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Reviewing the thermo-chemical recycling of waste polyurethane foam

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The worldwide production of polymeric foam materials is growing due to their advantageous properties of light weight, high thermal insulation, good strength, resistance and rigidity. Society creates ever increasing amounts of poly-urethane (PU) waste. A major part of this waste can be recycled or recovered in order to be put into further use. The PU industry is committed to assist and play its part in the process. The recycling and recovery of PU foam cover a range of mechanical, physical, chemical and thermo-chemical processes. In addition to the well-documented mechanical and chemical processing options, thermo-chemical treatments are important either as ultimate disposal (incineration) or towards feedstock recovery, leading to different products according to the thermal conditions of the treatment. The review focuses on these thermo-chemical and thermal processes. As far as pyrolysis is concerned, TDI and mostly polyol can be recovered. The highest recovery yields of TDI and polyols occur at low temperatures (150–200 °C). It is however clear from literature that pure feedstock will not be produced, and that a further upgrading of the condensate will be needed, together with a thermal or alternative treatment of the non-condensables. Gasification towards syngas has been studied on a larger and industrial scale. Its application would need the location of the PU treatment plant close to a chemical plant, if the syngas is to be valorized or considered in conjunction with a gas-fired CHP plant. Incineration has been studied mostly in a co-firing scheme. Potentially toxic emissions from PU combustion can be catered for by the common flue gas cleaning behind the incineration itself, making this solution less evident as a stand-alone option: the combination with other wastes (such as municipal solid waste) in MSWI's seems the indicated route to go.

1. Introduction

1.1. PU production and applications

In Europe, Polyurethane (PU) represents about 7% of the polymer consumption (Europe, 2016). The worldwide consumption of PU was valued at 60.5 billion USD in 2017 (Gama et al., 2018), with about 27% consumed in Europe as PU foams and other products. Worldwide, PU ranks 6th in the polymer production. Its total production reached 18 Mton in 2016 (Cornille et al., 2017). The PU consumption is expected to grow, driven by its versatility towards new applications, uses and further improved properties. The growing demand for lightweight and high-performance materials considerably increases the research attention in PU foam, using the conventional and modified foaming techniques (Cyzio and Lubczak, 2017; Gama et al., 2018). European applications and post-consumer disposal are illustrated in Fig. 1.

PU is mainly produced by reacting poly-isocyanates with multi-functional hydroxyl compounds (Debuissy et al, 2017a, 2017b). PU contains soft segments and hard segments (Laurichesse and Avérous, 2014), and its properties can be tuned for specific applications by modifying the chemical nature and ratio of soft and hard segments. PU is an attractive polymer family and is available in a wide variety of macromolecular structures (Furtwengler et al., 2017). Six main application fields are listed in Table 1 (IAL Consultants, 2020).

PU's are frequently used in long-term applications due to the highly resistant and strong urethane bonds. The wide application of PU however causes its persistent presence as solid waste stream in the environment, usually as discarded consumer and industrial products. From for a total of 70 samples collected on a British beach, Turner and Lau found 39 pieces of foamed PU plastic products (Turner and Lau, 2016). Similarly, Vermeulen et al. and Soo et al. reported a major contribution of end-of-life automobile PU waste foams in Europe and Australia (Vermeulen et al., 2011; Soo et al., 2017). The analysis of the material

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Abbreviations			
ADP	Abiotic resource depletion potential	GWP	Global warming potential
AP	Acidification potential	LCA	life cycle assessment
BFB	Bubbling fluidized bed	MSW, MSWI	Municipal solid waste, Municipal solid waste incinerator, respectively
CFC, HFC	Chlorofluorocarbons, Hydrofluorocarbons, respectively	PCDD/Fs	Dioxins/furans
CHP	Combined Heat and Power	PEG	Poly(ethylene glycol)
DAT	Diamino toluene	PU	Polyurethane
DSC	Differential scanning calorimetry	PUF	Flexible Polyurethane foam
EG	Ethylene glycol	PUR	Rigid Polyurethane foam
ELV	End-of-life vehicles	RIM	Reaction injection molding
EN	Energy use	SVZ	SVZ-Schwarze Pumpe GmbH (Germany)
EP	Eutrophication potential	SR	Shredder residues
GHG	Greenhouse gas emissions	TDI	Toluene di-isocyanate
		TGA	Thermo-gravimetric analysis

moreover shows that the levels of Sn, Zn, Sb can be relatively high, thus needing additional and more expensive processing.

1.2. Properties of PU foam

Polyurethane foam has a cellular structure and is used in different of applications as illustrated in Table 1 (mainly healthcare, vehicles, household applications and insulation boards. PU foam represents 67% of the global PU consumption, and corresponds to 50% of the polymeric foam market (Szycher, 2012). Polyurethane foams are a substantial enabler of significantly improved flexibility, durability, and cushioning for related solutions. PU foams are good insulating materials due to blowing gas trapped within the cell structure, and resulting in a heat conductivity at 20 °C of about 0.015–0.035 W/m K (VDI Heat Atlas, 2010).

Polyurethane foams are classified based on the densities and hardness/rigidity including mostly flexible (PUF) and rigid polyurethane (PUR) (Thirumal et al., 2008). They are also divided in open cell or closed cell foams. Other classifications consider end uses as already illustrated in Table 1 (Szycher, 2012).

PUF and PUR foams are different, each with specific advantages and drawbacks towards the intended uses. PUFs have a nearly complete open-cell structure with densities as low as 20 kg/m³ (Kausar, 2018). PUF is prone to burning with the release of extremely toxic and combustible gases. Research efforts have hence targeted to improve the PUF foam characteristics of heat resistance, flammability, and thermal properties. PUR foams are mostly of closed cell structure (only a few % of open cells) with bulk densities typically between 30 and 35 kg/m³,

Table 1
Categories of PU applications.

Categories	Applications	Production
Flexible foams	Vehicles, seating, mattresses	36%
Rigid foams	Household appliances, insulation board, packaging, ...	32%
Elastomers	Medical applications, glues, ...	8%
Adhesives and sealant	Casting, sealants	6%
Coatings	Vehicles (bumpers, side panels)	14%
Binders	Assembling of wood boards, rubber or elastomeric flooring surfaces	4%

although densities up to 80 kg/m³ are commercially offered. The blowing agent gas contributes to the very low thermal conductivity, low density, low moisture permeability and absorption, high rigidity and dimensional stability. PUR foams are mostly used in construction and industrial applications such as insulating boards or for insulating refrigerators and freezers. The auto ignition temperature is about 415 °C. Dynamic foam properties need to be considered under impact loading conditions for e.g. aircrafts, vehicles, and shock resistant packaging materials. Various nanoparticles such as carbon nanotubes, derivatives from graphene, nano-clays/silica can be added to PU foams to improve the mechanical and thermal characteristics, while also affecting the electrical conductivity, the bio-degradation, and the behavior during foaming. Some chemical properties of PUF and PUR are illustrated in Table 2.

