m)
1	Closed	38	6	1	10
2	Open	26	6	2	26 30
3	Closed	24	10	6	20
4a	Closed	22	13	2	19
4b	Closed	22	10	5	25
5	Open	10	27	5	13
6	Closed	38	10	5	19
7	Closed	20	10	7	19
8	Open	20	22	1	22
9	Closed	28	4	2	20

only) extracted from site 8. The combustible fractions were separated, dried overnight and ground to <10 mm using a Retsch SM 2000 shredder.

2.3 Metal content of waste fractions

The metal content was determined as described by Gutiérrez-Gutiérrez et al. (2015). To achieve the highest quantity of the extracted metals, samples were submitted to nitric acid digestion followed by a digestion with aqua regia (HNO_3 + HCl in a ratio of 1:3), as it was not technically possible to use HF to digest the samples. Briefly, for the nitric acid digestion, 0.5 g of sample was mixed with 8 ml of HNO_3 (70%, 1.42 density, Fisher Scientific) in Teflon tubes and left overnight. The samples were placed in a microwave digester (Multiwave 3000, Anton Paar) for 45 minutes at 800 W. The mixtures were then filtered (150 mm, hardened low ash paper, Fisher Scientific) and the remaining liquid was diluted to 100 ml with distilled water and retained for analysis. The filter paper and residue was then dried for 2 hours at 105°C and placed into a digestion tube with 6 ml of HCl (37%, 1.18 density, Fisher Scientific) and 2 ml of HNO_3. The mixture was subjected to microwave irradiation at 800 W for 45 minutes. The solution was filtered and the liquid diluted to 100 ml and retained for analysis.

The retained solutions were analysed for metal content using inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX) using several certified standard solutions for calibration.

The organic/fines fraction from sites 1-4 was analysed for rare earth elements and critical/valuable metals (Gutiérrez-Gutiérrez et al., 2015). To further investigate the distribution of metals, along with heavy metal elements, all fractions of waste extracted from site 9 were analysed.

3. RESULTS AND DISCUSSION

The results of the compositional analysis, as an average for each site, is illustrated in Figure 1. The soil-like organic material (fines) ranges between 30-74% (w/w), which is expected due to the relatively high proportion of food waste in household and general commercial wastes, along with the common practice of applying a daily soil cover to landfills during operation. The soil-like fraction had a similar consistency to soil, however is a mixture of the soil cover and humic material formed from the biodegradation of organic wastes. This finding is in agreement with previous studies on the characterisation of excavated waste samples (Garcia et al., 2016; Mor et al., 2006; Quaghebeur et al., 2013) where the composition of fine materials increases with depth (Frank et al., 2017).

Plastics were prominent in many samples, in particular across sites 2, 5, 6 and 7, with the plastic content ranging from 8.5% in site 9 to 44% in site 5. Quaghebeur et al (2013) observed a plastic content of up to 25%, so the waste extracted from sites 2, 5, 6 and 7 are higher than expected. This could be due to the age of the material and extent of degradation (i.e. reduction of the biodegradable proportion), or could be due to the waste types deposited; the sites predominantly accepted MSW, however some commercial and industrial wastes were disposed of, which is typically lower in organic content at the time of disposal.

The presence of such a significant organic/fines fraction suggests that for any enhanced landfill mining operation to be viable, this material would need to be separated and managed. Soil and complex organic matter are able to bind to metals, such as those mobilised in leachate material. This phenomenon was explored (Gutiérrez-Gutiérrez et al., 2015), with the results of this analysis from sites 1-4 presented in Figure 2 (rare earth elements and selected critical metals) and Table 2 (Cu, Ag, Au and Al).

