Review

Automotive shredder residue (ASR): Reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals' valorisation

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ABSTRACT

ASR is in Europe classified as hazardous waste. Both the stringent landfill legislation and the objectives/legislation related to ELV treatment of various countries, will limit current landfilling practice and impose an increased efficiency of the recovery and recycling of ELVs. The present paper situates ASR within the ELV context. Primary recovery techniques recycle up to 75% of the ELV components; the remaining 25% is called ASR. Characteristics of ASR and possible upgrading by secondary recovery techniques are reviewed. The latter techniques can produce a fuel- or fillergrade ASR, however with limitations as discussed. A further reduction of ASR to be disposed of calls upon (co-)incineration or the use of thermo-chemical processes, such as pyrolysis or gasification. The application in waste-to-energy plants, in cement kilns or in metallurgical processes is possible, with attention to the possible environmental impact: research into these impacts is discussed in detail. Pyrolysis and gasification are emerging technologies: although the sole use of ASR is debatable, its mixing with other waste streams is gradually being applied in commercial processes. The environmental impacts of the processes are acceptable, but more supporting data are needed and the advantage over (co-)incineration remains to be proven.

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1. Introduction: The broad problem of ELVs

The worldwide production of cars grew steadily over the past 30 years despite a dip in 2008–2009 due to the economic crisis (decrease by about 3.7% in 2008 and a further 12.8% in 2009) [1]. In 2007 about 73 million vehicles were produced worldwide, compared to about 38 million in 1980. Western Europe, North America and Japan are the main car producers [2]. The automotive industry is facing significant challenges as vehicles have a considerable environmental impact at all stages of their life cycle: resource consumption, emissions to air and waste generation during material/component production and during car assembly; energy (fuel) consumption and emissions of greenhouse gases and pollutants (CO_2, NO_x, particulate matter) during their use; and finally waste generation and release of hazardous substances when the car becomes an end-of-life vehicle (ELV).

To reduce the environmental impact of cars and to increase sustainability, all phases of the life cycle should be addressed, leaving in mind that the decrease of the impact in one stage of the life cycle can lead to an increase of the impacts in other stages. The use of petrol and its associated emissions can e.g. be reduced by designing lighter cars that usually incorporate more plastics to replace ferrous materials, but ferrous materials are more easily recycled than their plastic substitutes.

There is a growing concern about the environmental impact of ELVs as the amounts of ELVs generated are ever increasing and because the waste generated during the final treatment may contain hazardous components or compounds. An estimate determined that in 2000, 8–9 million tonnes of ELVs were generated per year in Europe [3,4]. Fig. 1 shows the projected number of ELVs in the period 2005–2030 [3] for the EU member states without Romania and Bulgaria (EU25), for the older EU countries (EU15) and for the new EU countries (EU10). The projection shows that the number of ELVs for the EU25 will likely increase by 45% between 2005 and 2030. When export of used cars is taken into account (about
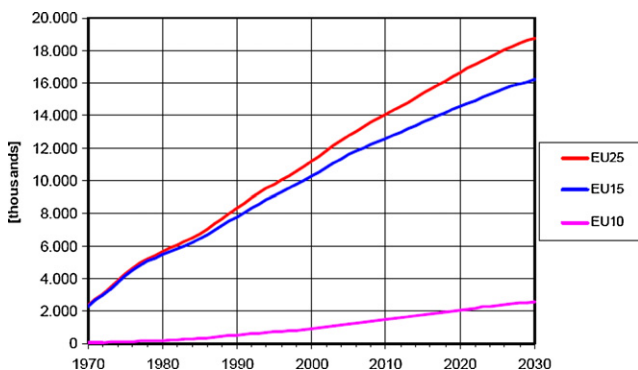
2 million), it can be expected that by 2030 the total mass of ELVs generated per year in the EU25 will reach 14–17 million tonnes [3].

Recycling of ELVs is not a recent concern, scrap cars have been recycled on an industrial scale for many decades and long before any national or European legislation was enacted [5]. The first industrial automobile shredder installation started operating in 1958. Recycling was driven by the recovery of valuable metals and the re-sale of used parts. In the mid-1990s and under increasing pressure from national governments, the automotive industry signed voluntary agreements to achieve higher recycling and recovery rates and to accept responsibility for the treatment of ELVs [5]. To date, most of the developed countries and hence the major car producing countries introduced legislations to encourage or make reuse, recovery and recycling of ELVs mandatory.

According to the EU-Directive 2000/53/EC on ELVs [6], member states must establish collection systems for waste arising from vehicles and must ensure that ELVs are exclusively transferred to authorised treatment facilities (ATFs). They must moreover encourage the reuse of suitable components, the recovery of components that cannot be reused, and must give preference to recycling when environmentally viable. Member states must meet the targets of "reuse and recovery" and of "reuse and recycling", which should increase to at least 85% and 80% respectively by the 1st of January 2006 and to at least 95% and 85% respectively by the 1st of January 2015. Reuse, recycling and recovery are defined as follows:

- reuse: using components of ELVs for the same purpose of their original conception;
- recycling: reprocessing waste materials for the original purpose or for other purposes, but excluding energy recovery;
- energy recovery: incineration of combustible waste, as such or mixed with other waste, with heat recovery;
- recovery: any of the applicable operations provided for in Annex IIB of the European Directive on ELVs.

Besides setting targets, the Directive aims at preventing waste from vehicles, by requiring that the member states encourage vehicle manufacturers, in liaison with their material and component manufacturers to:

- limit the use of hazardous substances in vehicles, so as to prevent their release into the environment, to make recycling easier, and to avoid the need to dispose of hazardous waste;
- design and produce vehicles which facilitate dismantling, re-use and recycling;
- increase the use of recycled materials in new vehicles.

The Directive furthermore requires that components of vehicles, sold after the 1st of July 2003, no longer contain Hg, Cr(VI), Cd or Pb (with a few exceptions, listed in Annex II of the Directive).

Contrary to the stringent legislation of the EU, the USA does not apply a specific legislation on ELV management [7], and both

Fig. 1. Projected development in the number of ELVs 1970–2030 (not including export and import of used cars) [3].

Table 1
Average composition of an ELV [2,7,10–12].

Material	% of total mass
Ferrous metal	65.4–71.0
Non-ferrous metals	7.0–10.0
Plastics	7.0–9.3
Rubber (including tires)	4.0–5.6
Glass	2.9–3.0
Fluids	0.9–6.0
Battery	1.0–1.1
Process polymers	1.0–1.1
Electrical/electronics	0.4–1.0
Other	1.0–5.9

waste materials and recycled materials are simply considered as solid waste. There is no federal legislation on solid waste and every state has its own legislation. In general ELV recycling receives less interest than in Europe, partly because of the widespread availability of waste disposal sites. Most ELV recycling facilities in the USA belong to the automotive industry and the major car manufacturers have programs to study both the improvement of car recyclability, and the reduction of the ASR burden. The USA Environmental Protection Agency (EPA) promotes the recycling concept among vehicle manufacturers [8].

In Japan recycling of ELVs is considered a priority area, and a law on automotive recycling was already implemented in 2004 [7]. Consequently, most car producers have branches in the recycling business and develop easy-to-recycle cars. Targets for recycling (including thermal recovery) of automotive shredder residue (ASR) were set at 50% by 2010 and at 70% by 2015, corresponding to an overall recycling rate of ELVs of about 95% by 2015, analogous to Europe, when the fraction represented by ASR in the total mass of ELVs is considered [9].

Table 1 illustrates the average composition of an ELV. Ferrous metals are by far the main component, followed by non-ferrous metals and plastics [2,7,10–12].

The use of materials such as plastics and aluminium in automobiles is expected to increase at the expense of ferrous metals, because the former are lightweight and have some desirable mechanical and physical properties resulting in the reduction of the total mass of the car and of its fuel consumption. The use of plastics increased by 50% over the past 20 years; the EU-Directive on ELVs might stimulate, however, using aluminium rather than

plastics, as the recycling of aluminium is easier and more cost effective [10].

The EU-Directive on ELVs had notable effects on numerous 'end-of pipe' solutions: it prompted innovations in post-shredder technologies (e.g. Galloo, Salyp, VW-Sicon, etc.) and led to new recycling applications of the fractions obtained, such as the use of fine sized ASR as filler in asphalt, concrete or composites. End-of life design considerations are so far not the highest priority for car manufacturers due to the delayed payback associated with long vehicle lifetimes [10]. However, as plastics are the most critical components for reaching the EU-targets, car manufacturers have both reduced the number of different plastics used in order to improve the possible recyclability, and often label plastic parts in order to facilitate identification during dismantling [13]. Recyclables are moreover increasingly used in car parts, albeit at low total volume. In general, the focus targets increasing the proportion of materials that can be recycled (usually downcycled), rather than increasing the quality of the recyclables [10]. There are also strong indications that the EU-Directive on ELVs led to reduced use of toxic substances. Nevertheless, innovations in end-of-life recovery technologies are still required for the processing of current ELVs (from older cars) despite of these design changes that will facilitate reuse and recycling in the future.