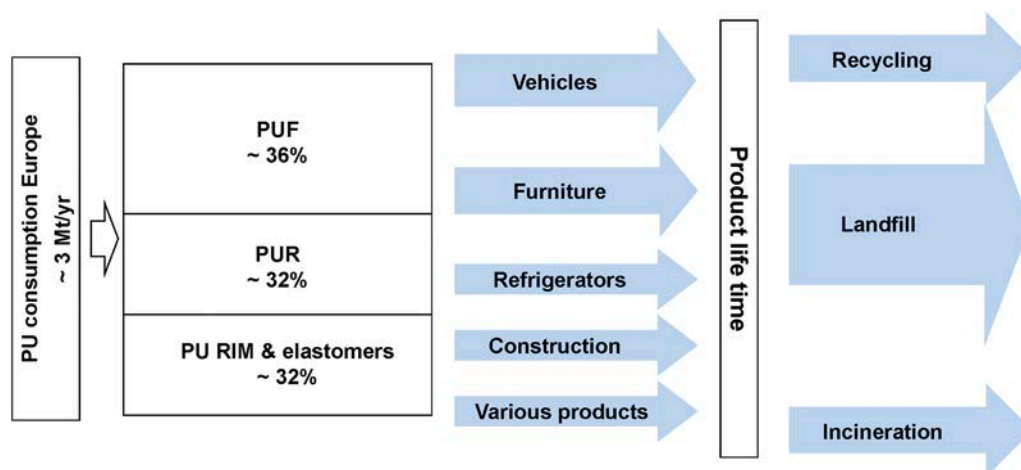


Fig. 1. European PU consumption, products and post-consumer disposal.

Table 2

Chemical Properties of PU foam materials (BASF, 2020; Eling et al., 2020; Nikje and Pooladian, 2019).

Chemical composition	Value	PU type
Volatiles (dry)	~88 wt%	PUF foam
Ash (dry)	~12 wt%	
Fixed carbon (dry)	0.3 wt%	
S, Cl, F (wt%)	<0.1, <0.3, 0	PUF foam
	<0.1, 1.5–13, 0.3–1.5	PUR foam
Sb + Sn (mg/kg)	10–250	PUR foam
	0.0	PUF foam

Since the PU waste, especially as insulation boards, can contain a multi-layer aluminum facing, 15 to 21 wt% of Al can be present in a 7 layer facing, against 8–9 wt% in a 5 layer facing. In a thermo-chemical treatment at moderate temperature such as pyrolysis, the aluminum foil can be recovered.

1.3. Foaming methods

The specific physical and chemical properties of PU foams depend mostly on the selected mix of raw materials, the obtained density and the foaming methods. These methods are briefly summarized in Table 3, and involve reactants, catalysts, surfactants, blowing agents and possibly nanoparticle fillers.

1.4. Polyurethane in waste streams

Recycling and recovery (including energy recovery) are gaining interest in Western Europe (European Commission, 2019). Some PU scrap (~3%) is also exported to North America (Garside, 2020). The processed flexible PU foam scrap is mostly from vehicle seats. Although landfill and incineration are still widely used as disposal method for all waste PU materials, the physical, chemical and thermo-chemical recycling recovery gains increasing interest with large scale industrial applications already in operation. Dow recently announced the installation of a major recycling plant at Orion Chemicals Orgaform (Semoy, France) (Volkova, 2020). Casey described an important development of chemically releasing the foaming agent prior to further recycling (Casey, 2020). The Repolyure process, developed by major waste polyurethane processors, combines several recycling techniques (European Commission, 2019).

If landfill is applied, mostly after compacting the PU scrap to a density of around 500 kg/m³, soil and groundwater pollution are of major concern, despite a low natural biodegradability of PU (Howard, 2002; Zevenhoven, 2004). Some bacteria, fungi and especially esterase enzymes, but also urease and papain, can break the ester bonds of the

Table 3

The foaming methods.

Processing Method	Processing conditions	Blowing agents	Products
One-pot free-rising (Liang and Shi, 2009; Thirumal et al., 2008)	Reactants are mixed in the required weight ratio, using cups or moulds. After degassing, the suspension is stirred and foam will form and set at ambient temperature over a period of hours.	n-pentane	Rigid foams, flexible foams
Water-blown (Molero et al., 2008)	Carbon nanotubes as nanofiller are used.	water	PUF
Batch foaming (Hirogaki et al., 2006; Yeh et al., 2013)	(Semi)-continuous foaming with controlled nanofiller dispersion and foaming. Sometimes equipped with a designed die and connected to a hot bath.	CO ₂ , N ₂	thermoplastic polyurethane-based foams, PU/nanofiller composite foams
Extrusion foaming (Kausar, 2018)	CO ₂ (pressure >7.6 MPa) is injected in the middle of the single-screw extruder within the polymer melt. The generated foam is discharged through a nozzle.	supercritical CO ₂	microcellular composite foams
Three-step method (Saha et al., 2008)	Sonication disperses the nanoparticles, while also mechanical mixing of particles with PU foam precursor is applied. After pouring the mixture in a preheated aluminum mould, it is oven-cured.	supercritical N ₂	Nanophased PU foams
Spray method (BASF, 2020; "Huntsman Ltd.," n.d.; Kausar, 2018)	Controlled curing times and expansion rate.	HFC, CO ₂	Open-cell and closed-cell PU spray foam

chain. Bacterial degradation of PU is very limited although *Bacillus* and *Pseudomonas* species lead to PU biodegradation (Espinosa et al., 2020; Magnin et al., 2020; Ru and Yang, 2020). The biological degradation is strongly affected by the PU crystallinity, the extent of repeating units, the PU structure and the cross-linking. It was recently demonstrated that bacterial strains of *Delftia acidovorans* TB-35 and *Staphylococcus epidermidis* are responsible for the microbial degradation of polyester and polyether bonds, respectively.

A major concern towards disposal is due to the presence of chlorinated and fluorinated blowing agents in older PU insulation foams. Liberated blowing agents must be collected and sent to an incinerator, with appropriate flue gas cleaning equipment such as catalytic thermal treatment (Everaert et al., 2003a, 2003b, 2004; Van Caneghem et al., 2012), or adsorption (Seville et al., 2021). Since the PU foam treatment routes will always include a primary milling step, the trapped blowing gases will be released upon mechanical treatment. CFC-11 was a serious ozone layer depleting compound. Non-halogenated compounds such as pentane, cyclopentane or CO₂ are however increasingly applied. It is hence important that these hazardous CFCs are trapped and destroyed during the milling. If the PU foam is landfilled, it will generate CFC-11 concentrations of 20–220 mg/m³ in the landfill gas, leading to potential corrosion in the gas engine-generators. The release of CFC-11 is however slow with 10% reported within a few weeks, and 50% released in a period of 1.35–135 years (Kjeldsen and Scheutz, 2003). Newer chloro-fluoro blowing agents have a higher diffusivity in the PU foam, and are released more rapidly. Their release is however strongly reduced if the shredded PU particles are coarse as illustrated in Figs. 2 and 3 below. Similar results are illustrated for a shredded refrigerator/freezer unit in Fig. 3. The collection and treatment of the released CFCs is required.

