



Mechanical and chemical recycling of solid plastic waste



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ABSTRACT

This review presents a comprehensive description of the current pathways for recycling of polymers, via both mechanical and chemical recycling. The principles of these recycling pathways are framed against current-day industrial reality, by discussing predominant industrial technologies, design strategies and recycling examples of specific waste streams. Starting with an overview on types of solid plastic waste (SPW) and their origins, the manuscript continues with a discussion on the different valorisation options for SPW. The section on mechanical recycling contains an overview of current sorting technologies, specific challenges for mechanical recycling such as thermo-mechanical or lifetime degradation and the immiscibility of polymer blends. It also includes some industrial examples such as polyethylene terephthalate (PET) recycling, and SPW from post-consumer packaging, end-of-life vehicles or electr(on)ic devices. A separate section is dedicated to the relationship between design and recycling, emphasizing the role of concepts such as Design from Recycling. The section on chemical recycling collects a state-of-the-art on techniques such as chemolysis, pyrolysis, fluid catalytic cracking, hydrogen techniques and gasification. Additionally, this review discusses the main challenges (and some potential remedies) to these recycling strategies and ground them in the relevant polymer science, thus providing an academic angle as well as an applied one.

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1. Introduction

1.1. The lifecycle of polymers

The lifecycle of polymer materials can be described by the scheme in Fig. 1: raw materials – be they virgin or recycled – are transformed into products via the various converting techniques (injection moulding, extrusion, etc.). This is the start-of-life phase for the (consumer) product. During the manufacturing process, a first type of solid plastic waste (SPW) is generated: post-industrial (PI) waste, which never makes it to the consumer. This could include runners from injection moulding, waste from production changeovers, fall-out products, cuttings and trimmings. Typically PI waste has the distinct advantages that it is clean and the composition of the polymer is known (Ignatyev et al., 2014). Quite often, these waste streams are also mono-streams, meaning they are uncontaminated by other polymers or non-polymers. In terms of recycling, these are often the higher-quality grades of polymer waste.

At end-of-life, the product is disposed and becomes post-consumer (PC) waste. Depending on the country, PC plastic waste is collected separately or not. If it is, the different regional collection schemes vary from very strict (such as the PMD¹ scheme in Belgium) to very open (such as the orange bags allowing all packaging waste in the Netherlands). Typically, PC plastic waste consists of mixed plastics of unknown composition and is potentially contaminated by organic fractions (such as food remains) or non-polymer inorganic fractions (such as paper) (Hubo et al., 2014), which makes it a more complex stream to recycle than PI waste.

From an environmental point of view, it remains preferable to avoid the creation of SPW altogether, by avoiding production in the first place (smarter packaging, alternative materials) or promoting re-use of plastics products, both of which are strongly related to raising the awareness of the consumer (European Commission, 2013). Such efforts run parallel to those on effective and efficient valorisation of the large amounts of SPW that inevitably continue to come into existence.

Once it does, the further processing options are similar for both PI and PC waste. The preferred option, which in fact closes the loop back to the – now secondary – raw materials, is recycling. In recycling, new raw materials are obtained via a mechanical (typically leading to regranulate) or chemical (typically leading to monomer building blocks) pathway. If polymer waste cannot be recycled, energy recovery is the preferred option. Landfill, the least-preferred option, should be avoided at all cost.

1.2. Material/Product-to-waste: polymer waste in the EU

Even within the two broad categories of PI and PC plastic waste, large differences can occur, based on the source of the waste, or (for PC waste) the locally implemented collection schemes. Fig. 2 presents an (non-restrictive) overview of the different possible origins of plastic waste, with examples and their typical further use. Some important properties will strongly affect the degree to which this waste can be effectively recycled. These include:

- Is the waste a mono-plastic (only one component) or a mixed plastic? As discussed further in this review, reprocessing of mixed polymer waste poses quite a few challenges. Therefore, mono-streams are always preferred.
- Is the plastic clean or contaminated with inorganic components, (small fractions of) other polymers or organic waste? In other words: are washing and purifying steps required?
- Are the composing polymers and their respective ratios in the mix known? This is always the case for mono-streams, but can also occur for mixed streams. It is an advantage to know the (pro rata) composition of a mixed plastic waste. Sadly, for mixed PC waste, this is seldom the case and ‘average bulk compositions’ are used as a rule-of-thumb instead.

Quantitative information about PI plastic waste is not publicly available, as this often remains in-company or is handled business-to-business. PC waste, on the other hand, is handled by municipalities and well tracked throughout Europe.

On average, 25 million tonnes of PC plastic waste (PlasticsEurope et al., 2015) is generated in Europe per year. In 2014, 29.7% of this was effectively recycled, 39.5% was sent to energy recovery and the remaining amount of 30.8% was landfilled.

¹ PMD = Plastics (bottles and fluid containers), Metals (cans) and ‘Drinkkarton’ (TetraPak).

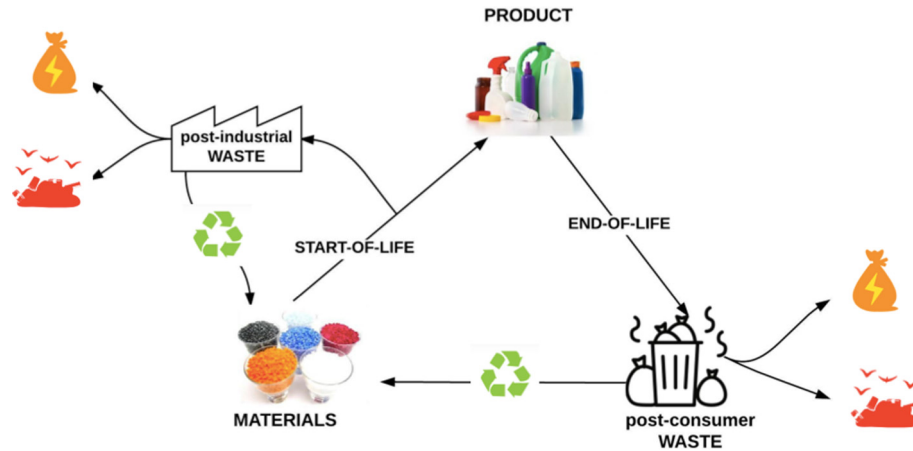


Fig. 1. Lifecycle of polymer materials. Depending on the chosen route, polymers will end up in recycling, energy recovery or landfill. Icons adapted from (PlasticsEurope et al., 2015).

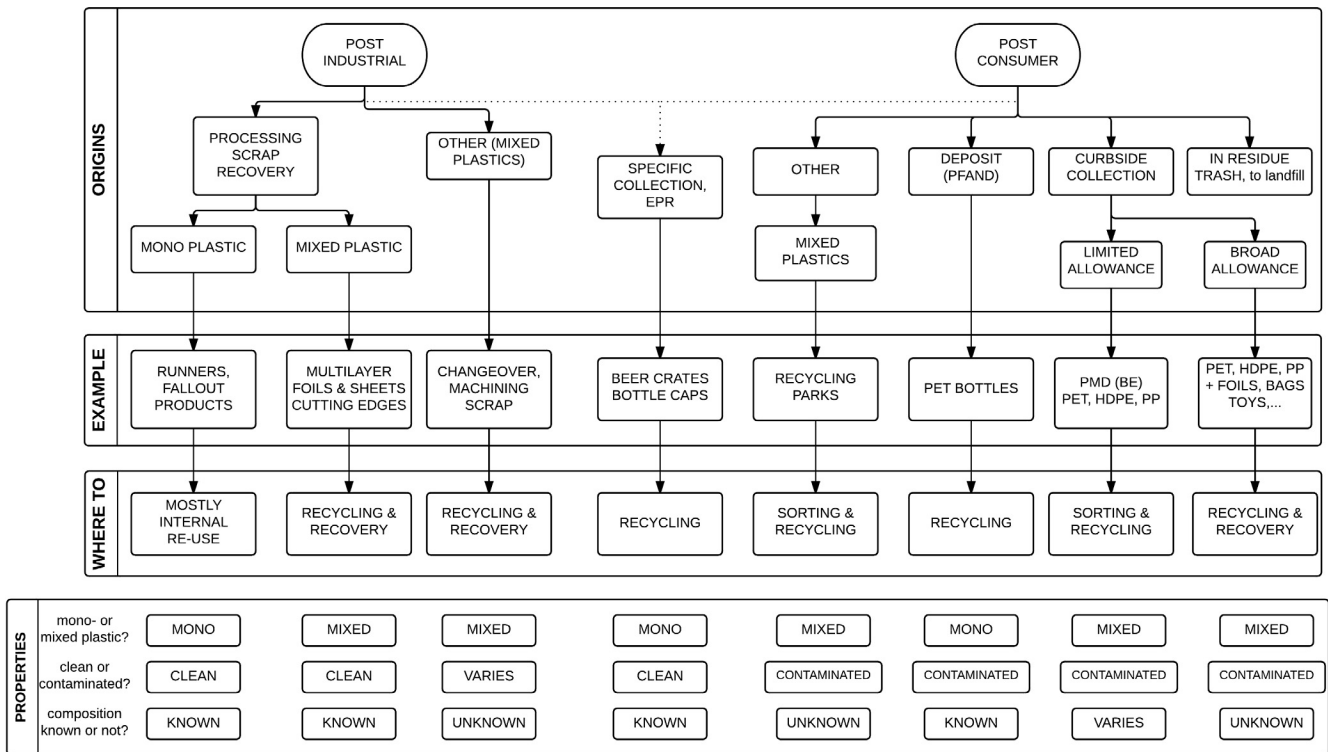


Fig. 2. Origins of SPW.

Over the past decade, recycling and energy recovery rates have steadily increased, which has significantly reduced landfilling. This evolution is shown in Fig. 3.

Landfilling rates are very uneven across Europe. In countries where landfill bans are in effect (Belgium, Luxembourg, Netherlands, Germany, Denmark, Switzerland, Austria, Norway and Sweden), less than 10% of plastic waste is landfilled. In other countries, such as Spain and Greece, a staggering amount of over 50% of all plastic waste still finds its way to landfill (PlasticsEurope et al., 2015).

Considering the types of polymer that make up the bulk of the collected plastic waste, a fair idea can be obtained by looking at the plastics demand for new products. This is shown in Fig. 4, which includes the dominant polymers listed with their respective shares

in those sectors that use the most plastics in their products (PlasticsEurope et al., 2015).

By far the largest share of all PC plastic waste is packaging waste. Packaging products are ubiquitous and tend to have short life times, especially when compared to other sectors such as building & construction, automotive and consumer products such as toys, which typically have a longer lifetime. With the exception of polyvinyl chloride (PVC), all of the other ‘big five’ polymers (high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) and polyethylene terephthalate (PET)) have their most sizeable application shares within packaging, so these will also dominate the composition of plastic waste.

Circular economy and reduction of (plastic) waste are high priorities for the European Union, resulting in ever stricter legislation

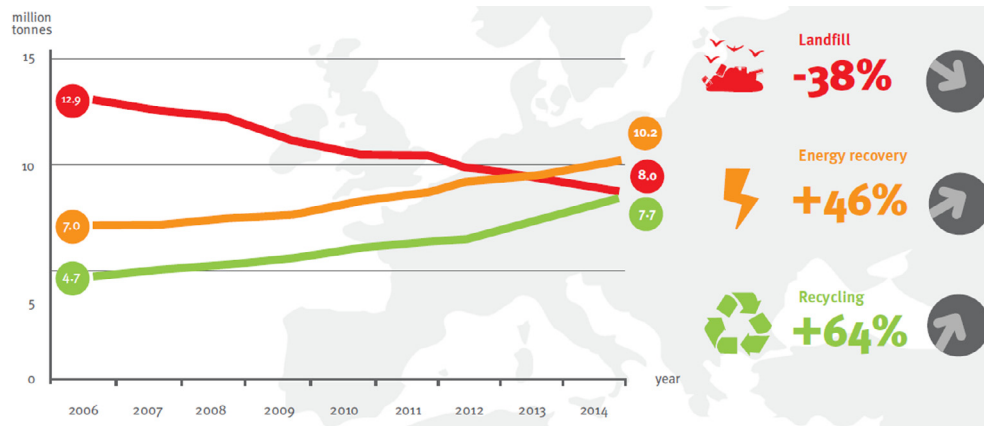


Fig. 3. Evolution of landfilling, recovery and recycling of SPW in EU (PlasticsEurope et al., 2015).

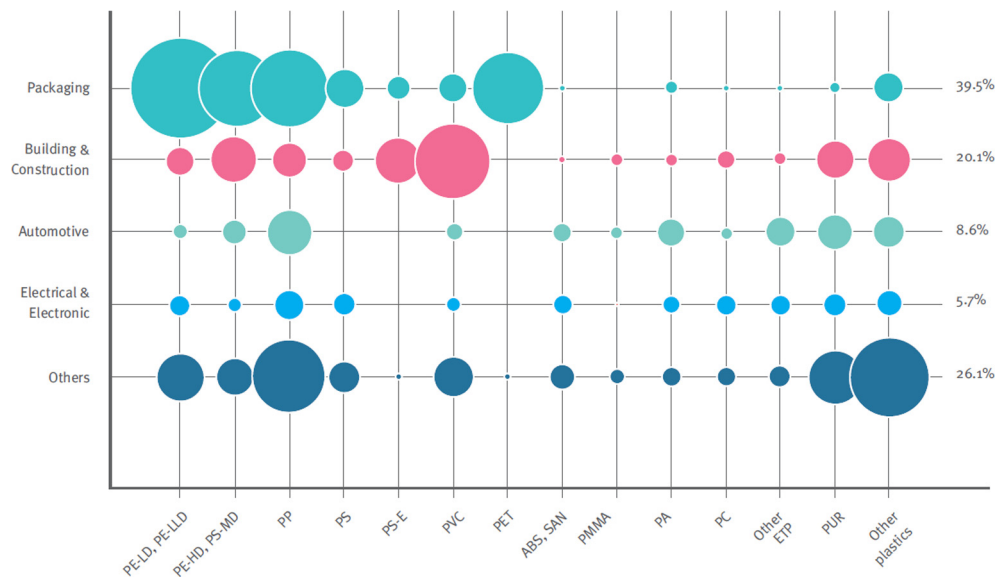


Fig. 4. Plastics demand per sector and per polymer type (PlasticsEurope et al., 2015).

such as complete landfill bans, extended producer responsibility (EPR) and specific recycling targets (European Commission, 2013). In the latest Circular Economy Package (CEP) (European Commission, 2015), released December 2015, the European Commission announces that it has ‘developed and will propose shortly to Member States *mandatory* product design and marking requirements to make it easier and safer to dismantle, reuse and recycle electronic displays’. The new CEP also includes an announcement of the revision of the Proposal on Waste, meant to promote industrial symbiosis (waste or by-products of one industry become inputs for another). This revision will include (the approach of) landfill bans, higher recycling targets – specifically for packaging industry – and more (or fiercer) EPR schemes (European Commission, 2015; World Economic Forum et al., 2016). In many EU member states, public procurement (representing 20% of the EU’s GDP) will (or already does) include an important ‘green’ aspect, e.g. the amount of recycled content in purchased products.

Additionally, the market in itself can be an excellent driver for more recycling as well. In their recently released report, ‘the new plastics economy – rethinking the future of plastics’ (World Economic Forum et al., 2016), the Ellen MacArthur Foundation proposes the creation of an effective after-use plastics economy as a main strategy to promote increased recycling rates

of (packaging) polymers. They argue that by creating this market, more materials will be captured, resource productivity will increase and an economical incentive will be provided to avoid ‘leakage’ of PC plastics into the environment. Additionally, increased recycling rates will contribute to the decoupling of the plastics industry from fossil feedstock. Recent studies indicate that in Europe alone, over 50% of plastic packaging could be recycled eco-efficiently with today’s available technologies (Denkstatt, 2015).

1.3. Waste-to-material: Pathways for the recycling of polymers

The most common method for the recycling of plastic waste is **mechanical recycling** (Al-Salem et al., 2009a). This process typically includes collection, sorting, washing and grinding of the material. Steps may occur in a different order, multiple times or not at all, depending on the origins and composition of the waste. Some examples from Fig. 2 include:

- Runners from injection moulding: this is clean PI waste of a well-known composition. It does not require collection (can be re-used in same company), sorting (it is a mono-stream) or washing (the material is clean).

- PC mixed plastics packaging waste: the broadest allowance of PC plastics waste, this stream requires collecting (from the consumer), sorting (for example select out the PET bottles), washing (removal of food and paper contaminants) and then grinding, often followed by regranulation.

Alternatively, the reuse of SPW in the construction industry can be considered for the disposal of plastic waste. The recycled plastics are used to substitute virgin construction materials in mortars and concrete (Gu and Ozbakkaloglu, 2016; Safi et al., 2013; Sharma and Bansal, 2016; Siddique et al., 2008).

Although a broad variation in recycling and recovery rate of waste plastics exists within Europe, almost 8 Mt of plastics waste were still landfilled in Europe in 2014 (PlasticsEurope, 2015). This amount of plastics corresponds to almost 100 million barrels of oil (PlasticsEurope, 2015). Worldwide, the amount of plastics ending up in landfill is almost half of the produced amount, being 150 Mt annually. This amount of plastics is quite considerable; hence it has high potential to be used as feedstock for the production of valuable products or to be used for **energy recovery**. The

latter being less favourable from an environmental point of view, the energy content of plastic is nonetheless comparable with heating oil (Kumar et al., 2011), respectively 42.6 MJ/l and 443.5 MJ/kg. Hence, a cheap source of energy can be found in using them as secondary fuel. However, incineration of plastics introduces the need of advanced pollution control measures, highly regulated by the EU Hazardous Waste Incineration Directive (Brems et al., 2012). Energy recovery of plastic waste yields toxic and noxious dioxins that should be carefully monitored. Processing difficulties such as those caused by the use of coatings and paints complicate the process of mechanical recycling. Also, contaminants can be not completely soluble and can induce phase separation, with a negative impact on the mechanical properties (Al-Salem et al., 2009a) as a result. This makes retaining high product quality very tough. Furthermore the market of recycled products is limited and the price is subjected to high fluctuations (as shown in Fig. 5), because of this establishing a profitable process is not straightforward.

All these drawbacks have led to the growing interest in a less frequent use type of recycling, namely **chemical recycling** (Angyal et al., 2007; Garforth et al., 2004; Kumar et al., 2011;

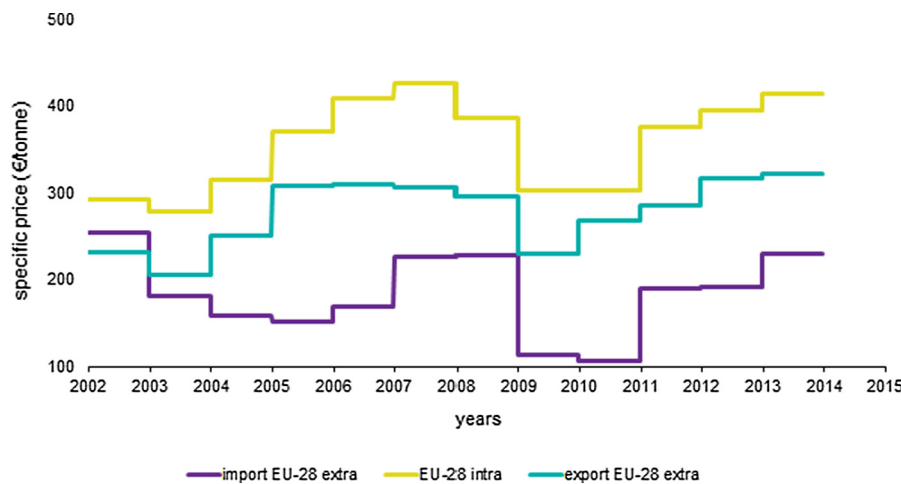


Fig. 5. Price indicator of plastic waste in EU-28 according to trade flows for period 2002–2015.

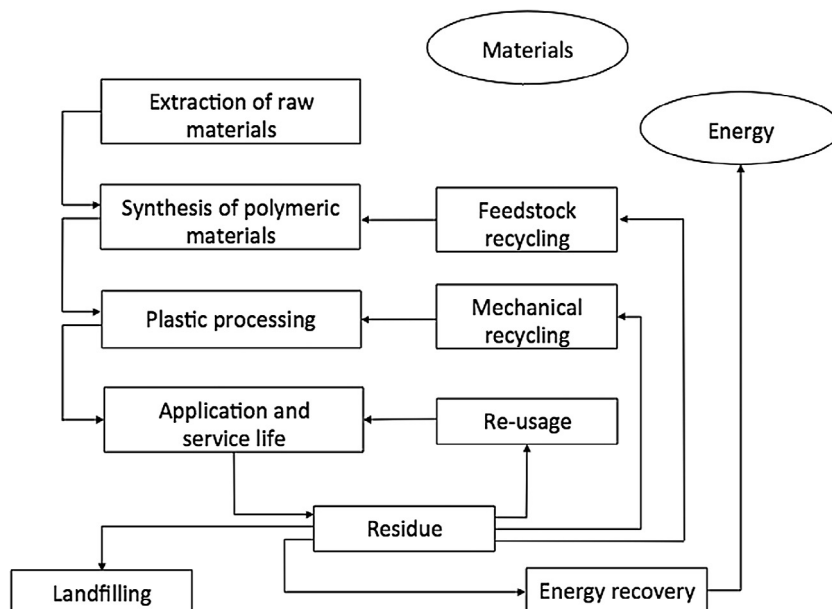


Fig. 6. Plastic waste management options in terms of the life cycle of polymeric products. Redrawn from Vilaplana and Karlsson (2008).

Okuwaki, 2004). This type of recycling has high potential for heterogeneous and contaminated plastic waste material if separation is neither economical nor completely technically feasible. It is based on converting the polymers into smaller molecules, which can be subsequently be seen as sustainable as it also reduces the amount of chemicals used for the production of fuels and virgin plastics (Al-Salem et al., 2009a; Garforth et al., 2004; Kaminsky et al., 2004; Lin and Yang, 2009; Okuwaki, 2004; Scheirs and Kaminsky, 2006a, 2006b). Recycling plastics is important to conserve natural resources and protect the environment, as this type of recycling can reduce the amount of fossil fuels needed to produce commodity plastics. Chemical recycling routes can be roughly divided into thermochemical and catalytic conversion processes. These will be discussed more extensively in one of the following sections.

An overview of the different pathways for recycling is shown in Fig. 6, including where their respective end products re-enter the lifecycle of plastics.

1.4. Material-to-product: from closed to open loop

Within circular economy thinking, the recycling of materials is often categorized based on the product which is manufactured from the secondary raw materials:

- In **closed-loop recycling**, the recycled plastics are used to produce the same product they were originally recovered from. The new product can be made up entirely of recycled plastics, or a mixture of the recycled plastic can be made with its virgin counterpart. This form of dilution ensures that the product can continue to be recycled and its recovered material added at the same rate. This is common practice for many PET packaging products, for example;
- In **open-loop recycling**, the recycled plastics are used for a different product than the one they were originally recovered from. This does not necessarily imply that the new application is of lower 'value'. Examples include manufacture of textile fibres from bottle-PET or printer components from water bottle polycarbonate (Kunststoffindustrie, 2015).

These two terms are essentially neutral, as they make an objective division based on the newly manufactured product. Therefore, they should be preferred to subjective labels such as 'up-cycling' and 'down-cycling', which immediately imply an appreciation of the added value of the recycling process. It is a known pitfall for those outside of plastics converting industry to consider open-loop recycling as some form of cascading into ever lower-valued applications.

2. Mechanical recycling

2.1. Steps in the mechanical recycling process

Prior to the actual reprocessing of recycled materials into new products, the conversion from waste to new raw materials needs to occur. This phase is generally termed the 'End-of-Waste' and begins after the collection step. For SPW, this process can include the following steps, each of which can occur anywhere between not at all and multiple times throughout the sequence:

- Separation and sorting: this occurs based on shape, density, size, colour or chemical composition.
- Baling: if the plastic is not processed where it is sorted, it is often baled in between for transport purposes.
- Washing: removal of (often organic) contaminants.

- Grinding: size reduction from products to flakes.
- Compounding & pelletizing: optional reprocessing of the flakes into a granulate, which is easier to use for converters than flakes.

PI waste tends to be better separated in advance according to composition, so sorting is applied to PC waste much more often than to PI waste. The same goes for washing, as PC waste is usually more contaminated.

Some of the most common sorting and washing techniques will be discussed by following the flow of two different plastic waste streams from Fig. 2:

- PMD (BE): A curbside collected mix with limited allowance.
- All plastics packaging waste bag (DE or NL): A curbside collected mix with broad allowance.

2.1.1. Example of industrial sorting: PMD

PMD is a separate collection scheme in Belgium for 'Plastics, Metalen en Drinkkarton' (plastics, metals and carton drink packages). This selected packaging waste is collected curbside by municipalities in a separate waste bag, for which the collection is made cheaper to the citizen than household waste. The bag allows for all 'solid bottle' packaging waste (water, lemonades, milk, soap and detergent bottles), metal cans (drink cans, canned goods and cosmetics such as deodorants) and carton drink packaging. For the plastics fraction this results in a majority of PET, followed by HDPE and a minority of PP (mostly caps). LDPE is included by ways of the attached labels.

The collected bags are delivered to sorting facilities, which sort out the different materials. For the plastics, this is into baled PET (clear, blue and green), HDPE and a rest fraction. Optionally, the PP fraction can be sorted out as well. A schematic of the sorting process is shown in Fig. 7.

2.1.1.1. From PMD to (mixed) plastics only. The (LDPE) bags are cut open in an automated sack opener and then the contents are passed through a **progressive rotating sieve** (= sorting by size). Both really small (bottle caps) and overly large objects (the bags themselves) are removed and go to the residue fraction.

A medium (40–120 mm) and large (120–220 mm) fraction continues, with an extra **wind sifter** in place to ensure that loose paper etiquettes and plastic bags are blown out. Plastic bags are not formally allowed in the PMD bag, but often end up in there anyway, due to bad sorting at the level of the consumer. Next, the mixed waste passes an overhead **magnet** for the removal of ferrous metals, an optical sorter for the removal of the carton and an **eddy current** for the removal of non-ferrous metals, which is mostly aluminium. The large fraction passes another **ballistic separator**, which removes all 'soft' plastics, meaning the foils. Only the 'hard' plastics, the bottles themselves, remain.

2.1.1.2. From mixed plastics to sorted plastics. The remaining mixed plastics are separated, first by **FT-NIR** (Fourier Transform Near Infrared) into PET and HDPE. **Optical colour recognition** sorters divide the PET into clear, blue and green. Finally, all these sorted streams pass through a sorting cabin, where trained operators check for false positives or negatives and correct any automated mistakes by **manual sorting**. After this final sorting step, the separated HDPE, blue PET, green PET and clear PET are baled for transport off-site.