Fig. 2 reviews the flow of a vehicle through the typical end of life operations [14]. Vehicles arrive at an authorized treatment facility (ATF) as the result of an accident (premature ELVs) or because they reached the end of their useful lives (natural ELVs). They are de-registered and de-polluted (removal of battery, fluids, tires, lubricants, break fluids and other hazardous substances). The treatment of these primary removed parts is described in Baeyens et al. [15,16]. Depending on their age and value, vehicles are further manually dismantled for reusable or recyclable parts. The remaining vehicle-hulk is then shredded using a hammer mill. The ferrous metals are removed using magnetic separation, whereas eddy current or dense media separation is used to separate non-ferrous metals. The residue of this process is called automotive shredder residue (ASR), also sometimes referred to as 'auto fluff' or 'auto shredder fluff', and traditionally sent to landfill. It is composed of plastics, rubber, foam, residual metal pieces, paper, fabric, glass, sand and dirt [11,17]. In Europe, ASR is classified as hazardous waste according to the list of hazardous wastes 2000-532-EEC (Chapter 1910, an annex of the European Directive 91-689-EEC on hazardous waste). In 2008, on average 74.1% of the ELVs initial mass was
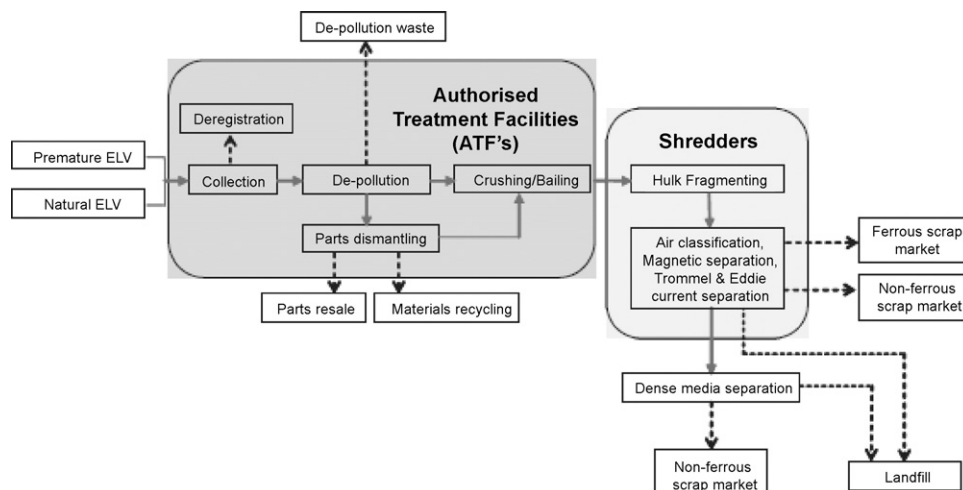

Fig. 2. Flow of a vehicle through the different end-of-life operations [14].
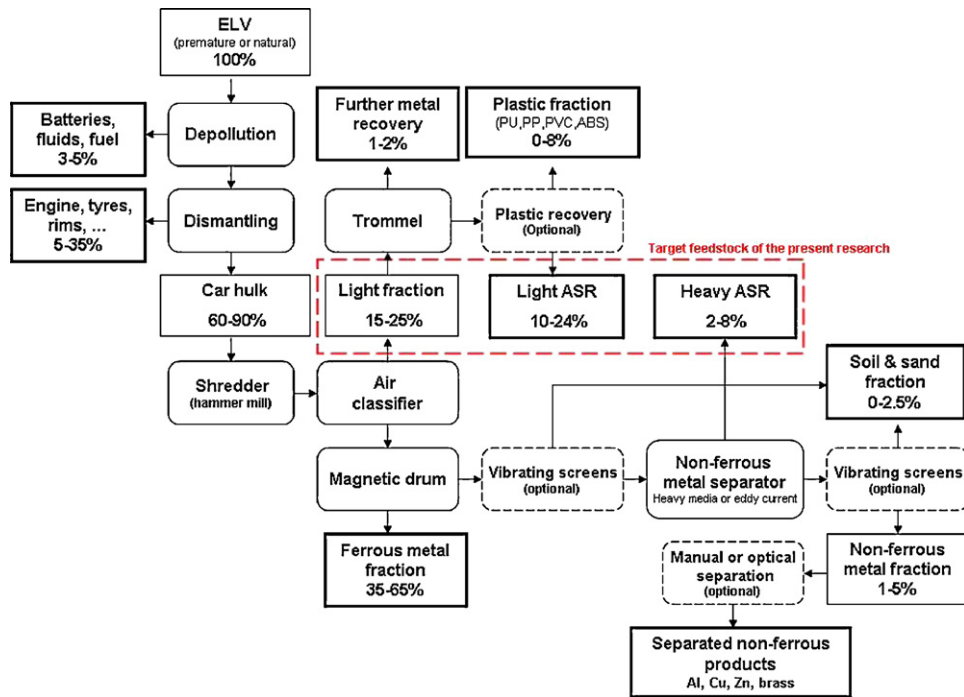
Fig. 3. Schematic representation of the processing of an ELV.

reused or recycled in the EU 15, an additional 2.7% was thermally recovered [4]. To meet the European targets for 2015, an extra 10.9% must be recycled and an extra 7.3% recovered, so that the target reuse and recovery rate of 95% is reached and only 5% of the ELV's is disposed of in landfills. An alternative would consist in dismantling more material before shredding, but this is not considered economically viable in Western countries.

The present paper will critically review all aspects of reuse, recycling and recovery of ELV components and materials, to complement existing papers that only address parts of these issues [11,17–20], and it will concentrate on post shredder technologies in which ASR is separated in different fractions in view of a more efficient recycling and energy recovery. The separation of metals is not considered in detail since reuse and recycling of metals is already well established. The ELV recovery and recycling process can be divided in four main steps: (i) dismantling, de-pollution and shredding: all primary actions, as briefly reviewed in Section 2, and giving rise to the production of ASR with characteristics as described in Section 3; (ii) secondary physical and mechanical treatment of ASR, and its possible direct uses (Section 4), (iii) the treatment of ASR by energy recovery (Section 5) or (iv) by thermo-chemical treatment (Section 6).

2. Primary ELV management: The production of ASR

The recycling rate of ELVs has always been high in comparison to other consumer products, due to their high metal content (of about 70%), making recycling economically feasible. The environmental impact of the non-recycled fraction of an ELV should nevertheless not be overlooked, as it often exhibits hazardous characteristics due to the presence of spent oils and lubricants, heavy metals, persistent organic pollutants (POPs), etc. [21]. It is thus not surprising that in 2000, Europe imposed quite stringent targets regarding reuse, recycling and recovery of ELVs [6], to limit this otherwise growing waste stream. Concerning the management of ELVs, this Directive prescribed the implementation of several measures, following the principles of extended producer responsibility (EPR) [14,22] and making economic stakeholders, such as manufacturers, dismantlers and shredder companies, responsible for setting up a system for the collection and treatment of ELVs. In order to reduce the amount of abandoned cars throughout Europe, vehicle manufacturers had to guarantee that by the year 2007, take back and treatment of ELVs was of no cost to the last owner. In 2000, for instance, 11% of the total amount of ELVs in the UK, were abandoned vehicles [23].

Table 2
Parts that can be recycled from ELVs [7].

Part	Material	Recycled as
Window	Glass	Tiles
Seat	Foam and fibre	Soundproofing materials for vehicles
Body, trunk, hood and door	Steel	Car parts and general steel products
Wire harness	Cu	Cu and engines products (cast Al reinforcement)
Bumper	Resin	Bumper, interior parts, toolbox, etc.
Radiators	Cu and Al	Gun metal ingots and Al products
Coolant, engine and gear oil	Oil	Alternative fuel for boilers and incinerators
Engine transmission, suspension and wheel	Steel and Al	General steel and Al products
Catalytic converter	Precious metals	Catalytic converters or precious metal (e.g. platinum) recycling
Tire	Rubber	Raw material and energy recovery (e.g. cement kilns)

Table 3
Composition, as wt%, of ASR.

	[2]	[11]	[25]	[26]	[27]	[35]	[36]	[42]	[75]	[145]	[150]	[157]	[162]	[163]	[164]
Metal				0.8–1.6											
Ferrous	8	3.1–3.7	3			12.0		11	6.4	6		2.2	8.1	13	11.4
Al		1.5–2			16									3	
Non ferrous	4	0.45–0.7			6.7									1	
Wire	5 (harness)		5			1.7	3	1				3.5	2.1		
Rubber	7	9.5–14.5	18	4.2–5.1	12.4	8.9	21 (elastomers)	13	2.7	38	20	9.4	5.3	23	
Plastics	33	35.6–44.2	33	20.6–23.6	39.8	14.2	41	37	21.9	20	20	29.3	19.3	22	42.6
Foam (PUR)	16		15	5.5–15.9	6.2			11	7.0	4.5		5.0	2.2	7	
Wood + cardboard	3		3		5.1				4.4	10		1	2.2	4	
Dirt + non-combustibles									8.6						
Textile	15	14.5–17.5	7	30.8–31.2		16.4	10	9	4.1	5	25	3.7	45.1	6	33.5
Glass	7			8.7–16.8	11.7	1.5	16		2.0	16.5			3.5	13	1.7
Others	2	21.3–31.8		6–8	13.4 (<40 mm)	34	9	18 (<5.6 mm)	42.9		35 ('inerts')	30.1 (<5 mm); 16.2 (non-detachable substances)	12.2	8	10.7 (miscellaneous)

Standards for storage, de-pollution, treatment and regulation of authorised treatment facilities (ATFs) were additionally established.

The actual processing of an ELV can be subdivided in several stages [11,14,19], each yielding a certain amount of the ELV's mass that can be reused, recycled or recovered, as schematically shown in Fig. 3.

Before dismantling, the potentially hazardous and toxic parts are removed from the ELV. De-pollution of an ELV typically addresses the parts that contain toxics (e.g. the battery) and to the liquids still present in the ELV (e.g. fuel, antifreeze, engine oil and brake fluid). Afterwards, during dismantling, reusable and recyclable components are removed, with special emphasis on components with a sufficient market value (e.g. aluminium rims) or containing valuable materials (e.g. catalytic converters). Table 2 lists parts of an ELV that can easily be recycled, indicating also possible end-products. In general, 5–35% of an ELV's mass is removed for reuse or recycling, depending on the age of the ELV (premature or natural ELV), on the market value of the removed parts, and on the labour costs to remove these parts. A large difference exists between for instance European countries, where only about 5–10% of an ELV's mass is removed during dismantling, and e.g. South Korea, where up to 35% of an ELV's mass is removed during this stage [11,19,24].