1.5. Objectives of the present research

The recycling and recovery of PU foam covers a range of physical, chemical and thermal processes, by which waste PU can either be crushed into particles and converted to basic hydrocarbon units, or transformed into constituent monomers for later reuse.

In view of the numerous publications on physical (mechanical) and chemical treatment options, these are only briefly dealt with in section 2. Thermo-chemical treatment methods allow the conversion of the PU waste to valuable monomers (pyrolysis) or syngas (gasification). Relevant literature data will be reviewed and discussed. The ultimate disposal of PU waste calls upon incineration. These thermal applications will be reviewed in section 3. Finally, an environmental assessment will be presented in section 4. Section 5 will conclude the review.

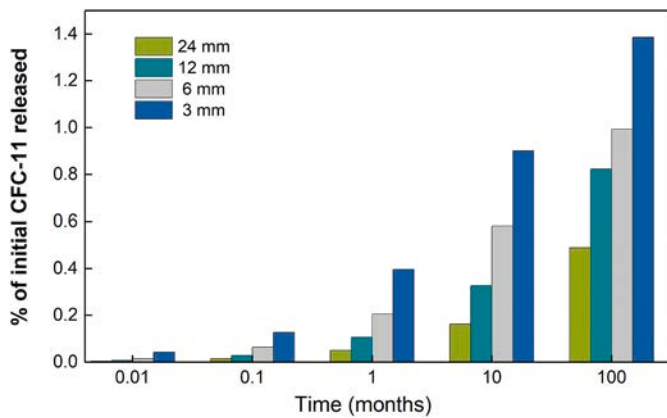


Fig. 2. Time-dependent CFC-11 release from shredded PU foam waste as a function of the shredded particle size in mm (adapted from Kjeldsen and Scheutz, 2003).

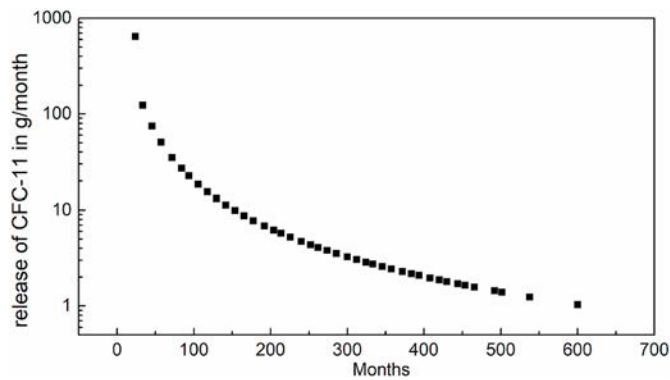


Fig. 3. Time-dependent CFC-11 release from PU foam waste of a shredded refrigerator/freezer (adapted from Kjeldsen and Scheutz, 2003).

2. Treatment of PU waste

2.1. The different options

In-line with a technology review of treating plastic solid wastes (Al-Salem et al, 2009, 2010; Brems et al., 2012), the options include 5 primary recovery treatment ways (repair and re-use, mechanical recycling through reuse in the polymer form, chemicals' recovery by decomposing the material into its different chemical components, thermo-chemical recycling and energy recovery) and a secondary treatment by biodegradation. These options are illustrated in Fig. 4.

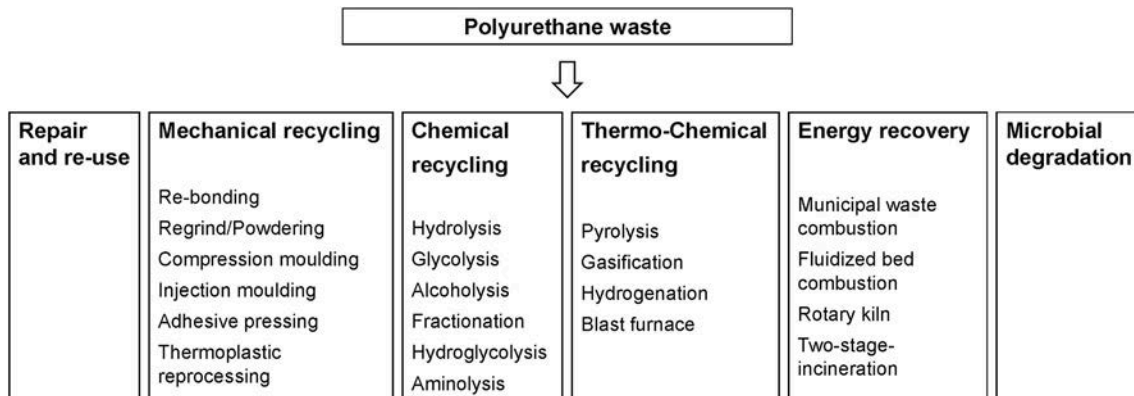


Fig. 4. Possible treatment and recycling processes.

Repair and re-use are generally not applicable for PU foam waste.

The mechanical and chemical primary treatment options are described in detail in review books (Datta and Wloch, 2017; Eling et al., 2020; Nikje and Pooladian, 2019) and papers (Matús et al., 2017; Yang et al., 2012) among others. They are not further detailed in this review, since outside its scope. The biological degradation depends upon many properties of the PU polymer, as discussed in section 1.4.

For sake of completeness, Table 4 summarizes the methods for physical and chemical recycling of PU wastes, the most general applied techniques being regrinding and glycolysis, respectively. The thermo-chemical and incineration with energy recovery are also included.

All of these options aim to minimize wastes and should avoid pollution by emissions. These emissions are significant in a physical process, and milling the scrap to a smaller size will increase the emission rate. The collection and treatment of the released emissions is required, as discussed in section 1.4.

The recovered polyol in a glycolysis process can only replace <50% of virgin polyol material for further application. The thermo-chemical recycling allows for dealing with significant amounts of scrap PU without significant problems, as discussed below.

3. Thermo-chemical recycling

3.1. Possible treatment

De-polymerisation can be applied on pure streams of particular PU-polymers, crushed to original building blocks. After recovering the composite chemicals, a re-polymerisation is possible. Since PU waste materials are generally of mixed composition, thermo-chemical feed-stock recycling processes have been developed to recover PU materials. Waste-to-energy applications should also be considered.

There are five main thermo-chemical processing routes: pyrolysis, blast furnace application, gasification, hydrogenation and incineration. The feed preparation and possible chemical products are illustrated in Fig. 5.

Details of these applications are discussed below.

3.2. Principles of the thermo-chemical degradation of PUF

An important factor in the thermo-chemical treatment is the thermal degradation of PU foams and various literature sources describe the mechanism by which PU is decomposed. Important factors are the temperatures at which the different types of chemical PU bonds break, since the thermal dissociation temperature is a function of the different structures of the polymer chain. Isocyanate, polyol and chain extenders used in the PU production are the most abundant compounds. The reported results vary due to the diversity of available waste PU. An overview of dissociation temperature ranges is included in Fig. 6 (Branca

Table 4

Description of various recycling and recovery processes.