FT-NIR is by far the most widely used technique for the automated sorting of plastics (Hopewell et al., 2009). It does have a few limitations, though, which are:

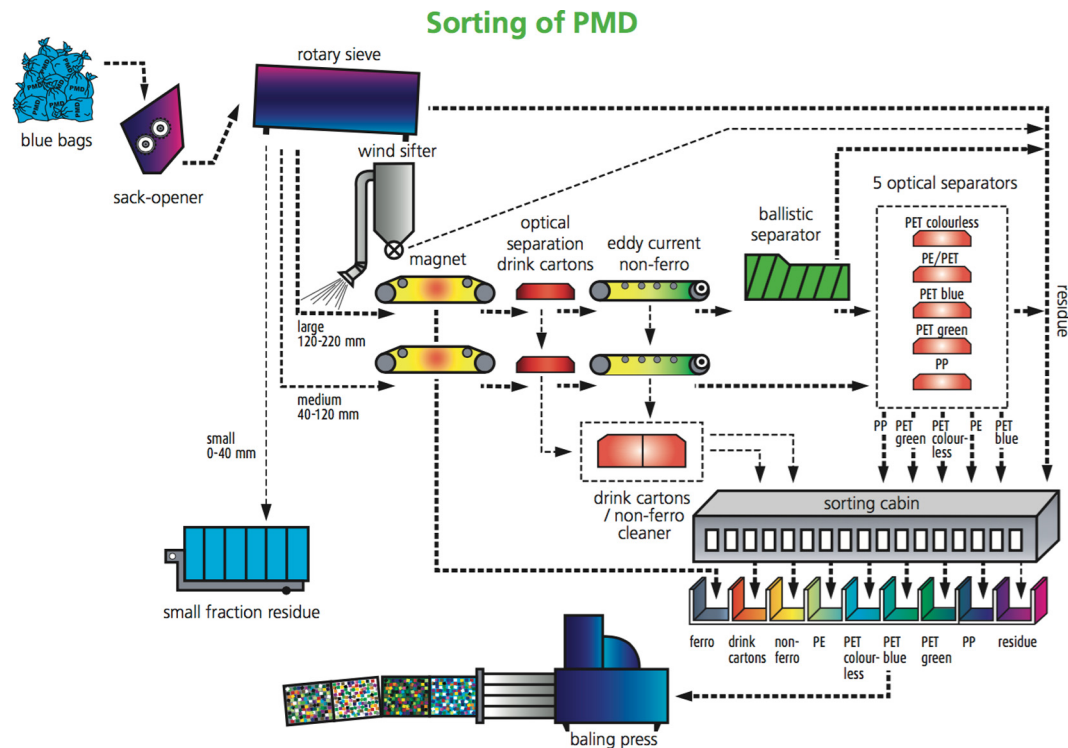


Fig. 7. Sorting of PMD waste (courtesy of Indaver, BE).

- It is an optical surface technique. Anything which leads to a false reading (the sensor 'sees' a label instead of the bottle underneath, products are inside one another, the light cannot reflect due to dirt) will give a false result;
- Products made up of more than one polymer (for example multilayer packaging), will be detected as the one that is presented towards the sensor at time of sensing;
- NIR cannot identify black or dark products.

Manual sorting by a trained operator is expensive but can be highly efficient. The operator is taught to sort based on product, which is coherent with certain material types. Within PMD recycling, the operator could sort out milk bottles (HDPE) or certain colours of soda bottles (green, blue, white PET). Manual sorting is also used in the sorting of other waste fractions, mostly for a mix of hard plastic products. Sorting examples would include garden furniture (talc filled PP), cable sleeves (HDPE), window profiles (PVC), children's swimming pools (PVC), plexi-glass (PMMA), etc.

While the PMD case has served well to highlight some leading sorting techniques at product level, it does not comprise the entire recycling process. The next example will demonstrate a more complete chain, where the separation of the mixed polymers is done at the level of grinded flakes.

2.1.2. Example of sorting: mixed packaging waste

Let us consider a broader format of curbside collected waste: the bag collection systems that allow for all plastic packaging waste (NL and DE). The resulting polymer mix is much more diverse and will contain PET, HDPE and PP as the example above. Additionally it will include fair amounts of L(L)DPE (tray packaging), polystyrene (PS) (yoghurt pots and trays) and – depending on the region – PVC (medical and cosmetic packaging). Furthermore non-packaging polymers such as acrylonitrile butadiene styrene (ABS), polyamide (PA), polycarbonate (PC) will contaminate the mix, as well as organic (food) remnants.

This challenging mixture of polymers can be sorted by a series of washing, grinding and separating. We discuss the operational flow of a small and medium-sized enterprise (SME) which takes in this waste (Eco-oh!, BE) to highlight the remaining dominant separation techniques.

The waste polymers, when delivered, are stored in a large hall. The sorting process starts by loading the material onto a belt system, which brings the mix to a crude **shredder**, which reduces the products to fist-sized particles (1st grinding). These are transported into a feed silo, from where the waste is led to the first washing. This is a **rotating drum washer** where rocks, metals and glass are separated gravitationally; a water flow provides the washing. Immediately after, **friction washers** (2nd washing) will remove the organic waste sticking to the plastics. The large particles are now fed into another **shredder** (2nd grinding) where they are further reduced to flakes sized roughly 1–12 mm. Immediately after, the flakes are washed again in **friction washers** (3rd washing). From there, they are led to the **float-sink separation** installation (1st separation, density based). In the water bath, PP and PE will float and the other polymers such as PET, PS, and PVC will sink. As this is a water-based technique, the flakes simultaneously undergo a 4th washing. We now have the float fraction (PP + PE, also known as mixed polyolefins or MPO) and the sink fraction. The sink fraction passes a strong overhead magnet (removal of ferrous remains) to a **mechanical drier** and is ready as secondary raw material, being a mix of technical plastics. The float fraction is also dried, but continues into a **wind sifter** (2nd separation, mass-based). Here the upward airflow will remove all 'soft' particles, i.e. the foils (mostly LDPE and PP). The heavier 'hard' particles will fall down against the airstream. The hard fraction MPO (PP and HDPE remaining) is now ready as secondary raw material. The soft fraction MPO (LDPE and some PP) is too low in bulk density to be used directly by converters, so it also undergoes a final **regranulation** (with **melt filtration**) step by extrusion. Now also this fraction is ready as a secondary raw material.

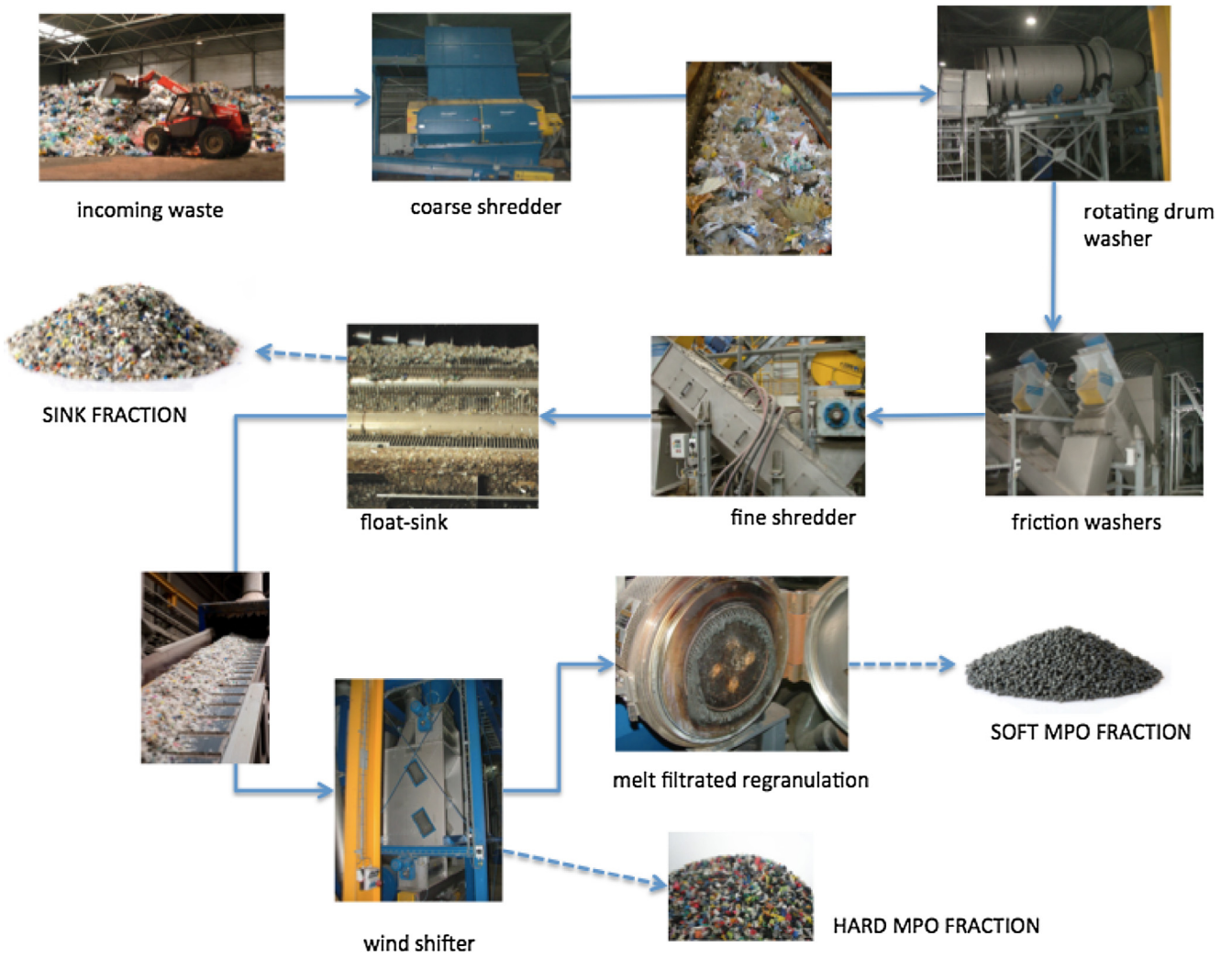


Fig. 8. Flow of the PC waste within Eco-oh! (courtesy of Eco-oh!, BE).

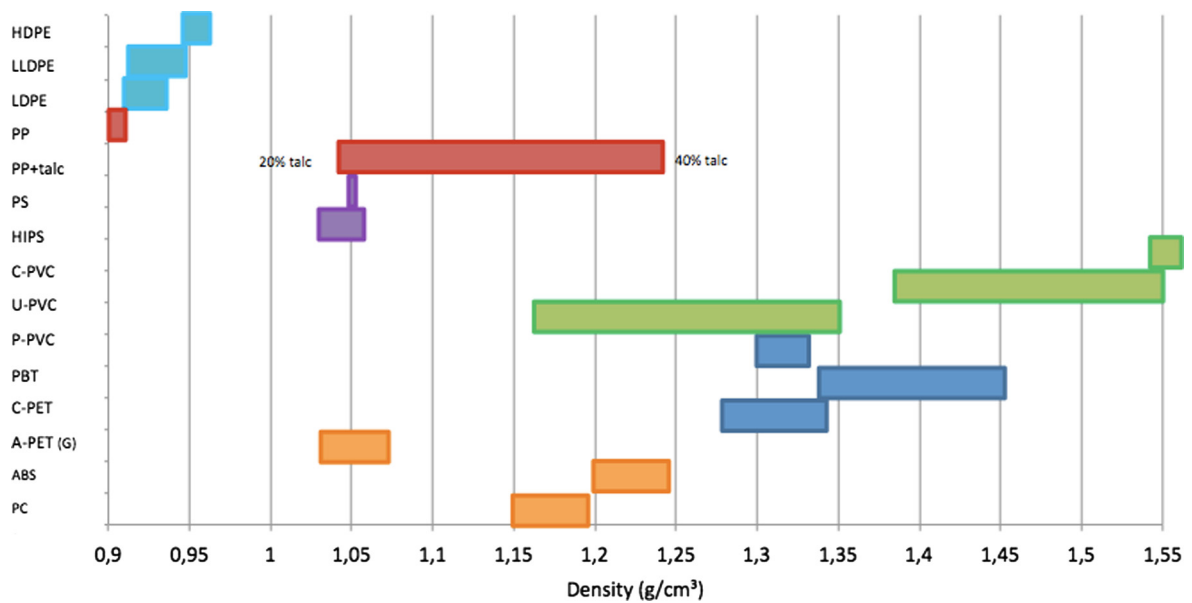


Fig. 9. Density ranges of some of the most common polymers in SPW (values based on Callister and Rethwisch (2010) and Kaiser et al. (2015)).

Flotation, also called float-sink separation, is a straightforward density-based separation technique. It is the dominant method for the sorting of shredded flakes, usually with water as a flotation agent (Wang et al., 2015a). In this relatively cheap sorting step, polymers with densities below 1 g/cm³ (unfilled PP and PE) will float and all other common polymers (PS, PET, PVC, ABS, etc.) will sink.

Flotation could (and is) equally be performed with denser media than water, to further separate the sink fraction. However, many polymers in PC waste have a ‘density range’ rather than a single density value and these ranges often overlap, thus making it impossible to completely separate these polymers effectively into mono-streams. Typical density ranges of packaging polymers are shown in Fig. 9.

During **regranulation** or subsequent reprocessing of the recycled materials, **melt filtration** is a useful technique to remove non-melting contaminations from the melt, as these would inevitably reduce the quality and properties of the extrudate (Stenvall and Boldizar, 2016). Typical removed fractions include wood, paper, aged rubber particles and higher-melting polymers (e.g. PET in PP processed at 220 °C) (Stenvall et al., 2013). Melt filters come in different mesh sizes. A smaller mesh size takes out more contaminations; it is more complex in production but will also lead to improved process stability and polymer quality (Luijsterburg et al., 2016).

Different options for melt filtration are listed here, in ascending order of installation cost:

- a *manually exchangeable sieve*, which is mechanically exchanged once it is sufficiently polluted (usually observed via pressure drop over the sieve). A clean sieve is levered into place, while the polluted sieve is rotated out so that it can be cleaned while the other sieve is active. This discontinuous method requires that the extrusion process be interrupted while the sieves are exchanged.
- A *semi-continuous sliding screen changer* utilizes a fast-acting hydraulic cylinder to move the screen packs in and out of the melt flow without interrupting the processing. However, during the exchange some off-specification material can (and will) be produced.
- The fully automated solution of *continuous melt filtration* ensures that a relatively equal amount of filtration area is exposed to the polymer flow at all times, minimizing processing effects due to screen changeover. Such continuous melt filtration is typically achieved either by an automated rotating sieve (a moving circular disk containing multiple screen packs) or a continuous belt screens exchangers. In advanced systems, there is no external power source, but the force of the extruder head pressure is used to move the filter screen.

2.1.3. Other sorting techniques

Other sorting techniques that are used (or developed) for the separating of mixed polymers include:

- **Tribo-electric (electrostatic) separation:** while this technique is theoretically applicable for complex mixes, the best results have been reported for separation of a binary mix (only two polymers) like ABS/PC, PET/PVC and PP/PE (Reinsch et al., 2014). In electrostatic separation, letting the polymer flakes collide in a charging unit causes one to be charged positively and the other to be charged negatively (or remain neutral) at the surface (Al-Salem et al., 2009a). They are then separated by their different deflection in an electric field. Some mixes, like PP+PE require an additional pre-treatment (e.g. electron-beam irradiation) to permit separation into homogeneous material fractions (Albrecht et al., 2011).

- **Froth flotation:** also called selective flotation separation, froth flotation is another method to separate polymers with similar densities (Censori et al., 2016). The basic principle of froth flotation is to have air bubbles adhere (or not) to a selected polymer surface, thus causing it to float (or sink). A precursor step is required wherein the surface characteristics of selected polymers are changed from hydrophobic to hydrophilic (= ‘selective wetting’, for a mixture of hydrophobic polymers) or the hydrophilicity of one of the polymers is increased (= ‘selective hydrophobization’, for partly wettable polymers) (Fraunholz, 2004). The technique is currently researched at lab-scale rather than widely used in industry. It is mostly used for the separation of mixed plastics with densities higher than water, primarily to separate binary mixes of a combination of mostly PS, PVC, PET, PC or POM (Wang et al., 2015a).
- **Magnetic density separation (MDS):** MDS is a refined density-based technique, with its origins in the mineral processing industry. By using a magnetic liquid (containing iron oxide) as the separation medium, the density of the liquid can be varied by use of a special magnetic field (Rem et al., 2013). Therefore, MDS can be applied to separate multiple polymer fractions in a single step. However, this is still a density-based technique and polymer fractions with overlapping densities will still contaminate one another. MDS has been successfully applied for the separation of PP and PE from MPO (Serranti et al., 2015) and PVC as well as rubbers from building & construction waste (Luciani et al., 2015).
- **X-ray detection:** useful for the separation of PVC containers, their high chlorine content makes them easy to distinguish (Arvanityannis and Bosnea, 2001).

2.2. Main challenges related to mechanical recycling

Different challenges arise when recycling both mono- and mixed plastics. The principal issue is the fact that polymers will degrade under certain conditions. These conditions are amongst others heat, oxidation, light, ionic radiation, hydrolysis and mechanical shear (Ravve, 2000). During mechanical recycling of polymers, two types of degradation prevail: degradation caused by reprocessing (thermal-mechanical degradation) and degradation during lifetime (La Mantia, 1996b).

Foremost is the thermal-mechanical degradation of polymers during reprocessing. Both PI as PC plastics recycling suffer from this type of degradation caused by a combination of heat and mechanical shear. The other type of degradation is the degradation occurring during lifetime by the long-time exposure to all sorts of factors in the environment (heat, oxygen, light, moisture, etc.). This type of degradation, however, is only important in the case of PC plastics recycling.

2.2.1. Thermal-mechanical degradation

Thermal-mechanical degradation is caused by the heating and mechanical shearing of the polymer during the melt processing. Different processes will be initiated in the polymer when it is subjected to a combination of temperature and shear (Beyler and Hirschler, 2002). The most common mechanisms occurring in commercial polymers are chain scission and chain branching. Depending on the type of polymer and aspects like initial molecular weight (M_w) and temperature, one or the other of these competing radical mechanisms becomes more dominant. Thermal-mechanical degradation begins, generally, with a hemolytic scission of a carbon-carbon covalent bond in the polymer backbone, generating free radicals. These free radicals may undergo some chemical reactions such as disproportionation, causing chain scission, or crosslinking also known as branching (Beyler and Hirschler, 2002) (see Fig. 10).

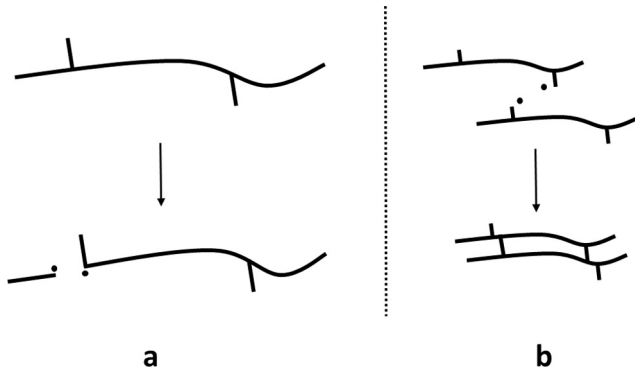


Fig. 10. Random chain scission (a) and crosslinking (b).

Chain scission mostly occurs in terminal pendent groups or in the polymer backbone and reduces the molecular weight of the polymer and hence also the properties. Chain branching results in crosslinking and increases the molecular weight. A typical example of chain scission occurs in PP (González-González et al., 1998), while some types of PE are more prone in displaying chain branching (Pinheiro et al., 2004). Both reactions result in a degree of unsaturation and the release of low-molecular volatile components.

Fig. 11 shows a typical example of molecular weight reduction due to thermal-mechanical degradation of a polypropylene sample

during a certain degradation time. Next to a decrease in M_w over time, also an increase in polydispersity and a shift in M_w distribution is often seen, which indicates the occurrence of different chain lengths in the polymer. An increasing MFI, as shown in Fig. 11b, is symptomatic of the decrease in M_w .

The change in M_w has a strong influence on the rheological and mechanical behaviour of polymers. Fig. 12a shows an example of the elongation at break of a PET sample, subjected to different extrusion steps mimicking a recycling process. A severe reduction in M_w already takes place in the first few extrusions, accompanied by the same decreasing trend in the elongation at break. Besides elongation at break, all mechanical properties will suffer changes depending on the change in M_w . In general, elongation at break and impact properties are the mechanical parameters which are immediately affected by thermal-mechanical degradation (La Mantia and Vinci, 1994). Fig. 12b shows the effect on the impact strength of a PA6 sample. The evolution of strength properties are very polymer dependent and can for some polymer even increase after recycling (Braun, 2002). Besides the variation in mechanical and rheological properties, also thermal properties (melting temperature, crystallization, etc.) and physical properties (surface properties, colour, etc.) are affected by thermal-mechanical degradation.

These effects of thermal-mechanical degradation can be compensated by adding different additives. A huge range of additives for increasing the recyclability of plastics can be found. Usually, heat stabilizers are re-added during the recycling because they

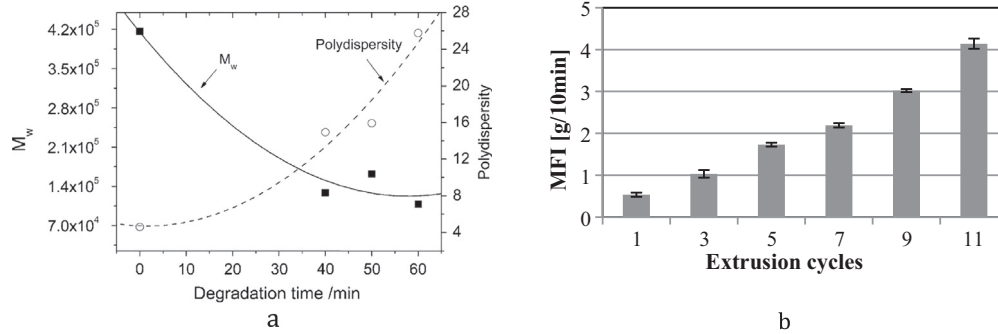


Fig. 11. (a) Molecular weight and polydispersity evolution of a PP sample (Qian et al., 2011). (b) MFI evolution of a multiple reprocessed PP sample (Delva et al., 2014).

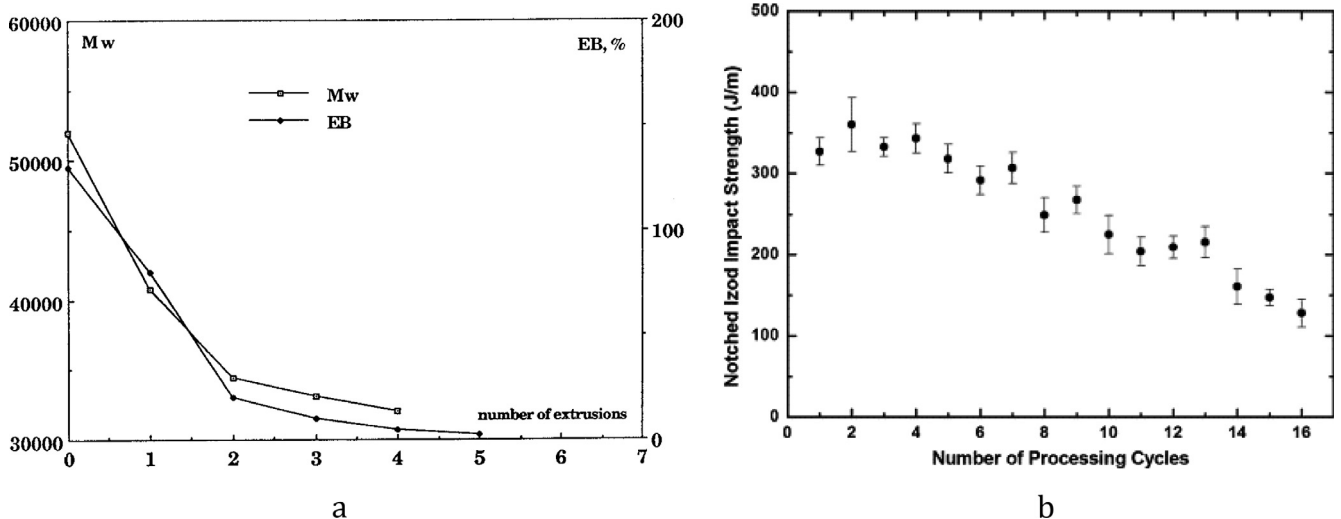


Fig. 12. (a) Molecular weight and elongation at break as function of number of extrusions for a PET sample (La Mantia, 1996b) and (b) Impact strength for a number of processing cycles of a PA6 sample (Su et al., 2007).

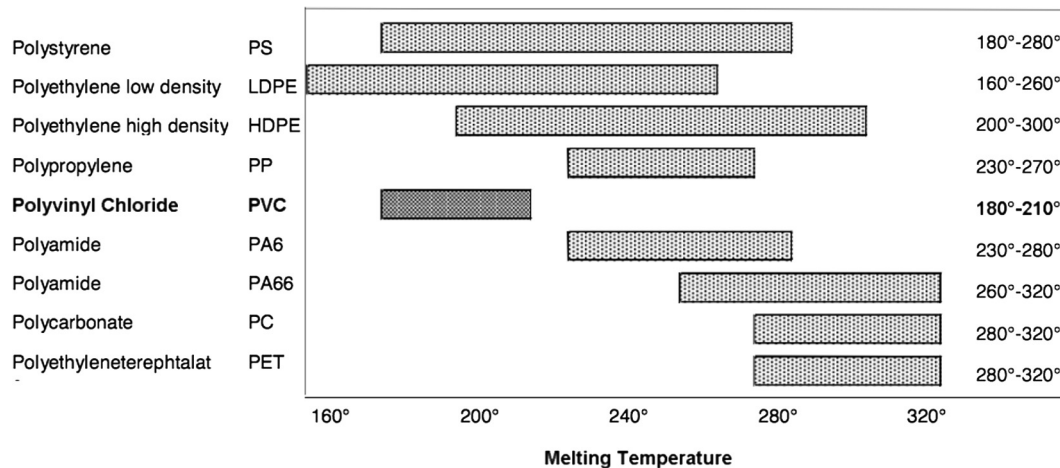


Fig. 13. Range of processing temperatures for common plastics (Moller and Jeske, 1995).

have mostly been consumed during the first lifetime and processing of the plastic (Ulatan, 2003). Next to heat stabilizers, also impact modifiers, crosslinkers, compatibilizers, pigments and fillers can be added (Murphy, 2001). A special case is the recycling of PET where postcondensation techniques are applied to improve the melt strength and mechanical properties (Dimonie, 2012). This will be discussed more in detail further on.

2.2.2. Degradation during lifetime

Plastic products are subjected to a combination of heat, oxygen, light, radiation, moisture and mechanical stress during their lifetime. The resulting degradation is mainly caused by photo-oxidation processes (La Mantia, 1996a). The structural changes in the polymer are very similar to the ones introduced by thermal-mechanical degradation. The main difference here is the presence of oxygen in the atmosphere (generally not present in processing machines). This leads to the formation of oxygenated groups on the polymer chain and will as such affect the final properties of the material.

Both degradation during lifetime and thermal-mechanical degradation yield low-molecular volatile compounds that are mostly trapped in the polymer when in the solid state. During reprocessing, however, these contaminants may diffuse through the melt and hinder the effective reprocessing. These contaminants cannot only compromise the product properties, but also the processing itself, since some may corrode the processing equipment. Proper degassing on recycling machinery is required to reduce this problem. These volatiles are small (oxygenated) fragments of the original polymer and can be identified by different analytical techniques like mass spectroscopy (Xiang et al., 2002).

2.2.3. Processing of complex mixtures

An additional challenge for the recycling of mixed plastic waste is the differences in melting points and processing temperatures between the polymers in the mixed plastics, as shown in Fig. 13. When reprocessing these mixtures, the recycler is often forced to reprocess them at the processing temperature of the highest melting component. This often leads to overheating and degradation of some lower melting components, which in turn reduces the final properties. This is especially relevant for mixtures containing both PVC and PET, wherein the elevated processing temperatures used for PET will accelerate the dehydrochlorination of the PVC (Moller and Jeske, 1995).

2.3. Mechanical recycling of mixed polymers

The mechanical recycling of mixed polymers ultimately always leads to the formation of polymer blends. A polymer blend consists of a mixture of two or more polymers (>2 wt%) (Utracki, 2002). The miscibility of blends is governed by their thermodynamics. The full thermodynamics of polymer blends is a complex matter, outside the scope of the current manuscript. A broad review concerning this topic can be found in the Polymer Blends handbook (Manias and Utracki, 2014). The following paragraph summarizes the most important parameters governing the (im)miscibility of blends.