The car hulk remaining after de-pollution and dismantling, is subsequently sent to a shredder facility. The shredding process generally makes use of a hammer mill to transform incoming hulks into small pieces, usually fist-sized or even smaller [11,24]. Ferrous metals are removed from this waste stream by a series of mechanical and magnetic separation processes. Purities of more than 99% can be reached using a magnetic drum, rendering this waste stream very suitable for recycling [11]. The removed ferrous metal fraction of an ELV, can mount up to 65% of the original ELV's mass. Non-ferrous metals are in general removed by eddy current or dense media separation; this fraction can mount up to 5% of the original ELV's mass. In some countries, also certain plastic fractions (including e.g. polypropylene, polystyrene and acrylonitrile butadiene styrene) are removed by applying physical or mechanical separation techniques, exploiting differences in density, solubility or melting point. As this separation step is not yet common practice, it is indicated as optional in Fig. 3 and further development within this field will be discussed in more detail in Section 4.

After all these process stages, the residual waste streams represent 15–25% of the original ELV's mass and are collectively termed "automotive shredder residue" or "ASR". This residual fraction is believed to further increase in the future, since the amounts of plastic used in vehicles will increase at the expense of the ferrous metal fraction (Section 1) and efficient separation of plastics is so far not common practice. Due to its highly heterogeneous nature and its classification as hazardous material, ASR is nowadays most often disposed of in dedicated and appropriate landfill sites [11,17,20,25].

To enhance the current European "reuse and recycling/recovery"-rates of ELVs, two major routes can be distinguished: more complete dismantling or development and application of ASR processing techniques. Increasing dismantling is currently not economically viable because of the high labour costs in combination with a rather low market value for low quantities of non-metallic materials [14]. Under the influence of the EU Directive, the car industry is introducing "design for disassembly": e.g. bonding agents and welded joints are avoided in order to reduce the time for disassembly. Yet, regardless of these design changes, innovations in ASR processing techniques remain required for processing ELVs, as the average lifetime of a vehicle ranges between 12 and 15 years, depending on the geographical region under consideration [3,11,12]. These innovative technologies for advanced physical and/or mechanical separation in view

of recycling, or for energy and thermo-chemical recovery will only gain importance in the near future. They will be dealt with from Section 4 onwards.

3. Characteristics of ASR

3.1. Definitions

Characterization of ASR is important to discern potentially combustible and valuable fractions in order to select and optimize recycling and recovery techniques. ASR is usually defined as the 15–25% of ELV's mass remaining after de-pollution, dismantling, shredding of the hulk, and removal of metals from the shredded fraction (Section 2, Fig. 3). The reader is cautioned since some authors define ASR as the residual fraction after shredding, but without removal of the metal fraction, which can account for up to 65% of the original ELV's mass [19,26,27]. In the present article the first definition of ASR will be used, i.e. the residue after shredding and removal of metals. It should moreover be remembered that shredders often not only process ELVs, but ELVs together with other consumer products such as white goods and other metallic manufacturing and construction waste [18,24,28]. In such cases the more general term "shredder residue (SR)" is used to describe the product of the shredding process.

The fact that this definition is not uniformly applied, introduces a lot of uncertainty in data concerning (A)SR and the present section therefore reviews and classifies the relevant literature data. ASR is a highly heterogeneous mixture of residual ferrous and non-ferrous metals (5–23%), plastics (20–49%), rubber (3–38%), textile and fibre material (4–45%), wood (2–5%), and glass (2–18%) [11,17,27,29,30]. The exact composition and physical properties of ASR depend mainly on the shredder input, shredder equipment, and post-shredder separation processes [17,18]. The heterogeneity of the material, with varying levels of contamination (chlorine, heavy metals, PCDD/Fs), moisture content, ash content and calorific value, constitutes a considerable challenge to select or design an appropriate treatment process for ASR [18,31].

In-line with the overall treatment scheme of Fig. 3, ASR can be classified based on its origin from the post-shredding scheme [18] into:

- *Light fluff:* fraction generated during shredding of the hulk and separated using air classification (ca. 75% of the total ASR; 10–24% of the total ELV)
- *Heavy fluff:* fraction remaining after metal separation from the shredded heavy fraction (ca. 25% of the total ASR; 2–8% of the total ELV).
- *A soil/sand fraction* is sometimes reported separately, but is usually included as part of the heavy ASR (ca. 0–2.5% of the total ELV)

ASR is, however, also frequently classified based on its particle size. As there is no standardized division between 'fine' and 'coarse' size fractions, the fine-sized fraction ranges from <2 to <20 mm throughout the different literature sources. In addition to fine and coarse particles, an intermediate fraction is sometimes defined.

Both the heterogeneity of ASR itself and the lack of a uniform definition and standard classification of ASR and its fractions, make it particularly difficult to unambiguously characterize "ASR" or some of its fractions. A further uncertainty is introduced when trying to visually classify ASR or its fractions [18].

3.2. Material composition and physical properties

Table 3 shows that the composition of ASR can differ considerably depending on the applied shredding and post-shredding

Table 4
Elemental composition and characteristics of ASR.

	[31]	[38]	[47]	[51]	[73]	[75]	[88]	[116]	[126]	[135] (mixed SR)	[144]	[145]	[149]	[152]	[157]
Energetic value (MJ/kg)	19.7(HHV) 18.7(LHV)	29.3			25.1	18.2					10.2	21.0	21.0	13.4–25 (LHV)	21.5
Ash (wt%)	44.7	18.4			24.5	42.77	18.3	3.7	68.2		58.1	27.3	24.2		30.7
Cl (wt%)	0.943	1.8		2.49	3.4		0.56				0.5		2.2	0–2.5	2.9
S (wt%)	0.28	0.52		0.19	0.33	0.25	0.32	0.3	0.56		0.3	0.3	0.02	0–0.6	0.36
Ca (wt%)				1.49	3.9									6–13	12.4
Si (wt%)														9–35 (SiO_2)	12.9
Fe (wt%)	4.1			4.67			10.6			1–18	17.6			3–10	2.8
Al (wt%)	15.2			1.15			31.9			0.7–3	8.6			4–10	5.3
As (ppm)			4.2–6.3			11								3–6	3.5
Cd (ppm)			12			160						80		0–30	6.2
Cr (ppm)	37.2		120–140	8200		280	489			1000–11,000		260		100–200	
Cu (ppm)	5747		14,000–30,000				5320	16,000		4000–30,000		12,350		10,000–60,000	34,000
Hg (ppm)	0.113		0.56–0.91			1.6								0–0.5	0.08
Ni (ppm)	33		180–230			100	366			400–1500		2910		50–100	
Pb (ppm)	2167		1500–1800	1400			2710	1400		1000–11,000		2000		0–5000	1700
Zn (ppm)	6646		8500–9300				8510	12,000		5000–30,000		17,370		0–15,000	8750
Moisture (wt%)	7.15	1			0.7	24.1			5.4		2.6	2	0.38	2–25	1.2

Table 5
(a) Composition, as wt%, of ASR, according to the origin: light fluff.

	[26]	[27]	[30]	[47]	[158]	[159]	[165]
Metals	1–1.7	21	8.8	2.5	3.7	0.3	
Wire	2.9–3		4.7	1	2.2		0.5
Rubber	3.8–4	3.1	2.6	3	8.8	10.3	4.1
Textile	37.5–39.6		36.1	32.5	26.2	8.3	7.9
PUR foam	6.6–20.6		35.3	8			3.8
Plastic	16.1–24.1	31.8	11.7	9	46.1	11.0	8.7
Wood	0.03–0.4			1	2.7	0.6	
Paper	0.8–1.0				0.8		
Soil/sand	6.4–21.6				4.3		
Glass	0	2.3		43 (minerals)			
Others	2.7–6.2		0.8		5.2	69.5 (<10 mm)	75 (fines)

(b) Composition, as wt%, of ASR, according to the origin: heavy fluff

	[26] (S&S + heavy)	[27]	[47]	[159]	[165]
Metals	0.2–1.4	1.6	5	0.7	
Wire	7.0–12.7		3		0.7
Rubber	14.1–17.3	9.3	55	43.7	44.8
Textile	7.7–11.6		3	10.5	10.5
PUR foam	0.9–2.8				3.3
Plastic	23.8–30.9	8	19	32.6	29
Wood	0.06–0.7		7	4.7	5.6
Paper	1–2.5				
Soil/sand	7.6–12.3		8 (minerals)		
Glass	8.3–11.0	9.4			
Others	4.6–14.0			7.8	6.1 (fines)

process, especially as far as the major fractions of metals, rubber, plastics and textiles are concerned. This is mainly due to differences in processing and sorting efficiency, although the cited authors moreover do not use the same classifications: foam (PUR) is sometimes mentioned separately, but is usually included in the plastic fraction; the same applies to 'wire', which is sometimes mentioned separately, but is usually included in the residual metal fraction or the non-ferrous fraction. Up to 27 different types of plastics are currently encountered in ASR, although the majority of the plastic components are made of polypropylene (PP), polyurethane (PUR), polyvinylchloride (PVC), acrylonitrile butadiene styrene (ABS), poly-methyl-methacrylate (PMMA) and polyethylene terephthalate (PET) [19,26,27]. ASR typically contains significant amounts of Cl, S and heavy metals as illustrated in Table 4. The particle size ranges from less than 125 μm up to approximately 10 cm [17,24,32–35]. The calorific value ranges from 14 to 30 MJ/kg and the ash content from 18% to 68%. The moisture content ranges from 0.7% to 25%.