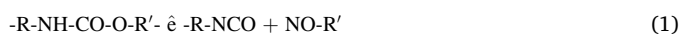
Type	Option	Description
Mechanical	Recycling to reuse PU with physical treatment. The wastes are crushed into small particles to be used as inert fillers.	
	Regrinding (Beran et al., 2020; European Commission, 2019; Zia et al., 2007)	<ul style="list-style-type: none"> After milling, preferably to below 0.1 mm, products can be re-used as filler in polyurethane foams or elastomers. The density and mechanical properties of PU powder is similar to the new produced foam.
	Particle bonding (Metzler, 2001)	<ul style="list-style-type: none"> After adding a binder to the PU scrap, the mixture is compressed. The addition of steam completes the binding to make padding type products, of varying mechanical properties. Higher density but lower hardness.
	Adhesive pressing (Metzler, 2001)	<ul style="list-style-type: none"> Granular polyurethane particles are pressure-coated with a binder and heat and pressure cured. Semi-finished product reobtained.
	Compression molding (Hulme and Goodhead, 2003; Matúš et al., 2017)	<ul style="list-style-type: none"> PU granules are molded at high temperature and pressure (180 °C, 350 bar) to produce rigid and hard high performance parts of e.g. pump and motor housings.
Chemical	Injection molding	<ul style="list-style-type: none"> Reaction injection molding (RIM) is applied to recycle PU into automotive parts Recycling cross-linked PU, and PU mixtures with other plastics (preferable added thermoplasts).
	Recovery of the initial feedstock, especially monomers of polyol, that can be included in the production of new PU.	
	Hydrolysis (Yang et al., 2012)	<ul style="list-style-type: none"> Waste PU foam is treated with steam and alkali hydroxide as a catalyst at high temperatures and pressures. Side reactions can occur and result in unwanted by-products di-amines.
	Glycolysis (Jutrzenka Trzebiatowska et al., 2019; Petri and Marker, 2006; Simón et al., 2018; Zhu et al., 2014)	<ul style="list-style-type: none"> PU foam is reacted with various diol compounds at 200 °C through trans-esterification reaction. Mostly targets the effective recovery for making new PU or producing a fuel alternative.
	Alcoholysis (Vanbergen et al., 2020)	<ul style="list-style-type: none"> The original the original reactants can be obtained, i.e., polyols and urethane products, by using alcohols and hydroxide (sodium, potassium hydroxides) at high temperature under high pressure,
Thermo-chemical	Acidolysis (Gama et al., 2020; Yang et al., 2012)	<ul style="list-style-type: none"> Using inorganic and organic acids, a series of products is obtained such as amides, polyols, amine salts, and oligo urea
	Hydroglycolysis (Gadhawe et al., 2018, 2019; Nikje et al., 2011)	<ul style="list-style-type: none"> PU reacts with water, diethylene glycol, and hydroxides (LiOH, NaOH, KOH) to produce polyols and various intermediate chemicals. The obtained mixture is normally of appropriate quality.
	Aminolysis (Zia et al., 2007)	<ul style="list-style-type: none"> Various degraded products (substituted polyol, polyamines, ...) are obtained by using hydroxyl and amino-derived compounds, Aminolytic chain cleavage and subsequent hydrolysis produce the original polyols and amines.
	Aminolysis-Hydrolysis (Campbell and Meluch, 1976)	
	Thermal conversion of the PU waste into feedstock chemicals	
Energy recovery	Pyrolysis (Uliana et al., 2020)	<ul style="list-style-type: none"> Oxygen-free thermal decomposition of the PU waste into gaseous, liquid and solid (char) products. Use of PU waste in blast furnace Fe reduction
	Blast Furnace (Rane et al., 2015)	
	Gasification (Branca et al., 2003; Schingnitz et al., 2000)	<ul style="list-style-type: none"> Produces heat, ashes and synthesis gas (H₂, CO), where CO can be used for synthesizing the PU required isocyanates; H₂ can also be used in the production of other PU feedstock (formaldehyde, polyether).
	Hydrogenation (Abdel-Rahman et al., 2019; Szycher, 2012)	<ul style="list-style-type: none"> High pressure thermal process, seldom applied but with a potential to decompose PUR.
	Complete or partial oxidation of PU to recover its heating value (mostly in a heat and power unit). Various techniques are used to decrease NO and CO emissions.	
Energy recovery	Municipal waste combustion (Rittmeyer et al., 1994; Van Caneghem et al., 2012)	<ul style="list-style-type: none"> Co-firing of CFC-containing PU foams
	Fluidized bed combustion (Van Caneghem et al., 2012; Weigand et al., 1996)	<ul style="list-style-type: none"> 39 MW_{th} coal-fired BFB combustion plant
	Rotary kiln (Zevenhoven, 2004).	<ul style="list-style-type: none"> Combustion of commingled plastic waste
	Two stage incineration. (Zia et al., 2007)	<ul style="list-style-type: none"> A primary pyrolysis/gasification reactor, followed by a combustion of the formed vapors and gases

et al., 2003).

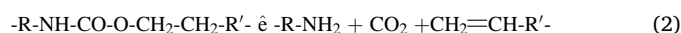
Within the matrix of flexible PUF, the thermally weakest links are allophanate and biuret with a dissociation at about 110 °C (although also 85 °C has already been reported for the allophanate links). Both biuret and allophanate start to regenerate their precursors, isocyanate and urethane upon pyrolysis. Urethanes and urea are slightly more stable, while the isocyanurate group (di-substituted urea) is the most stable of the N-based derivatives. The ether group is markedly more stable than any of these, while the isocyanurate group is stable up to 270 °C.

The principles of the thermo-chemical degradation were proposed during the early years of research. Cullis and Lattimer provide a 3-route pathway of the mechanisms behind the degradation and cleavage of PU at 200–300 °C (Cullis and Hirschler, 1981; Lattimer and Williams, 2002):

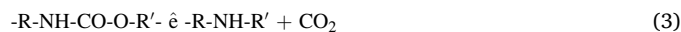
The cleavage to isocyanate is also called retro-polymerisation or depolymerisation since the original starting materials are obtained.



The cleavage to primary amine, CO₂ and olefins is reported to proceed via a 6-membered ring transition state, with carbamic acid (-R-NH-COOH) as possible intermediate.



The dissociation of carbamic acid into CO₂ and secondary amines, proceeds through a concerted intra-molecular displacement of CO₂ with a 4-membered ring transition state.