2.3.1. (Im)miscibility of polymer blends

The simplest way of predicting the miscibility of polymers is by the Gibbs free energy of mixing (Manias and Utracki, 2014). The fundamental thermodynamic relationship between mixtures is shown in Eq. (1).

$$\Delta G_{mix} = \Delta G_{AB} - (G_A + G_B) \leq 0 \quad (1)$$

In this equation, the Gibbs free energy of the polymer mixture ΔG_{AB} has to be lower than the summation of the Gibbs free energy of the different polymeric constituents A and B. This can be rewritten to Eq. (2), showing that the Gibbs free energy consists of two terms, namely the enthalpy of mixing (ΔH_{mix}) and the entropy of mixing (ΔS_{mix}). T is the absolute temperature.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \leq 0 \quad (2)$$

Mixtures of different polymers can be (partially) miscible or immiscible depending on the thermodynamic equilibrium. A completely miscible blend will be formed if the Gibbs free energy is negative and moreover if the criterion in Eq. (3) is also fulfilled. φ is the volume fraction of component B.

$$(\partial^2 G / \partial \varphi) > 0 \quad (3)$$

Favourable mixing requires a negative Gibbs free energy. The increase in entropy for mixing of polymers (in contrast to smaller molecules) is however negligible, meaning that the enthalpy of mixing should be negative for most common polymeric systems. This is dependent on the specific interaction between both blend components (hydrogen bonding, ion-dipole, dipole-dipole, donor-acceptor and Van der Waals interactions). The more 'chemically alike' the two polymers are, the more compatible they will be (Koning et al., 1998). The basic theory for the calculation of the

Gibbs free energy was done by Flory and Huggins (Flory, 1942). By rewriting both the enthalpy and the entropy of mixing in Eq. (2), Eq. (4) is called the Flory-Huggins equation.

$$\Delta G_{mix} = kTN(\chi_{AB}\varphi_A\varphi_B + \varphi_A \ln(\varphi_A) + \varphi_B \ln(\varphi_B)) \quad (4)$$

In this equation, k is the Boltzmann constant, N is the mole fraction, T is the absolute temperature, φ_i is the volume fraction of component i and χ_{AB} is the Flory-Huggins interaction parameter, which has to be negative before spontaneous mixing occurs. χ_{AB} is a dimensionless parameter and is considered a measure for the interaction-energy between polymer A and polymer B in a blend. In the Flory-Huggins theory, χ_{AB} is a constant. In reality however, this parameter is strongly dependent on temperature, pressure and concentration. The exact calculation of this parameter is therefore rather complicated (Manias and Utracki, 2014). By using the Hildebrand solubility concept however, χ_{AB} can be calculated using Eq. (5). In this equation, V_m represents the mixing volume, R the gas constant, T the absolute temperature and δ_i the solubility parameter of polymer i . The solubility of the polymers is governed by the possible interactions between both components. The interactions are divided in dispersive (Van der Waals) forces (δ_{id}), polar forces (δ_{ip}) and hydrogen bonds (δ_{ih}) (Eq. (6)).

$$\chi_{AB} = \frac{V_m}{RT} [(\delta_A - \delta_B)^2] \quad (5)$$

$$\delta_i^2 = \delta_{id}^2 + \delta_{ip}^2 + \delta_{ih} \quad (6)$$

Completely miscible blends are called homogeneous blends and display a one-phase morphology. Immiscible blends on the other hand can have different kinds of morphologies (Utracki, 2002): spherical drops, cylinders, fibres, sheets or co-continuous phases (Fig. 14).

The resulting morphology of the blends depends on different parameters: the nature of the polymers (structure and molecular weight), their concentration and the processing parameters (equipment, temperature and viscosity ratio).

In typical polymer waste, the dominant polymers in quantity are the polyolefins (PP, PE), PET and PVC (PlasticsEurope et al., 2015). Blending a combination of these polymers always yields immiscible blends. A typical SEM (scanning electron microscopy) image of an incompatible PP/PET 85/15 blend is shown in Fig. 15. Within the PP matrix, spherical micron-sized PET droplets are dispersed.

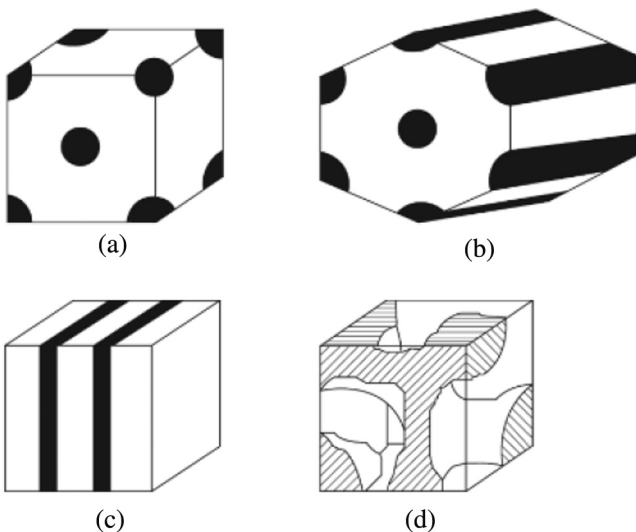


Fig. 14. Morphologies of immiscible polymer blends: (a) droplets (b) cylinder (c) lamellar and (d) co-continuous (Maier and Calafut, 2008).

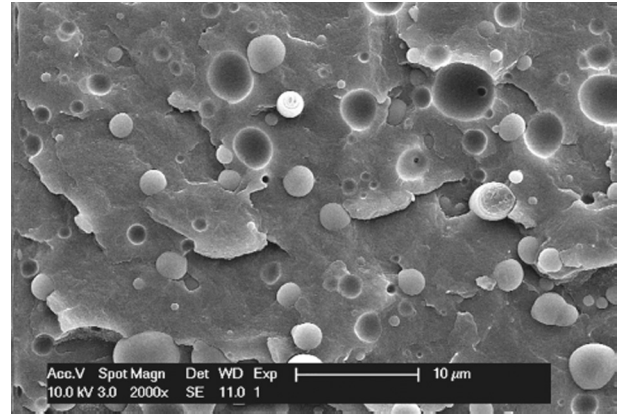


Fig. 15. Incompatible PP/PET 85/15 blend (van Bruggen et al., 2016).

2.3.2. Properties of polymer blends

Depending on the miscibility and the compatibility between the polymers, polymer blends can display synergistic, antagonistic or additive behaviour (Fig. 16). Most properties do not simply follow the additive law. However not every property behaves in the same way for the same polymer pair. For example, the tensile strength for an MPO-PP system follows the additive law, while the elongation at break displays the curve of a typical incompatible blend (Hubo et al., 2015). The elongation at break and impact properties are usually very sensitive to the distribution and dispersion of the second phase. Even the mixing of two types of PP (low and high molecular weight e.g.) can lead to a loss in properties due to differences in crystallization.

2.3.3. Use of compatibilizers

This immiscibility of polymer blends can be mitigated by different techniques. The go-to strategy is often the introduction of compatibilizers (Koning et al., 1998). A compatibilizing agent is a third component, which is introduced in the polymer blend and lowers the interfacial tension, thus promoting the interfacial adhesion between the immiscible polymers. This results in a uniform (and small) distribution of the dispersed phase and a stable morphology. The mechanism of compatibilization has to fulfil the following requirements in order to be effective (Utracki, 2002):

1. Lowering of the interfacial tension, resulting in a finer dispersion.
2. Stabilization of the resulting morphology against the effect of shear and temperature during processing.

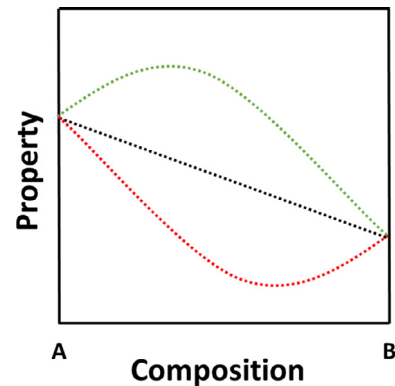


Fig. 16. Property - composition curve of blends; green = synergistic; red = antagonistic and black = additive. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Improving the adhesion between the different phases in the solid state.

Three main compatibilizer groups can be distinguished based on the interactions between the compatibilizer and the blend:

- Block or graft copolymers: these compatibilizers are built out of different polymer segments, and one of the polymer segment will be more compatible with the matrix phase and the other one with the dispersed phase. The compatibilizer will migrate towards the interface and reduce the interfacial tension. An example of this type is a block copolymer of PE and PP, used in mixed PE/PP blends.
- Non-reactive polymers containing polar groups: the interfacial tension is reduced by the secondary intermolecular interactions between these polymers. The non-reactive polymer will be compatible with the matrix. The compatibilization will be influenced by the type of secondary interaction (Van der Waals < dipoles < hydrogen bonding). PMMA and polycaprolactone (PCL) are example of this type of compatibilizers.
- Reactive functionalized polymers: the reactive group will covalently bond to the dispersed phase and the polymer backbone is compatible with the matrix. The adhesion between phases will be the highest for these types. Examples of this type of compatibilizer are PP grafted with maleic anhydride (PP-g-MA) or PP grafted with glycidyl methacrylate (PP-g-GMA).

An example of the different compatibilization mechanisms of SEBS-g-GMA (triblock copolymer styrene/ethylene butylene/styrene grafted with GMA) on a blend of PP and PET is showed in Fig. 17. Different types of interactions simultaneously occur and all contribute to the reduced interfacial tension and the improved

adhesion. This can also be seen on the SEM micrographs in Fig. 18. Fig. 18a is the incompatible PP/PET blend with PET dispersions in a range between 1 and 3 μm . Adding 2.5 wt% SEBS-g-GMA (Fig. 18b) to this blend reduces the PET dispersions size below 1 μm . The change in morphology also increases the final mechanical properties (van Bruggen et al., 2016).

Quite a lot of research has been done on selecting the most appropriate compatibilizer for a certain polymeric system. Table 1 shows commonly used compatibilizers for different polymeric systems.

2.4. Typical examples of mechanical recycling

2.4.1. PET

The recycling of PET is a typical example of a broadly implemented PC recycling process. According to Petcore, the PET recycling rate in 2014 for bottles and containers in Europe was at 57% (Petcore). This recycling rate is very high compared to other disposed plastics. The process of PC PET recycling consists of different parts: collection, sorting and reprocessing into a product. Collection of PET in Europe is governed by the European Union directive on Packaging and Packaging Waste (2004/12/EC). This directive states that each member state must set up a collection scheme, but is free to choose the most suitable method themselves. Existing collection methods are curbside collection, drop-off locations or the refill and deposit system. The important factors here are the overall collection quantities and the amount of contamination. Each system has its advantages and drawbacks. Between the different member states, collected quantities differ quite a lot.

After collection, the PET is sorted from the other contaminating plastic waste (HDPE, PVC, etc.) through hand sorting or automated systems and afterwards compressed into bales for easier trans-

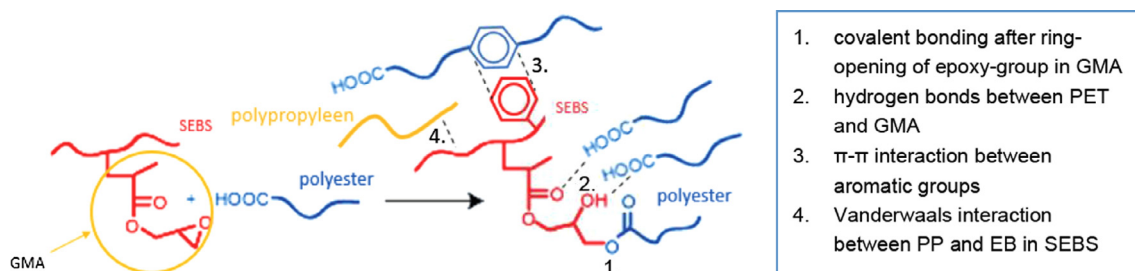


Fig. 17. Interactions between SEBS-g-GMA (red) and PP (yellow) - PET (blue, marked as polyester). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

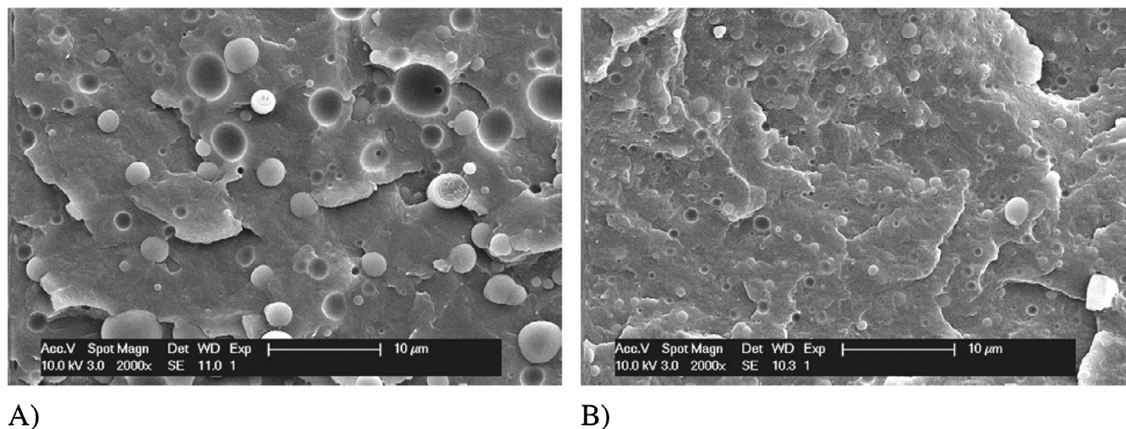


Fig. 18. (a) Incompatible PP/PET 85/15 blend and (b) PP/PET 85/15 blend compatibilized with 2.5 wt% SEBS-g-GMA (van Bruggen et al., 2016).

Table 1
Commonly used compatibilizers for different polymeric systems.

Polymeric system	Commonly used compatibilizer	References
PE-PET	PE-g-AA, PE-g-IA, PE-g-GMA, SEBS, SEBS-g-GMA, SEBS-g-MA	El-Nashar et al. (2008), Jeon et al. (2005), Koning et al. (1998), Pluta et al. (2001), Sanchez-Valdes et al. (2013), and Zhang et al. (2011))
PP-PET	PP-g-AA, PP-g-MA, SEBS, SEBS-g-MA, SEBS-g-GMA, EVA, EVA-g-MA	Champagne et al. (1999), Koning et al. (1998), Lepers et al., (19970, Pang et al. (2000), Papadopoulou and Kalfoglou (2000), van Bruggen et al. (2016) and Xanthos et al. (1990)
PP-PE	EVA, EPDM, SEBS	Blom et al. (1998), Kallel et al. (2003), Koning et al. (1998), and Souza and Demarquette (2002)
PP-PA	PP-g-GMA, PP-g-MA, SEBS-g-MA	Holsti-Miettinen et al. (1994), Koning et al. (1998), and Lin et al. (2013)
PE-PA	PE-g-MA, PE-g-GMA	Chiono et al. (2003), Dasedemir et al (2015), Jiang et al. (2003), and Yao et al. (2000)
PP-PS	SBS, SEBS, EVA	Hlavatá et al. (2001) and Ismail and Nasir (2002)
ABS-PC	ABS-g-MA, PP-g-MA, epoxy resins, PMMA	Elmaghor et al. (2004), Jin et al. (1998), Tjong and Meng (2000), and Zhang et al. (2001)
PC-PS	PC-g-PS, PS-Par, SEBS-g-PC	Chevallier et al. (2013), Ohishi et al. (2001), and Pu et al. (1998)

portation. Finally, these PET streams are reprocessed into new products, mostly packaging applications (bottles and containers), but also turned into fibres or new applications. These PET streams

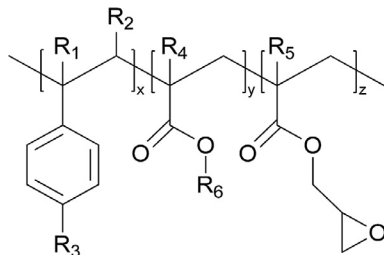


Fig. 19. Chemical principle of a PET chain extender.

must be as clean as possible to avoid contaminations, which inevitably lead to a decrease in final properties or difficulties in reprocessing (Awaja and Pavel, 2005).

Different techniques are used to counter the thermal-mechanical degradation and accompanied M_w reduction of recycled PET. This is mostly done to increase the melt strength and facilitate further processing. The most common techniques are:

- Solid-state post-condensation: this process involves heating of the PET at a temperature between the glass transition temperature and the melting temperature in a reactor. Condensation reactions occur between the chains terminal groups in the amorphous phase of the polymer, in a temperature range of 200–240 °C. The reaction proceeds under vacuum to remove by-products (Welle, 2011);

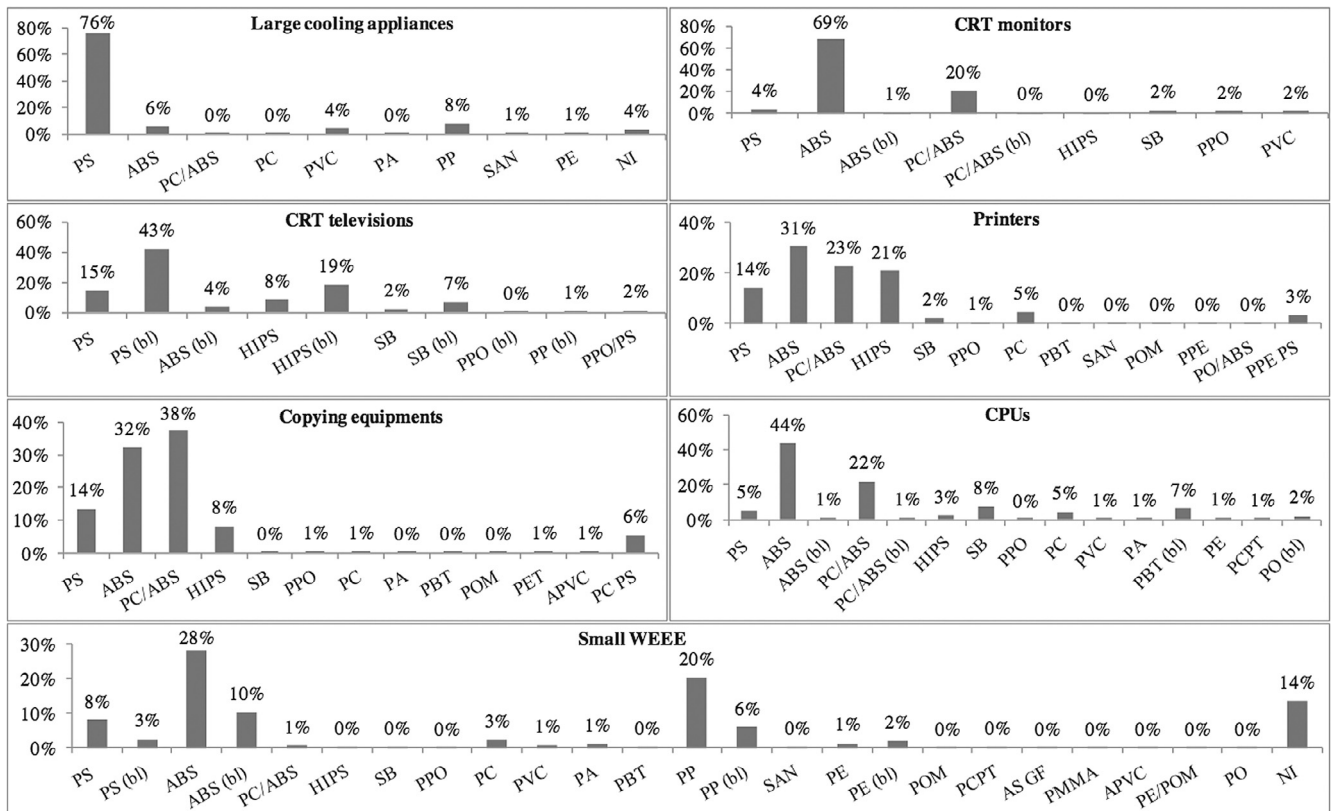


Fig. 20. Plastic composition for WEEE appliances (Martinho et al., 2012).

- Addition of chain extenders (Awaja and Pavel, 2005): in this process, a low (or moderate) molar mass compound with different functional groups reacts with the hydroxyl PET end-groups to crosslink the affected polymer chains, resulting in chain extension and/or branching and an increase of M_w . A commercial example of a chain extender is Joncryl from BASF (Baden Aniline and Soda Factory), which is a multifunctional epoxy-based oligomer (Fig. 19).

2.4.2. SPW from WEEE and ELV

Both WEEE (Waste of Electric and Electronic Equipment) and ELV (End-of-Life Vehicles) provide an abundant source for the more technical (non-polyolefin) thermoplastic polymers like ABS, PC, (High Impact)PS and ABS-PC blends (Beigbeder et al., 2013; Buekens and Yang, 2014; Guo et al., 2009; Stenvall et al., 2013; Tarantili et al., 2010). A sample composition of WEEE plastics per product type is shown in Fig. 20. This mix is often further separated into the individual polymers with heavy-medium flotation (Al-Salem et al., 2009a).

Of these polymers, the most effectively recycled is ABS. However, ABS is sensitive to degradation both during its lifetime (UV and oxygen induced) and during processing (thermo-mechanically induced). The mechanisms involved are both chain scission and crosslinking (Arostegui et al., 2006; Peydro et al., 2013; Scaffaro et al., 2012), as shown in Fig. 21. Additionally, volatile components (mainly styrene derivatives) may develop during the product lifetime due to environmental degradation. These are freed during the reprocessing of the ABS, potentially leading to void formation in the recycled ABS extrudate (Arnold et al., 2009) and reduction of impact strength (Bai et al., 2007).

This degradation will inevitably lead to inferior mechanical properties of rABS, when compared to virgin ABS. Impact strength and ductility are foremost among these (Bai et al., 2007; Boldizar and Moller, 2003; Brennan et al., 2002; Peydro et al., 2013).

Routes for upgrading recycled ABS primarily include blending with virgin ABS (Scaffaro et al., 2012; Van Damme et al., 2016), and the addition of impact modifiers like SEBS rubber (Peydro et al., 2013; Van Damme et al., 2016) or chain extenders (Wang et al., 2015b).

Some specific WEEE products like printed circuit boards contain mostly (thermoset) phenolic resins as polymer component, up to 40 wt% (Mou et al., 2007). Currently, the only viable pathway for mechanical recycling of these waste streams is pulverization and subsequent use as a filler in both thermosetting and thermoplastic resins (Guo et al., 2009). Similar to the use of talc (Leong et al., 2004), it is possible to use pulverised epoxy waste from circuit

boards as strengthening filler in PP. With a loading of up to 30%, it has been found that (both tensile and flexural) strength and modulus increase proportionally for a PP matrix, as does temperature resistance (expressed by an increase in Vicat softening temperatures) (Zheng et al., 2009).

The mechanical recycling of polymers from WEEE and ELV is currently complicated by the presence of certain brominated flame retardants (BFR) like pentabrominated diphenyl ethers (PBDE) and decabrominated diphenyl ethers (DBDE), which have been banned as an additive for new products (Stenvall et al., 2013; Vilaplana and Karlsson, 2008). However, methods for detection of BFR-holding polymers do exist (Vilaplana and Karlsson, 2008) and even the extraction of BFR from the melt is possible with techniques like supercritical-fluid extraction (Altwaiq et al., 2003) or ultrasonic extraction (Pohlein et al., 2005).

2.4.3. SPW from post-consumer packaging waste

In several EU countries (e.g. NL, DE, IT), PC packaging waste (PC-PPW) is collected and processed separately. In some countries, like BE, pilot projects are running to evaluate the feasibility (FostPlus, 2014). Typically, such countries also have a separate collection system (often based on a deposit system) in place for PET bottles. Therefore, PET bottles are considered exclusive to this waste stream. The dominant polymers in PC-PPW are PET (from thermoformed food trays), PP (trays), LDPE (foils), PVC (flexible packaging), ABS and (E)PS (yoghurt pots, food trays) (Bonifazi et al., 2016). A detail of a typical composition for such waste is given in Table 2.

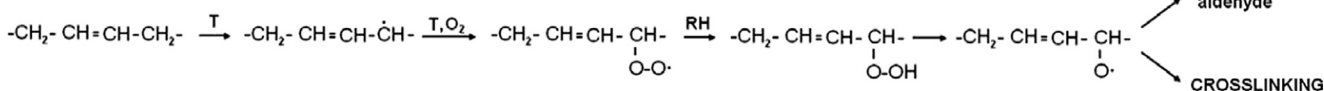
An important fraction of PC-PPW materials is made up of multilayer products (Luijsterburg and Goossens, 2014). These include PET/PE, PET/PE/EVOH or PA/PE. Typically, initial sorting of PC-PPW is done by flotation in water: the polyolefins (PP and PE) will

Table 2

Typical composition of a sample PC-PPW (Bonifazi et al., 2016).

Waste	% Weight
PET	26.80
PVC	24.90
Rubber	3.10
PS/ABS	9.60
PA/PBT and other polymers	5.40
PE/PP (added)	11.90
PE/PP	5.50
PAPER/FIBRE	4.20
METAL/INERTS	8.60

a PB phase



b PB-SAN grafting sites

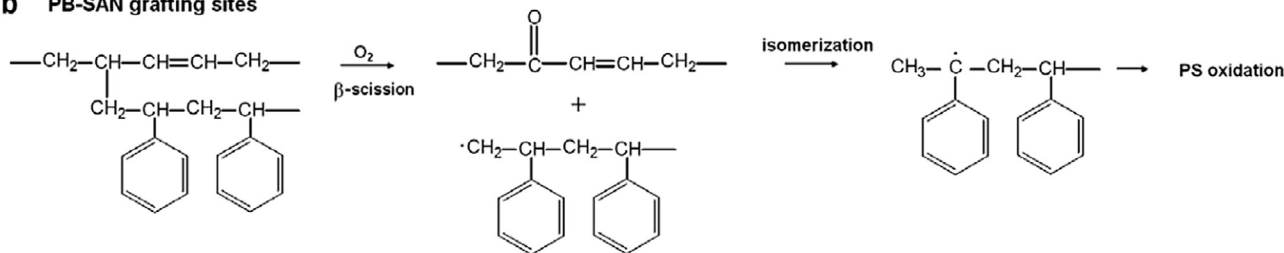


Fig. 21. Degradation mechanisms in ABS. (a) in the poly-butadiene (PB) phase and (b) at the PB-SAN grafting sites (Scaffaro et al., 2012).

Table 3

typical properties for hard and soft MPO fractions (Hubo et al., 2014) values are shown as mean \pm standard deviation.

Material	Notched Charpy impact (23 °C) [kJ/m ²]	Young's modulus [MPa]	Tensile strength [MPa]
Hard MPO	3.22 \pm 0.15	1095 \pm 95	14 \pm 0.5
Soft MPO	9.88 \pm 1.12	569 \pm 31	14 \pm 0.6

float and the sink fraction will contain mostly PET (around 50%), multilayers, PP (talc-filled), PS and PVC (Bonifazi et al., 2016). Small amounts of ABS, PMMA, PC and PA might occur.

This complex sink fraction is currently sent to energy recovery (Bonifazi et al., 2016). The MPO fraction, however, is usually valorised through mechanical recycling. MPO fractions are commonly a combination of PP and (mostly) HDPE from 'hard plastics' or a combination of PP and (mostly) LDPE from 'soft plastics', i.e. foils. This equates to the hard MPO and soft MPO fractions discussed in the sorting scheme of Fig. 8. By experimental estimation, the composition of a hard MPO fraction is about 60% PP and 30% PE (Hubo et al., 2014). The rest is a mixture of non-polyolefin plastics and floating contaminations like wood or cork.