Light and heavy fluff are both characterized by a high content of combustibles such as plastics (38 MJ/kg), rubber (23 MJ/kg) and textile (17 MJ/kg) (Table 5a and b). Heavy fluff contains more rubber; light fluff contains more textiles and low density plastics [30,33]. Heavy fluff is generally characterized by a higher ash content than light fluff. The reported calorific values vary significantly among the literature sources cited in Table 4. Light fluff can contain up to 70% of 'fine' sized material as illustrated in Table 5a.

The subdivision of (A)SR on the basis of its particle size in a fine and a coarse fraction is generally applied to the total ASR fraction, but sometimes it is also applied to light and heavy ASR separately [24,29,32,33,35,36]. Although the coarse fraction can be defined as the fraction of particles exceeding either 2 or even 20 mm, roughly about 50% of the ASR exceeds 20 mm (coarse fraction), while the other half is expected to be smaller (fines) [17,24,32,35]. Generally, a small fraction of ASR (2%) is larger than 100 mm and consists of large pieces of foam, rubber or plastics that have not been broken during the shredding process.

The coarse fraction mainly consists of PUR (foam), plastics, rubbers and textiles. It has the lowest ash content and the highest calorific value (15–30 kJ/kg) and can thus easily be used as a fuel.

The coarser particle size allows mechanical separation into recyclable fractions. The fine fraction consists of pieces of glass, plastics and metals along with dust and dirt [17]. It generally has a higher ash content and a lower calorific value (11–21 MJ/kg) than the coarse fraction and is thus less suited for combustion [17]. Despite their significant share in the total ASR mass, fines are not currently considered for recycling due to their complex composition and the difficulty to allocate the different constituents to a single category of material [17,24]. Alternative techniques such as energy recovery (incineration), thermo-chemical recovery (pyrolysis/gasification) or direct incorporation of ASR in products (use as filler, binder, aggregate, etc.) are hence necessary in order to divert this fraction from being landfilled [17,24,37].

3.3. Contaminants

ASR may contain significant concentrations of chlorine and heavy metals (Table 4). The chlorine content of ASR ranges from 0.5 to 4 wt% [17,28,30] and is mainly due to the presence of chlorinated plastic components such as PVC or halobutyl rubber [32]. Also brominated flame retardants are present. Incineration of ASR may therefore lead to the formation of toxic compounds such as PCDDs (dioxins), PCDFs (furans) and hydrochloric acid (HCl), needing a proper flue gas treatment to avoid emission in the environment [38].

In Van Caneghem et al. [39] concentrations for PCDD/Fs, dioxin-like PCBs, PCBs and PAHs of 242–329 ngTEQ/kg, 481–631 ngTEQ/kg, 13–15 mg/kg and 37–140 mg/kg, respectively, were reported. Other sources report PCB concentration ranging from 0.5 to 7 mg/kg; PCBs are in general more concentrated in the coarse fraction than in the fines [17,28]. Van Caneghem et al. [40], reported a PCDD/F-fingerprint of ASR dominated by higher chlorinated PCDD congeners: approximately 90% of the total PCDD/F content of the ASR was accounted for by hepta- and octa-CDD while the PCDFs represented only ca. 3%, with hepta-CDF and octa-CDF being most abundant. Hedman et al. [41] reported a PCDD/F fingerprint of the textile and leather fraction of RDF from MSW; the relative contribution of the different congeners to the total PCDD/F content agrees with the PCDD/F fingerprints of the ASR reported by

Table 6
Elemental composition and characteristics of ASR as a function of particle size.

	[17] (<20 mm)	[17] (20–50 mm)	[17] (>50 mm)	[32] (<2 mm)	[32] (<12.7 mm)	[32] SR (12.7–38.1 mm)	[32] SR (>38.1 mm)	[33] (<2 mm)	[33] (>2 mm)	[36] (<2 mm)
Energetic value (MJ/kg)	11.7(HHV) 10.7(LHV)	16.4(HHV) 15.2(LHV)	20.7(HHV) 19.3(LHV)		12.4	21.3	30.4			16.7
Ash (wt%)	40.4	16.4	21.3		57.9	37.1	20.5			36.2
Cl (wt%)			0.09		0.8	2.1	3.2			0.5
S (wt%)	0.15	0.1			0.27	0.31	0.49			0.2
Ca (wt%)					3.11	2.45	1.74			
Si (wt%)					0.44	0.28	0.11			2.1
Fe (wt%)				12.1	2.0	1.3	1.4	12–14	6.0	25.7
Al (wt%)				1.3	1.2	0.9	0.4	1.2–2	0.7	
As (ppm)	16	20	9		9	4	4			
Cd (ppm)	6.7	7.0	5.5	99				30–120	20	
Cr (ppm)	270	390	194	272	130	67	101	180–300	88	800
Cu (ppm)	34	16	32	11,692	15,839	26,958	15,735	2300–22,000	2000–5000	12,000
Hg (ppm)	0.65	0.9	1.0							
Ni (ppm)	230	210	144	271	224	162	148	140–550	80–280	700
Pb (ppm)	3800	5000	2000	4310	738	354	64	1030–10,200	1200–3000	2000
Zn (ppm)				14,385	6787	7441	3415	7900–16,000	3900–5000	19,000
Moisture (wt%)	13.8	4.4	12.3							

Van Caneghem et al. [40]. ASR can contain up to 40% of textiles and leather [17,19,42], suggesting that this fraction might be a contamination source of PCDD/Fs in ASR. As the reported fingerprint of ASR [40] also resembled the PCDD/F fingerprint of diesel exhaust reported by Chang et al. [43], these exhausts can be considered another possible contamination source of PCDD/Fs in ASR.

Table 4 reviews some literature concentrations of heavy metals in ASR. Table 6 details the different size fractions of ASR. Lanoir [30] and OVAM [27] reported total (heavy) metal concentrations in ASR ranging from 13.5% to 22%. These percentages are high compared to those reported by other authors (see Table 3). The metals with the highest concentrations are Al (0.7–8.6%), Fe (1–18%), Cr (0.037–11 mg/g), Cu (4–60 mg/g), Zn (0–30 mg/g) and Pb (1.4–11 mg/g). The fine ASR fraction generally contains the highest heavy metal concentrations [17,29]. For some heavy metals, such as Cu, Cd, Pb, Ni, Zn, concentrations may exceed the limit values of applicable landfill regulations [44] and pose a threat for the environment as these metals can leach from the ASR [33]. Table 7 summarizes leaching results for different ASR fractions and compares them to the European limit values for non-hazardous waste. As can be seen, there is a very large variety among the different literature sources and no unambiguous conclusion can be made. Further research concerning leaching of heavy metals from ASR and from its different fractions (subdivided by origin and/or size) is necessary to correctly assess its hazardous nature.

4. Secondary recovery of ASR

4.1. Post-shredder technologies: Physical and mechanical upgrading of ASR

The physical and mechanical upgrading of ASR can be seen as an extension of the shredding process and has been researched intensively over the past decades [5,11,20,45–47]. Recovery of all recyclable materials from ASR in a single step is not feasible due to its heterogeneity. In currently operating technologies, as summarized in Table 8, the applied techniques to separate and concentrate the different types of materials are similar: air classification, magnetic and eddy current separation and screening or trommel separation. The post-shredder technologies (PSTs) mentioned in Table 8 are designed to treat the residual material stream remaining after de-pollution, dismantling and shredding of an ELV. The indicated overall recovery rates for ASR have to be critically assessed since they are based on the current ASR composition, that is, however, expected to change over the coming years for reasons explained in Sections 1 and 2, and since they assume optimum dismantling and de-pollution before shredding. The energetic valorisation of some upgraded streams has been taken into account in the given recovery rates. The largest difference among post-shredder technologies stems from the techniques used for the separation of plastics. Different steps of float/sink separation are most commonly used, as this is a well established technique for the separation of mixed plastics, where the density differences of the plastics makes them respectively to sink or float in a tank filled with a liquid of suitable density (e.g. water, brine or supercritical CO_2). Other techniques for plastic separation, not (only) exploiting the difference in density, have been developed and applied in several PSTs: froth flotation, thermo-mechanical sorting or static hydrodynamic separation (Table 8).

According to Ferrão et al. [11], increasing the recycling of the plastics from ASR is the key issue to achieve the European *reuse and recycling* target of 85% by 2015, as it is expected that in this

Table 7
Leaching values (mg/l) for heavy metals from ASR.

Metal	[19] (Shredder dust)	[33]	[34]	European limits (L/S = 10)
As	<0.4		1.08	2
Cd	ND	<0.005	1.42	1
Cr	0.007–0.016		0.12	10
Ni		<0.03–0.13		10
Pb	0.8–1.1	<0.03	1.27	10
Zn		0.06–0.175		50
Cu	0.14–0.5	<0.03		50
Hg	ND			0.2
Se			1.46	0.5

way an additional 6-10% of the total ELVs mass can be recycled. It is furthermore expected that the share of plastics in ASR will increase in the coming years because of the trend towards lowering the vehicle's mass. The introduction of the EU-directive on ELVs moreover gave a strong incentive to reduce the number of different plastics used and to label plastic parts in order to facilitate identification during dismantling [13,25]. The major plastics used in a vehicle are polypropylene (PP), polyurethane (PUR), polyvinylchloride (PVC) and acrylonitrile butadiene styrene (ABS), which represent together over 60% of the plastic fraction [5,19,25]. Several studies pointed out that these plastics can be physically and mechanically recovered from ASR with a sufficient purity to warrant high quality recyclates [11,20,25,48]. The quality of the recycled plastics indeed remains a major issue in this context and is the subject of much research. Plastics should however not only be separated and recycled because of their intrinsic value; their occurrence can also cause problems in some subsequent treatment methods e.g. in pyrolysis: PUR is difficult to crack, PVC can contaminate the pyrolysis gas with methylchloride, rubbers form tars and major quantities of a carbonaceous residue, whereas PE and PP tend to form waxes.