Whereas these mechanisms originally concerned non-polymeric urethanes, they also apply to commercial PU, with similar dissociation temperature ranges observed for urethanes containing primary and secondary alcohols. Ravey and Pearce pyrolyzed PUF produced with toluene di-isocyanate (TDI): with a long residence time in the reaction zone the formation of diamino toluene (DAT) sets in via routes (2) and (3) cited above (Ravey and Pearce, 1997), thus confirming other studies stressing a high polyol but low isocyanate recovery. Ravey and Pearce moreover reported the formation of a “yellow smoke” poly-urea aerosol, when TDI and DAT recombine in the vapor phase. Heating to 360 °C avoided the formation of diamino-toluene and CO₂ and resulted in vapors of TDI representing ~33 %-wt of the initial PU mass and ~96% of initial PU nitrogen.

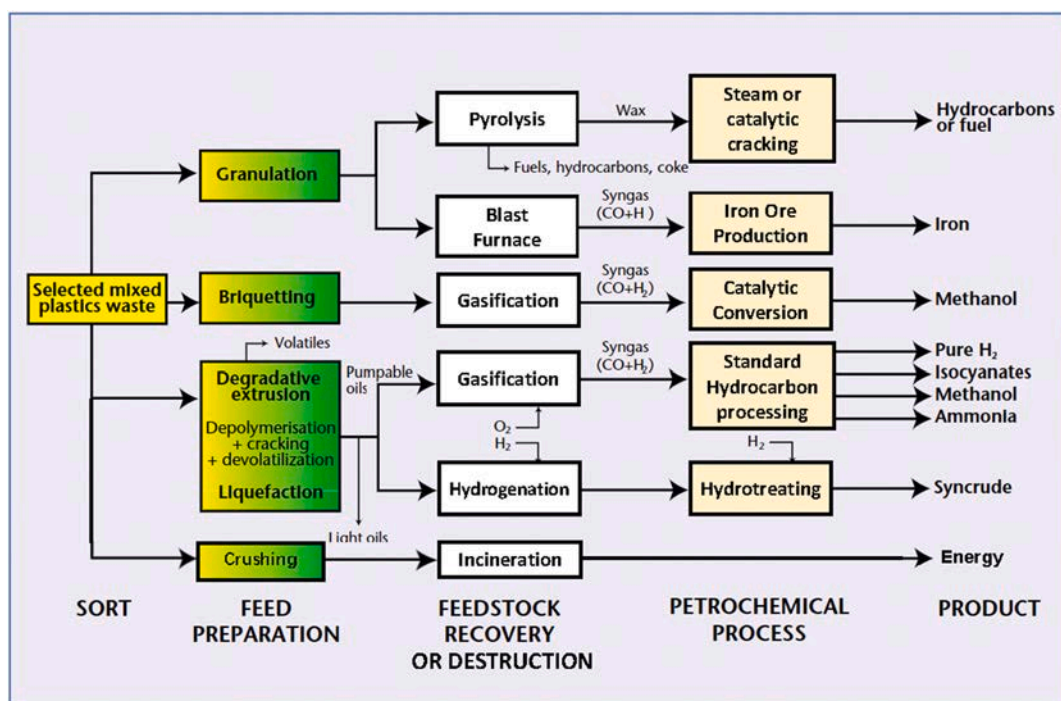


Fig. 5. Possible products of thermo-chemical and energy recovery.

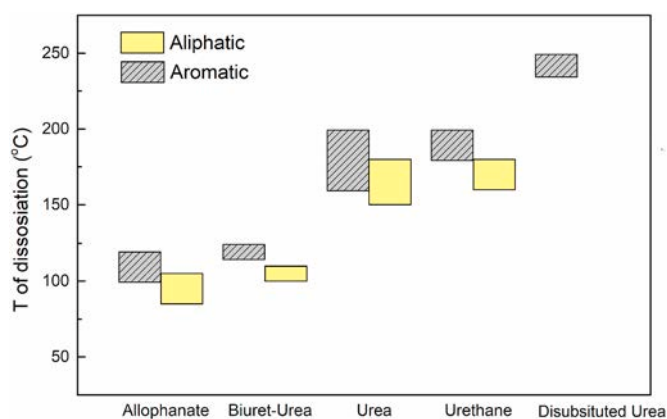


Fig. 6. Ranges of dissociation temperatures for PU.

3.3. Pyrolysis

The pyrolysis process consists of thermally decomposing the PU waste in an oxygen-free (or oxygen-lean) environment. The macromolecules are disrupted and yield gaseous, liquid and solid products. Char (solid product) is being formed as an unwanted by-product, although the amount of chars generated is very limited.

In most literature sources, the pyrolysis process is studied through small-scale thermo-gravimetric analysis (TGA) under a N_2 atmosphere. TGA measures the weight loss of the PU sample as a function of time, and hence temperature due to the fixed temperature ramp (K/min). In some studies, these measurements were combined with a differential scanning calorimetry (DSC) analysis), for measuring the reaction heat flux, again as a function of the temperature. Various pyrolysis studies were reported, all treating different chemical compositions or industrial blends/applications. Depending on the exact composition of the PU material, different results were obtained. Relevant studies are summarized below.

A low temperature (250–350 °C) pyrolysis was used by Lattimer et al.. Whereas no N_2 was found at temperatures >300 °C, the

depolymerization followed route (1) for temperatures below 300 °C leading to the formation of pure polyester and urethane polyester. When exceeding 300 °C, dehydration of the linear and cyclic polyester pyrolyzates produced unsaturated olefinic end groups, while primary and secondary amine products, as in mechanisms (2) and (3) above, were not detected (Lattimer et al., 1998). This was later contradicted when primary amine formation through mechanism (2) was detected (Lattimer and Williams, 2002).

PUF from the furniture industry was pyrolyzed in a TGA up to 450 °C (Font et al., 2001). The 95% decomposition of the PU occurred between 230 and 380 °C. At 500 °C, large fractions of aromatics and alkanes/alkynes were measured, shifting to mainly benzene, ethane + ethylene, and methane at 900 °C. Earlier pyrolysis studies demonstrated that the decomposition of TDI-based polyester and polyether urethane foams showed a fast and complete loss of TDI unit (200–300 °C) with a polyol residue and the formation of the characteristic “yellow smoke” (Woolley, 1972). At temperatures in excess of 300 °C, Matuszak and Frisch degraded polyurethanes based on poly (ethylene glycol) (PEG) and different diisocyanates to predominately amine and CO_2 . Aliphatic polyurethanes were more thermally stable than the aromatic-based materials. Studies by Hileman et al. and Voorhees et al. confirmed that pyrolysis proceeded according to reactions (1), (2) above (Hileman et al., 1975; Matuszak and Frisch, 1973; Voorhees et al., 1978). Reaction (1) dominated the pathway at low pyrolysis temperatures. Lattimer et al. confirmed the above findings, with a dominant reaction (1) at temperatures <300 °C. The decomposition of PU to cyclic oligomers became prominent at higher temperatures (Lattimer and Williams, 2002).