Mechanical properties for these unmodified industrial MPO's have been reported as shown in Table 3. Typically, the hard MPO will have higher strength properties but lower toughness and the soft MPO, with its large amount of LDPE, will have high impact strength but inferior stiffness.

Even these similar polymers like PP and PE turn out to be immiscible in the melt (Liu and Truss, 1996; Teh et al., 1994; Utracki and Dumoulin, 1995). Furthermore, it has been shown that the properties of the MPO blends strongly depend on (i) the individual polyolefin characteristics and (ii) the mixture composition. The latter will affect blend morphology, which will in turn determine whether or not the resulting mechanical properties like modulus and elongation at break follow a proportional law-of-mixtures. Impact strength, which is strongly dependent on interfacial adhesion, usually does not follow any law-of-mixtures and will display the antagonistic behaviour from Fig. 16 (Delva et al., in press; Hubo et al., 2015).

Typical products for mechanical recycling of MPO include garden furniture, outdoor flooring and boards for stables or water edges. Industry would like to move into higher-level products as well. Therefore, much research is conducted on improving either the stiffness or the impact toughness of the MPO materials.

Common low-cost strategies to improve the toughness of recycled MPO, through a combination of impact modification and compatibilization effects, include the addition of EPDM (ethylene propylene diene monomer) rubbers (Banerjee et al., 2016; Delva et al., 2013) or ethylene/propylene block copolymers (EPR) (Radonjic and Gubeljak, 2002). Results strongly depend on the quality of the recycled MPO, as contaminations are known to adversely affect the effectiveness of the compatibilization (Kazemi et al., 2015). For improvement of strength, additives like inorganic (ceramic or glass) fibres (Borovanska et al., 2016; Kuram et al., 2014) or natural fibres (Akeson et al., 2016; Ares et al., 2010; Twite-Kabamba et al., 2011) have been used. Other efforts to upgrade the properties of recycled MPO include blending with virgin LDPE (Delva et al., in press; Guerfi and Belhaneche-Bensemra, 2014) or high-quality recycled mono-PP (Hubo et al., 2015). It has also been shown that MPO could be considered for specialty applications like mirror welding, where the can replace high-purity recycled PP. It was found that HDPE 'contaminations' up to 20 wt% do not adversely affect the mirror welding process (Hubo and Ragaert, 2016).

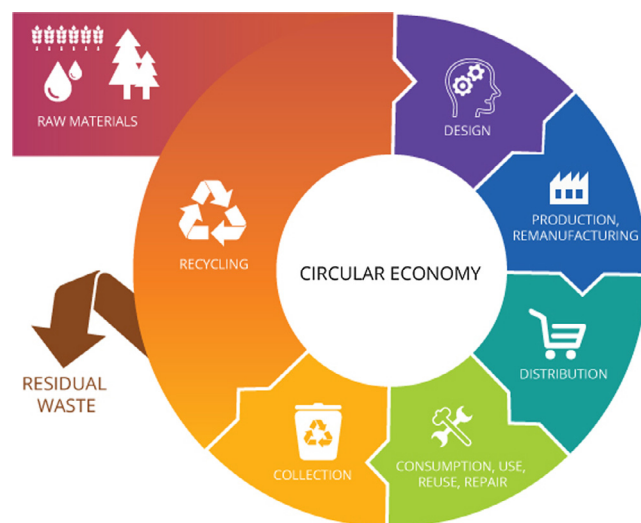


Fig. 22. Schematic of the principles of the Circular Economy (EU-Parliament, 2015).

2.5. Design and recycling

The design of plastic products has a large impact on both their recyclability (at end-of-life, EoL) and the degree to which they can incorporate recycled materials (at start-of-life, SoL).

Design for Recycling is, via the Ecodesign Directive (European Commission, 2009), heavily promoted by the EU within the framework of the Circular Economy, a schematic of which is shown in Fig. 22. It is a well-known product development strategy in which new products are developed so that they can be recycled at their EoL. It entails easy separation of different materials and an all-round efficient material use (Rodrigo and Castells, 2002). The strategy is part of a virgin material's SoL.

In the European Commission's latest Circular Economy Package (CEP), it was proposed to make mandatory a 'product design...to make it easier and safer to dismantle, reuse and recycle electronic displays' (European Commission, 2015). It is expected that other product categories will follow. Additionally, Design for Recycling is encouraged via the implementation of Extended Producer Responsibility (EPR) schemes, wherein the EoL costs will factor as an economic incentive to producers (European Commission, 2015). Design for Recycling, as such, only covers the EoL in terms of recycling/recyclability.

The authors would like to advocate also considering design at the product's SoL and this is where Design from Recycling comes in (Ragaert, 2016; Ragaert et al., 2016). In Design from Recycling, the secondary raw material originating from the recycled polymer waste of a previous product's EoL is the starting point of a new product development. Design from Recycling involves the following key aspects (Ragaert, 2016):

- Identifying the recycled polymer's strengths and weaknesses through extensive characterization.
- Matchmaking between the recycled material's characteristics and potential (new or existing) products.
- Adapted product (and mould) design for manufacturing of the products in recycled polymers.
- If needed, identifying acceptable (cost-effective) strategies for the upgrading of the material quality (to product requirements) where necessary. This usually involves small amounts of additives like stabilizers or compatibilizers.
- Through life cycle analysis (LCA), life cycle costing (LCC) and Resource Efficiency calculations, quantifying the overall resource efficiency of the whole process, thus ensuring the best

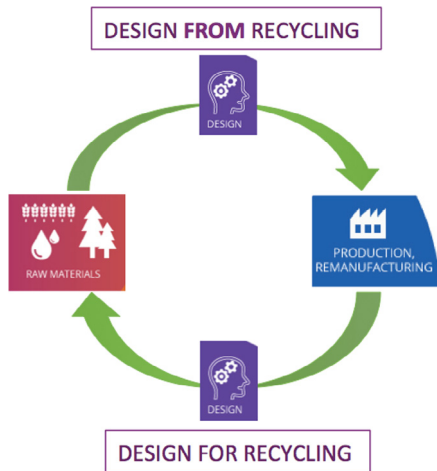


Fig. 23. The complementarity of Design for and from Recycling in the Circular Economy (icons). adapted from EU-Parliament (2015)

possible use of the recycled polymers as well as demonstrating to the broader public the gain that is to be had by using these secondary material sources.

Design from Recycling needn't be closed-loop. It is perfectly valid – and often necessary – to valorise a recycled material outside its original product application. For example, this could be because a packaging material cannot (legally) be re-used in a food-contact application or because the recycled material has an entirely different composition and properties set compared to the virgin (recycling of multilayers, which become blends).

Design from Recycling, being a relatively new concept, is not without its challenges. It requires a close collaboration between (materials) engineers and product designers, two classes of professionals that typically think and speak in a different 'language'. A tool for harmonisation between the two is required (Veelaert et al., 2016). Furthermore, the volatile feedstock prices of virgin materials steadily undermine the economic incentive for industry to take up recycled materials in production.

Design for and from Recycling are in fact complementary strategies that, when applied together, can truly bring a material full-circle. Simplifying the schematic from Fig. 22, this principle is illustrated in Fig. 23.

3. Chemical recycling

Plastic waste seems to be a very promising feed in the production of valuable chemicals and fuels. The current interest is not only in recovering energy or in mechanical recycling but also in the production of valuable products such as monomers or petrochemical feedstocks.

For some feedstocks such as PET, PUR and nylon, chemical recycling options exist. The interest in using them as feedstock has been growing steadily, as these are closely related to the conventional petroleum fractions and have high hydrocarbon content. Unlike biomass, plastic waste and in particular polyolefin waste, do not contain significant amounts of oxygen. Therefore, higher carbon efficiency can be expected and hence, higher gross margins. In the following section, different types of technologies for processing these SPW streams are reviewed. Known processes to handle this feed stream are gasification, pyrolysis, fluid-catalysed cracking and hydrocracking. The main focus of this section will be those

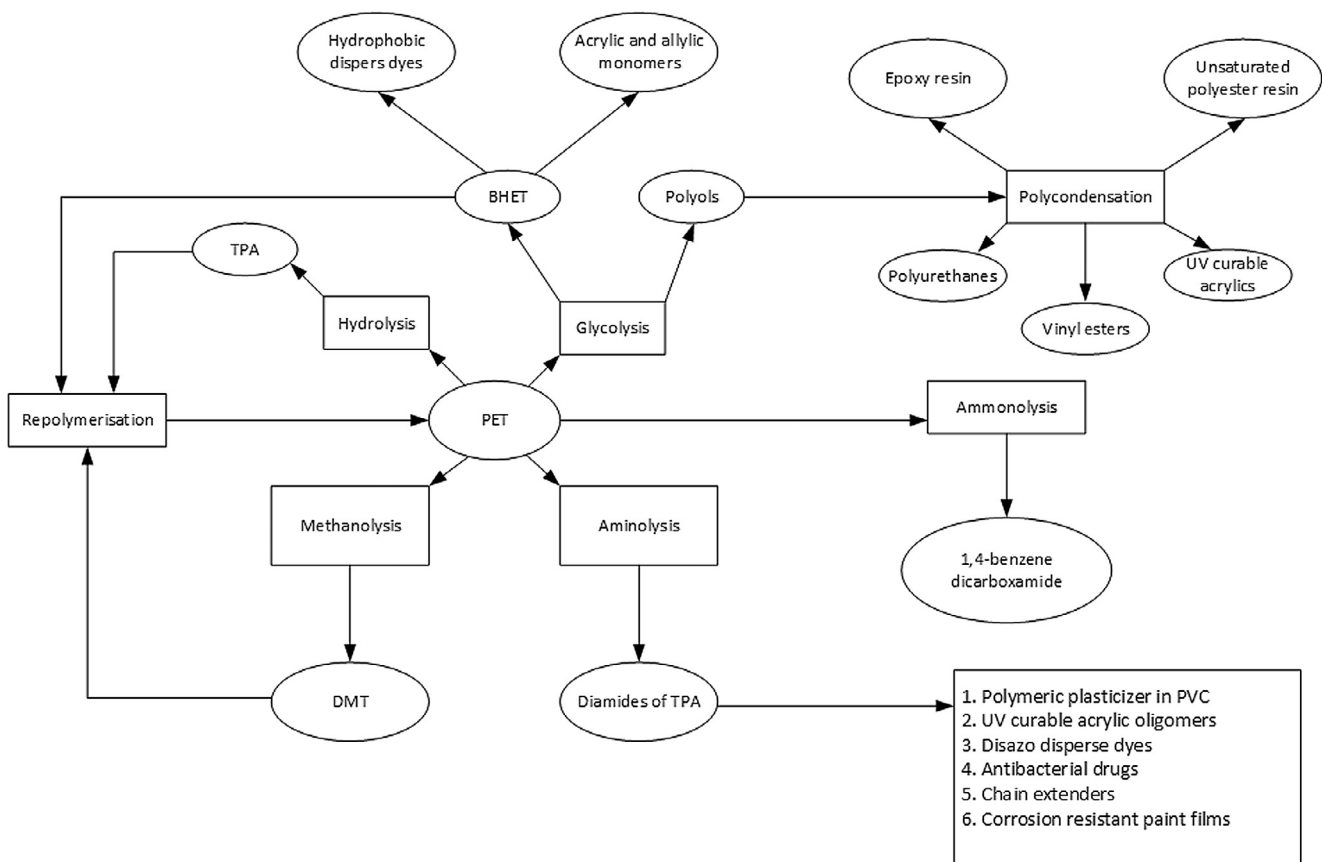


Fig. 24. Different methods of PET chemolysis and the value-added products derived thereof (Aguado and S, 1999).

types of chemical recycling that consist of either monomer recycling or feedstock recycling. Both paths have been recognized as ideal methods for the preservation of limited resources and for the protection of the environment by decreasing the volume of non-degradable waste (Al-Salem et al., 2009a, 2010).

3.1. Chemolysis

Chemical recycling is an accepted recycling method that follows the principles of “sustainable development”. The fact that chemically recycled plastics can be well-suited for food applications has steadily increased an interest in the various chemolysis possibilities. Chemical recycling methods are opening newer pathways for using waste as a precursor in generating pure value-added products for various industrial and commercial applications. However, it has to be stressed that chemically recycled polymers are more expensive than the virgin material because of the raw material cost, capital investment, and scale of operation. For example, it has been calculated that for a PET chemolysis facility to be economically viable, a minimum throughput of 1.5×10^4 tonnes per annum is required (George and Kurian, 2014).

3.1.1. Chemical recycling of PET

Chemical recycling of PET can completely depolymerize it into its monomers terephthalic acid (TPA), dimethyl terephthalate (DMT), bis(hydroxyethylene) terephthalate (BHET), and ethylene glycol (EG). In this case, depolymerization is the reverse reaction of the polymer formation route. PET can also be partially depolymerised to oligomers or other chemical substances. There are different depolymerization routes such as methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and hydrogenation, depending on the chemical agent used for the PET chain scission. Fig. 24 summarizes the different options for PET chemolysis, as well as the type of products that can be derived from PET depolymerisation.

PET methanolysis is based on the treatment of PET with methanol at relatively high temperatures (180–280 °C) and pressures (20–40 atm), which leads to the formation of DMT and EG as the main products. The degradation products of PET after glycolysis and aminolysis find potential applications as plasticizers, cross-linking agents, chain extenders, corrosion inhibitors, and precursors in the generation of value-added products such as UP resins, polyurethanes, textile dyes, antibacterial drugs, epoxy resins, and vinyl esters.

Hydrolysis, i.e. the reaction of PET with water under neutral, acidic, or basic conditions at high temperature and pressure, breaks the polyester chains into TPA and EG. The main drawbacks are the low purity of TPA and the fact that this is a comparatively slow option because water is a weak nucleophile.

Glycolysis is the simplest and oldest method of PET depolymerization. It is even a commercial PET recycling method practiced by renowned companies worldwide such as DuPont/DOW, Goodyear, Shell Polyester, Zimmer, and Eastman Kodak (Scheirs, 1998). It is a versatile recycling method because, besides the formation of monomers, specialized oligomeric products such as α,ω -dihydroxy materials (polyols) are also produced. The latter can be further utilized for the synthesis of polymers such as unsaturated polyesters, polyurethanes, vinyl esters, epoxy resins, etc. Glycolysis is the preferred recycling option when the incoming PET feed is of high quality. It is absolutely not suited for the removal of low levels of copolymers, colorants or dyes. It is best suited to the recovery of PI scrap (Scheirs, 1998). Glycolysis involves the transesterification of PET with an excess of glycol at temperatures in the range of 180–250 °C, promoting the formation of BHET. Different glycols, such as EG, diethylene glycol (DEG), propylene glycol (PG), polyethylene glycol (PEG), 1,4-butanediol and hexylene

glycol, can be used for the glycolysis of PET. Because the process is sluggish in the absence of any catalyst, transesterification catalysts are usually employed (George and Kurian, 2014). Glycolysis of waste PET proceeds through three stages: oligomers, dimers, and monomers. The glycol diffuses into the polymer, causing the polymer to swell, thus increasing the diffusion. The glycol subsequently reacts with an ester bond in the chain and degrades the PET into lower fractions. George and Kurian showed that the reaction parameters such as reaction time, temperature, catalyst concentration, and PET:reagent ratio have great significance on the efficient depolymerization of PET. These reaction conditions can be ranked according to decreasing importance as: catalyst concentration > reaction temperature > reaction time (George and Kurian, 2014).

3.1.2. Other chemical recycling processes

Sub- and supercritical fluids such as water and alcohol are excellent reaction media for depolymerization or decomposition of plastics. By using sub- and supercritical fluids, polymer decomposition can in some cases proceed rapidly and selectively. In this way it is possible to convert condensation polymers with ether, ester, or acid amide linkages by solvolysis back to their monomers. Indeed, these condensation polymers are relatively easily depolymerized into their monomers without using a catalyst in water or alcohol, which act as reactant as well as solvent. Also, addition polymers can be decomposed with or without catalysts in sub- and supercritical fluids. Composite plastics such as fibre-reinforced plastics are decomposed into smaller molecular components and fibre materials (Goto, 2009; Oliveux et al., 2012).

PA6, which is a polymer synthesized by ring-opening polymerization of ϵ -caprolactam, can be depolymerized by hydrolysis in sub- and supercritical water. ϵ -Caprolactam and ϵ -aminocaproic acid can be collected in the liquid phase. The total yield of these monomers was about 100% for reactions at 573 K in 60 min and at 603 K in 30 min.

Matsushita Electric Works, Ltd., Japan has been developing a technology for the depolymerisation of flame retardant polymers (FRP) using hydrolysis in subcritical water. In their technology, thermosetting resin in FRP can be recycled into basic materials with a material recycling rate of 70%. The concept of their subcritical water recycling process is illustrated in Fig. 25. After subcritical water hydrolysis, the resin is dissolved into a liquid. The recovered components such as glycols and fumaric acid can then be separated from the aqueous solution and polymerized into polyester with fresh resin material to produce recycled resin. Also, a styrene-fumaric acid copolymer (SFC) could be separated from the aqueous phase.

3.2. Pyrolysis

Pyrolysis is an interesting technology for plastic waste feeds that are difficult to depolymerize and that are currently not (mechanically) recycled but incinerated and/or dumped to landfill such as mixed PE/PP/PS, multilayer packaging, fibre-reinforced composites, polyurethane construction and demolishing waste. Especially these newer multilayered films seem to be much harder to recycle than the simpler metal, paper, and glass containers they replace. Fig. 26 shows such a typical structure of a highly engineered multilayer package material. The workhorse is PE, because it will be the least expensive. PE gives the packaging its bulk and structural integrity. If more toughness is needed, a packaging company might opt for PET, the resin of choice for beverage containers. Most food packages need a barrier layer to protect against oxygen. Ethylene-vinyl alcohol (EVOH) is popular because it is more effective in blocking oxygen than PE, PET, or nylon. If even more barrier is needed, a package might incorporate metallized film. One can

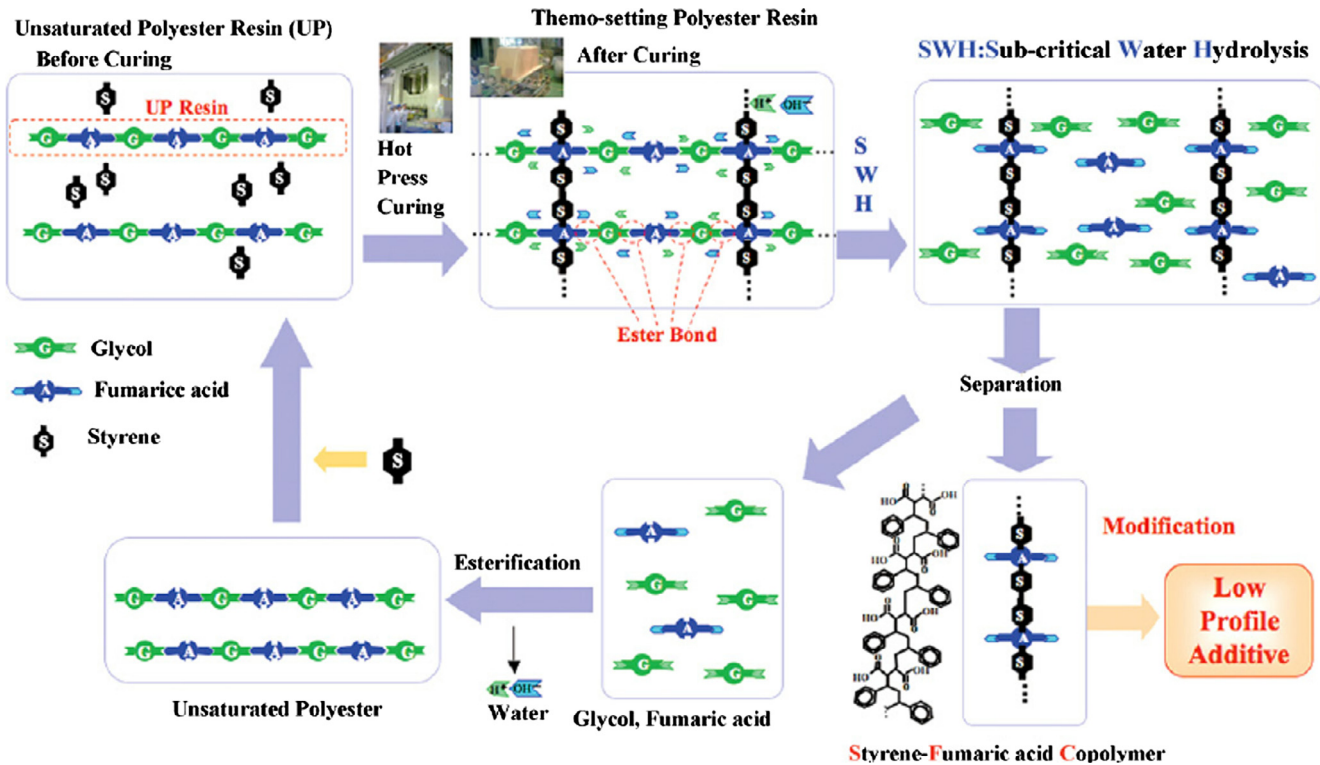


Fig. 25. Concept of FRP recycling developed at Matsushita Electric Works, Ltd.

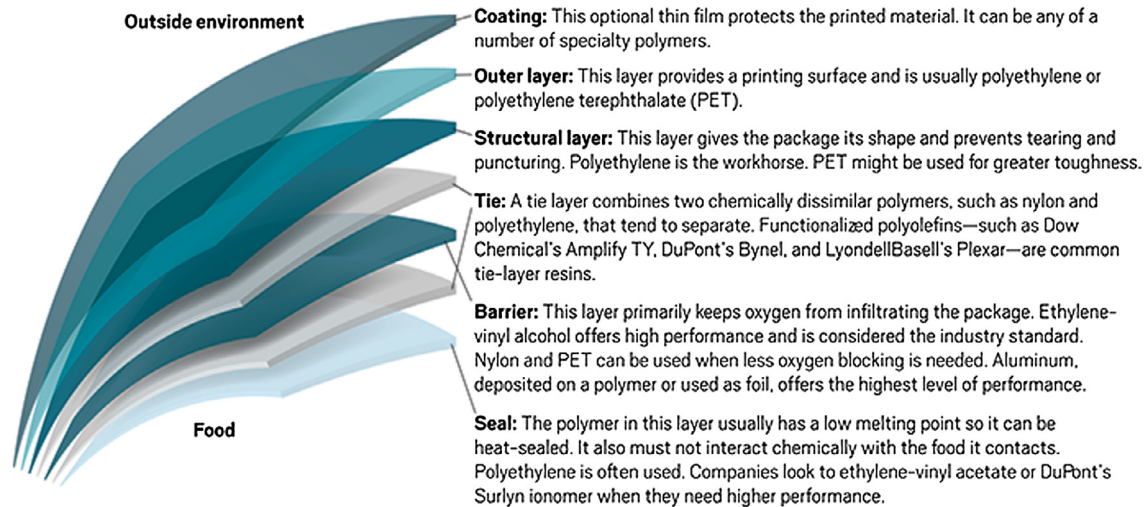


Fig. 26. Architecture of modern multilayer packaging materials (Tullo, 2016).

immediately see that depolymerization or mechanical recycling is no longer an option and tougher methods are needed, and here pyrolysis comes into play. Unlike mechanical recycling, this option can handle highly contaminated, such as automotive shredder residue, and highly heterogeneous mixtures of plastics increasing the flexibility of the process with respect to feedstock (Vermeulen et al., 2011). This is the main advantage as economic viable and satisfactory separation of all the different types of plastic is hardly achievable (Al-Salem et al., 2010).

The pyrolysis process takes place at moderate to high temperatures (500 °C, 1–2 atm) in absence of oxygen. The high temperatures allow to break down the macrostructure of the polymer to form smaller molecules (Angyal et al., 2007). Depending on the

nature of the polymer, either depolymerisation or random fragmentation will dominate. The pyrolysis products of SPW can be decomposed into three fractions: gas, liquid and solid residue (Al-Salem et al., 2009a,b, 2010). As an example, the process scheme in Fig. 27 shows the implementation of a novel vortex reactor technology in a classical plastic waste pyrolysis plant design equipped with a conventional separation section. Several demonstration plants have been built and are operational as summarized in Table 4.

A key difficulty of the pyrolysis process is the complexity of reactions that occur, especially when mixed streams are processed. Different polymers give rise to completely different product spectra, according to their dominant decomposition pathway. Even

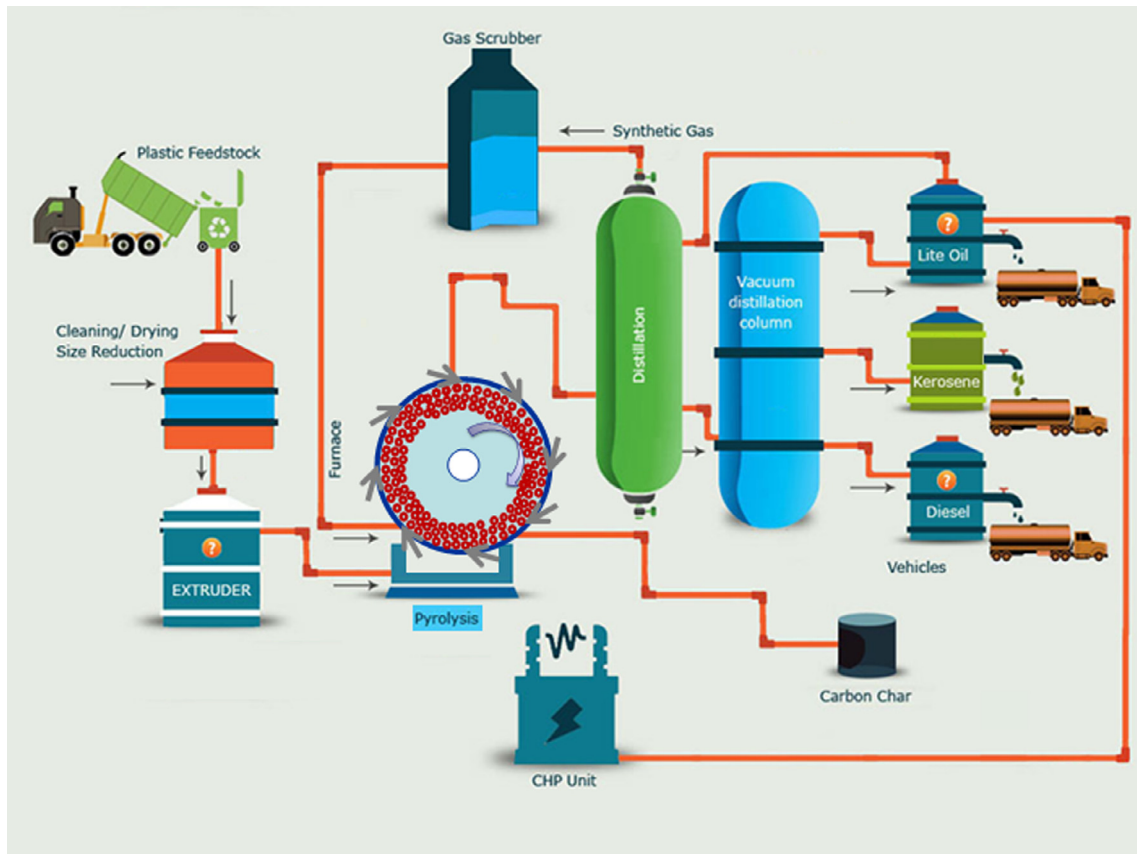


Fig. 27. Process Flow Diagram of a classical pyrolysis plant with a novel vortex reactor technology.