Industrial applications by shredding companies, using these post-shredder techniques for plastic separation, e.g. Galloo in Belgium, have shown that the European reuse and recycling target of 85% can indeed be reached [27,45].

4.2. Advanced secondary recovery of ASR

4.2.1. Upgrading to fuel

ASR has a favourable calorific value (14–30 MJ/kg), but the high ash content and the elevated chlorine and heavy metal concentrations may limit its use as fuel substitute, if used as such. The aim of advanced secondary recovery techniques is to segregate ASR and to isolate the combustible materials with low ash content and with low contaminant concentrations.

The finest fraction of ASR generally has the highest ash and mineral oil content, combined with the lowest calorific value (Section 3). Screens, shaker tables, rotary drums or float/sink separation techniques can be applied to remove this fine sized fraction and thus improve the fuel characteristics of the ASR [17,37,42,49]. In order to improve the ease of transportation and storage, the ASR density can be increased by pelletization [50].

Chlorinated plastic components such as PVC or (halobutyl) rubber are the main sources of the high chlorine concentrations often found in ASR (Section 3.3). As PVC contains about 50% of chlorine, PVC removal from ASR is a simple way of lowering the overall chlorine concentration. Several studies pointed out that density separation, using a bath density of 1100–1200 kg/m³, can remove the majority (up to 68%) of chlorinated plastics (density of about 1400 kg/m³ or more) from the combustible materials of ASR [32,42]. Hwang et al. [42] reported another technique to

Table 8
Overview of post-shredder technologies.

	Argonne	Galloo	MBA-polymers	Salyp process	Stena	R-plus (WESA-SLF)	VW-Sicon
Separation techniques							
Air classification	X	X	X	X	X	X	X
Magnetic separation	X	X	X	X	X	X	X
Eddy current separation	X	X	X	X	X		X
Screening		X		X	X	X	X
Trommel separation	X	X		X	X		
Optical sorting				X			X
Manual sorting					X		
Drying						X	
Float/sink separation		X		X	X		X
Froth flotation	X						
Thermo-mechanical sorting				X			
Wet grinding			X				
Hydrocyclone			X				
Static, hydrodynamic separation tanks		X					
Heavy media separation					X		
Status of development	Operating plants	Operating plants	Operating plants	Operating plants	Operating plants	Operating plants	1 trial plant + 2 under construction
Overall recovery rate	90% of polymers > 6 mm 90% of metals > 6mm	90%	Not given	86%	80%	92%	95%

decrease the chlorine content of ASR plastics, by combining thermal treatment of ASR (heating to 300 °C) to remove chlorine from PVC, followed by washing of the char to remove soluble chlorides: overall de-chlorination reached 81% when applied after density separation. The use of thermal energy to reduce the chlorine concentration is however debatable due to the high energy costs [42]. Other recently studied de-chlorination techniques of ASR include the extraction of chlorine with calcium hydroxide ($Ca(OH)_2$) or with a sodium hydroxide/ethylene glycol mixture (NaOH/EG) [38,51]. At ambient temperature, only inorganic chlorine is removed; when the temperature is increased to 100–200 °C, organic chlorine can also be extracted. A ball mill reactor can be used to improve contact between the ASR and the solution and thus enhance the extraction efficiency [51].

In some cases heavy metals must be removed from ASR before recycling or energy recovery in order to meet the regulatory limits of the final application. Certain heavy metals can easily be removed by mechanical separation [29,34]. Granata et al. [29] found that the ASR fraction smaller than 0.5 mm contained the highest Cr, Ni, Pb and Zn concentrations: removing this fraction can reduce the overall concentration of these elements in the ASR by more than 77%. Kurose et al. [34] demonstrated that Cr, Cd and Pb concentrations in ASR could be reduced by at least 83% by eddy current separation of non-ferrous metals.

Further heavy metal removal can be obtained by washing ASR with an acid extraction agent [29,33,34]. Depending on the way heavy metals are bound to the matrix, different extraction agents, such as CH_3COOH, KCl/HCl, NH_4OH/HCl or H_2O_2/CH_3COONH_4, give the best results. Granata et al. [29] found that Cd and Zn were rather weakly bound to the matrix, so that extraction with a weak acid was sufficient to reduce their concentration. This technique can also be used to recover Zn from the ASR fraction smaller than 0.5 mm, as it is one of the most abundant metals in this fraction and it has a fair market value.

4.2.2. Incorporation into manufactured products

It is inherently difficult to mechanically separate the fine sized ASR fraction (<20 mm) in e.g. ferrous and non-ferrous metals, plastics, etc. Furthermore, this fraction generally exhibits the worst combustion characteristics (Sections 3 and 4). As a consequence, several studies investigated the possibilities of directly incorporating this fine sized ASR fraction into products such as composites, concrete or asphalt. Most of these applications are, however, still in a research phase and further investigation remains necessary before real scale application is possible.

Incorporation of ASR in composites may close a recycling loop when this composite material is used for new automotive components. Sendijarevic et al. [52] prepared rigid composites from ASR using isocyanate-based binders: strength properties were evaluated for composites prepared by incorporation of various fractions and amounts of ASR. Robson and Goodhead [53] investigated the dual-injection moulding process to incorporate ASR into composites. A skin of virgin polymer is moulded over the core material, containing ASR. Polypropylene (PP) was used as skin material, while the core consisted of a 50/50 vol% mixture of PP and ASR granules. The properties of this composite were found acceptable to manufacture low strength components such as housings, casings and covers or for products where the mechanical strength can be provided by large cross-sections.

The fine sized ASR fraction can also be used as filler in concrete. This fraction typically contains about 30% of organic matter, as well as inorganic substances such as quartz, calcite, magnetite, hematite, anhydrite [54,55]. If calcium sulfoaluminate cement is used, ASR can be directly incorporated into the concrete: heavy metals, such as Zn and Pb, were found to be successfully integrated and immobilized into the structure. The ASR-concrete mixture can be used for various applications including road construction.

Another application is the use of fine sized ASR as a binder and/or aggregate in asphalt [56,57]. Incorporation of ASR in asphalt reduces the oxidation of the asphalt and increases the elastic memory, thus preventing fatigue cracking [56]. Rosetti et al. [57] showed that granules, produced by mixing ASR with binding materials (lime or cement), fly ash and a densifying agent, were a suitable aggregate in asphalt mixes. In their experiments, the optimum ASR to fly ash ratio was 1 to 1, but the optimum mix of the different constituent materials and the possibility of industrial production still need further investigation.

The Reshment Process, developed by CTC Umwelttechnik of Switzerland, combines mechanical and thermal treatment of ASR to recover metals and to produce a vitrified material, that can be recycled in the road construction sector [11,46,58]. A mechanical separation is applied as a first step to remove the metal fractions (mainly Al, Cu and Fe) for recycling. The residual product is mixed with fly ash of MSW incinerators and undergoes thermal treatment in a CONTOP melting cyclone, operated at about 2000 °C. According to Sauert et al. [59], this process results in the thermal valorisation of ASR (47%), in recycling of metals (8%) and in the recovery of the vitrified granulate as construction material (37%). Due to the high energy requirements of this process, it is expected to be economically less interesting than other recycling or recovery options of ASR.

5. Direct ASR-to-energy applications

Due to the ASR heterogeneity in particle sizes and elemental composition, the technical and economic feasibility of its recycling and mechanical recovery is limited (Section 3), [60–63]. Thermal treatment methods such as co-incineration with other wastes in waste-to-energy (WtE) installations or application as (energy) feedstock in the foundry and cement industries may constitute a cost effective and more sustainable alternative to landfilling of ASR. However, according to the EU-Directive 2000/53/EC, the fraction of ASR that is not recycled, but from which energy is recovered, should by 2015 not exceed 10% of the original ELV's mass. Therefore, the thermal treatment should be considered as a complement to intensive dismantling and primary and/or secondary recovery activities, allowing a further increase of the recovery of ELVs. Moreover, thermal treatment of ASR considerably reduces volume and mass: only the resulting inert ash must be landfilled.

Processing of ASR through thermal treatment was studied in various research, pilot and full scale projects and showed high potential, as ASR has a heating value ranging from 14 to 30 MJ/kg (Section 3). The exact calorific value of ASR largely depends on its organic fraction, typically about 50 wt% [17,28,46,60,62]. Whereas the small particle size of the fine ASR fraction often hinders further mechanical recovery (Section 3.3), this fraction can largely be handled by thermal treatment.

5.1. Co-incineration with other waste streams

In general ASR is not suited for mono-incineration, due to possible carry-over of unburned fines and melting characteristics [64]. A mixture with lower calorific wastes enhances the incineration potential and efficiency in waste-to-energy plants, while still maintaining the advantages of considerable mass and volume reduction, along with recovery of energy. Co-incineration of ASR can be conducted in various incinerator types, such as grate furnaces, fluidized bed combustors, rotary kilns and cement kilns.

5.1.1. Grate furnace

Over the past decades, co-incineration of ASR with municipal solid waste (MSW) in a grate furnace was studied by several researchers. Many of the conducted pilot and full-scale studies pointed out that this practice can be both economically and environmentally sound, on condition that best available techniques (BAT) are applied [60,63,65,66]. Co-incineration with MSW in a grate furnace has the advantage that the technique is well known and that grate furnaces, using best available techniques for energy recovery and flue gas cleaning, are operational in many countries throughout Europe and abroad.