The quantities of rare earth elements (REE) and other critical materials in relatively low concentrations suggest that mining for these materials alone would not be economically viable (Gutiérrez-Gutiérrez et al., 2015). However, when recovered as part of a large enhanced landfill

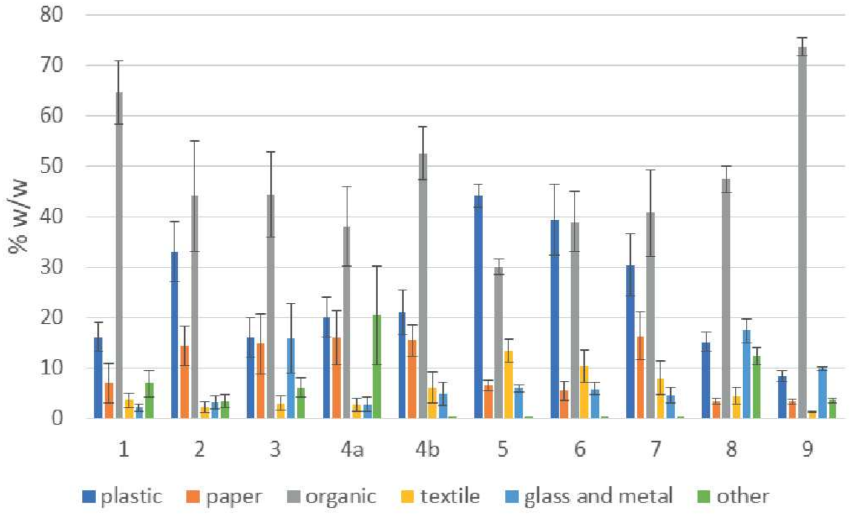

FIGURE 1: Average waste composition of sites 1-9 (error bars shown as standard error of the mean).

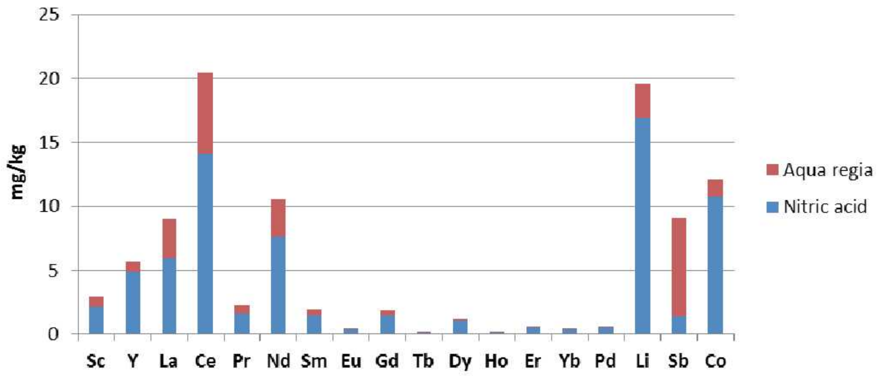

FIGURE 2: Rare earth elements and selected critical metal content of the fines (soil-like organic) fraction from sites 1-4.

mining undertaking then the recovery could be viable. This study focuses on the total metals present, however further work would be required to understand the recoverability of each metal. The Cu and Al concentrations measured are significant, and across the 4x sites analysed this represents a potentially viable resource of these metals. The combined value of aluminium and copper from within the fines fraction across the four sites is around $400 million (Gutiérrez-Gutiérrez et al., 2015), which is assuming complete recovery.Complete recovery wouldn't be expected in any recovery operation, therefore these values provide perspective of the scale of the metals. Due to the varied composition of waste within landfills, excavation solely for the purpose of these metals would be a significant technical challenge, in addition to the commercial viability previously mentioned.

To expand the work described by Gutiérrez-Gutiérrez et al. (2015) a further site was characterised in detail. Each fraction from site 9 was analysed for the REE and critical metals, the results of which are shown in Table 3a-c.

The REE observed in the fines fraction are closely aligned to the values in sites 1-4, however the Cu and Al values are lower, with the reasons for this requiring further research. Of the heavy metals Cr, Pb and Zn are most abundant, with the Cr content being significantly higher than values reported for non-landfilled wastes and MSW incinerator residues (Jung et al., 2004; Øygard et al., 2004). Chromium is, therefore, likely to chemically mobile in landfills through leachate movement arising from hazardous materials such as paints, batteries and chemical/industrial residues. However the values observed in wood materials suggests that the wood fraction separated in this study was treated with copper chromium arsenate [CCA], previous a widely-used wood preservative. The presence of such high Cr levels does suggest that any enhanced landfill mining operation would need to take into consideration environmental and human health risks posed by Cr, and other hazardous elements present.