Table 4
Overview of commercial or pilot plant of plastic pyrolysis processes (Butler et al., 2011).

Process	Location	Capacity	Status
Mogami-Kiko	Japan	3 t/d	Operational
Royco Beijing	China	6 kt/d	Unknown status
Sapporo/Toshiba	Japan	14.8 kt/a	Operational
ALTIS	Japan	Unknown	Commercially applied
Gossler Evitec	Germany	1 kt/a	Status unknown
Changing World Technologies	USA	10 Mgal/year	Demo

the presence of certain impurities can substantially affect the product distribution and make that the obtained product lose a substantial part of its value, for example certain oxygenates that lead to the formation of methanol or formaldehyde. To make it even more difficult, PE and PP have the tendency to randomly fragmentize while polytetrafluoroethylene (PTFE), PA, PS and PMMA can be pyrolysed into products containing mostly their respective monomers. For example PMMA pyrolysis has a remarkable monomer yield of near 98% (Garforth et al., 2004). These polymers can be depolymerized and hence both from an economical and environmental point of view, this is the most interesting route to valorised these waste streams. On the other hand, the product spectrum of PE and PP is very broad and is characterized by a skewed distribution. This is due to the random fragmentation mechanism of these resins (Ranzi et al., 1997). Hence, further processing is needed, resulting finally in petrochemical feedstock such as naphtha or diesel.

Although pyrolysis is a simple technology it is only economically viable when carried out in large volumes at present. The latter

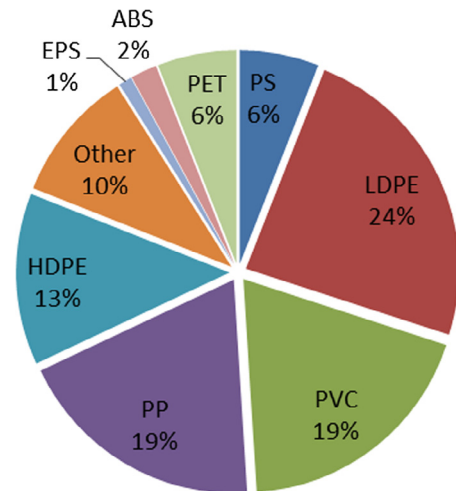


Fig. 28. Average plastic consumption by polymer type in an European context (Brems et al., 2012).

implies that today only the most common polymers and their mixtures are suitable for conversion to either monomers or liquid energy carriers/petrochemical streams. These are PE, PP, PS and PVC and they represent approximately 80% of the polymers being produced in Europe, see Fig. 28. Other waste plastics have a marginal contribution to the waste stream and hence specific valorisation of these streams cannot significantly contribute to a commercial high scale production facility such as a pyrolysis plant. This is primarily related to the complexity of the separation section if complex mixtures are used. At present, distillation is the only

technique that can be used to purify the obtained monomers and the formed liquids. In some cases, even complex extractive separation technologies are needed, such as for the recovery of certain aromatics. Moreover, the strict specifications on the monomers' purity imply that large distillation towers are needed, with high cooling duties. However, by integrating pyrolysis in an existing olefin complex, investment costs could be drastically reduced.

One of the other main issues with pyrolysis of SPW is the presence of PVC in the stream (Bhaskar et al., 2003; Okuwaki, 2004; Rijpkema, 1999; Sadat-Shojai and Bakhshandeh, 2011). Notwithstanding the significant difference in density to other types of plastics, there will always remain a small fraction of PVC in the mixture, as a result of imperfect separation. This requires special attention, as the formed HCl will have to be removed from the products. Furthermore, the presence of this acid will impose severe metallurgic constraints on the equipment material. Note that the presence of even small amounts of halogens in the oil/waxes prevents the use of it as fuel or petrochemical feedstock. A typically used specification indicates that the amount of chlorine should not exceed 10 ppm (Bhaskar et al., 2003). To tackle the challenge of PVC contaminants in the SPW stream, pyrolysis at lower temperature (300 °C) has been suggested (Bhaskar et al., 2003;

Okuwaki, 2004; Sadat-Shojai and Bakhshandeh, 2011). In a pre-pyrolysis reactor the plastics are melted and degradation of PVC takes place while other types of plastics remain almost unaffected. Chlorine removal of 98 wt% has been reported (Okuwaki, 2004). The remaining chloride in the effluent can be neutralized via reaction by addition of CaCO_3 , CaO , NaHCO_3 , $\text{Na}_2(\text{CO}_3)_2$ or NH_3 . Nevertheless, proper sorting of the starting material is paramount, as these last techniques will lead to waste streams that need to be processed, increasing the overall operating cost of the plant. In addition, the use of these neutralization agents is less favoured from an environmental point of view. The formed HCl will be contaminated by some light hydrocarbons and economically viable valorisation is not possible today. Last but not least, the different product fractions will also contain some traces of sulphur or other elements as most plastics contain anti-flame or antioxidant additives (Miskolczi et al., 2004).

The primary pyrolysis reactor can be of several design types, as schematically depicted in Fig. 29. Bubbling fluidized bed, stirred tank reactors and screw/auger reactors are the main designs and have been extensively reviewed (Butler et al., 2011). Most authors conclude that fluidized bed reactors are the most favourable option for plastic pyrolysis, due to a vast number of advantages such as

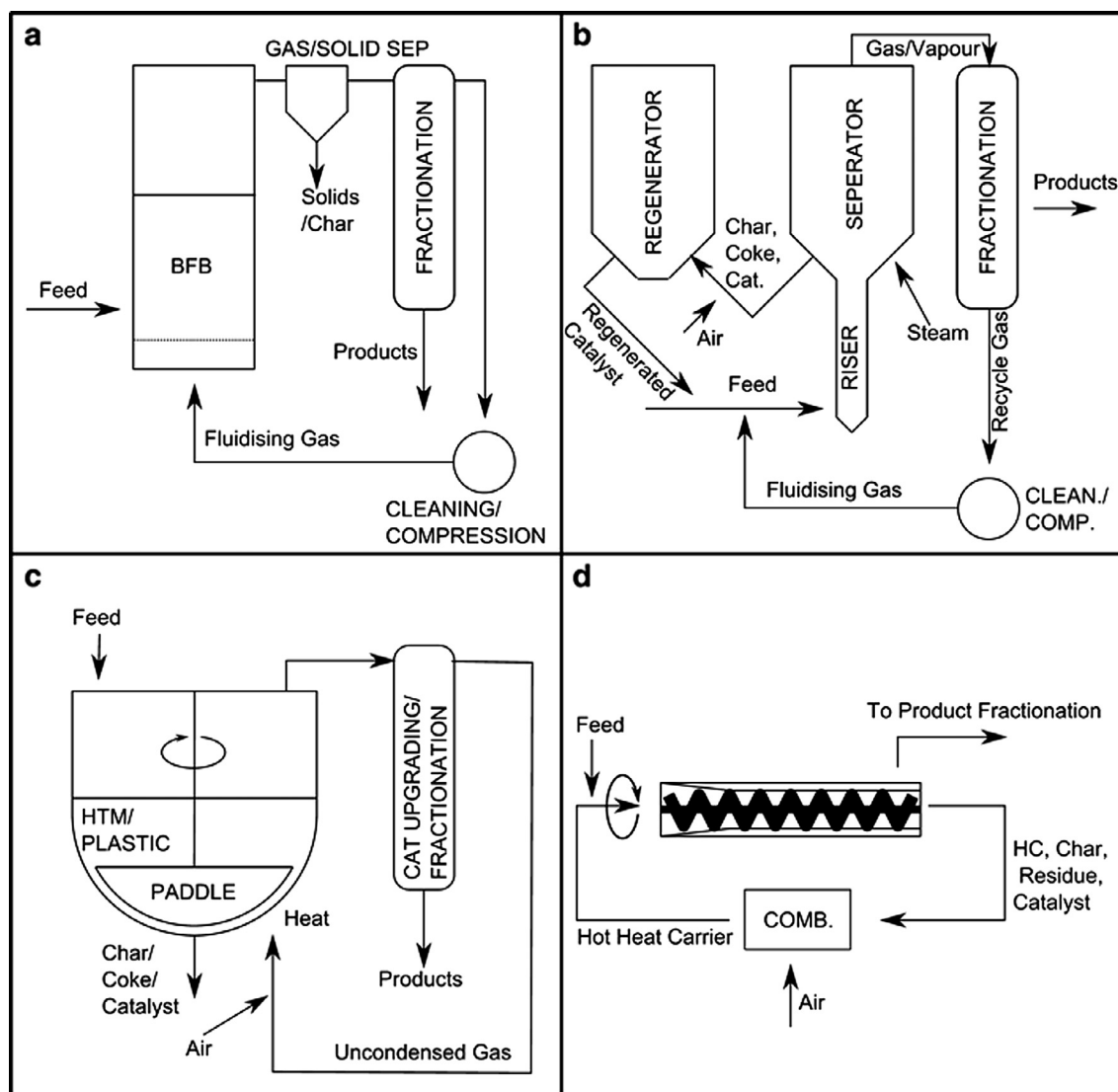


Fig. 29. Different designs for plastic solid waste pyrolysis (Butler et al., 2011): (a) Bubbling Fluidized Bed, (b) fluid catalytic cracker, (c) stirred tank reactor and (d) screw/auger reactor.

uniform product and higher conversion rates (Westerhout et al., 1998). However, recently a new, disruptive reactor concept has been introduced, that makes use of a rotating bed, the so-called the gas-solid vortex reactor in a static geometry (GSVR-SG) or vortex reactor, as shown in Fig. 26. The unique attributes of the vortex reactor allow it to significantly improve certain processes that suffer from convective heat or mass transfer limitations between phases. Other advantages may arise from the ability to work with different fluidisation agents such as steam or hydrogen (de Broqueville, 2009). The high centrifugal acceleration ($>30g$'s) generates much higher slip velocities and more intense heat and mass transfer between phases. Since the GSVR-SG technology is relatively new, the state of the art is still at the level of cold flow assessment analyses, experimentation and modeling, with valuable experimental studies carried out for different applications (Ashcraft et al., 2012; Ashcraft et al., 2013; De Wilde and de Broqueville, 2007, 2008; Dutta et al., 2010; Ekature et al., 2011; Kovacevic et al., 2014; Kovacevic et al., 2015).

For the fluidized bed reactor, the molten plastic stream coming from the pre-treatment step in which removal of the chlorine takes place is fed to the reactor. The formed gasses are rapidly cooled to prevent undesired secondary gas phase reactions. In order to fluidize the bed, a fluidizing gas is needed. Theoretically, nitrogen, steam or a recycle gas can be used. When targeting high small olefins yields, recycle gas is a questionable option as secondary reactions will dominate and hence will decrease the small olefins yields. Nitrogen is not a good option either as separation of the products nor is it economically feasible from an industrial point of view. Steam has been found to be the best option in that respect (Westerhout et al., 1998).

As stated previously, the products of the reaction can mainly be divided into three generic fractions: gas, liquids and char. The temperature of the reactor has a big influence on the mass distribution among these fractions.

Beside the temperature, a vast number of parameters influence the product spectra of the plastic pyrolysis process: composition, macrostructure of the polymer, level of micro mixing, residence time of the gas, temperature and fluidizing gas (Al-Salem et al., 2009b; Faravelli et al., 2003; Faravelli et al., 1999; Marongiu et al., 2007; Ranzi et al., 1997; Walendziewski and Steininger, 2001; Yan et al., 2015). Therefore, detailed modeling of the process is necessary to raise the performance of the process to unprecedented levels of efficiency and maximize profit. Although the kinetics are highly complex due to the condensed phase, the free radical mechanism and the vast number of species, detailed models are an indispensable tool, allowing to reduce the uncertainty, while increasing the credibility and hence proving the economic viability of the process. Many groups have been conducting experiments and developing kinetic models for the pyrolysis of SPW. In particular, this has been done for the polyvinyl polymers such as PE, PP and PS, as these give rise to products with favourable properties for further applications. Thermogravimetric analyses have been mainly used to understand the mechanism of pyrolysis of virgin plastics and to determine kinetic parameters of rather simple kinetic models consisting of several lumped fractions and power law equations, i.e. the so-called Coats-Redfern method. These models have focused on describing isothermal of dynamic thermogravimetric data. One disadvantage is that these thermogravimetric data have been measured at quite low temperatures and hence, extrapolation towards industrially relevant temperatures might be error-prone. Differences in thermal decomposition were noticed, most likely related to the presence of contaminants and additives in the plastics. For example, it has been observed that waste plastics have a lower initial decomposition temperature (Yan et al., 2015).

Ranzi et al. have published models for the pyrolysis of polyolefins by assuming a typical radical chain mechanism consisting of initiation, H-abstraction, β -scission and radical recombination (Ranzi et al., 1997). Further extension has been done in the modeling of the process. Faravelli et al. (Faravelli et al., 2003, 1999) paid more attention to the product distribution and later the thermal decomposition of PE and PS mixtures where the amount of macromixing was taken into account (Faravelli et al., 2003, 1999). More recent developments were accomplished by extending the number of reaction possibilities by Marongiu et al. (2007). The amount of ordinary differential equations which has to be solved is very high and different solution methods have been compared (Marongiu et al., 2003, 2007). Compact, yet sufficiently detailed kinetic models that have been validated with reliable experimental data are still lacking, and this leads to scale-up problems, which is therefore one of the key difficulties to improve the flexibility of plastic waste pyrolysis.

Another major challenge is stable waste supply, with the focus on quantity, composition and quality. For example the BASF feedstock recycling process was designed to handle the recycling of mixed plastic waste supplied by the DSD (Dual System Germany Ltd) collection system. A pilot plant was started in 1994 in Ludwigshafen, with a capacity of 15,000 ton/yr. Uncertainties in the feedstock supply caused that no agreement could be reached on a waste supply guaranteed in the long term for a gate fee that would be sufficient to cover the costs of a full-scale plant. Particularly due to the long mortgaging periods of such industrial installations, long-term commitments are essential to reduce the financial risks for the investor to reasonable levels. The pilot plant was closed in 1996.

3.3. Fluid catalytic cracking (FCC)

Thermal decomposition of SPW yields a skewed carbon distribution of the reactor effluent, as shown in Fig. 30. Therefore catalytic decomposition of SPW seems to be a better alternative as the product spectra will be narrower by the intrinsic shape selectivity that a catalyst exhibits, as shown in Fig. 30.

Another advantage is that the product spectra can be directed towards fuel, commodity chemicals and fine chemicals, depending on the process conditions. Also, the use of catalyst allows to use less stringent reaction conditions, lowering energy consumption of the overall process and as such affecting the total operating cost (Lin and Yang, 2009; Passamonti and Sedran, 2012; Thegarid et al., 2014). In Fig. 30 a comparison has been made between the reactor effluent of the thermal and catalytically cracked plastics. As can be seen, the product spectrum has been shifted towards smaller carbon numbers and has a smaller tail. Furthermore, the aromatic and naphthenic compounds are selectively formed in presence of a classical FCC-catalyst (Buekens and Huang, 1998; Li et al., 2014). Catalytic cracking increases the gasoline yield as shown in Fig. 31.

Two different types of catalytic cracking can be distinguished: liquid phase and vapour phase (Buekens and Huang, 1998). In the liquid phase process the catalyst comes in direct contact with the molten polymer phase. In this mode the catalyst aids with converting the partially degraded oligomers. In vapour phase contact processes, the vapours formed during cracking are brought into contact with the catalyst. The use of solid catalysts such as silica-alumina, ZSM-5, zeolites, and mesoporous materials for these purposes are all possible and have been tested. The reactor design is very similar to the FCC-unit shown in Fig. 29.

As stated previously, one of the main advantages over SPW pyrolysis is that conversion can be achieved at lower temperatures, having a positive effect on the overall heat requirement and hence on the economics of the process. The required temperature to

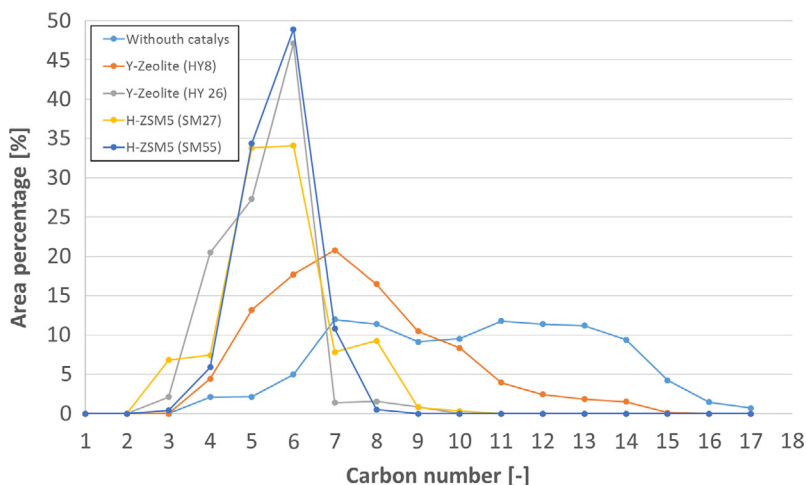


Fig. 30. Products distribution of the liquid products of the pyrolysis by Schirmer et al. (2001).

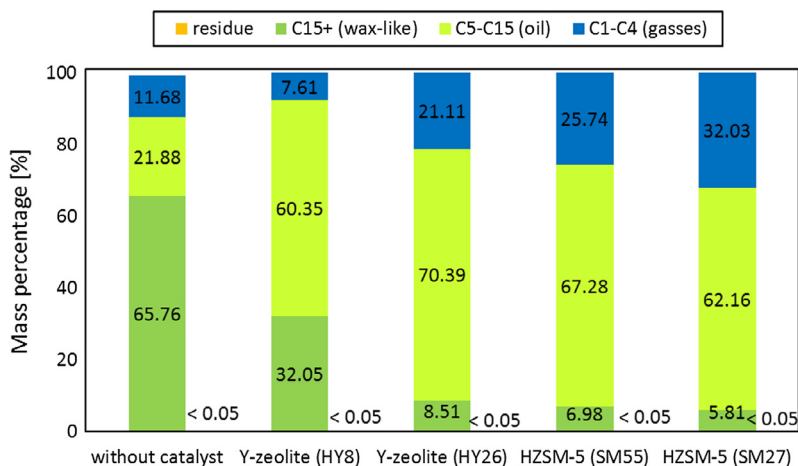


Fig. 31. Products yields of various catalysts at 440 °C by Schirmer et al. (2001).

Table 5
Overview of current catalytic cracking plants for plastics (Butler et al., 2011).

Process	Temperature	Catalyst	Feedstock	Capacity	Yield
Zadgaonkar Process	400 °C	Unknown catalyst	PE, PP, PS, PVC, PET	5 Mt (India)	10–20% gas, 60–80% liquid, 7–10% residue
Smuda Process	300–450 °C	Ni-silicate, Fe-silicate	PE, PP, PS, PVC, PET	10 kt/a (Poland)	32.3 vol% gasoline, 43 vol% diesel, 29.7 vol% residue
T-Technology	390–420 °C	Unknown	PE, PP, PS	10kt/a (USA)	15–20% gasoline, 60–70% light oil, fuel oil and diesel

achieve reasonable conversion for pyrolysis is above 450 °C, while the temperature can be lowered to 300–350 °C when using a catalyst (Buekens and Huang, 1998). Moreover, the yields towards isoalkanes and aromatics in the range of C₅–C₁₅ are increased, which are the higher valued gasoline components, as can be seen in Fig. 31.

Nevertheless catalytic cracking also suffers from several drawbacks. Carbonaceous deposits, being Cl and N components present in the raw waste stream, rapidly deactivate the catalyst. Furthermore, inorganic materials tend to block the pores of the catalyst, which sometimes results in a permanent deactivation of a large number of active sites. Therefore, harsh pre-treatment steps are quite often required to protect the catalyst. Sometimes light pyrolysis of the feed as pre-treatment allows dealing with highly contaminated feeds or feeds containing significant amounts of heteroatoms. The presence of these contaminants can also deteri-

orate the quality of the products, and hence special care is needed (Miskolczi et al., 2009).

Several commercial catalytic processes are available. Their main goal is to produce high yields of transport grade fuels such as gasoline and diesel. An overview of current pilot and commercial processes is given in Table 5.

Note that the results presented in Table 5 should be evaluated with a certain level of scepticism. This is for example illustrated in the work of Pinto and co-workers. They studied plastic waste pyrolysis, originating from Portuguese MSW, in an autoclave reactor using several zeolite and several metallic catalysts at 415 °C and 33 atm (Pinto et al., 1999). The waste feedstock was a mixture of PC plastics and consisted of 68% PE, 16% PP and 16% PS. All catalysts gave an oil yield of approximately 90 wt%. The oil fraction consists of alkanes (55%), aromatics (35%) and alkenes (10%). However, when evaluating the research of the octane numbers (RON) of

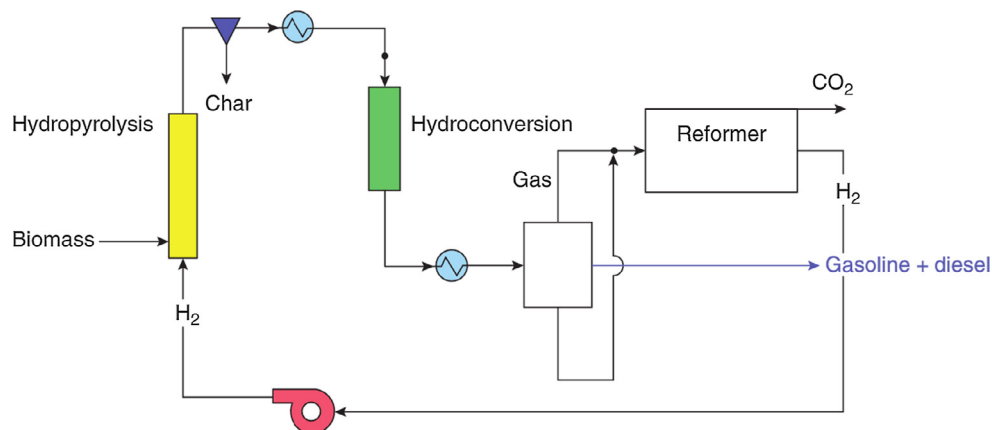


Fig. 32. Integrated hydropyrolysis and hydroconversion of biomass in the IH² process. Reprinted from Linck et al. (2014).

the produced gasoline, Pinto and co-workers measured values in the range between 15 and 30. This is much lower than conventional gasoline because of the presence of large amounts of *n*-paraffins and the low amounts of *iso*-paraffins and aromatics. Therefore, the liquid fraction should be further treated or blended in order to be used as fuel (Pinto et al., 1999), which is a substantial additional cost.

Major challenges that need to be overcome are related to the bulky nature of the polymers. This makes the activity too limited and deactivation by coking to be severe (Serrano et al., 2012), as also indicated by the Ellen MacArthur Foundation. The absence of a suitable reactor technology, in which catalytic fast pyrolysis can be carried out, is considered as the second major bottleneck (Ellen MacArthur Foundation, 2017).

3.4. Hydrogen technologies

3.4.1. Hydrocracking

The main difference with catalytic cracking of plastics is the addition of hydrogen. The process takes place at elevated hydrogen pressures, roughly 70 atm and temperatures in the range of 375–400 °C. The catalyst can be a Ni/S or NiMo/S supported catalyst. Due to the presence of inorganic matter in the raw SPW, the plastics are initially liquefied and filtered to remove non-distillable material. This happens via low temperature pyrolysis. The liquid is then sent over the catalyst bed. The presence of hydrogen improves significantly the product quality, i.e. a higher H/C ratio and lower aromatic content. Experiments for different types of catalysts revealed high yield of paraffin (Ding et al., 1997). Other main advantages to upgrade the liquid yield of plastic pyrolysis are that heteroatoms are handled excellently and no toxic products such as dioxins are produced or survive the process. On the other hand, a hydrogen stream is necessary which is known to be an expensive utility. For example, electrically produced hydrogen costs about €2500 per tonne.

Some advantages of hydrocracking are that good quality naphtha feed can be produced and that mixtures of plastics can be used. This comes at the high cost of hydrogen and the high operating pressures and related investment/operational costs.

3.4.2. Integrated hydropyrolysis and hydroconversion (IH²)

Integrated hydropyrolysis and hydroconversion, also known as IH², is a catalytic thermochemical conversion process able to convert organic material into a range of hydrocarbon fuels. The process can deal with virtually all types of feedstock, including cellulosic fractions, wood and agriculture residues, municipal waste and mixtures thereof (Marker et al., 2013, 2012). The technology has

been developed by Gas Technology Institute (GTI) of Des Plaines. A simplified process scheme is presented in Fig. 32. The process consists of three reactors, being hydropyrolysis, hydroconversion and reforming.

The hydropyrolysis reactor is a fluidized bed reactor containing catalyst particles. The catalyst is exclusively licensed by CRI (Criterion Catalyst Company). The inlet of the reactor consists of the renewable feedstock and hydrogen. Operating temperatures and pressures are respectively between 400–500 °C and 15–35 atm. Note that the temperature range corresponds to typical fast pyrolysis temperatures. Hence, similar to fast pyrolysis, volatile components are released from the biomass in the hydropyrolysis reactor. In the gas-phase, the formed molecules react with hydrogen and catalyst. Deoxygenation takes place and the oxygen atoms end up in water (dehydration), CO (decarbonylation) and CO₂ (decarboxylation). These reactions are exothermic and offset the endothermicity of pyrolysis. The effluent of the hydropyrolysis reactor has a low oxygen content and an acid number of less than 1, compared to 200 for fast pyrolysis oil (Marker et al., 2013, 2012, 2014). Acid catalyzed polymerization, aromatization, and coking reactions are suppressed in hydropyrolysis, compared to thermal pyrolysis and catalytic cracking. The remaining solid residue can be removed through cyclones while the catalyst, which has a higher density, remains in the fluidized bed.

Subsequently, the gaseous stream enters the hydroconversion reactor. The second reactor is a fixed bed reactor, again using a CRI proprietary catalyst. Operating pressure is similar to the first reactor. The amount of heteroatoms are further reduced in this stage, the oxygen content goes from approximately 2.7 wt% to less than 1 wt% (Marker et al., 2014).

The product stream is condensed and gas and liquid streams are separated. The liquid consists of two phases, an organic phase with very low oxygen content and an aqueous phase. The gas stream consists of small molecules such as methane, ethane, propane, CO and CO₂. The gas is sent to a steam reformer together with the produced water. The steam reformer can produce the required amount of hydrogen for hydropyrolysis and hydroconversion. This does require a proper hydropyrolysis catalyst and selection of operating conditions in the hydropyrolysis reactor that balances dehydration reactions, which consumes hydrogen, as well as decarboxylation reactions, which do not consume hydrogen.

Similar to pyrolysis followed by hydrotreatment, the IH² process enables the production of liquid hydrocarbons directly starting from plastic waste. The IH² process, however, does not require an external import of hydrogen, making the process more attractive. Furthermore, the IH² process omits treatment of the pyrolysis oil, which has high acidity and hence imposes higher

constraints on the construction material of reactor and storage vessels. Because of its efficiency, simplicity, moderate pressures (compared to ex situ hydrotreatment of fast pyrolysis oil), and integrated nature, this technology has been shown to have good overall economic potential. All different individual elements of the IH² process are all already commercialized, minimizing investment risk and allowing fast implementation of the technology.

The IH² process, which is based on an integrated hydropyrolysis and hydroconversion mechanism, is shown to be a promising technology for the production of liquid fuels out of biomass. The creators of the IH² technology claim that the process can be operated based on a solid recovered fuel feedstock including plastics from SPW, but further investigation is required on this statement (Narasimhan and Del Paggion, 2017; Shell, 2017).

Table 6
Location, size and year of installation of KDV plants around the world (GmbH).