Extensive co-incineration tests were carried out in the MSW incinerators at Horgen and at Bazenheid, both in Switzerland [46,66–68]: up to 10% of shredder residue was co-incinerated to assess the technical feasibility and environmental impact. The co-incineration was reported to meet the regulatory environmental limits. Switzerland was the first country in the world to treat all of its shredder residue, including ASR, by thermal processing [69]. Co-incineration tests of ASR and MSW were also conducted in Germany, Spain and Sweden [11,60]: the largest waste incineration facility in Sweden (Renova), successfully co-incinerated up to 20% ASR with MSW [60]. It was shown that flue gas emissions did not change significantly compared to the incineration of MSW. PCBs appeared the most critical organic pollutants: their concentration increased by a factor of 3–5 in the flue gases and by a factor of 5 in the bottom ashes, but all regulatory limits were still met. Mark [65] compared different alternatives (co-incineration with MSW, co-incineration in a cement kiln and co-incineration with hazardous waste) and concluded that co-incineration of ASR with MSW was most appropriate.

Although most authors do not recommend co-incinerating high percentages of ASR with MSW, Mark and Fisher [63] demonstrated that up to 31% of ASR can be co-incinerated with MSW, without significantly changing the composition of the flue gases, the plant operation, the burnout of the waste or the potential use of the bottom ashes. However, the concentrations of Zn, Pb, Sn, Sb and Co in the fly and boiler ashes increased significantly: the respective concentrations of Pb and Zn were even up to 18 and 16 times higher than the average baseline level. For higher amounts of ASR, over 40%, problems of bridging and plugging of the conveyer transfer chutes and additional problems in the feed system were reported [70].

In many countries, bottom ashes from MSW incineration are used as a secondary raw material in building applications [71,72]. Therefore, it is important to monitor toxic components (heavy metals, POPs) in the bottom ashes when ASR is co-incinerated, as ASR contains in general higher amounts of these components than MSW. In this way, legal concentration limits for toxic elements in bottom ashes limit the amount of ASR that can effectively be co-incinerated [64].

5.1.2. Fluidized bed combustor

Saxena et al. [75] investigated mono-incineration of ASR in a FBC, in view of achieving optimum combustion conditions and acceptable flue gas and ash composition. The heterogeneity of the ASR was found to cause lots of difficulties in the operation of the fluidized bed.

More recent studies [39,40,73–77] focus on the co-incineration of ASR in a fluidized bed combustor (FBC). Good practice in such installations is to incinerate low calorific waste streams such as waste water treatment (WWT) sludge along with high calorific, non recyclable waste from industrial sources, such as carpets, textiles, refuse derived fuel and ASR, in order to maintain temperatures of about 650 °C in the sand bed and of about 900 °C in the freeboard [78].
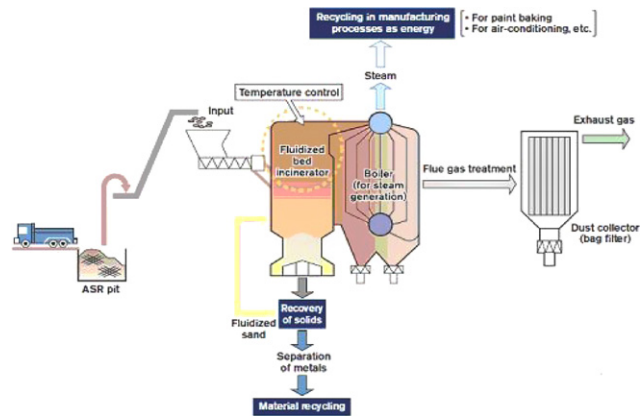

Fig. 4. System for energy recovery from ASR at Oppama plant [74].

Nissan modified an FBC at its Oppama plant to recover energy from ASR [74]. Full scale operation i.e. co-incineration of 4,800 tonnes of ASR per year along with other waste from the Nissan plants, started in 2005 (Fig. 4). Nissan was the first car manufacturer to thermally treat its own ASR with energy recovery. The produced steam is used in the manufacturing process. Optimum temperature control appeared essential for successful co-incineration of ASR. Kobyashi et al. [73] investigated the flue gases from a FBC, co-incinerating different refuse derived fuels with ASR, and concluded that the composition of the input as well as the excess oxygen strongly affect the flue gas composition.

During an extensive trial, heavy ASR was added to the usual waste feed of the SLECO FBC at the Indaver site in Antwerp, Belgium, Europe's largest FBC for WtE conversion [39,40,76]. In this full scale trial PCDD/F, PCB, dioxin-like PCB, PAH and heavy metal concentrations were determined in all input and output streams. During the trial, the input waste stream consisted of 25% ASR, 25% RDF and 50% WWT sludge, whereas the usual waste feed consisted of 70% RDF and 30% WWT sludge. Because incineration of ASR generates less non-biogenic CO_2 per delivered MJ of energy than incineration of RDF, the impact on global warming decreased when ASR was co-incinerated. NO_x and SO_2 emissions did not change significantly; neither did the emissions of persistent organic pollutants (POPs), despite the increased input. The POPs in the input streams were destroyed during incineration and the formation of new POPs during the cooling of the flue gas appeared to a great extent independent of the POP concentrations in the input [39]. As also reported by other authors [73,79–82], the increased Cu and Fe concentrations in the fly ash and boiler ash enhanced de novo synthesis of PCDD/Fs. During the co-incineration trial, the amount of bottom ashes generated per ton of incinerated waste was at most 48% higher than with the usual waste feed. The concentrations of heavy metals in these ashes increased on average by 10%, but still complied with local legal requirements for use as secondary raw materials (road construction), except for copper. The total heavy metal concentration in the flue gas also increased (by about 60%) during the co-incineration of ASR, but remained well below the local regulatory limits (Vlarem). Fly and boiler ash and flue gas cleaning residue, corresponding to 16.5 wt% of the original input, were landfilled after moistening and physicochemical treatment (e.g. stabilisation/solidification), respectively. It was concluded that co-incineration of heavy ASR with RDF and WWT-sludge is a valid method to increase the reuse and recovery rate of ELVs. The quality of the generated ashes was found to determine the proportion of ASR that can effectively be co-incinerated [76].

5.1.3. Rotary kiln

A rotary kiln allows to process solid, liquid and gaseous waste streams and is generally applied for the thermal treatment of hazardous industrial wastes such as POP-containing waste, medical waste, chemical waste, sludge, etc. In the kiln and the post combustion chamber temperatures of 900–1200 °C are reached. A residence time of at least 2 s at these temperatures guarantees complete burnout of the waste input [61,83,84]. At temperatures in excess of 1100 °C, also mixtures of high chlorinated wastes (>1 wt% Cl) can be treated [83]. The use of a small-scale rotary kiln incinerator for on-site power generation from ASR was investigated by Hubble et al. [85]. In the flue gases heavy metal and inorganic emissions were acceptable; organics were not measured. The ASR volume and mass was reduced by 80% and 55%, respectively. Some samples of the ashes exceeded the regulatory limits on lead leaching, but addition of sodium silicate, lime or cement type reagents resulted in a reduced leaching.

A rotary kiln is very robust and is thus also suitable for co-incineration of ASR with hazardous waste. Thermal recovery in a rotary kiln is however often more expensive than in a grate furnace or FBC due to both the more intensive flue gas cleaning and the additional treatment and disposal of the ashes, while in general less energy is recovered [65,86].

5.1.4. Cement kiln

Cement manufacturing is energy-intensive, with energy costs of up to 50% of the production costs. The economic benefits of using waste as alternative fuel are thus obvious. Over the past decades, experience with substitute fuels such as plastics, tires, paint, used oil and other solid and liquid wastes was gained [32,61,87]. In Europe, the cement industry became the largest consumer of secondary fuels from industrial waste, with over 100 kilns co-incinerating different types and quantities [88,89]. In some cement kilns, waste-derived fuels replace up to 80% of the fossil fuel demand [87]. Beside the use as energy feedstock, cement manufacturers also use different materials as mineral substitutes, such as spent catalysts, aluminium production wastes, glass, industrial ashes, filter cake, etc. [32].

A cement kiln is a rotary kiln with a length that can mount up to 200 m [61,90]. The solid input flows counter-current with the combustion gases. The length of the kiln ensures a sufficient residence time of the incineration gases at high temperatures: about 8 s at temperatures above 1200 °C [87]. Given these typical process conditions, a cement kiln seems in principle ideal for the use of waste materials as fuel. However, to guarantee that the quality standards of the clinker are met, extensive chemical analysis of the waste materials and required pre-treatments should be conducted before using a waste as an alternative fuel or resource [87,88,91].

ASR is a potential alternative fuel and mineral feedstock for cement production as about 50 wt% of ASR consists of combustible matter such as plastic or rubber, and another 40 wt% is made up of silicates, calcium, aluminium and iron [32]. Nevertheless, Gendebien et al. (2003) [88] reported strong negative effects on the quality of the clinker when ASR was used in a cement production process in Switzerland: when the fuel of the cement kiln contained 50% of ASR, instead of the regular fossil fuel mix, the concentrations of Cl, Pb, Cd, Cu and Zn in the clinker increased by one order of magnitude or more, as shown in Table 9. In this case, the Swiss product specification for clinker was not met for Cl, Cd, Cu, Pb and Zn (Table 9). In general, upgrading and purification of ASR is required before its use as fuel substitute in high percentages in a cement kiln, as already discussed in Section 4. The required pre-treatment is, however, often uneconomic or impractical. Other problems related to co-incineration of ASR in cement kilns are increased ash formation, clogging of the fuel injection zone, volatilization of mercury and increased concentrations of hazardous elements in the cement kiln dust [62,92].
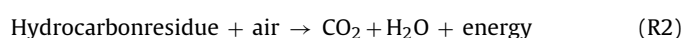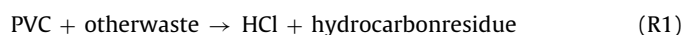
5.1.5. Major environmental concerns when ASR is co-incinerated

Co-incineration of ASR can be challenging due to high concentrations of chlorine, persistent organic pollutants (POPs) and heavy metals (Section 3). The concentration of these components can be reduced by the advanced upgrading techniques as discussed in section 4, when economically feasible. Optimum control of the process conditions in combination with adequate flue gas cleaning will limit the emission of harmful substances.