For the samples from Site 8, the average gross calorific value [GCV] of the combustible fraction measured with the calorimeter is 18.2 ± 5.7 MJ/kg (GCV, dry). Figure 3 illustrates the net calorific value [NCV] on dry basis for each sample in comparison with the composition of combustible materials. On an as-received basis, the GCV and NCV for the combustible fraction were 12.9 MJ/kg and 11.0 MJ/kg respectively.

The samples analysed here provide an indication of the contents of such landfill sites, however are not absolute values due to the volume of the landfill sites in comparison with the number of samples analysed. Obtaining representative samples from a whole landfill site presents a significant challenge, and further work is required to consider the statistically valid number of samples required. Further work could also involve innovative whole-site characterisation techniques, including electromagnetic measurements (Bobe et al., 2018).

Research groups have investigated the use of excavated landfill material for use as RDF, or solid recovered fuel [SRF], with challenges mostly arising due to the need to separate significant volumes of fines. Wolfsberger and Hollen (2014) concluded that the separation process was not efficient due to the 42% moisture and 69% fines contents in the waste material (Wolfsberger and Hollen, 2014). Results for the current project show a lower moisture content (26,3%) and a reduced percentage of fines (47.4%). Thus, the process' efficiency could be expected to be higher, al-

TABLE 2: Content of Cu, Ag, Au and Al (in mg/kg) for sites 1-4.

Metal	Average content (mg/kg)			
	Site 1	Site 2	Site 3	Site 4
Cu	1,076	1,027	2,595	1,830
Ag	2.26	2.77	3.63	5.02
Au	0.18	0.13	0.16	0.05
Al	17,274	12,357	12,594	12,079

TABLE 3: Critical metals (a), light REE (b) and heavy metal (c) content of waste fractions from site 9. All numbers presented as mg/kg.

Critical metals (a)						
	Cu	Ag	Li	Sb	Co	Al
Paper	134.38	0.85	5.85	7.08	10.53	10.707
Wood	166.40	2.21	3.49	8.59	24.73	5.045
Fines	254.22	16.66	8.91	58.32	8.49	12.806
Film plastics	148.43	1.71	4.30	182.64	12.21	6.269
Dense plastics	588.75	2.61	8.37	16.49	17.43	8.238
Textiles	377.86	2.91	11.94	13.88	19.11	14.182

LREES (b)					
	La	Ce	Pr	Nd	Sm
Paper	4.17	8.84	1.00	3.67	0.69
Wood	3.97	9.00	0.99	3.76	0.71
Fines	10.07	21.25	2.40	9.22	1.79
Film plastics	4.09	9.08	1.00	4.07	0.72
Dense plastics	7.15	15.92	1.78	6.75	1.24
Textiles	8.78	20.52	2.26	8.64	1.69

Heavy metals (c)						
	Cd	Cr	Pb	Zn	Sn	As
Paper	0.51	1.056	94.10	215.55	18.44	2.97
Wood	0.77	2.435	175.91	325.32	18.88	6.59
Fines	1.11	834	303.73	565.66	30.83	4.81
Film plastics	1.27	1.187	293.97	519.89	18.98	3.00
Dense plastics	1.48	59.14	529.09	1.652	104.96	5.13
Textiles	1.69	1.866	567.91	650.75	35.47	6.23

though an industrial scale testing would have to be undertaken.

On the other hand, the process described by Jones et al. (2013) could be viable for RDF recovery from the present landfill, though it would also need to be evaluated in large scale. The fines fraction, in this case, was lower (39%) than in the work presented here. In short, RDF production is strongly influenced by the amount of fines present in the waste. Extensive sieving and separation of the fines are vital in order to obtain high quality RDF.