Location	Size	Year of installation	Remarks
Monterey, Mexico	KDV500	2004	
Bulgaria	KDV500	2007	
Ontario, Canada	KDV500	2007	1st generation plant
Hoyerswerda, Germany	KDV500	2008	1st generation plant
Tarragona, Spain	KDV1000	2009	1st generation plant
Massachusetts, USA	KDV500	2010	Installed by Covanta Energy Corp 1st generation plant
Eppendorf, Germany	KDV150	2010	
Bary, Italy	KDV150	2012	
Ethiopia	KDV150	2012	
Lesmierz, Poland	KDV1000	2012	First compact KDV1000
Tekirdag, Turkey	KDV1000	/	Compact KDV1000
Schwyz, Switzerland	KDV150	/	

3.5. KDV process

KDV, a German acronym for Katalytische Drucklose Verölung or the catalytic pressure-less depolymerization process, was developed by the German company Alphakat GmbH and claims the catalytic conversion of biomass and plastic waste towards liquid fuels at nearly atmospheric pressure. The advantage of the products of this process is the almost complete removal of oxygen atoms, making the final liquid fuel directly applicable in conventional combustion engines. As such, this technology would make it possible to obtain diesel oil, kerosene and petroleum from all substrate types that contain hydrocarbons of both organic and mineral origin. In this way, the possible feedstock of the process can range from polymer plastics such as PET and PP to lignocellulose. The oxygen will generally be removed as CO₂. A second advantage of the process is the mild reaction conditions at which the reaction takes place in comparison to alternative processes such as pyrolysis (Reza and Bahram, 2015). According to the licensors, the technology is ready for industrial use and many demonstration and full-scale facilities of the KDV process have been built in various countries with outputs ranging from 150 to 5000 L/h of diesel fuels proving feasibility and scale up possibilities. In Table 6 different installed KDV-plants are summarized.

Before sending the feedstock to the reactor, a pre-treatment is necessary to reduce the water content to around 5 wt%, and the particle diameter to less than 3 mm. The shredded feedstock, catalyst and lime are subsequently mixed with carrier oil and heated to a temperature of 180 °C. The catalyst applied in this process is a 100% crystalline alkali-doped aluminium silicate, such as a sodium doped zeolite of type Y with faujasite structure (Broach et al., 2012). By using this catalyst of natural origin, the inventors claim

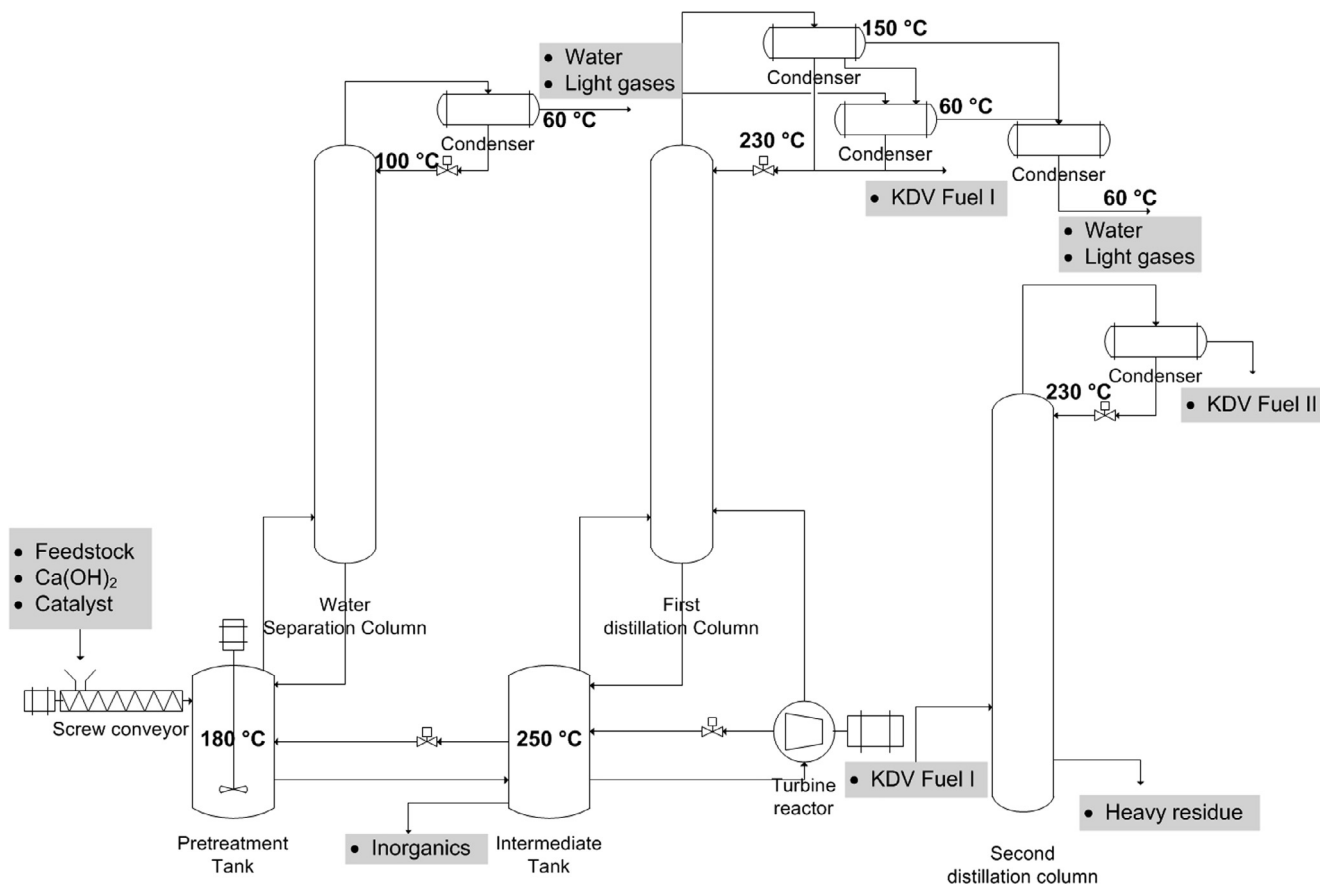


Fig. 33. Schematically overview of the KDV-process.

to imitate the natural process of oil creation on an accelerated basis (GmbH; Koch, 2011). The lime, $\text{Ca}(\text{OH})_2$, is added to control the pH at a value of around 9, which is the optimal environment for the catalytic reaction (see Fig. 33).

The oil mixture is subsequently sent to the turbine reactor in which the temperature is raised to 250 °C. This increase in temperature will be the result of in a high-shear inline mixer connected in circuit to the reactor. Liquid and solid material is dragged by high-speed rotation of the turbine blades. Due to the centrifugal forces, the preheated and dewatered material is forced towards the periphery and the hydrocarbons are separated from the residues. At the same time, the mixing and frictional energy will increase the temperature leading to depolymerisation and deoxygenation of the extracted hydrocarbons. A reaction temperature between 250 and 320 °C results in a product distribution in the middle distillate range, i.e. diesel fuel. Both the initial mixer and turbine reactor will operate at pressures slightly beneath atmospheric pressure (90 kPa).

The reactions in the KDV reactor are not studied intensively. It is argued that before the hydrocarbon plastics are thermally cracked, they are first dechlorinated and dehalogenated by neutralization of the ion exchanging catalyst (Scheirs and Kaminsky, 2006a, 2006b). As such, issues are avoided with HCl generation and chlorine contamination, which are encountered in other waste-to-fuel processes. Furthermore, this ion exchange capability of the catalyst will enable using considerably lower cracking temperatures compared to conventional catalysts. Furthermore, in a study conducted by Kemi-information AB, a theoretical evaluation of the process based on a claimed energy efficiency of 70% was performed. This study pointed out some discrepancies in the mass and energy balances presented by Alphakat (Reza and Bahram, 2015).

Thermal cracking will occur in the turbine reactor where the temperature is raised by friction. In this way coke deposition on the wall can be omitted instead of using direct heating via the wall (Koch, 2011). The acid cracking catalyst will produce carbonium ions by the abstraction of hydride ions from the hydrocarbon molecules. This is subsequently followed by chain scission yielding C_{30} – C_{50} oligomeric hydrocarbons. Secondary cracking by β -scission of these hydrocarbons will then give rise to liquid hydrocarbon fuel located in the middle distillate range (C_{10} – C_{25}) (Scheirs and Kaminsky, 2006a, 2006b).

A part of the reaction product is returned to the mixer to maintain the oil circulation. Since not only diesel is recycled but also water and gaseous products, the presence of a distillation column is required for the removal of these products. Also, the water present in the reactor feed will be separated as such, as it evaporates at the operation temperature of the mixer. The other part of the reaction product is separated from the turbine reactor by distillation. By running through condensers at different temperatures the water and gaseous products will be parted from the KDV fuel. The temperatures of these condensers will be determined by closed cooling water and oil cycles. Afterwards, the KDV fuel is sent to a distillation column where it is separated in the actual diesel oil and bitumen. This latter could be used as asphalt for road construction or as fuel for combustion. Van Geem and co-workers compared the most important properties of two of these KDV fuels with conventional petroleum diesel and showed that, with minor upgrading, direct use in refineries is possible, see Table 6 (Gonzalez-Quiroga et al., 2016). More specifically, the organic fractions recovered from demolition waste and municipal solid waste were liquefied and deoxygenated in a CPD pilot plant with 150 L h^{-1} ($4.2 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$) liquid fuel capacity. The produced fuels were characterized by elemental analysis, comprehensive two-dimensional gas chromatography, and the ISO tests for automotive diesel established by the EN 590:2009 Standard. The studied fuels showed very low oxygen contents (<0.4 wt%) and a high

share of paraffins (>40 wt%). The carbon range of the fuel obtained from demolition wood was wider than that of the fuel obtained from municipal solid waste (C-5-C-29 vs. C-6-C-22). The flash points (54, 46 °C), the sulphur contents (40, 80 ppmw), and the cetane numbers (43, 33) did not comply with the respective requirements for automotive diesel (i.e., ≥ 55 °C, <10 ppmw, and ≥ 51). Nevertheless, both fuels showed salient cold filter plugging points (–14, –15 °C) and cloud points (–15, –44 °C), which are indicative of good fuel performance at extreme winter conditions. The wide carbon number distribution, especially toward the lower range (i.e., carbon number < C), suggests that the studied fuels can be split into a kerosene-like and a diesel-like cut. Overall, the fuels from the CPD process exhibit great potential as alternative transportation fuel. However, properly selecting the starting material is crucial for minimizing costly hydrotreating (see Table 7).

An additional expansion of the KDV process is the off-line removal of ashes from the turbine reactor. These residuals still contain a significant amount of KDV fuel. The ashes are therefore heated to 500 °C at which the remaining fuel is removed and separated via a distillation column. The residual ashes, which contain a considerable amount of minerals, could be applied as fertilizer for agricultural usage (Koch, 2011).

KDV diesel suffers from a high sulphur content, see Table 6 (Labeckas and Slavinskas, 2013). Due to emission regulations in the EN 590:2009 norm, the sulphur content has become one of the most important fuel properties and this is problematic for the KDV fuel. Although the sulphur content strongly depends on the feedstock composition, it is consistently found to be high. Another issue is that the cetane number is in general slightly lower than what is required by the European Standards (Labeckas and Slavinskas, 2013). In addition, increased NO_x , CO and HC emissions as compared to regular diesel were reported. Although these emissions would be within the limits permitted by the Emission Standards (Labeckas and Slavinskas, 2013).

The KDV process has been demonstrated to be able to convert SRF into synthetic fuel. In contrast to other WtE processes, KDV offers the opportunity of processing oxygen and halogenated compounds. The chemistry behind this process, however, is still unknown. However, it shows many similarities with deoxygenation process. In addition to the lack of chemical information, there is also a lack of technical information about the KDV process and hence further investigation is required (Gonzalez-Quiroga et al., 2016).

3.6. Gasification combined with methanol production

In the Netherlands, a partnership comprised of AkzoNobel, Van Gansewinkel, Air Liquide, AVR and Enerkem is looking to build its waste-to-chemicals plant in Rotterdam. The new chemical plant will use Enerkem's innovative technology to convert residual waste into methanol, a raw material used in the chemical industry. The methanol will then be converted into chemicals such as acetic acid (e.g., for fibres and adhesives), thickening agents and dimethyl ether (clean propellant gases). These chemicals are currently produced almost entirely from fossil fuels. The planned facility will therefore provide a sustainable alternative by producing a renewable chemical and will represent a significant step toward a sustainable and circular approach to waste management in Rotterdam.

Syngas is a valuable intermediate in the chemical industry and can be produced from any carbonaceous source such as natural gas, coal, biomass or even organic wastes (Wender, 1996). The lowest production cost of syngas so far is based on methane and, hence, the main focus has been on using associated gas (Dry, 2002). Associated gas is a byproduct during the exploitation of crude oil and comes at low or even negative value. Syngas can

Table 7
Standardized fuel properties of the CPD fuels compared to those of petroleum diesel and the requirements for diesel established by the EN 590:2009 Standard (Gonzalez-Quiroga et al., 2016).

Property (Standard)	CPD fuel from SRF-DW	CPD fuel from SRF-MW	Petroleum diesel (Labeckas and Slavinskas, 2013)	EN 590:2009 requirement
Density at 15 °C (ISO 12185), kg m ⁻³	840	807	842	820–845
Kinematic viscosity at 40 °C (ISO 3104) mm ² s ⁻¹	2.52	1.49	2.94	2.0–4.5
Flash Point (ISO 2719), °C	53.5	46.0	68	≥55
Cold Filter Plugging Point (EN 116), °C	–14	–47	–5	n.s. ^a
Cloud Point (EN 23015), °C	–15	–44	6	n.s.
Content of ashes (ISO 6245), ppmw	350	<10	n.r. ^b	≤100
Sulfur content, ppmv	40	80	9.0	<10
Ash content (ISO 6245), ppmw	350	<10	n.r.	≤100
Nitrogen content, ppmv	<100	150	n.r.	n.s.
High Heating Value (ISO 8217), MJ kg ⁻¹	42.9	43.2	43.0	n.s.
Iodine number (EN 14111), g I ₂ (100 g) ⁻¹	8.8	12.2	12	n.s.
Water content (ISO 12937), ppmw	118	96	21	≤200
Cetane number (ISO 5165)	43.0	33.1	51.6	≥51

^a n.s. non-specified.

^b n.r. non-reported.

be produced from any organic source and it has profiled itself as important intermediate to the production of petroleum like products through FTS or via methanol and DME synthesis followed by MTG/MTO (Wender, 1996). Syngas is a mixture of carbon monoxide and hydrogen. The quality of syngas is measured via the H₂/CO ratio. This is an important specification as different downstream process steps have different optimal ratios. At present, these process steps are applied at industrial scale if fossil feedstocks, mainly gas and coal, are used and can be considered as proven and mature technologies.

3.6.1. Gasification

Gasification is one the best known technologies to convert a solid starting material whether pre-treated or not. This process converts almost every feed (Puig-Arnavat et al., 2010), composed of organic material, to a gaseous mixture containing CO₂, CO, H₂, CH₄ and other light hydrocarbons via partial oxidation (Heidenreich and Foscolo, 2015; Kumar et al., 2009; Ruiz et al., 2013). The process requires an oxidation agent, which is usually a mixture of steam and pure oxygen or solely air (Trippe et al., 2011). However, the use of air, the cheapest option in terms of operational costs, has several disadvantages such as higher gas flow rate, resulting in lower throughputs and tougher separation which negatively impacts the overall costings (Wilhelm et al., 2001). Moreover, from an environmental point of view, this yields higher amount of noxious NO_x, which should be carefully monitored. During the gasification process the feed undergoes several reactions from which nature can be both exothermic as well as endothermic. The overall process is endothermic (Munasinghe and Khanal, 2010). Gasifiers are frequently used to yield higher thermal efficiency for power generation. Besides this higher thermal efficiency, it also reduces the emission of harmful products into the atmosphere. The produced syngas contains, besides the before mentioned gases, also some impurities such as NH₃, H₂S, NO_x, alkali metals, and tars (Dudyński et al., 2015; Ruiz et al., 2013; Spath and Dayton, 2003). Special attention should be given to the potentially presence of contaminants, as these are known poisons for downstream processes, in particular for catalytically conversion processes (Spath and Dayton, 2003). The purification step is the major contributor to the costs of producing the syngas (Haro et al., 2013; Munasinghe and Khanal, 2010; Spath and Dayton, 2003; Wilhelm et al., 2001).

As stated previously, the main product of the gasification step is syngas. Syngas is a valuable flammable gas mixture of hydrogen and carbon monoxide and smaller quantities of methane,

carbon dioxide and hydrocarbons. Syngas can be seen as the basis for a lot of different products through C₁-chemistry. Methanol can be formed via the Methanol-To-Olefins (MTO) process, while paraffinic hydrocarbons can be formed through the Fischer-Tropsch process or Methanol-To-Gasoline (MTG) process. The carbon distribution of the effluent is much narrower for MTG than for FTS. Syngas is characterized by the molar H₂/CO ratio. For biomass a ratio of hydrogen over carbon monoxide of roughly 1.5–1.8 is obtained. Therefore energy intensive water gas shift facilities should be installed to increase this ratio, i.e. negatively impacting the carbon efficiency (carbon loss in the form of CO₂) and the capital investment and operational costs. Different types of gasifiers exist, of which fluidized, fixed bed and entrained flow are the most common ones. The gasification of SPW can certainly be developed into a valid recycling route for SPW, producing a syngas, rich in H₂ and CO. Although references of industrial scale application are given in the literature, the future break-through of the process will require further experimental work to improve the equipment design and product optimisation. Advances in that area will aid in the improvement and more widespread use of gasification reactors (Brems et al., 2012).

The Texaco gasification process is by far the most common and well-known technology. First pilot scale experiments (10 tonnes/day) were carried out in the US. Fig. 34 reviews the process, which consists of two parts: a liquefaction step and an entrained bed gasifier. In the liquefaction step, the plastic waste is mildly thermally cracked (depolymerisation) into synthetic heavy oil and some condensable and non-condensable gas fractions. The non-condensable gases are reused in the liquefaction as fuel (together with natural gas). Oil and condensed gas produced are injected to the entrained gasifier. The gasification is carried out with oxygen and steam at a temperature of 1200–1500 °C. After a number of cleaning processes (amongst others, HCl and HF removal), a clean and dry synthesis gas is produced, consisting predominantly of CO and H₂, with smaller amounts of CH₄, CO₂, H₂O and some inert gases (Brems et al., 2015).

3.6.2. Methanol synthesis

Methanol is one of the largest produced chemicals in the world as it is used as reactant for the production of several commodity chemicals, as depicted in Fig. 35, such as formaldehyde, acetic acid and methyl amine (Spath and Dayton, 2003). Methanol can be produced via different paths, including an oxidative route from methane and catalytically via syngas (Spath and Dayton, 2003).

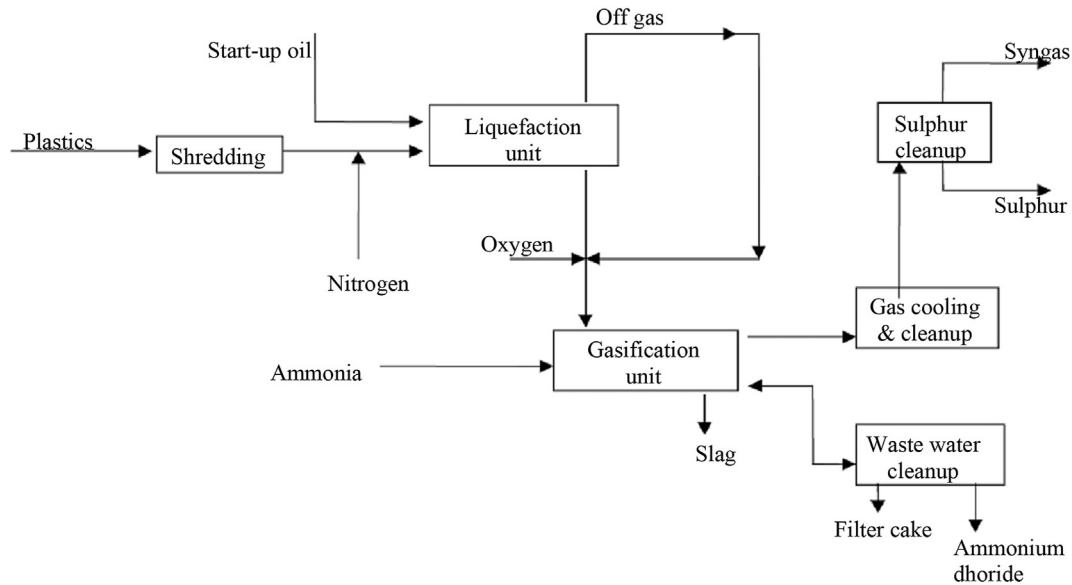


Fig. 34. Texaco gasification process schematic diagram (Brems et al., 2015).

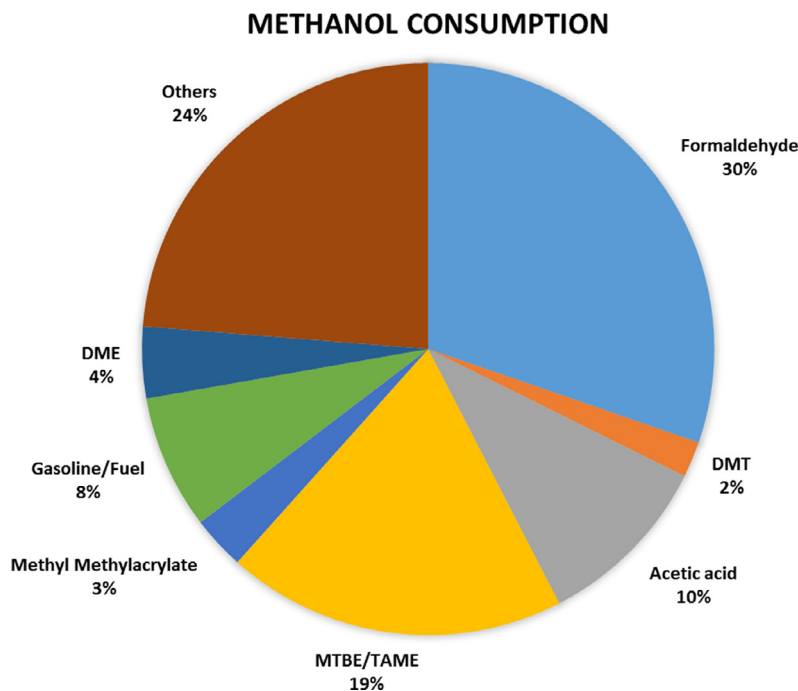


Fig. 35. Methanol usage (Ali et al., 2015).

The latter is most applied industrially (Spath and Dayton, 2003; Waugh, 1992). The conversion of syngas to methanol is performed at high temperature and high pressure. The reaction itself is exothermal and equilibrium limited. This has as major consequence for the reactor design, as care has to be taken to prevent runaway and severe catalyst deactivation. The produced methanol can then further be deployed in the production of olefins or petroleum like products via respectively methanol-to-olefins (MTO) and methanol-to-gasoline (MTG), possibilities that are discussed in the following paragraph.

The first catalytic system used to produce catalytically methanol was $\text{ZnO/Cr}_2\text{O}_3$ (Spath and Dayton, 2003). The reactor was operated at high temperature (350 °C) and at very high pressure

(250–300 atm) (Spath and Dayton, 2003). The technology was developed by BASF in the mid-1920 (Waugh, 1992). Due to newer technologies with respect to syngas purification, the interest of easily poisoned Cu catalyst was renewed. In 1966, ICI (Imperial Chemical Industries) introduced a new more active catalyst $\text{Cu/ZnO/Al}_2\text{O}_3$ (Spath and Dayton, 2003; Waugh, 1992). This allowed operating the reactor at lower temperature (220–275 °C) and significant lower pressure (50–100 atm). A generic scheme of the process is given in Fig. 36. The catalyst is highly sensitive to S-poisoning. The preferable purity of syngas should be below 0.1 ppm of S in order to retain the activity of the Cu sites and have sufficient activity to ensure a run length of 5 years (Spath and Dayton, 2003).

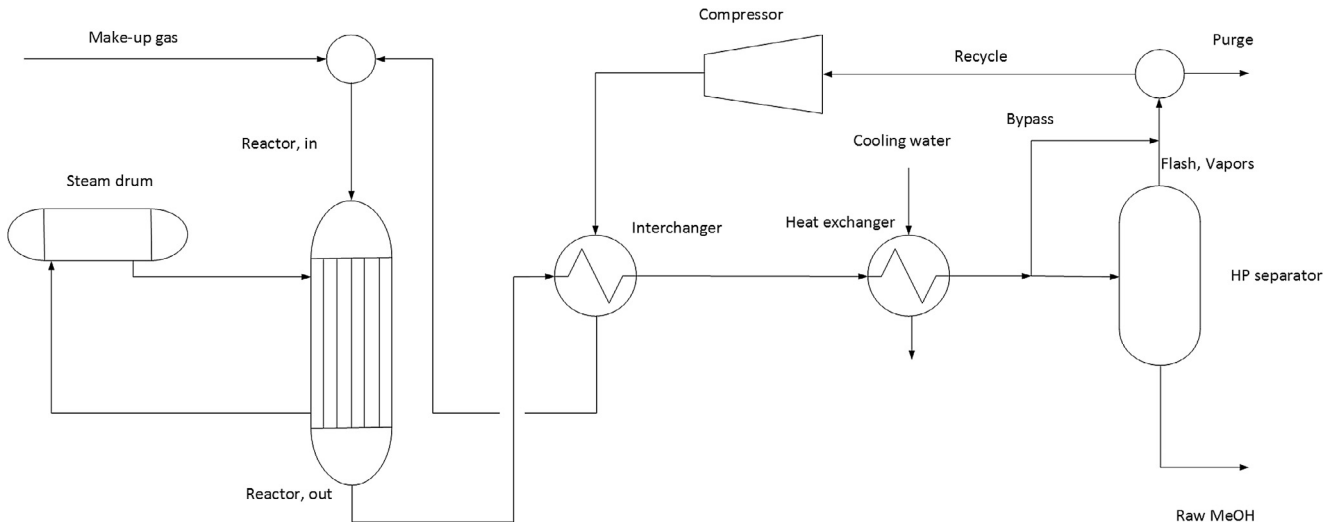


Fig. 36. Generic scheme of the methanol production (Abrol and Hilton, 2012).

Syngas is mixed with the recycle stream and conducted over the catalyst bed. Due to equilibrium limitation the syngas conversion is limited to 25% for a single pass. So the reactor effluent consists mostly of unreacted syngas. The effluent is then distilled and the unreacted syngas is recycled.

Methanol can be further used as commodity chemical or further processed to yield olefins and fuels through respectively MTO and MTG. Further dehydration to yield DME is also a possibility.

3.6.3. MTG/MTO

The methanol to gasoline (MTG) process, developed by Mobil Oil Corporation, converts methanol catalytically to hydrocarbons over a zeolite catalyst. The process is considered to be the first new synthetic fuel process since FTS. The process was discovered by accident by two independent groups of Mobil scientists when trying to convert methanol to ethylene oxide and attempting to methylate isobutene with methanol (Keil, 1999). The process has successfully been commercially accomplished in 1985 at New

Zealand, Mobil's Motunui plant. The gasoline contains high amounts of durene (1,2,4,5-tetramethylbenzene) that needs to be converted into components with lower boiling points to prevent blockages in engines at low temperatures. This can be done in a heavy gasoline treatment (HGT) plant, also patented by Mobil (Keil, 1999). The gasoline is virtually sulphur free. Initially, a fixed bed reactor was used. However, later a fluidized bed has been developed to deal with deactivation of the catalyst because of coke deposits. In the case of a fluidized bed, continuous removal and regeneration via oxidation of the catalyst can be performed. The process is typically conducted at 350 °C and pressures of about 30 atm (Keil, 1999; Spath and Dayton, 2003). The process is schematically depicted in Fig. 37. Methanol is heated and mixed with catalyst. ZSM-5 or SAPO-34 are mainly used as catalyst. Due to cokes formation the catalyst is burned off for catalyst regeneration.