High concentrations of *chlorine* in waste result in high concentrations of hydrogen chloride (HCl) in the combustion gases, which may reduce the service life of incineration equipment due to chemical corrosion and fouling [28]. Traditional acid components, such as HCl, are therefore removed from combustion gases by wet, semi-wet, dry or semi-dry scrubbing, using lime (CaO), hydrated lime (Ca(OH)$_2$), sodium bicarbonate (NaHCO$_3$), sodium carbonate (Na$_2$CO$_3$) or limestone (CaCO$_3$) as a solid, in suspension or in solution [93–95]. Wet scrubbers are more efficient, but have the disadvantage of producing waste water. In many recent thermal treatment plants, a dry contactor/reactor and filter are therefore followed by a wet gas scrubber [72,93].

The EU-Directive 2000/76/EC [83] sets stringent regulations on the operating conditions of waste incinerators depending on the chlorine content of the waste: a gas temperature of at least 850 °C and a residence time of at least 2 s are required for waste containing less than 1 wt% chlorine; for waste containing more chlorine, a gas temperature of at least 1100 °C and a residence time of at least 2 s are imposed. As ASR can contain up to 4 wt% of chlorine, de-chlorination techniques for ASR, as outlined in section 4, are intensively researched in order to make ASR more suitable for co-incineration in installations that operate at temperatures lower than 1100 °C. Another way to overcome the problems related to the high chlorine content was proposed by Zevenhoven et al. [77], who developed a two-stage waste combustion process that makes use of the specific properties of PVC, the main contributor of chlorine in ASR. The process consists of two fluidized bed reactors with heat recovery and involves the following chemical conversions:

$$PVC + otherwaste \rightarrow HCl + hydrocarbonresidue \qquad (R1)$$

$$Hydrocarbonresidue + air \rightarrow CO_2 + H_2O + energy \qquad (R2)$$

The de-hydrochlorination of the input waste takes place at 200–400 °C according to Reaction R1, in the first reactor which is operating with oxygen free fluidisation gas to prevent formation of PCDD/Fs. The mixture of sand and particulate hydrocarbon residue is subsequently fed to the second reactor, operated as combustor at 700–900 °C (Reaction R2). The hot sand is recycled to the first reactor after heat recovery. Advantages of this process include reduced acidity of the flue gases from the second FBC, recovery of HCl from the first FBC and avoidance of residues from sorbents used to trap HCl and PCDD/Fs from the flue gases [77].

Public opinion in general opposes co-incineration of ASR, due to the possible release of *persistent organic pollutants* (*POPs*), such as PCDD/Fs, PCBs and PAHs. Co-incineration of ASR may indeed lead to the release of POPs, due to the elevated concentrations of chlorine, POP-precursors and POPs contained in the ASR (Section 3). Several studies investigated the influence of co-incineration of ASR on POP emissions [39,40,60,96–99]. It is generally assumed that the incoming POPs are destroyed during incineration and that upon cooling of the flue gases new POPs form via the heterogeneous pathway either through the precursor route or through de novo synthesis [100–102]. This assumption can be supported by analysis of the congener distributions or so called 'chemical fingerprints' of the POPs [103–105]. Van Caneghem et al. [39,40] investigated the con-

Table 9
Heavy metal concentration in the cement clinker; co-incineration ratio of ASR: 50% [88].

Element	Unit	Without waste	With ASR	Swiss Buwal[a]
Cl	mg/kg	134	1180	1000[b]
As	mg/kg	13	14.9	40
Pb	mg/kg	16.2	554	100
Cd	mg/kg	0.3	6.6	1.5
Cr	mg/kg	34.6	129	150
Cu	mg/kg	17.9	1070	100
Ni	mg/kg	27.3	98.5	100
Hg	mg/kg	0.12	0.08	0.5[b]
Zn	mg/kg	59.6	1750	350

[a] Swiss product specifications for clinker.
[b] Guide values for Portland cement.

gener fingerprints for PCDD/Fs, dioxin-like PCBs, PCBs and PAHs in a full-scale FBC, co-incinerating 25% ASR with 25% RDF and 50% waste water treatment (WWT) sludge. For PCDD/Fs, it was found that the fingerprint of the flue gas, fly and boiler ash, and flue gas cleaning residue were dominated by PCDFs (mainly hepta- and octaCDFs), in contrast to the PCDD/F fingerprint of the RDF and ASR input, which were dominated by PCDDs. Also for the dioxin-like PCBs, the fingerprint of the outputs differed significantly from the one of the inputs: high chlorinated dioxin-like PCBs were more abundant in the outputs than in the inputs. Van Caneghem et al. [39,40] concluded that the differences between the fingerprints of the input and the outputs confirm that waste incinerators destroy POPs present in the waste and that new POPs are formed during the cooling of the raw flue gases. These findings are consistent with results from other authors, concluding that the POP-output of an incineration process is to a great extent independent from the POP concentration in the incinerated waste [60,96]. Moreover, if wastes such as ASR, containing high levels of POPs, are co-incinerated with for instance MSW, the incinerator is a POP sink, as less POPs are formed than destroyed [39,99].

New formation of PCDD/Fs upon cooling of the flue gas occurs via the heterogeneous pathway either through the precursor mechanism or through de novo synthesis. Formation and chlorination of PCDD/Fs via the precursor pathway can be enhanced by the presence of ash particles, copper and iron. As ASR contains high concentrations of both copper and iron, this could enhance the formation of PCDD/Fs in the flue gas when ASR is co-incinerated with wastes containing lower amounts of these elements. Van Caneghem et al. [40] found that a waste mix containing 25% ASR, 25% RDF and 50% WWT sludge contained 7.5 times more copper than a 70% RDF and 30% WWT sludge mix, the usual feed of the FBC studied. The concentrations (expressed as ng/kg) of the individual PCDD/F congeners increased mainly in the fly and boiler ash; the highest increase was noticed for the HpCDD/Fs and OCDD/F. As these congeners have low TEF-values, the incinerator's total PCDD/F output, expressed in equivalent TEQ-values, did however not increase significantly.

Aae Redin et al. [60] found that PCB concentrations (expressed in ng/Nm^3 or ng/kg respectively) increased with a factor of 3–5 in the flue gases and with a factor of 5 in the bottom ash, when ASR was co-incinerated with MSW compared to the sole MSW incineration. Other studies by e.g. Ishikawa et al. [97] and Van Caneghem et al. [99], reported similar increases of the total PCB concentration of incinerator outputs.

Common practice for capturing POPs in the flue gas is adsorption on powdered activated carbon, which is subsequently retained by fabric or baghouse filters [106–109]. A new development is the use of 'catalytic filters', based on two proven technologies: catalysis and surface filtration [110,111] with reported efficiencies of destruction in excess of 99.5% for all PCDD/Fs. However, contrary to catalytic filters, activated carbon also removes mercury from the flue gas and is even increasingly efficient at lower temperatures.

Another important environmental concern related to co-incineration of ASR is the increasing concentration of *heavy metals* in the flue gases and in the solid residues. As already mentioned in Section 3, automotive shredder residue is rich in certain heavy metals, such as copper, nickel, lead and zinc. Before incineration, the concentrations of heavy metals can be reduced by the advanced secondary recovery techniques of Section 4.

Transfer of heavy metals into the different outputs during incineration can be influenced by the occurrence and distribution of heavy metals in the incinerated waste, by physicochemical conditions influencing the incineration, and by parameters influencing the combustion kinetics [112–114]. The partitioning of heavy metals over the different incinerator outputs is very complex. Several studies show that e.g. chlorine enhances the volatilization of heavy metals such as copper, lead and zinc. [113,115,116]. The presence of hydrogen in the system however limits this effect, as HCl is more likely formed than metal chlorides [116]. Another important element in the waste is sodium, which increases adsorption of heavy metals in the bottom ash due to its affinity for chlorine [114]. The partitioning of heavy metals between the different outputs is often simplified by assuming that it mainly depends on the physicochemical properties (e.g. volatility) of the metals in combination with the working conditions of the incinerator [113,117–120]. Metals with different volatilization characteristics of the metal as such, of the metal oxides or of the metal chlorides, are transferred into the flue gas by different mechanisms. Zhang et al. [114] found that Hg and Cd are transferred into the flue gas by volatilization, whereas the volatilization temperatures of Cr, Cu and Ni (and their oxides or chlorides) are so high that they are only transferred by entrainment with ash particles; As, Pb and Zn are transferred by both mechanisms. Upon cooling of the flue gases, heavy metal vapours (except mercury) condense quite easily on particulates, thus facilitating their abatement by common de-dusting techniques, such as electrostatic precipitators, fabric, ceramic or cartridge filters [61]. More efficient particulate removal results thus in more efficient heavy metal removal. Activated carbon or coke, injected in the flue gas, adsorbs 80–93% of the mercury in the flue gas, so that mercury only becomes an important environmental concern when the input contains large amounts of it, which is generally not the case for ASR [112,121].

Iron and aluminium are, if present as metal, often mechanically removed from the bottom ashes. Bottom ashes originating from MSW incinerators (grate furnace or FBC) are in many countries used as secondary raw material for building applications [60,64,71,72,88]. Co-incineration of ASR in small proportions will in general cause no significant change in metal concentration and leaching [122]. Incineration of high quantities of ASR may

increase the heavy metal concentrations in the bottom ashes to such extent that the limit values for leaching are no longer met, thus limiting the use of bottom ashes as secondary raw material or imposing more intensive treatment of the ashes. Especially the high amount of copper present in ASR, mainly transferred into the bottom ash, may limit the application of this ash as a raw material. A possible way to decrease copper leaching below the limit value, is extraction with solutions of organic complexants, like ammonium citrate, or acid washing with dilute HCl solutions [123,124]. Another possibility is heating the bottom ashes (at about 400 °C) in order to destroy fulvic and humic acids that form extractable complexes with copper [71,125].