The relatively high proportion of plastics in landfill contributes to the CV, which is comparable to SRF produced from fresh MSW (Velis et al., 2012; Wagland et al., 2011). As the plastics are likely to be degraded and/or contami-

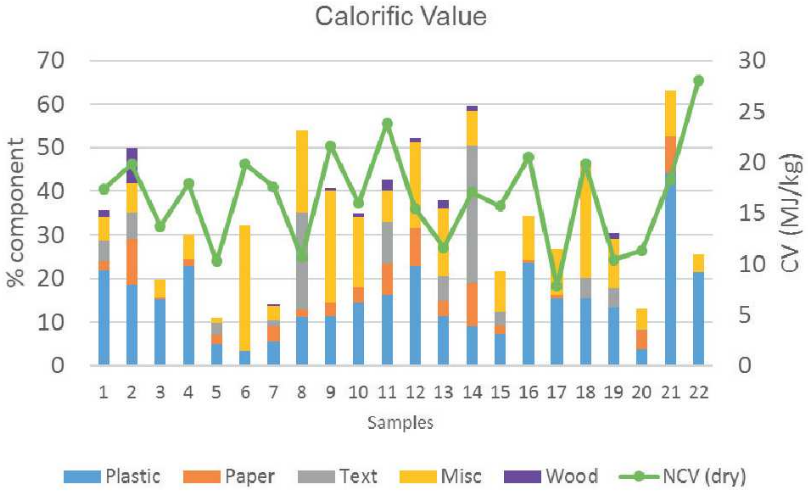

FIGURE 3: Combustible fraction and composition of site 8 with the NCV (dry), MJ/kg, for each sample.

nated through long-term exposure to leachate and landfill gas, it is not likely that all plastics recovered from landfill can be recycled conventionally (Joseph et al., 2007). Therefore, advanced options such as pyrolysis and gasification of plastics could upcycle these materials into chemicals and liquid fuels; this is a topic which has not been fully explored and so further work is required.

In summary, RDF production from enhanced landfill mining operations is one potential outlet, however successful valorisation of landfilled material is likely to comprise a flexible approach utilising options such as the recovery of recyclable materials (metals, for example), upcycling of plastics, refining of the fines material and the production of RDF.

4. CONCLUSIONS

The findings have highlighted that the waste composition varied across sites and between samples, however the percentage of fines (soil-like organics) is consistently high in comparison to other materials. This volume of fines presents a challenge in managing materials excavated from ex-situ landfill mining operations however the results presented here, and in previous studies, suggests that this material also contains valuable secondary raw materials.

Direct recycling of remaining plastics/paper/textiles might not be economically viable due to contamination and degradation. However options for managing these resources include the use of the combustible fraction as RDF or as a feedstock for advanced thermal conversion, potentially to produce valuable chemicals and/or liquid fuels.

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CHARACTERISATION OF EXCAVATED PLASTICS FOR THERMOCHEMICAL UPCYCLING TO PLATFORM CHEMICALS AND LIQUID FUELS

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Introduction

If the European Parliaments has its way, the concept of Enhanced Landfill Mining (ELFM) will be integrated into the EU Landfill Directive in the near future.[1] Landfilled waste will become a potentially valuable resource which is valorised as material (WtM) and energy (WtE).[2] In Europe, between 1995 and 2015, 5.25 billion tonnes of waste were deposited in landfills,[3] of which the plastic fraction represents between 5-25 wt% of the total landfilled waste.[4,5,6] Changes in physical and chemical properties of plastic waste during its storage in landfill have not been thoroughly studied, and further work is required to properly address this topic. This paper presents an early investigation on the degradation of plastics in landfills, focusing on the characterisation of excavated plastic waste from three different landfills in UK.