The MTG plant ceased to operate in 1997 and only the methanol production facilities remain. In 2009, a second generation MTG

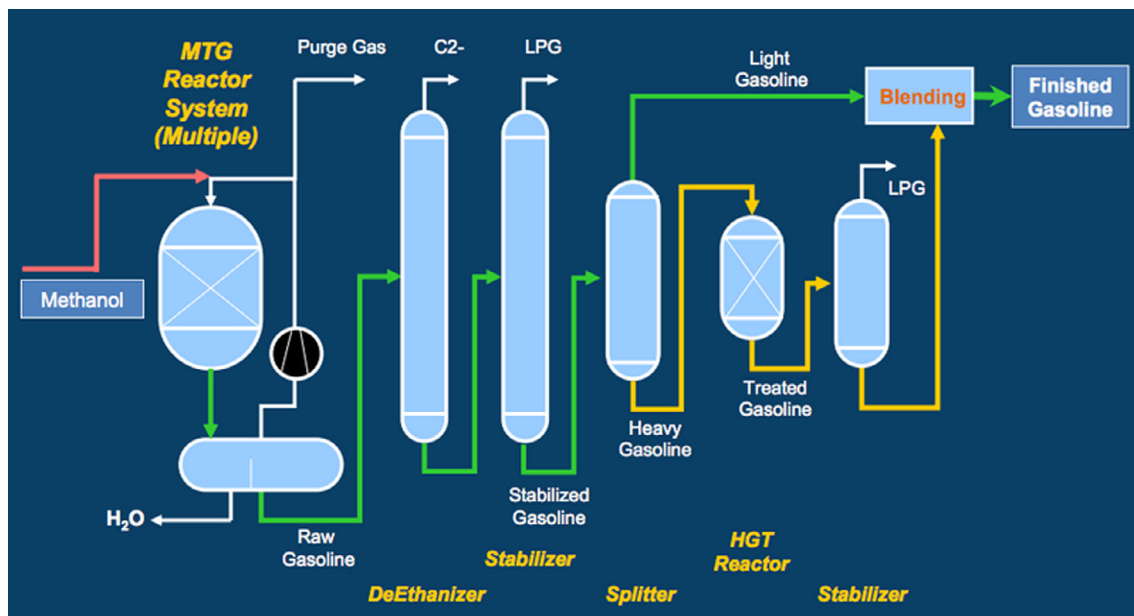


Fig. 37. The schematic representation of the fluidized bed MTG-process (Keil, 1999).

plant started to operate in China by Jincheng Anthracite Mining Group (JAMG). The production capacity is much less than the Mobil's Motunui plant and amounts up to 2500 bpd. This plant was the first coal-based MTG plant and successfully demonstrated the coal-to-gasoline concept.

The occurring reactions in the reactor can be summarized as follows. The first reaction of the sequence raw methanol is partially dehydrated yielding dimethyl ether. This dimethyl ether is then converted into light olefins, which in the last stage will be converted into hydrocarbons with longer chains. One can understand that the reaction conditions can be optimized to enhance the yields towards light olefins and prevent further reaction toward gasoline like molecules as occurring during MTG. This consideration has led to the second process, namely MTO, where the main products are light olefins. This process has been patented by several companies including ExxonMobil (Brown et al., 2005) and UOP/HYDRO (Barger et al., 1993). The process is depicted in Fig. 38.

The process conditions are in contrast with MTG at near atmospheric pressure, higher temperature and a less stronger acid active site of catalyst (Spath and Dayton, 2003). Methanol to olefin process converts methanol into light olefins. Unlike steam cracking, the yield of propylene over ethylene ratio in MTO is more flexible and hence gives the possibility to optimize the production towards the actual market demand. However, the technology is still not competitive with highly optimized steam crackers.

3.7. Toxicity of pyrolysis and gasification products

The gaseous products generated under various thermal decomposition conditions and the toxicity of those products is a substantial concern. A series of literature reviews was undertaken by the National Bureau of Standards to examine the toxicity and chemistry of the effluents produced when seven plastics were decomposed under various thermal and atmospheric condition. These plastics are: acrylonitrile-butadiene-styrenes, nylons, polyesters, polyethylenes, polystyrenes, poly(vinyl chlorides) and rigid polyurethane foams (Levin, 1987). For polyurethane foams,

carbon monoxide (CO) and hydrogen cyanide (HCN) were the predominant toxicants found among more than 100 other gaseous products (Paabo and Levin, 1987). In general, the combustion products generated from rigid polyurethane foam in the flaming mode appear to be more toxic than those produced in the non-flaming mode. For PVC, the major products of thermal decomposition include hydrogen chloride, benzene and unsaturated hydrocarbons (Huggett and Levin, 1987; Yu et al., 2016). In the presence of oxygen, carbon monoxide, carbon dioxide and water are included among the common combustion products. The main toxic products from PVC fires are hydrogen chloride (a sensory and pulmonary irritant) and carbon monoxide (an asphyxiant). The LC50 value, i.e. the lethal concentration of the chemical in air, calculated for a series of natural and synthetic materials thermally decomposed according to the NBS toxicity test method, ranged from 0.045 to 57 mg l⁻¹ in the flaming mode and from 0.045 to >40 mg l⁻¹ in the non-flaming mode. The LC50 results for a PVC resin, decomposed under the same conditions, were 17 mg l⁻¹ in the flaming mode and 20 mg l⁻¹ in the non-flaming mode. These results indicate that PVC decomposition products are not extremely toxic when compared with those from other common building materials. When the combustion toxicity (based on their HCl content) of PVC materials is compared with pure HCl experiments, it appears that much of the post-exposure toxicity can be explained by the HCl that is generated. The use of Cl-containing oil will cause severe unit corrosion and the release of environmental toxins. Therefore, necessary measures should be taken in terms of conversion of PVC into high quality oil. Compared with conventional pyrolysis, catalytic cracking can inhibit the formation of chlorinated hydrocarbons, lowering the reaction temperature, shortening residence times and enhancing the selectivity of products (Aguado et al., 2006). Catalytic dechlorination involves the selective cleavage of one or more C–Cl bonds, lowering toxicity and generating reusable raw materials. The toxicity of ABS degradation products was found to be comparable with the toxicity of the thermal decomposition products of other common polymeric materials (Rutkowski and Levin, 1986).

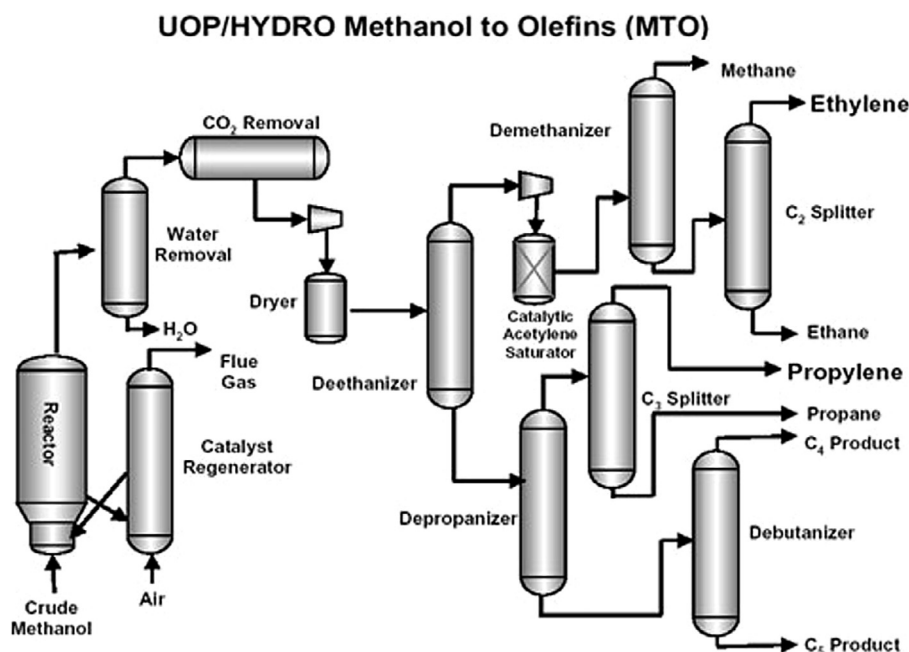


Fig. 38. Process flowsheet of the UOP/HYDRO MTO process.

Table 8
Summary of discussed techniques for recycling of SPW, including their advantages and challenges.

		Technique	Advantages	Challenges
Mechanical recycling	sorting	Flotation (sink-float)	Well-known technology Cost-effective Particle size Useful to remove non-melting contaminants	Efficiency determined by density differences plastics Mainly limited to binary mixtures
		Melt filtration		Potential pressure fluctuations in production
		FT-NIR	Additional melt pressure Post-drying not required Well-known	Black undetectable Plastic should be dry Pre-treatment
		Tribo-electric (electrostatic) separation	Efficient for various plastics Small particle sizes allowed	
		Froth flotation	Efficiency	Precursor step required In development for recycled plastics Density overlaps remain
		Magnetic density separation	Improved density-based technique Multiple polymer fractions in a single step	
	X-ray detection	Accuracy Useful for PVC	Cost-effectiveness	
	Reprocessing		High value recycling Well-known technology Straightforward	Thermal-mechanical degradation Challenging for complex mixtures Miscibility of polymer blends
Chemical recycling	Chemolysis		Generates pure value-added products	Requires high volumes to be cost-effective Mainly limited to condensation polymers
			Operational for PET	Complexity of reactions
	Pyrolysis		Suitable for highly heterogeneous mixtures of plastics Simple technology	Requires high volumes to be cost-effective Low tolerance for PVC Stable waste supply
				Deactivation of catalyst Absence of suitable reactor technology
	Fluid Catalytic cracking		Narrow product outcome Less stringent reaction conditions leads to favourable economics	
	Hydrogen technologies	Hydrocracking	Quality of produced naphta Suitable for mixtures of plastics	Presence of inorganics High cost of hydrogen High investment and operational costs
		IH ² process	Promising technology for the production of liquid fuels out of biomass Different elements already commercialized	Further research required
KDV process		Also suitable for oxygen and halogenated compounds	Chemistry still unknown Lack of technical information	
Gasification		Syngas is a valuable intermediate Cost of air Well-known technology	Amount of noxious NO _x Specific drawbacks of air	

4. Conclusion

This paper has reviewed the current state-of-the-art in the field of recycling of SPW, discussing both mechanical and chemical recycling. Mechanical recycling is the current industrially ubiquitous technique for the recovery of waste polymers. Different technological aspects of sorting and reprocessing have been discussed, as well as the materials science behind challenges associated with efficient mechanical recycling such as contaminations or the mixing of different plastics types in waste. These affect the product quality and give rise to limited economies of scale and fluctuating price of recycled materials. It is these potential limitations, which have led to the growing interest in a currently less frequently used type of recycling, namely chemical recycling. We have given an overview of the different pathways for the conversion of polymers into smaller molecules, which can be subsequently used for production of chemicals, fuels or virgin plastics with identical performance as the original materials. This type of recycling has high potential for heterogeneous and contaminated plastic waste material, where separation is either not economically viable or not completely technically feasible. A summary of all the discussed techniques for recycling of SPW is made in Table 8, including their advantages and remaining challenges. This review shows that both mechanical and chemical recycling have high industrial potential

and can be complimentary pathways for closing the loop on polymers; in any case they remain vastly preferable to energy recovery and landfilling.

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References

- Abrol, S., Hilton, C.M., 2012. Modeling, simulation and advanced control of methanol production from variable synthesis gas feed. *Comput. Chem. Eng.* 40, 117–131.
- Aguado, J., Serrano, D.P., Escola, J.M., 2006. *Catalytic Upgrading of Plastic Wastes, Feedstock Recycling and Pyrolysis of Waste Plastics*. John Wiley & Sons Ltd, pp. 73–110.
- Aguado, J., S., D.P., 1999. *Feedstock Recycling of Plastic Waste*.
- Akesson, D., Fuchs, T., Stoss, M., Root, A., Stenvall, E., Skrifvars, M., 2016. Recycling of wood fiber-reinforced HDPE by multiple reprocessing. *J. Appl. Polym. Sci.*, 133.
- Al-Salem, S., Baeyens, P., Baeyens, J., 2009a. Recycling and recovery routes of plastic solid waste (PSW): a review. *Waste Manage.* 29, 2625–2643.
- Al-Salem, S., Lettieri, P., Baeyens, J., 2009b. Thermal treatment of different grades and types of Polyethylene (PE) wasted articles. In: *Proceedings of 8th World Congress of Chemical Engineering Montreal (Quebec)*, pp. 1–4.
- Al-Salem, S., Lettieri, P., Baeyens, J., 2010. The valorization of plastic solid waste (PSW) by primary to quaternary routes: from re-use to energy and chemicals. *Prog. Energy Combust. Sci.* 36, 103–129.

- Albrecht, V., Simon, F., Gohs, U., Kretzschmar, B., Reinsch, E., Peuker, U.A., 2011. Influence of Additives and Filler on the Electrostatic Separation of Polyolefin Mixtures. Eurofillers, Dresden, Germany.
- Ali, K.A., Abdullah, A.Z., Mohamed, A.R., 2015. Recent development in catalytic technologies for methanol synthesis from renewable sources: a critical review. *Renew. Sustain. Energy Rev.* 44, 508–518.
- Altwaig, A.M., Wolf, M., van Eldik, R., 2003. Extraction of brominated flame retardants from polymeric waste material using different solvents and supercritical carbon dioxide. *Anal. Chim. Acta* 491, 111–123.
- Angyal, A., Miskolczi, N., Bartha, L., 2007. Petrochemical feedstock by thermal cracking of plastic waste. *J. Anal. Appl. Pyrol.* 79, 409–414.
- Ares, A., Bouza, R., Pardo, S.G., Abad, M.J., Barral, L., 2010. Rheological, mechanical and thermal behaviour of wood polymer composites based on recycled polypropylene. *J. Polym. Environ.* 18, 318–325.
- Arnold, J.C., Alston, S., Holder, A., 2009. Void formation due to gas evolution during the recycling of Acrylonitrile-Butadiene-Styrene copolymer (ABS) from waste electrical and electronic equipment (WEEE). *Polym. Degrad. Stabil.* 94, 693–700.
- Arostegui, A., Sarriónandía, M., Aurrekoetxea, J., Urrutibeascoa, I., 2006. Effect of dissolution-based recycling on the degradation and the mechanical properties of acrylonitrile-butadiene-styrene copolymer. *Polym. Degrad. Stabil.* 91, 2768–2774.
- Arvanitoyannis, I.S., Bosnea, L.A., 2001. Recycling of polymeric materials used for food packaging: current status and perspectives. *Food Rev. Int.* 17, 291–346.
- Ashcraft, R.W., Heynderickx, G.J., Marin, G.B., 2012. Modeling fast biomass pyrolysis in a gas-solid vortex reactor. *Chem. Eng. J.* 207–208, 195–208.
- Ashcraft, R.W., Kovacevic, J., Heynderickx, G.J., Marin, G.B., 2013. Assessment of a gas-solid vortex reactor for SO₂/NO_x adsorption from flue gas. *Ind. Eng. Chem. Res.* 52, 861–875.
- Awaja, F., Pavel, D., 2005. Recycling of PET. *Eur. Polymer J.* 41, 1453–1477.
- Bai, X.J., Isaac, D.H., Smith, K., 2007. Reprocessing acrylonitrile-butadiene-styrene plastics: structure-property relationships. *Polym. Eng. Sci.* 47, 120–130.
- Banerjee, J., Soliya, P., Mukhopadhyay, P., Bandyopadhyay, D., Chakrabarty, D., Dutta, K., 2016. Impact modification of isotactic polypropylene with ethylene-propylene diene monomer rubber. *Int. Polym. Proc.* 16.
- Barger, P.T., Wilson, S.T., Holmgren, J.S., 1993. Process for Converting Methanol to Olefins Using an Improved Metal Aluminophosphate Catalyst. Google Patents.
- Beigbeder, J., Perrin, D., Mascaro, J.F., Lopez-Cuesta, J.M., 2013. Study of the physico-chemical properties of recycled polymers from waste electrical and electronic equipment (WEEE) sorted by high resolution near infrared devices. *Resour. Conserv. Recycl.* 78, 105–114.
- Beyler, C.L., Hirschler, M.M., 2002. Thermal decomposition of polymers. *SFPE Handb. Fire Protect. Eng.* 2, 110–131.
- Bhaskar, T., Uddin, M.A., Kaneko, J., Kusaba, T., Matsui, T., Muto, A., Sakata, Y., Murata, K., 2003. Liquefaction of mixed plastics containing PVC and dechlorination by calcium-based sorbent. *Energy Fuels* 17, 75–80.
- Blom, H.P., Teh, J.W., Rudin, A., 1998. PP/PE blends. IV. Characterization and compatibilization of blends of postconsumer resin with virgin PP and HDPE. *J. Appl. Polym. Sci.* 70, 2081–2095.
- Boldizar, A., Moller, K., 2003. Degradation of ABS during repeated processing and accelerated ageing. *Polym. Degrad. Stabil.* 81, 359–366.
- Bonifazi, G., Di Maio, F., Potenza, F., Serranti, S., 2016. FT-IR analysis and hyperspectral imaging applied to postconsumer plastics packaging characterization and sorting. *IEEE Sensors J.* 16, 3428–3434.
- Borovanska, I., Cerrada, M.L., Zipper, P., Djoumaliski, S., 2016. Recycled polyolefin blends: effect of modified natural zeolite on their properties and morphology. *Polym. Plast. Technol. Eng.* 55, 486–497.
- Braun, D., 2002. Recycling of PVC. *Prog. Polym. Sci.* 27, 2171–2195.
- Brems, A., Baeyens, J., Dewil, R., 2012. Recycling and recovery of post-consumer plastic solid waste in a European context. *Therm. Sci.* 16, 669–685.
- Brems, A., Dewil, R., Baeyens, J., Zhang, R., 2015. Gasification Of Plastic Waste As Waste- To- Energy Or Waste- To- Syngas Recovery Route, Solid Waste as a Renewable Resource. Apple Academic Press, pp. 241–263.
- Brennan, L.B., Isaac, D.H., Arnold, J.C., 2002. Recycling of acrylonitrile-butadiene-styrene and high-impact polystyrene from waste computer equipment. *J. Appl. Polym. Sci.* 86, 572–578.
- Broach, R.W., Jan, D.-Y., Lesch, D.A., Kulprathipanja, S., Roland, E., Kleinschmit, P., 2012. Zeolites. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Brown, S.H., Shinnar, R., Weber, W.A., 2005. Process for Converting Methanol to Olefins. Google Patents.
- Buekens, A., Yang, J., 2014. Recycling of WEEE plastics: a review. *J. Mater. Cycles Waste* 16, 415–434.
- Buekens, A.G., Huang, H., 1998. Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. *Resour. Conserv. Recycl.* 23, 163–181.
- Butler, E., Devlin, G., McDonnell, K., 2011. Waste polyolefins to liquid fuels via pyrolysis: review of commercial state-of-the-art and recent laboratory research. *Waste Biomass Valoriz.* 2, 227–255.
- Callister, W., Rethwisch, D., 2010. Materials Science & Engineering. Wiley & Sons.
- Censori, M., La Marca, F., Carvalho, M.T., 2016. Separation of plastics: the importance of kinetics knowledge in the evaluation of froth flotation. *Waste Manage.* 54, 39–43.
- Champagne, M.F., Huneault, M.A., Roux, C., Peyrel, W., 1999. Reactive compatibilization of polypropylene/polyethylene terephthalate blends. *Polym. Eng. Sci.* 39, 976–984.
- Chevallier, C., Becquart, F., Taha, M., 2013. Polystyrene/polycarbonate blends compatibilization: morphology, rheological and mechanical properties. *Mater. Chem. Phys.* 139, 616–622.
- Chiono, V., Filippi, S., Yordanov, H., Minkova, L., Magagnini, P., 2003. Reactive compatibilizer precursors for LDPE/PAG blends. III: ethylene-glycidylmethacrylate copolymer. *Polym.* 44, 2423–2432.
- Dasdemir, M., Maze, B., Anantharamaiah, N., Pourdeyhimi, B., 2015. Reactive compatibilization of polyamide 6/polyethylene nonwoven based thermoplastic composites. *Eur. Polymer J.* 63, 194–206.
- de Broqueville, A., 2009. Process for the thermal and/or catalytic conversion of reactive fluids passing through various longitudinal reaction volumes of a rotating fluidized bed.
- De Wilde, J., de Broqueville, A., 2007. Rotating fluidized beds in a static geometry: experimental proof of concept. *AIChE J.* 53, 793–810.
- De Wilde, J., de Broqueville, A., 2008. Experimental investigation of a rotating fluidized bed in a static geometry. *Powder Technol.* 183, 426–435.
- Delva, L., Cardon, L., Ragaert, K., 2015. Evaluation of post-consumer mixed polyolefines and their injection moulded blends with virgin poly-ethylene. *Environ. Eng. Manage. J.* (in press).
- Delva, L., Ragaert, K., Degrieck, J., Cardon, L., 2014. The effect of multiple extrusions on the properties of montmorillonite filled polypropylene. *Polymers* 6, 2912–2927.
- Delva, L., Verberckmoes, A., Cardon, L., Ragaert, K., 2013. The use of rubber as a compatibilizer for injection moulding of recycled post-consumer mixed polyolefines. In: 2nd international conference WASTES: Solutions, Treatments and Opportunities. CVR, Braga, Portugal, pp. 689–694.
- Denkstatt, 2015. The potential for plastics packaging to contribute to a circular and resource-efficient economy, Identiplast.
- Dimonie, D., 2012. Overview on Mechanical Recycling by Chain Extension of POSTC-PET Bottles. InTech.
- Ding, W., Liang, J., Anderson, L.L., 1997. Hydrocracking and hydroisomerization of high-density polyethylene and waste plastic over zeolite and silica-alumina-supported Ni and Ni-Mo sulfides. *Energy Fuels* 11, 1219–1224.
- Dry, M.E., 2002. High quality diesel via the Fischer-Tropsch process—a review. *J. Chem. Technol. Biotechnol.* 77, 43–50.
- Dudyński, M., van Dyk, J.C., Kwiatkowski, K., Sosnowska, M., 2015. Biomass gasification: influence of torrefaction on syngas production and tar formation. *Fuel Process. Technol.* 131, 203–212.
- Dutta, A., Ekapture, R.P., Heynderickx, G.J., de Broqueville, A., Marin, G.B., 2010. Rotating fluidized bed with a static geometry: Guidelines for design and operating conditions. *Chem. Eng. Sci.* 65, 1678–1693.
- Ekapture, R.P., Suryawanshi, V.U., Heynderickx, G.J., de Broqueville, A., Marin, G.B., 2011. Experimental investigation of a gas-solid rotating bed reactor with static geometry. *Chem. Eng. Process.* 50, 77–84.
- El-Nashar, D.E., Maziad, N.A., Sadek, E.M., 2008. Improving low-density polyethylene/poly(ethylene terephthalate) blends with graft copolymers. *J. Appl. Polym. Sci.* 110, 1929–1937.
- Ellen Macarthur Foundation, 2017. The New Plastics Economy: Catalysing Action.
- Elmaghor, F., Zhang, L., Fan, R., Li, H., 2004. Recycling of polycarbonate by blending with maleic anhydride grafted ABS. *Polym.* 45, 6719–6724.
- EU-Parliament, 2015. Circular economy: the importance of re-using products and materials.
- European Commission, 2013. On a European Strategy on Plastic Waste in the Environment, Green Paper. European Commission, Brussels.
- European Commission, 2009. Ecodesign Directive (Directive 2009/125/EC). Brussels.
- European Commission, 2015. Closing the Loop - An EU Action Plan for the Circular Economy (COM(2015) 614/2). Brussels.
- Faravelli, T., Bozzano, G., Colombo, M., Ranzi, E., Dente, M., 2003. Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *J. Anal. Appl. Pyrol.* 70, 761–777.
- Faravelli, T., Bozzano, G., Scassa, C., Perego, M., Fabini, S., Ranzi, E., Dente, M., 1999. Gas product distribution from polyethylene pyrolysis. *J. Anal. Appl. Pyrol.* 52, 87–103.
- Flory, P.J., 1942. Thermodynamics of high polymer solutions. *J. Chem. Phys.* 10, 51–61.
- FostPlus, 2014. Fost Plus onderzoekt uitbreiding PMD-zak. Fostpost, Brussel.
- Fraunholz, N., 2004. Separation of waste plastics by froth flotation - a review, part I. *Miner. Eng.* 17, 261–268.
- Garforth, A.A., Ali, S., Hernández-Martínez, J., Akah, A., 2004. Feedstock recycling of polymer wastes. *Curr. Opin. Solid State Mater. Sci.* 8, 419–425.
- George, N., Kurian, T., 2014. Recent developments in the chemical recycling of postconsumer poly(ethylene terephthalate) waste. *Ind. Eng. Chem. Res.* 53, 14185–14198.
- GmbH, A.
- González-González, V.A., Neira-Velázquez, G., Angulo-Sánchez, J.L., 1998. Polypropylene chain scissions and molecular weight changes in multiple extrusion. *Polym. Degrad. Stab.* 60, 33–42.
- Gonzalez-Quiroga, A., Djokic, M.R., Van Geem, K.M., Marin, G.B., 2016. Conversion of solid waste to diesel via catalytic pressureless depolymerization: pilot scale production and detailed compositional characterization. *Energy Fuels* 30, 8292–8303.
- Goto, M., 2009. Chemical recycling of plastics using sub- and supercritical fluids. *J. Supercrit. Fluids* 47, 500–507.
- Gu, L., Ozbakkaloglu, T., 2016. Use of recycled plastics in concrete: a critical review. *Waste Manage.* 51, 19–42.