Polyurethane foams were pyrolyzed based on TDI and glycerol/propylene oxide/ethylene oxide (Ravey and Pearce, 1997). At 320–360 °C in a reactor with continuous evacuation of the vapors, the loss of nitrogen (as TDI) was near quantitative with the regenerated polyol in the residue fraction. When pyrolyzed in confined conditions, diamine (diaminotoluene) was produced. It demonstrated that both reactions (1) and (2) occur, but the reversible reaction (1) is faster. An equilibrium is established when TDI produced by the reversible reaction (1) is confined in the reactor, although then the irreversible reaction (2) is favored. Pan and Webster studied the kinetics of PUF decomposition

during pyrolysis, and confirmed the importance of reaction (1) (Pan and Webster, 2012).

Bilbao et al. performed TGA studies under N₂ flow of PUF foam and demonstrated the two-step degradation to a weight loss of 90% below ~400 °C (Bilbao et al., 1996). Activation energies were determined and were a strong function of the operating temperature, ranging from 28.8 kJ/mol (200–240 °C) to 180.9 kJ/mol (315–393 °C). The decomposition in air is considerably faster than in N₂, with an activation energy of 97.7 kJ/mol at 230–300 °C. Similar TGA results when treating PU foam in air were found by Branca et al. (2003), although 3 consecutive decomposition ranges were observed, each with a corresponding mass loss of respectively 8% (205–230 °C), 38% (320–360 °C) and 50% (540–590 °C). The respective activation energies were 134 kJ/mol, 81 kJ/mol and 180 kJ/mol, respectively.

Flash pyrolysis (milliseconds) at 700 °C, combined with Pyrolysis-GC/mass spectroscopy (Py/GCMS) was performed and resulted in the decomposition to -CH₃, -CN, HCNO and CO₂/N₂O (Zevenhoven, 2004). Entrained flow N₂-pyrolysis of the PUF at 750–950 °C, produced the same products, although 10 to 15 wt% of PUF was collected as char, that contained 15% of C and 16% of N.

US patents US2998395, US3983087, US4450583 and US5462971 described a technology for N₂-driven pyrolysis of scrap flexible or semi-rigid PUF at 450–800 °C for a reaction time of about 5 min. The organic phase of the products consisted of alcohols and re-useable polyols. Details are given in the appropriate patents.

The possible presence of multilayer aluminum facing in applications of construction insulation materials adds an extra objective to the pyrolytic recycling, since scrap aluminum can be recovered without significant residual PU contamination.

3.4. Gasification

Among the thermo-chemical feedstock recycling processes, gasification is of particular interest for PU materials, mostly as a two stage process of preheating and subsequent air or O₂ blown gasification. This forms mostly H₂ and CO (syngas), which can be sent to a reforming process for the production of various products like methanol, ammonia, and oxo-alcohols. Commercial gasification units have been operated worldwide for a variety of feedstock. A pilot plant at The SVZ GmbH used the high-temperature BG-Lurgi slagging-bed gasification (Buttker et al., 2005) to gasify waste materials, including pelletized shredder residues (SR), including densified PUF and MSW. The mass flow chart for treating SR is illustrated in Fig. 7.

3.5. Blast furnace application

Bremer Steelworks (Germany) uses a range of mixed plastics wastes including crushed and densified PUF to replace 30% of fossil-based reducing agent (heavy oil or coal dust), to convert iron ore in the blast furnace (Al-Salem et al., 2009, 2010; Metzler, 2001), as illustrated in Fig. 8. The waste plastics are converted into syngas, which then accounts for part of the iron ore reduction.

In general, numerous blast furnace operators are using a similar reduction route, and it is a potential method to deal with mixed waste plastics.

3.6. Energy recovery (combustion/incineration)

Incineration with energy recovery is the ultimate disposal method for materials without short or medium term markets. This should hence be considered for contaminated PU scraps (PU laminates to wood, aluminium, leather or fabrics), or mixed plastic materials. Since PU with traditional flame retardants (brominated retardants, Sb₂O₃, ...) cannot easily be recycled, incineration is a potential solution. For PU waste, incineration leads to a volume reduction of >99%, while fully destroying harmful PU blowing agents (Tohka and Zevenhoven, 2002; Vermeulen et al., 2011). The energy recovery from scrap rigid PU foam from construction and demolition waste in co-fired solid waste incineration plants (MSWIs), was initially promoted by Rittmeyer et al. (1994). Initial tests were conducted in Germany at an incinerator of the Karlsruhe Research Centre and at a full-scale MSWI plant, with specific objectives of measuring the waste burn-out and the emission of combustion pollutants (e.g. CFCs, HF, HCl, dioxins/furans (PCDD/Fs). Emissions of CFC-11 and chloro-fluoromethanes were between 0 and 10 µm/m³ (against an ambient of ~4 µg/m³). Table 5 summarizes the averages of other emissions measured, with measurement errors given in the original publication.

It was demonstrated that PU foam waste could be co-fired at ~1 wt% of the input of the MSWI without process modifications and avoiding the risk of fires starting in the feeding hopper and waste bunker, PCDD/F emissions were significantly below the 0.1 ngTEQ/Nm³ standards. CFCs in PU foams could be successfully destroyed in MSWI facilities and chlorinated organises in the flue gas could be captured and destroyed (Everaert et al., 2003a, 2003b; Everaert, 2004).

Ravey and Pearce studied the pyrolysis and combustion of PUF foam from vehicle seats (Ravey and Pearce, 1997). When using air as carrier gas, hence simulating incineration, TGA/DTA and DSC tests revealed an onset reaction at ~250 °C, a conversion of ~80% at 300 °C, and a

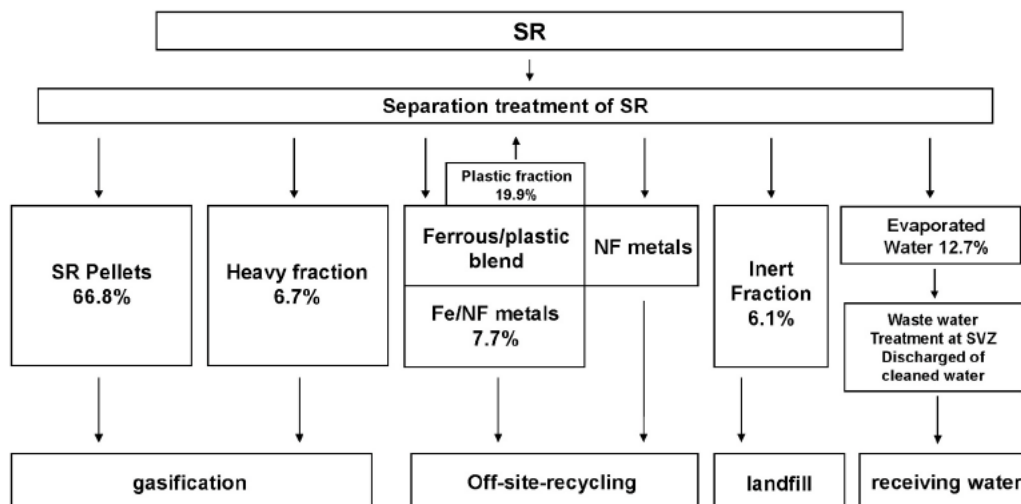


Fig. 7. SVZ flow chart.