Materials and methods

Sample collection

A total of 8 excavated waste samples were collected from 3 different landfills located in the UK, at a depth ranging between 5 to 39 meters (Table 1). The excavated waste has been manually sorted and was divided in 10 fractions (Table 2). [5,8]

Table 1: Overview of excavated waste samples

Sample no.	1	2	3	4	5	6	7	8
Depth (m)	39.0	5.0	6.5	18.5	8.0	18.0	6.0	18.0
Quantity (g)	8,448	5,838	553	870	390	603	595	876

Plastic characterisation

The excavated plastic samples were washed with cold water, air dried at room temperature and then weighed to calculate the percentage of impurities, such as soil and semi-degraded paper. The excavated plastic samples of approximately 4 x 4 cm were analysed by a visual-NIR spectrometer (ASD Inc Releases LabSpec 2500) with a spectral range of 350-2500 nm and compared with fresh plastic spectra. The percentages for each plastic type identified were calculated. Similar plastic types were grouped based on their origin and depth. Samples 3, 5 and 7 were collected from the same landfill and depths between 6.0 and 8.0 m, and grouped by plastic type as Sample A. Similarly, samples 4, 6 and 8 were collected from the same landfill and depths between 18.0 and 18.5 m, and grouped by plastic type as Sample B. SEM-EDS (Environmental Scanning Electron Microscope Philips XL30 ESEM and Energy Dispersive Spectroscopy) was used to characterise the surface morphology and the chemical elements present in the surface of a representative plastic sample for each plastic type and to evaluate degradation and contamination levels. The ash C, H, N and metal content were determined following the British Standard method.[9,10,11]

Results and discussion

Excavated waste sample composition

Table 2 shows the percentage of each waste fraction found in the excavated waste samples. The largest fraction is represented by the soil with a range between 53 and 81 wt%, followed by plastic fraction ranging 5-26 wt%. The fraction 'Other' comprises mostly stones and unidentified materials. This distribution is consistent with previous studies which identified the fines fraction, which includes soil-type material as the major fraction in excavated waste followed by the plastic fraction.[4,5]

Table 2: Classification and quantification (in wt% as received) of waste fractions present in the excavated waste samples from landfill

Waste Fraction / Sample no.	Pl	P/C	M	G/C	T	W	S/F	B	WE	O
1	26	1	1	0	1	9	53	0	0	8
2	11	1	0	1	2	2	62	0	0	21
3	16	0	0	7	0	1	65	0	0	10
4	8	0	0	4	2	1	81	0	0	5
5	20	1	0	5	1	1	55	0	0	18
6	5	6	0	0	1	2	75	0	0	11
7	24	1	0	1	7	1	63	0	0	4
8	6	0	0	4	0	5	77	0	0	8

Pl =plastic; P/C = Paper/cardboard; M = Metal; G/C = Glass/ceramic; T = Textile; W = Wood; S/F = Soil/fine fraction; B = Batteries; WE = WEEE; O = Other.

Excavated plastic waste characterisation

The percentage of impurities in excavated plastic ranges between 62 and 87 wt% mainly including soil, semi-degraded paper and moisture. Zhou *et al.*[7] observed similar results, with impurities ranging from 61.8 and 84.4 wt%. The results from NIR spectroscopy (Table 3) highlights that the main fraction of the municipal waste plastic is composed of thermoplastics (including PE, PET, PP, PVC, and PS), which is to be expected as thermoplastics represent 80 wt% of the plastic consumed worldwide.[12,13,14] PE is found as the predominant plastic type in all excavated waste samples (Table 3).

Table 3: Plastic types found in the excavated plastic waste, with wt% of total plastics shown

Sample	PE		PET		PP		PVC		PS		Rest	
no.	g	%	g	%	g	%	g	%	g	%	g	%
1	184.0	50.1	143.0	38.9	11.5	3.1	3.5	1.0	2.0	0.5	23.5	6.4
2	121.5	60.9	1.5	0.8	23.0	11.5	5.5	2.8	5.0	2.5	43.0	21.6
3	7.0	32.1	-	-	7.0	32.1	-	-	-	-	7.8	35.8
4	5.5	56.1	-	-	1.5	15.3	0.5	5.1	0.5	5.1	1.8	18.4
5	9.5	70.4	-	-	1.5	11.1	-	-	-	-	2.5	18.5
6	3.5	43.8	0.5	6.3	0.5	6.3	-	-	-	-	3.5	43.8
7	16.0	47.1	-	-	0.5	1.5	-	-	2.0	5.9	15.5	45.6
8	4.0	37.0	0.5	4.6	1.5	13.9	0.5	4.6	-	-	4.3	39.8

PE = polyethylene; PET = polyethylene terephthalate; PP = polypropylene; PVC = polyvinyl chloride; PS = polystyrene; Rest = other plastic types.