- Guerfi, N., Belhaneche-Bensemra, N., 2014. Preparation, characterization and valorization of regenerated low density polyethylene/polypropylene blends. *Environ. Eng. Manage. J.* 13, 2609–2613.
- Guo, J.Y., Guo, J., Xu, Z.M., 2009. Recycling of non-metallic fractions from waste printed circuit boards: a review. *J. Hazard. Mater.* 168, 567–590.
- Haro, P., Trippé, F., Stahl, R., Henrich, E., 2013. Bio-syngas to gasoline and olefins via DME—a comprehensive techno-economic assessment. *Appl. Energy* 108, 54–65.
- Heidenreich, S., Foscolo, P.U., 2015. New concepts in biomass gasification. *Prog. Energy Combust. Sci.* 46, 72–95.
- Hlavatá, D., Horák, Z., Lednický, F., Hromádková, J., Pleska, A., Zanevskii, Y.V., 2001. Compatibilization efficiency of styrene-butadiene multiblock copolymers in PS/PP blends. *J. Polym. Sci., Part B: Polym. Phys.* 39, 931–942.
- Holsti-Miettinen, R.M., Seppälä, J.V., Ikkala, O.T., Reima, I.T., 1994. Functionalized elastomeric compatibilizer in PA 6/PP blends and binary interactions between compatibilizer and polymer. *Polym. Eng. Sci.* 34, 395–404.
- Hopewell, J., Dvorak, R., Kosior, E., 2009. Plastics recycling: challenges and opportunities. *Philos. Trans. R. Soc. B-Biol. Sci.* 364, 2115–2126.
- Hubo, S., Delva, L., Van Damme, N., Ragaert, K., 2015. Blending of recycled mixed polyolefins with recycled polypropylene: effect on physical and mechanical properties. In: Holzer, C. (Ed.), *Polymer Processing Society 2015*, Graz Austria.
- Hubo, S., Leite, L., Martins, C., Ragaert, K., 2014. Evaluation of post-industrial and post-consumer polyolefin-based polymer waste streams for injection moulding. In: 6th Polymers & Mould Innovations International Conference. Guimaraes, Portugal, pp. 201–206.
- Hubo, S., Ragaert, K., 2016. Mirror welding of recycled polyolefins. In: Maazouz, A. (Ed.), *Polymer Processing Society 2016*. Lyon, France.
- Huggett, C., Levin, B.C., 1987. Toxicity of the pyrolysis and combustion products of poly(vinyl chlorides): a literature assessment. *Fire Mater* 11, 131–142.
- Ignatyev, I.A., Thielemans, W., Vander Beke, B., 2014. Recycling of polymers: a review. *Chemoschem* 7, 1579–1593.
- Ismail, H.H., Nasir, M., 2002. The effect of various compatibilizers on mechanical properties of polystyrene/polypropylene blend. *Polym. Test.* 21, 163–170.
- Jeon, B.H., Yoon, H., Hwang, S.S., Kim, J., Hong, S.M., 2005. Enhancement of compatibility and toughening of commingled packaging film wastes. *Polym.-Korea* 29, 127–134.
- Jiang, C., Filippi, S., Magagnini, P., 2003. Reactive compatibilizer precursors for LDPE/PA6 blends. II: maleic anhydride grafted polyethylenes. *Polym.* 44, 2411–2422.
- Jin, D., Shon, K., Jeong, H., Kim, B., 1998. Compatibility enhancement of ABS/polycarbonate blends. *J. Appl. Polym. Sci.* 69, 533–542.
- Kaiser, G., Schmolzer, S., Strasser, C., Pohland, S., Turan, S., 2015. *Handbook Differential Scanning Calorimetry*. Netzsch, Selb, Germany.
- Kallel, T., Massardier-Nageotte, V., Jaziri, M., Gérard, J.-F., Elleuch, B., 2003. Compatibilization of PE/PS and PE/PP blends. I. Effect of processing conditions and formulation. *J. Appl. Polym. Sci.* 90, 2475–2484.
- Kaminsky, W., Predel, M., Sadiki, A., 2004. Feedstock recycling of polymers by pyrolysis in a fluidised bed. *Polym. Degrad. Stabil.* 85, 1045–1050.
- Kazemi, Y., Kakroodi, A.R., Rodrigue, D., 2015. Compatibilization efficiency in post-consumer recycled polyethylene/polypropylene blends: effect of contamination. *Polym. Eng. Sci.* 55, 2368–2376.
- Keil, F.J., 1999. Methanol-to-hydrocarbons: process technology. *Microp. Mesop. Mater.* 29, 49–66.
- Koch, C., 2011. *The KDV Technology [Company Presentation]*. Alphakat GmbH.
- Koning, C., van Duin, M., Pagnoulle, C., Jerome, R., 1998. Strategies for compatibilization of polymer blends. *Prog. Polym. Sci.* 23, 707–757.
- Kovacevic, J.Z., Pantzali, M.N., Heynderickx, G.J., Marin, G.B., 2014. Bed stability and maximum solids capacity in a gas-solid vortex reactor: experimental study. *Chem. Eng. Sci.* 106, 293–303.
- Kovacevic, J.Z., Pantzali, M.N., Niyogi, K., Deen, N.G., Heynderickx, G.J., Marin, G.B., 2015. Solids velocity fields in a cold-flow gas-solid vortex reactor. *Chem. Eng. Sci.* 123, 220–230.
- Kumar, A., Jones, D.D., Hanna, M.A., 2009. Thermochemical biomass gasification: a review of the current status of the technology. *Energy* 2, 556–581.
- Kumar, S., Panda, A.K., Singh, R., 2011. A review on tertiary recycling of high-density polyethylene to fuel. *Resour. Conserv. Recycl.* 55, 893–910.
- Kunststofindustrie, F.N.Re., 2015. *Casguide Ontwerpen met Kunststof Recyclaat*.
- Kuram, E., Sahin, Z.M., Ozcelik, B., Yilmaz, F., Medar, M.M., 2014. Recyclability of polyethylene/polypropylene binary blends and enhancement of their mechanical properties by reinforcement with glass fiber. *Polym. Plast. Technol. Eng.* 53, 1035–1046.
- La Mantia, F.P., 1996a. *Basic Concepts on the Recycling of Homogeneous and Heterogeneous Plastics. Recycling of PVC and Mixed Plastic Waste*. ChemTec Publishing.
- La Mantia, F.P., 1996b. *Recycling of PVC and Mixed Plastic Waste*. ChemTec Publishing.
- La Mantia, F.P., Vinci, M., 1994. Recycling poly(ethyleneterephthalate). *Polym. Degrad. Stabil.* 45, 121–125.
- Labeckas, G., Slavinskis, S., 2013. Performance and emission characteristics of a direct injection diesel engine operating on KDV synthetic diesel fuel. *Energy Convers. Manage.* 66, 173–188.
- Leong, Y.W., Abu Bakar, M.B., Ishak, Z.A.M., Ariffin, A., Pukanszky, B., 2004. Comparison of the mechanical properties and interfacial interactions between talc, kaolin, and calcium carbonate filled polypropylene composites. *J. Appl. Polym. Sci.* 91, 3315–3326.
- Lepers, J.C., Favis, B.D., Tabar, R.J., 1997. The relative role of coalescence and interfacial tension in controlling dispersed phase size reduction during the compatibilization of polyethylene terephthalate/polypropylene blends. *J. Polym. Sci., Part B: Polym. Phys.* 35, 2271–2280.
- Levin, B.C., 1987. A summary of the NBS literature reviews on the chemical nature and toxicity of the pyrolysis and combustion products from 7 plastics - acrylonitrile butadiene styrenes (ABS), nylons, polyesters, polyethylenes, polystyrenes, polyvinyl chlorides) and rigid polyurethane foams. *Fire Mater* 11, 143–157.
- Li, X., Li, J., Zhou, G., Feng, Y., Wang, Y., Yu, G., Deng, S., Huang, J., Wang, B., 2014. Enhancing the production of renewable petrochemicals by co-feeding of biomass with plastics in catalytic fast pyrolysis with ZSM-5 zeolites. *Appl. Catal. A* 481, 173–182.
- Lin, Y.-H., Yang, M.-H., 2009. Tertiary recycling of commingled polymer waste over commercial FCC equilibrium catalysts for producing hydrocarbons. *Polym. Degrad. Stabil.* 94, 25–33.
- Lin, Z., Guan, Z., Xu, B., Chen, C., Guo, G., Zhou, J., Xian, J., Cao, L., Wang, Y., Li, M., 2013. Crystallization and melting behavior of polypropylene in β -PP/polyamide 6 blends containing PP-g-MA. *J. Ind. Eng. Chem.* 19, 692–697.
- Linck, M., Felix, L., Marker, T., Roberts, M., 2014. Integrated biomass hydrolysis and hydrotreating: a brief review. *Wiley Interdisc. Rev.: Energy Environ.* 3, 575–581.
- Liu, Y., Truss, R.W., 1996. Study of dispersion morphologies of isotactic polypropylene and linear low density polyethylene blends by scanning electron microscopy. *J. Appl. Polym. Sci.* 60, 1461–1473.
- Luciani, V., Bonifazi, G., Rem, P., Serranti, S., 2015. Upgrading of PVC rich wastes by magnetic density separation and hyperspectral imaging quality control. *Waste Manage.* 45, 118–125.
- Luijsterburg, B., Goossens, H., 2014. Assessment of plastic packaging waste: Material origin, methods, properties. *Resour. Conserv. Recy.* 85, 88–97.
- Luijsterburg, B.J., Jobse, P.S., Spoelstra, A.B., Goossens, J.G.P., 2016. Solid-state drawing of post-consumer isotactic poly(propylene): effect of melt filtration and carbon black on structural and mechanical properties. *Waste Manage.* 54, 53–61.
- Maier, C., Calafut, T., 2008. *Polypropylene: The Definitive User's Guide and Databook*. Elsevier Science.
- Manias, E., Utracki, L.A., 2014. *Thermodynamics of Polymer Blends*. In: Utracki, L.A., Wilkie, C. (Eds.), *Polymer Blends Handbook*. Springer Science.
- Marker, T., Roberts, M., Linck, M., Felix, L., Ortiz-Toral, P., Wangerow, J., McLeod, C., Del Paggio, A., Gephart, J., Starr, J., 2013. Long Term Processing Using Integrated Hydrolysis plus Hydroconversion (IH2) for the Production of Gasoline and Diesel from Biomass. *Gas Technology Institute*.
- Marker, T.L., Felix, L.G., Linck, M.B., Roberts, M.J., 2012. Integrated hydrolysis and hydroconversion (IH2) for the direct production of gasoline and diesel fuels or blending components from biomass, part 1: proof of principle testing. *Environ. Prog. Sustain.* 31, 191–199.
- Marker, T.L., Felix, L.G., Linck, M.B., Roberts, M.J., Ortiz-Toral, P., Wangerow, J., 2014. Integrated hydrolysis and hydroconversion (IH2[®]) for the direct production of gasoline and diesel fuels or blending components from biomass, Part 2: continuous testing. *Environ. Prog. Sustain.* 33, 762–768.
- Marongiu, A., Faravelli, T., Bozzano, G., Dente, M., Ranzi, E., 2003. Thermal degradation of poly(vinyl chloride). *J. Anal. Appl. Pyrol.* 70, 519–553.
- Marongiu, A., Faravelli, T., Ranzi, E., 2007. Detailed kinetic modeling of the thermal degradation of vinyl polymers. *J. Anal. Appl. Pyrol.* 78, 343–362.
- Martinho, G., Pires, A., Saraiva, L., Ribeiro, R., 2012. Composition of plastics from waste electrical and electronic equipment (WEEE) by direct sampling. *Waste Manage.* 32, 1213–1217.
- Miskolczi, N., Angyal, A., Bartha, L., Valkai, I., 2009. Fuels by pyrolysis of waste plastics from agricultural and packaging sectors in a pilot scale reactor. *Fuel Process. Technol.* 90, 1032–1040.
- Miskolczi, N., Bartha, L., Deák, G., Jover, B., 2004. Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons. *Polym. Degrad. Stabil.* 86, 357–366.
- Moller, R., Jeske, U., 1995. *Recycling von PVC*. Forschungszentrum Karlsruhe, Karlsruhe, Grundlagen, Stand der Technik, Handlungsmöglichkeiten.
- Mou, P., Xiang, G., Duan, G., 2007. Products made from nonmetallic materials reclaimed from waste printed circuit boards. *Tsinghua Sci. Technol.* 12, 276–283.
- Munasinghe, P.C., Khanal, S.K., 2010. Biomass-derived syngas fermentation into biofuels: opportunities and challenges. *Bioresour. Technol.* 101, 5013–5022.
- Murphy, J., 2001. CHAPTER 20 - Other Types of Additive: Additives for Recycling. *Additives for Plastics Handbook (Second Edition)*. Elsevier Science, Amsterdam, pp. 237–244.
- Narasimhan, L., Del Paggio, A., 2017. *Hydrocarbon Fuels from Bio-Waste – An Integrated Energy-Environmental Solution* <http://www.fipi.org.in/attachments/11_May_16/Session%20I/3_C%20S%20Laxmi.pdf>.
- Ohishi, H., Ikehara, T., Nishi, T., 2001. Phase morphologies and mechanical properties of high-impact polystyrene (HIPS) and polycarbonate blends compatibilized with polystyrene and polyarylate block copolymer. *J. Appl. Polym. Sci.* 80, 2347–2360.
- Okuwaki, A., 2004. Feedstock recycling of plastics in Japan. *Polym. Degrad. Stabil.* 85, 981–988.
- Oliveux, G., Bailleul, J.L., La Salle, E.L., 2012. Chemical recycling of glass fibre reinforced composites using subcritical water. *Compos. Part A-Appl. Sci.* 43, 1809–1818.
- Paabo, M., Levin, B.C., 1987. A review of the literature on the gaseous products and toxicity generated from the pyrolysis and combustion of rigid polyurethane foams. *Fire Mater* 11, 1–29.

- Pang, Y.X., Jia, D.M., Hu, H.J., Hourston, D.J., Song, M., 2000. Effects of a compatibilizing agent on the morphology, interface and mechanical behaviour of polypropylene/poly(ethylene terephthalate) blends. *Polym.* 41, 357–365.
- Papadopoulou, C.P., Kalfoglou, N.K., 2000. Comparison of compatibilizer effectiveness for PET/PP blends: their mechanical, thermal and morphology characterization. *Polym.* 41, 2543–2555.
- Passamonti, F.J., Sedran, U., 2012. Recycling of waste plastics into fuels. *LDPE conversion in FCC. Appl. Catal. B* 125, 499–506.
- Petcore.
- Peydro, M.A., Parres, F., Crespo, J.E., Navarro, R., 2013. Recovery of recycled acrylonitrile-butadiene-styrene, through mixing with styrene-ethylene/butylene-styrene. *J. Mater. Process. Technol.* 213, 1268–1283.
- Pinheiro, L.A., Chinelatto, M.A., Canevarolo, S.V., 2004. The role of chain scission and chain branching in high density polyethylene during thermo-mechanical degradation. *Polym. Degrad. Stabil.* 86, 445–453.
- Pinto, F., Costa, P., Gulyurtlu, I., Cabrita, I., 1999. Pyrolysis of plastic wastes: 2. Effect of catalyst on product yield. *J. Anal. Appl. Pyrol.* 51, 57–71.
- PlasticsEurope, 2015. *Plastics The Facts 2014/2015: an Analysis of European Plastics Production. Demand and Waste Data*, PlasticsEurope Brussels, Belgium.
- PlasticsEurope, EuPC, EuPR, EPRO, 2015. *Plastics - the Facts 2015. An Analysis of European Plastics Production, Demand and Recovery for 2015*.
- Pluta, M., Bartczak, Z., Pawlak, A., Galeski, A., Pracella, M., 2001. Phase structure and viscoelastic properties of compatibilized blends of PET and HDPE recyclates. *J. Appl. Polym. Sci.* 82, 1423–1436.
- Pohlein, M., Llopis, A.S., Wolf, M., van Eldik, R., 2005. Rapid identification of RoHS-relevant flame retardants from polymer housings by ultrasonic extraction and RP-HPLC/UV. *J. Chromatogr. A* 1066, 111–117.
- Pu, H., Tang, X., Xu, X., 1998. Studies on polycarbonate/polystyrene/polycarbonate-graft-polystyrene blends. II. Compatibility and morphology of PC/PS/PC-g-PS blends. *Polym. Int.* 45, 169–174.
- Puig-Arnavat, M., Bruno, J.C., Coronas, A., 2010. Review and analysis of biomass gasification models. *Renew. Sustain. Energy Rev.* 14, 2841–2851.
- Qian, S., Igarashi, T., Nitta, K.-H., 2011. Thermal degradation behavior of polypropylene in the melt state: molecular weight distribution changes and chain scission mechanism. *Polym. Bull.* 67, 1661–1670.
- Radonjic, G., Gubeljak, N., 2002. The use of ethylene/propylene copolymers as compatibilizers for recycled polyolefin blends. *Macromol. Mater. Eng.* 287, 122–132.
- Ragaert, K., 2016. Trends in mechanical recycling of thermoplastics. In: Pinter, G., Pilz, G. (Eds.), 25. *Leobener Kunststoff-Kolloquium 2016*. Leoben, Austria.
- Ragaert, K., Hubo, S., Van Damme, N., Veelaert, L., De Meester, S., Du Bois, E., 2016. Design from Recycling: Identifying applications for recycled polymers. In: Maazouz, A. (Ed.), 32nd *Polymer Processing Society*, Lyon, France.
- Ranzi, E., Dente, M., Faravelli, T., Bozzano, G., Fabiani, S., Nava, R., Cozzani, V., Tognotti, L., 1997. Kinetic modeling of polyethylene and polypropylene thermal degradation. *J. Anal. Appl. Pyrol.* 40, 305–319.
- Ravve, A., 2000. *Principles of Polymer Chemistry*. Kluwer Academic/Plenum Publishers.
- Reinsch, E., Frey, A., Albrecht, V., Simon, F., Peuker, U.A., 2014. Continuous electric sorting in the recycling process of plastics. *Chem. Ing. Tec.* 86, 784–796.
- Rem, P., Di Maio, F., Hu, B., Houzeaux, G., Baltes, L., Tieren, M., 2013. Magnetic fluid equipment for sorting secondary polyolefins from waste. *Environ. Eng. Manage. J.* 12, 951–958.
- Reza, F., Bahram, S., 2015. Feasibility study and quality assurance of the end-product of Alphakat KDV technology for conversion of biomass.
- Rijkema, L., 1999. *PVC and Municipal Solid Waste Combustion: Burden or Benefit?* TNO Institute of Environmental Sciences, Energy Research and Process Innovation TNO-MEP 99, p. 462.
- Rodrigo, J., Castells, F., 2002. *Electrical and Electronic Practical Ecodesign Guide*.
- Ruiz, J.A., Juárez, M.C., Morales, M.P., Muñoz, P., Mendiávil, M.A., 2013. Biomass gasification for electricity generation: Review of current technology barriers. *Renew. Sustain. Energy Rev.* 18, 174–183.
- Rutkowski, J.V., Levin, B.C., 1986. Acrylonitrile-butadiene-styrene copolymers (ABS): Pyrolysis and combustion products and their toxicity—a review of the literature. *Fire Mater* 10, 93–105.
- Sadat-Shojai, M., Bakhshandeh, G.-R., 2011. Recycling of PVC wastes. *Polym. Degrad. Stabil.* 96, 404–415.
- Safi, B., Saidi, M., Aboutaleb, D., Maallem, M., 2013. The use of plastic waste as fine aggregate in the self-compacting mortars: effect on physical and mechanical properties. *Constr. Build. Mater.* 43, 436–442.
- Sanchez-Valdes, S., Ramirez-Vargas, E., de Valle, L.F.R., Mendez-Nonell, J., Martinez-Colunga, J.G., Gutierrez-Villarreal, M.H., Lopez-Quintanilla, M.L., Sanchez-Adame, M., Mendoza-Garcia, D., 2013. Effect of functionalized polyethylenes on clay dispersion in high density polyethylene nanocomposites. *Polym. Bull.* 70, 535–547.
- Scaffaro, R., Botta, L., Di Benedetto, G., 2012. Physical properties of virgin-recycled ABS blends: effect of post-consumer content and of reprocessing cycles. *Eur. Polymer J.* 48, 637–648.
- Scheirs, J., 1998. *Polymer Recycling: Science, Technology, and Applications*. Wiley.
- Scheirs, J., Kaminsky, W., 2006. *Feedstock Recycling and Pyrolysis into Diesel and Other Fuels*.
- Scheirs, J., Kaminsky, W., 2006b. *Feedstock Recycling and Pyrolysis of Waste Plastics*. John Wiley & Sons.
- Schirmer, J., Kim, J., Klemm, E., 2001. Catalytic degradation of polyethylene using thermal gravimetric analysis and a cyclod-spheres-reactor. *J. Anal. Appl. Pyrol.* 60, 205–217.
- Serrano, D.P., Aguado, J., Escola, J.M., 2012. Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *ACS Catalysis* 2, 1924–1941.
- Serranti, S., Luciani, V., Bonifazi, G., Hu, B., Rem, P.C., 2015. An innovative recycling process to obtain pure polyethylene and polypropylene from household waste. *Waste Manage.* 35, 12–20.
- Sharma, R., Bansal, P.P., 2016. Use of different forms of waste plastic in concrete – a review. *J. Clean. Product.* 112 (Part 1), 473–482.
- Shell, 2017. *Back to the Future: Could Cars One Day be Powered by Waste?* <<http://www.shell.com/inside-energy/back-to-the-future.html>>.
- Siddique, R., Khatib, J., Kaur, I., 2008. Use of recycled plastic in concrete: a review. *Waste Manage.* 28, 1835–1852.
- Souza, A., Demarquette, N., 2002. Influence of coalescence and interfacial tension on the morphology of PP/HDPE compatibilized blends. *Polym.* 43, 3959–3967.
- Spath, P.L., Dayton, D.C., 2003. *Preliminary Screening-Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas*. DTIC Document.
- Stenvall, E., Boldizar, A., 2016. Mechanical and thermal characterization of melt-filtered, blended and reprocessed post-consumer WEEE thermoplastics. *Recycling* 1, 89–100.
- Stenvall, E., Tostar, S., Boldizar, A., Foreman, M.R.S., Moller, K., 2013. An analysis of the composition and metal contamination of plastics from waste electrical and electronic equipment (WEEE). *Waste Manage.* 33, 915–922.
- Su, K.-H., Lin, J.-H., Lin, C.-C., 2007. Influence of reprocessing on the mechanical properties and structure of polyamide 6. *J. Mater. Process. Technol.* 192–193, 532–538.
- Tarantili, P.A., Mitsakaki, A.N., Petoussi, M.A., 2010. Processing and properties of engineering plastics recycled from waste electrical and electronic equipment (WEEE). *Polym. Degrad. Stabil.* 95, 405–410.
- Teh, J.W., Rudin, A., Keung, J.C., 1994. A review of polyethylene-polypropylene blends and their compatibilization. *Adv. Polym. Technol.* 13, 1–23.
- Thegarid, N., Fogassy, G., Schuurman, Y., Mirodatos, C., Stefanidis, S., Iliopoulou, E., Kalogiannis, K., Lappas, A., 2014. Second-generation biofuels by co-processing catalytic pyrolysis oil in FCC units. *Appl. Catal. B* 145, 161–166.
- Tjong, S.C., Meng, Y.Z., 2000. Effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly(acrylonitrile-butadiene-styrene) blends. *Eur. Polymer J.* 36, 123–129.
- Trippie, F., Fröhling, M., Schultmann, F., Stahl, R., Henrich, E., 2011. Techno-economic assessment of gasification as a process step within biomass-to-liquid (BtL) fuel and chemicals production. *Fuel Process. Technol.* 92, 2169–2184.
- Tullo, A.H., 2016. The cost of plastic packaging. *Chem. Eng. News* 94, 32–37.
- Twite-Kabamba, E., Fehri, Z.F., Rodrigue, D., 2011. Properties of recycled LDPE/Birch fibre composites. *Prog. Rubber Plast. Recycl. Technol.* 27, 1–20.
- Ulutan, S., 2003. Influence of additional thermal stabilizers on the reprocessing of postconsumer poly(vinyl chloride) bottles. *J. Appl. Polym. Sci.* 90, 3994–3999.
- Utracki, L.A., 2002. *Polymer Blends Handbook*. Kluwer Academic Pub.
- Utracki, L.A., Dumoulin, M.M., 1995. *Polypropylene alloys and blends with thermoplastics*. In: Karger-Kochis (Ed.), *Polypropylene: Structure, Blends and Composites*. Chapman and Hall, London, p. 50.
- van Bruggen, E.P.A., Koster, R.P., Picken, S.J., Ragaert, K., 2016. Influence of processing parameters and composition on the effective compatibilization of polypropylene-poly(ethylene terephthalate) blends. *Int. Polym. Proc.* 31, 179–187.
- Van Damme, N., Leroy, S., Van Loocke, S., Hubo, S., Veelaert, L., Cardon, L., Dubois, E., Ragaert, K., 2016. Upgrading of recycled ABS from ELV and WEEE. In: 7th *International Polymer and Materials Innovations Conference*. Ghent, Belgium.
- Veelaert, L., Ragaert, K., Hubo, S., Van Kets, K., De Bois, E., 2016. Bridging design and engineering in terms of materials selection. In: 7th *Polymers and Moulds Innovations Conference*. Ghent Belgium.
- Vermeulen, I., Van Caneghem, J., Block, C., Baeyens, J., Vandecasteele, C., 2011. Automotive shredder residue (ASR): reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals' valorisation. *J. Hazard. Mater.* 190, 8–27.
- Vilaplana, F., Karlsson, S., 2008. Quality concepts for the improved use of recycled polymeric materials: a review. *Macromol. Mater. Eng.* 293, 274–297.
- Walendziewski, J., Steininger, M., 2001. Thermal and catalytic conversion of waste polyolefines. *Catal. Today* 65, 323–330.
- Wang, C.Q., Wang, H., Fu, J.G., Liu, Y.N., 2015a. Flotation separation of waste plastics for recycling—a review. *Waste Manage.* 41, 28–38.
- Wang, J., Li, Y.C., Song, J.F., He, M.Y., Song, J.J., Xia, K., 2015b. Recycling of acrylonitrile-butadiene-styrene (ABS) copolymers from waste electrical and electronic equipment (WEEE), through using an epoxy-based chain extender. *Polym. Degrad. Stabil.* 112, 167–174.
- Waugh, K.C., 1992. Methanol synthesis. *Catal. Today* 15, 51–75.
- Welle, F., 2011. Twenty years of PET bottle to bottle recycling—an overview. *Resour. Conserv. Recycl.* 55, 865–875.
- Wender, I., 1996. Reactions of synthesis gas. *Fuel Process. Technol.* 48, 189–297.
- Westerhout, R., Van Koningsbruggen, M., Van Der Ham, A., Kuipers, J., Van Swaaij, W., 1998. Techno-economic evaluation of high temperature pyrolysis processes for mixed plastic waste. *Chem. Eng. Res. Des.* 76, 427–439.
- Wilhelm, D., Simbeck, D., Karp, A., Dickenson, R., 2001. Syngas production for gas-to-liquids applications: technologies, issues and outlook. *Fuel Process. Technol.* 71, 139–148.

- World Economic Forum, Ellen MacArthur Foundation, Company, M., 2016. The New Plastics Economy - Rethinking the Future of Plastics.
- Xanthos, M., Young, M., Biesenberger, J., 1990. Polypropylene/polyethylene terephthalate blends compatibilized through functionalization. *Polym. Eng. Sci.* 30, 355–365.
- Xiang, Q., Xanthos, M., Mitra, S., Patel, S., Guo, J., 2002. Effects of melt reprocessing on volatile emissions and structural/rheological changes of unstabilized polypropylene. *Polym. Degrad. Stabil.* 77, 93–102.
- Yan, G., Jing, X., Wen, H., Xiang, S., 2015. Thermal cracking of virgin and waste plastics of PP and LDPE in a semi-batch reactor under atmospheric pressure. *Energy Fuels*.
- Yao, Z., Yin, Z., Sun, G., Liu, C., Tong, J., Ren, L., Yin, J., 2000. Morphology, thermal behavior, and mechanical properties of PA6/UHMWPE blends with HDPE-g-MAH as a compatibilizing agent. *J. Appl. Polym. Sci.* 75, 232–238.
- Yu, J., Sun, L.S., Ma, C., Qiao, Y., Yao, H., 2016. Thermal degradation of PVC: a review. *Waste Manage.* 48, 300–314.
- Zhang, X., Chen, Y., Zhang, Y., Peng, Z., Zhang, Y., Zhou, W., 2001. Effects of ABS-g-MAH on mechanical properties and compatibility of ABS/PC alloy. *J. Appl. Polym. Sci.* 81, 831–836.
- Zhang, Y., Zhang, H.S., Guo, W.H., Wu, C.F., 2011. Effects of different types of polyethylene on the morphology and properties of recycled poly(ethylene terephthalate)/polyethylene compatibilized blends. *Polym. Adv. Technol.* 22, 1851–1858.
- Zheng, Y., Shen, Z., Cai, C., Ma, S., Xing, Y., 2009. The reuse of nonmetals recycled from waste printed circuit boards as reinforcing fillers in the polypropylene composites. *J. Hazard. Mater.* 163, 600–606.