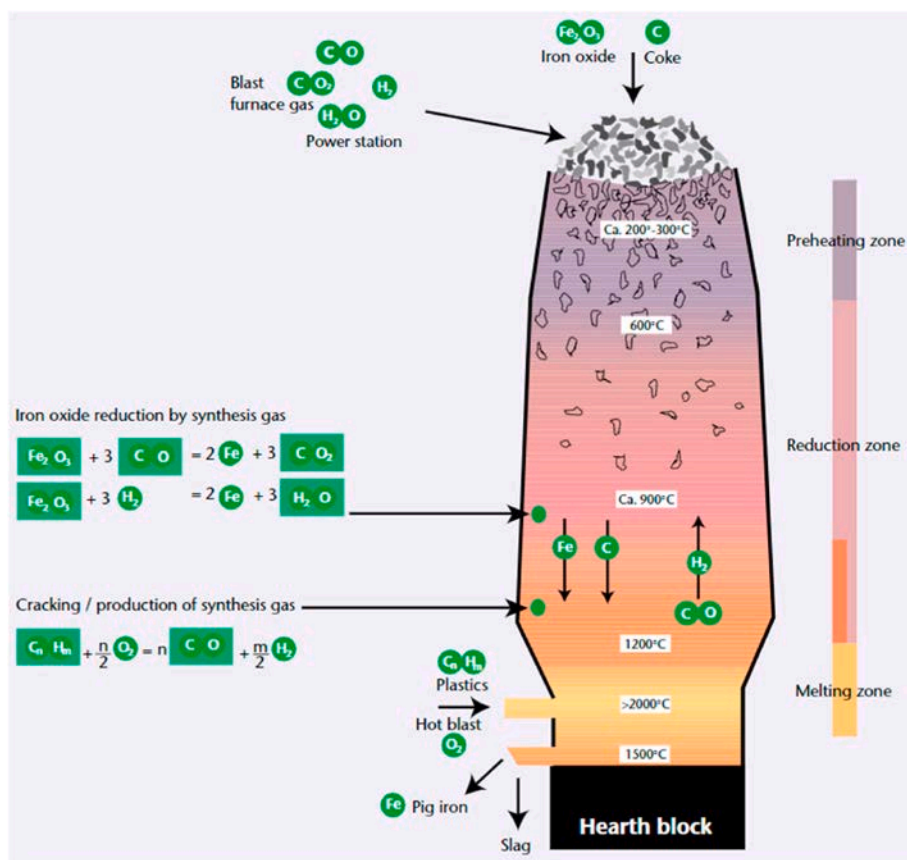


Fig. 8. PU and plastics gasification in a blast furnace (Al-Salem et al, 2009, 2010; Metzler, 2001).

complete incineration at 500 °C. These two-step decomposition results were confirmed in a furnace, with firstly the production of yellow smoke and a viscous liquid, followed by the slow cracking of the liquid into gaseous products. Independent of the residence times, considerable amounts of CO, CH₄, HCN, NH₃ and NO, and some minor amounts of C₂H₄ and C₂H₂ were released. Atom balances are presented in the original paper. CO and NO were formed from intermediates such as HNCOO, but the direct release of as NO followed a significant release of HCN, oxidized in the gas phase as a possible alternative decomposition route.

Weigand et al. co-fired PUF wastes (compressed mattresses, car seats and furniture) in a 39 MW_{th} bubbling fluidized bed coal combustion plant (Weigand et al., 1996). The PUF waste of heating value 24–30 MJ/kg was fed at 13–20% of the energy input. Emissions were all within the legal limits. The concentration of heavy metal trace elements increased from 0.06 to 0.32 mg/m³ mostly through Sn (tin), used as catalyst in the PU foam PU production. The costs for co-incinerating PUF wastes were estimated at ~50 €/ton. Rigid and flexible PU foams without flame retardants were suitable for co-firing with coal. Other PU

wastes such as RIM PU waste and demolition rigid PU waste were problematic for combustion in the fluidized bed.

Further combustion tests of PUF foams from automobile seats in grate incinerators were published (Rogaume et al., 1999), optimizing operating conditions towards minimum NO_x and CO emission. An excess air factor up to 1.6 significantly reduced the CO emission, while NO_x emissions increased. Optimum operating conditions were selected at a total excess air factor of 1.35, and flue gas recycling further reduced the CO and NO_x emissions by 15% and 45%, respectively. Zevenhoven performed additional combustion tests of a PUF foam between 750 and 950 °C in a mixed O₂/N₂ feed environment (7% O₂, 93% N₂) (Zevenhoven, 2004). When the PUF nitrogen content was 6.6 %wt, less than 10% of the PUF-N was emitted as NO + NO₂. Minor emissions of toxic elements such as HCN, CO, benzonitril and other nitrils and TDI, together with some toxic components from burning PU additives (acidic gases, dioxins/furans or toxic zinc ferrocyanide, used as smoke suppressant in PU and other polymers) (Cullis and Hirschler, 1981; Levin et al., 2006; Tohka and Zevenhoven, 2002).

The effect of flame retarded polyurethane or thermo-chemical processes is also described in literature since they hamper the thermal decomposition of the material and the flame chemistry, resulting in enhanced charring or carbonization. The previously used chlorinated and brominated flame retardants are now replaced by (organo-) phosphorus or nitrogen flame retardants (Cullis and Hirschler, 1981; Tohka and Zevenhoven, 2002). An enhanced thermal stability of PU was reported when P is integrated in the structure of the polyol used, and when flame retardants with up to ~10 %wt phosphorus in the polyols are applied. An overview is given by (Nikje et al., 2011). The presence of a P-containing PU (PU-P) slightly increases the degradation temperature to ~290 °C instead of 270 °C. When co-incinerating PU-waste, an additional amount of dust emission was measured, although this emission can be reduced by an increased cross-linking of the material,

Table 5
Emissions from the Karlsruhe tests for MSW/PU foam co-firing (Rittmeyer et al., 1994).

Component	Average values of on-line monitoring			
PUF feed [wt %]	0	1	2	3
HCl [mg/m ³]	524	571	589	761
CO [mg/m ³]	<5	<5	<5	<5
NO [mg/m ³]	209	209	202	209
O ₂ [%]	11	11,2	11,4	11,1
SO ₂ [mg/m ³]	274	306	248	278
Temperature [°C]	943	961	957	985
Waste [kg/h]	298	280	253	240

using cyanurate structures, or by adding smoke suppressants such as furfuryl alcohol into the polymer structure (Zia et al., 2007).

4. Environmental

The review focused upon thermal and thermo-chemical processes for the treatment/disposal of PU foam. Landfilling will however also be included in the assessment, since still widely practiced. To study the environmental aspects and potential impacts throughout a product's life, a life cycle assessment (LCA) provides a useful tool. Pyrolysis, incineration and landfill can be easily compared on equal grounds, however providing different outputs such as recovered materials or energy. The environmental benefits of recovered resources are accounted for by including avoided burdens of conventional production.