Figure 1 compares the surface of excavated plastic samples and the surface of fresh plastic waste of the same plastic type established by SEM-EDS. In general, the surfaces of fresh plastic waste (Figures 1A, 1B, 1D and 1I) appear more homogeneous than the surfaces of excavated plastic, which seem altered. Table 4 presents a description of the surface characteristics and level of imperfection which can be associated with the first visual effect of degradation.[20]

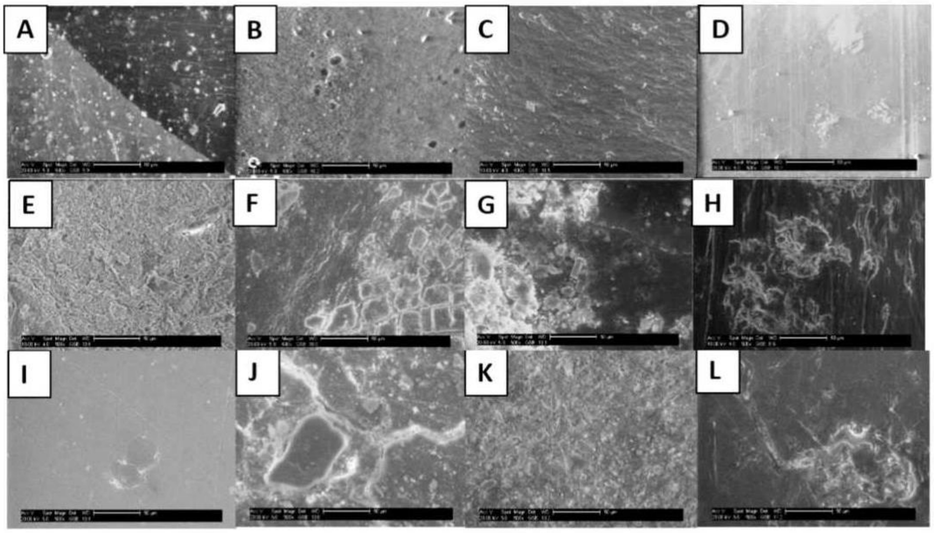

Figure 1: Surface images of fresh plastic waste (A, B, D, I) and excavated plastics (C, E, F, G, H, L, M, N) under 500x magnification. A: HDPE white carry bag; B: LDPE coloured packaging; C: Excavated PE (sample 1); D: PET; E: Excavated PE (sample 2); F: Excavated PE (sample B); G: Excavated PE (sample A); H: Excavated PET (sample 1); I: PP; J: Excavated PP (sample 1); K: Excavated PP (sample 2); L: Excavated PP (sample A)

Table 4: Surface characteristics and chemical elements detected by SEM-EDS (minimum concentration detected 0.08 wt%) of fresh and excavated samples

Sample	Figure	Surface texture	Surface degradation level	Main elements	Minor elements (< 5 wt%)	Trace elements (< 0.5 wt%)
HDPE	1A	F, AP	**Medium**	C, O, Ca		S, Cl
LDPE	1B	P	**Medium**	C, O, Ti	Al, Cl, Ba	Si, P, S, Cu
1 PE	1C	Fl, AP	**Medium**	C, O, Ca	Al, Si, Cl, K, Ti, Fe	Na, Mg, P, S, Cu, Zn
2 PE	1E	Fl, AP, Gr	**High**	C, O, Si, Ca	Al, K, Fe	Mg, P, S, Ti, Mn
A PE	1G	AP, Gr	**High**	C, O	Al, Si, Ca, Fe	Mg, P, S, K, Ti
B PE	1F	F, AP, Gr	**High**	C, O	Mg, Si, Ca	Al, P, S, Cl, Ti, Fe, Cu, Mo
PET	1D	S	**Low**	C, O		Al
1 PET	1H	G, AP, Gr	**High**	C, O	Al, Si, Ca, Fe	Mg, P, S, K, Ti
PP	1I	S	**Low**	C	Ca, Ti, Fe	Mg, Al, Si, Cl
1 PP	1J	F, AP, Gr	**High**	C, O	Si, Ca, Ti, Fe	Mg, Al, S, Cl, K, Zn
2 PP	1K	Fl, AP, Gr	**High**	C, O, Si, Ba	Al, S, K, Ca, Fe, Zn	Mg, P
A PP	1L	F, AP, Gr	**Medium**	C, O	Al, Si, Ca, Fe	Cl, K, Zr

F = fractures; AP = adhering parts; P = pits; Fl = flakes; G = grooves; Gr = granulates; S = smooth.

Calcium, which can be linked with the commonly used filler calcium carbonate ($CaCO_3$),[15, 16] is present in fresh HDPE and all the excavated plastic samples. Other identified elements can be related to the use of additives in plastics, such as quartz (SiO_2), wollastonite ($CaSiO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$), fire retardant $Mg(OH)_2$, magnetite (Fe_3O_4), titanium carbide (TiC), and pigment (TiO_2).[16, 17] Ti and Al are Ziegler-Natta catalysts used to produce PP and PE.[18] The presence of Si and Al may be associated to impurities of soil which major constituents are SiO_2 and Al_2O_3. Indeed, these elements are detected in larger quantities in excavated plastics than in fresh plastic waste. This result agrees with Zhou *et al.* study.[7] The roughness of excavated plastic surface could be explained by the presence of these impurities in the excavated plastics even after washing. The ash content of excavated waste is found to be higher than fresh waste for PP and PET, while PE is found to generally follow an opposite trend (Table 5; the ash content of 1 PP, A PP and 2 PP are 18.9 wt%, 1.3 wt% and 13.3 wt% respectively, not shown in the table). The higher level of ash in fresh PE might be related to the high level of titanium present in the sample compared to the excavated PE waste.[19] The excavated plastic samples present a lower level of Ni, Pb, Cu, Cr, As compared to other studies.[5,21]

Table 5: Characteristics of excavated plastic waste and fresh plastic waste

	39 m		18 m	6-8 m	5 m	Fresh plastic waste		
	1 PE	1 PET	B PE	A PE	2 PE	PE	PP	PET
C (wt .% db)	79.6	62.6	80.8	83.2	83.8	72.9	84.2	62.3
N (wt .% db)	0.5	0.3	0.4	0.3	0.3	0.3	0.2	0.3
H (wt .% db)	13.1	5.0	13.3	13.7	13.9	11.9	13.6	4.9
Ash (wt .% db)	4.5	1.2	11.8	6.2	3.1	7.6	2.2	0.2
Hg (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Cd (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Tl (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Sb (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
As (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Cr (mg/kg)	2.2	7.9	1.4	2.0	<1	<1	1.6	4.4
Co (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Cu (mg/kg)	5.9	13	6.8	7.4	10	11	4.8	12
Pb (mg/kg)	6.7	<1	2.0	1.9	5.8	1.1	5.1	3.7
Mn (mg/kg)	1.3	3.2	1.8	6.2	<1	4.9	2.7	1.1
Ni (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
Sn (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1
V (mg/kg)	<1	<1	<1	<1	<1	<1	<1	<1

db = dry basis.

Conclusion

The analyses of excavated plastic waste highlight the presence of a larger quantity of impurities than those in fresh plastic waste probably due to soil impurities. The surface analysis indicates that the excavated PP and PET have degraded more than excavated PE. Excavated PP and PET show higher ash content than fresh PP and PET waste. Furthermore, the ash content of excavated PP reaches the maximum level in the sample from greater depth (39 m) compared to the shallow depth (6-8 m and 5 m). However, the ash content of excavated PE did not exhibit a clear trend which can be related to the difference in depth.

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