Numerous LCA studies were presented in literature. Results in literature seem fairly consistent, showing that mechanical recycling has the lowest impact on total energy use and global warming potential in most of the assessed cases (Bjorklund and Finnveden, 2005). Feedstock recycling produces a high-value output, but typically at a high energy consumption, hence reducing the overall performance. Landfilling PU waste can be preferable to incineration regarding the global warming potential due to the very slow PU biodegradation (time perspective of 100 years). With landfill as baseline, three environmental indicators were analyzed: the global warming potential (greenhouse gas emissions), acidification of wet and dry deposits, and consumption of (scarce) energy resources. The environmental impact of greenhouse gas emissions (GHG) caused by the incineration is higher than that of landfill (+0.96 kg CO₂/kg). Feedstock recycling reduces the GHG emissions by 0.08 to 0.37 kg CO₂/kg due to feedstock substitution. Acidic emissions of incineration and feedstock recycling are reduced in comparison with landfill. Lazarevic et al. provide an overall analysis of available studies based on the LCA framework (Lazarevic et al., 2010). The impact categories evaluated are global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), abiotic resource depletion potential (ADP), energy use (EN) and residual solid waste destined for landfill (SW). Mechanical recycling seems the preferred scenario for GWP, EP and AP. Feedstock recycling seems the preferred scenario for GWP, EP and AP. Feedstock recycling produced less SW. EN was heavily dependent upon the technology chosen. In the comparison of incineration with feedstock recycling, feedstock recycling uses fewer abiotic resources than incineration. It also produces less SW when single waste streams are investigated, whereas incineration is preferred for mixed waste streams. Finally, when comparing incineration and landfill, landfill scenarios have a lower GWP than incineration scenarios, whereas all other categories favor incineration.

Results are illustrated in Fig. 9 and Fig. 10.

Although landfill performs well compared to other options due to the low energy inputs in managing a landfill, Incineration with energy recovery (albeit with relatively low efficiency) generally has a better environmental performance than landfill. Of all scenarios assessed, it results in the lowest solid waste production, but has the most adverse global warming impact. In most impact categories pyrolysis performed better than landfill and incineration. A more thorough LCA of the pyrolysis process is certainly recommended in additional research.

5. Conclusions

Waste PU is versatile in composition as a result of the diversity of applications. The waste can only be considered as non-hazardous when heavy metals or Sb₂O₃ and/or brominated flame retardants are absent. Various waste processing options are available. In addition to the well-documented and widely applied mechanical and chemical processing options, thermo-chemical treatments also achieve feedstock recovery, leading to different products according to the applied thermal conditions of the treatment. Incineration is the ultimate disposal route.

As far as pyrolysis is concerned, mostly polyol can be recovered.

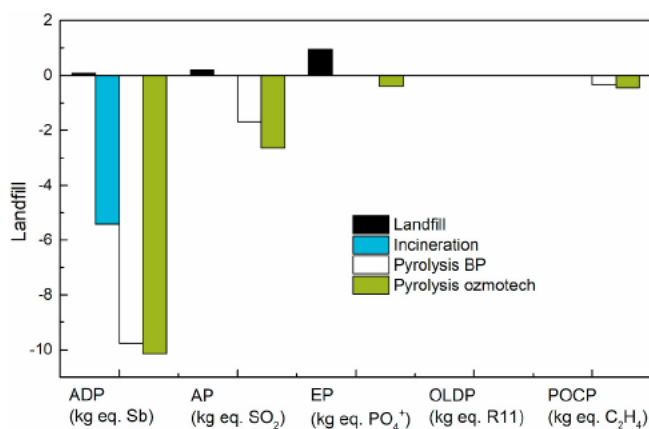


Fig. 9. LCA comparing landfill, incineration with energy recovery and pyrolysis towards ADP, AP, EP, OLDP and POCP (WRAP, 2020).

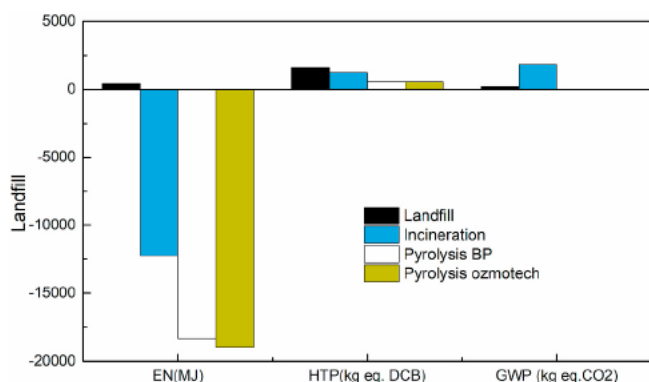


Fig. 10. LCA comparing landfill, incineration with energy recovery and pyrolysis for EN, HTP and GWP (WRAP, 2020).

These studies were however mainly conducted on a small scale by thermo-gravimetric analysis. Despite the lack of pilot-scale experiments, pyrolysis seems to offer a good potential for feedstock recovery, with advantages of a low temperature of the operation. Clearly more experimental work, on a laboratory and pilot-scale is required. In view of the low density of the PU waste, we recommend the use of an entrained pyrolysis reactor (short residence time, use of injected milled waste) or the use of a fluidized bed pyrolysis reactor, where a densified PU-waste will be required. It is however clear from literature that pure feedstock will not be produced, and that a further upgrading of the condensate will be needed, together with a thermal or alternative treatment of the non-condensable.

Gasification towards syngas has been studied on a larger and industrial scale. Its application would need the location of the PU treatment plant close to a chemical plant, if the syngas is to be valorized in chemical synthesis or in conjunction with a gas-fired Combined Heat and Power plant. The whole process however is of a complex nature, with H₂ and CO being formed, adding to the complexity towards safety and health issues.

Incineration has been studied mostly in a co-firing scheme. Potentially toxic emissions from PU combustion can be catered for by the common flue gas cleaning behind the incineration itself, make this solution less evident as a stand-alone solution: the combination with other wastes (such as municipal solid waste) in MSWI's seems the indicated route to go. In this respect however, a first step pyrolysis combined with a second step incineration of non-condensables and possibly chars seems attractive.

A tentative LCA assessment ranks pyrolysis ahead of incineration

with energy recovery, both being more favorable than landfilling.

Authors' contribution

Yimin Deng, Investigation, Methodology, Data curation, Original Draft, Writing - Review & Editing, Visualization. Raf Dewil, Validation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition. Lise Appels, Data Curation, Visualization, Writing - Review & Editing. Renaud Ansart, Methodology, Writing - Review & Editing, Validation. Jan Baeyens, Investigation, Methodology, Data curation, Writing - Review & Editing, Visualization. Qian Kang, Conceptualization, Methodology, Writing - Original Draft, Writing - Review & Editing, Project administration.

Declaration of competing interest

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

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