The fly and boiler ashes are most often landfilled together with the FGC-residue, possibly after an appropriate treatment if required. Especially the higher concentrations of Cd, Pb and Zn might require removal or stabilization of these heavy metals before landfilling [123,126]. Possible methods for the reduction of heavy metal leaching from these ashes include separation, solidification, chemical stabilization, encapsulation, sintering or vitrification [127].

The economic aspects of the treatment of the different ashes will determine the proportion of ASR effectively co-incinerated. Yet, Lopes et al. [126] found that the ashes of a FBC were more stable and resistant to aggressive environmental conditions (acidification) than the untreated ASR, so that the environmental risks associated with landfilling are decreased through co-incineration.

5.2. The use of ASR as fuel in metallurgical processes

5.2.1. Blast furnace

A blast furnace is a reactor used in the iron and steel industry that transforms iron ore into molten iron [128,129]. It can be considered as one of the largest, most complex industrial reactors due to its various material inputs, including gaseous and liquid energy carriers, granular material and powders. Furthermore, over thirty major reactions and phase changes take place [129]. Iron ore and coke are alternately fed onto the top of the furnace, while hot air and auxiliary fuels (pulverized coal, oil or natural gas) are introduced through lances in the lower furnace part, thus making the process comparable with a counter current moving bed reactor. In the area located in front of the lance injection zone, the so-called raceway, auxiliary fuels are cracked and produce syngas that flows upward through the moving bed [36,61,129]. This way, the auxiliary fuels also act as reducing agents. Besides the use of traditional fuels, such as pulverized coal, oil or natural gas, economic incentives have encouraged the use of waste materials as auxiliary fuels. This was found possible due to the high intrinsic stability of the blast furnace process. Indeed, process conditions in the raceway assure complete destruction of all persistent organic pollutants and prevent formation of new ones [36]. Trace elements such as heavy metals dissolve into the hot metal and in the slag. The key issue for iron makers when using waste as auxiliary fuel in the blast furnace is to assure a smooth, highly efficient operation and suitable metal quality at decreased production costs.

Injection of high calorific plastics into the raceway has become normal blast furnace operational practice since the late 1990s [61,130]. Several simulations, lab scale and industrial tests have been conducted in order to analyse the possible use of ASR in blast furnaces both as auxiliary fuel and as auxiliary reducing agent [20,36,129–133]. Most of these studies concluded that, due to the presence of certain chemical components as well as due to the physical nature of ASR, it is only cost-effective to co-combust small proportions (up to 3%). Injecting higher amounts of ASR leads to disturbances in the operation of the blast furnace and can only

be considered after suitable pre-treatment. Important parameters that influence the use of ASR in blast furnaces are the physical properties, the calorific value, the chemical composition and the concentration of non-ferrous metals. A study, conducted by the Competitive Analysis Center Inc. and Economic Associates Inc. [134] has set the following criteria for the organic fraction of ASR: moisture content below 7.5%, particle size between 3.2 and 6.4 mm and ash content below 10% [46]. Besides these criteria, also the chlorine, copper, lead and zinc concentrations are limiting factors [62,132,133]. Chlorine can accumulate in the blast furnace dust, part of which is recycled in the furnace. When the chlorine accumulates, the concentration of hydrogen chloride (HCl) in the off gas might exceed regulatory limits [133]. As for waste incinerators, release of HCl may reduce the service life of the incineration equipment via chemical corrosion and fouling. The concentration of copper in the hot metal is a very important parameter and has to be maintained below certain limits as copper makes the steel brittle [62]. Besides copper, also heavy metals such as lead and zinc were found problematic for the iron making process, since they generally increase coke and energy consumption and cause productivity losses due to the formation of scaffolds in the blast furnace [133]. Intensive advanced secondary recovery of ASR is generally necessary to comply with the requirements of a specific blast furnace plant (Section 4). As this may be quite expensive, the use of ASR as an alternative fuel in blast furnaces is often not economically interesting [132]. From a metallurgical point of view, in the blast furnace, the use of the gas or oils produced by gasification or pyrolysis of ASR is preferred to direct secondary recovery [20,132]. Continuous supply of ASR with adequate and constant quality and sufficient quantity, is a fundamental requirement of the iron makers, but is unfortunately difficult to guarantee by the producers [130].

The Thermobath® process [11,20] is a thermal pre-treatment process, facilitating ASR injection into a blast furnace. It separates ASR in floats (plastics) and sediments (metals, glass and sand) on the basis of their different specific density, using an oil bath at 280 °C. The floating plastics can be injected into the blast furnace as auxiliary fuel and as reducing agent, while the remaining metals can be recycled in the steel-making process.

5.2.2. Pyro-metallurgical non-ferrous metal production processes

Pyrometallurgical processes can be applied for the separation of non-ferrous metals from minerals, ores or concentrates. Copper smelting, for instance, is a pyrometallurgical treatment requiring elevated amounts of energy. Due to the continuous price increase of copper and fossil fuels, electronic scrap smelters have also become interested in certain ASR fractions. Co-smelting of ASR or of its ash from preceding energy recovery treatments (incineration, pyrolysis or gasification) in non-ferrous metal plants may be considered as a low cost recycling route, as no complex, energy consuming mechanical pre-treatment is necessary. In order to be of economic interest for copper smelters, the waste mixture should contain over 5 wt% of copper [135], which is in general not the case for ASR or its ashes (Sections 3 and 5). A possible solution, discussed by Jalkanen [135], is the co-smelting of ASR and shredder residues from electric and electronic scrap (ESR), resulting in a waste stream with sufficient concentrations of copper (mainly due to the ESR) and with an elevated heat content (mainly due to the ASR). Typical impurities or hazardous metallic components present in ASR and ESR, such as Pb, Sn and Zn, do not require any special measures or pre-treatment. Only the presence of aluminium can cause problems in the smelting process: due to its high reactivity, its presence leads to slag splashing [135].

6. Thermo-chemical treatment of ASR

6.1. ASR as feedstock for the thermo-chemical treatment

Thermo-chemical treatment refers to advanced technology processes that convert ASR components liable to decomposition under the application of heat into liquids and/or gases. A solid residue remains, containing a carbonaceous char, mineral ash and metals present in the ASR feedstock.

The liquids and the gas have mostly been found suitable for use as fuel. Their possible recovery for use as feedstock for the production of petrochemicals is less obvious due to the complex composition of ASR. Often the char is found difficult to be recycled due to the high concentrations of heavy metals and minerals, and has to be send to landfill.

Within the thermo-chemical treatment technologies, pyrolysis and gasification are generally considered as the emerging technologies for waste and biomass as illustrated for plastic solid waste by Al-Salem et al. [61,136] and Brems et al. [137] and for biomass by Van de Velden et al. [138].

Although the industrial development of these technologies into the sole treatment of ASR is rather slow due to its very heterogeneous nature, the pressure to deal with ASR is however constantly growing, and has become a priority in view of the European Directive on ELVs and the constantly increasing landfill costs. ASR pyrolysis and gasification are therefore being extensively researched. Up till now, most ASR pyrolysis and gasification processes, applied on an industrial scale, lack a designed end-product procedure, especially for the char [61,139,140]. The problems encountered by Donaj et al. [140] clearly illustrate the complexity of the treatment of the char from ASR pyrolysis.

6.2. ASR pyrolysis

Pyrolysis is commonly operated at moderate temperatures (400–600 °C) and either in the absence of oxygen, or with such low levels of oxygen that feedstock combustion does not significantly occur. The products are a solid residue, condensable organic vapours called pyrolytic liquids, and gases. The relative yield of these 3 products largely depends on the composition of the feedstock and on the operating conditions of the pyrolysis reactor: mainly operating temperature, rate of heat transfer to the ASR particles, and residence times of the ASR and the products in the reactor. Char production generally ranges from 33-68 wt% [18], thus exceeding common char quantities encountered when pyrolysing plastics or biomass as such [137,138,141].

Fundamental research of ASR pyrolysis mostly used thermogravimetric analysis as e.g. reported by Rausa and Pollesel [142], and small-scale reactors as reported by e.g. di Marco et al. [143], Day et al. [144], Zolezzi et al. [145], Chiarioni et al. [146,147] and Joung et al. [148,149]. Both thermogravimetric and lab-scale pyrolysis reactors were always coupled with product identification and characterisation.

The use of pilot-scale experiments is very limited, with Galvagno et al. [150] being the only detailed example retrieved from literature. Vacuum pyrolysis experiments were reported by Roy and Chaala [151], whereas Donaj et al. [139],[140] presented results of microwave pyrolysis experiments.

A critical review of the developments in the full-scale pyrolysis of ASR has been presented by Harder and Forton [18], giving a complete analysis of the evolution of the pyrolysis processes, and of the competing environmental, legislative and commercial drivers towards a further development. Among the processes recognised as being commercially proven or having a commercial potential, the authors describe the Ebara process, the PKA process, the Pyromelt Process (Lurgi) and the TWR process (Siemens; Schwel-Brenn;

TWR/Mitsui). It is noteworthy that all processes mix ASR with other wastes, such as MSW waste or biomass to regulate the variations in material characteristics and calorific value. The application of the Ebara concept via sequential pyrolysis/gasification and combustion is reported in great detail by Viganò et al. [152], confirming the appealing energy and environmental performances. In addition to the processes described by Harder and Forton [18], other combined waste processes have been described in literature.

The ConTherm® technology pyrolyses shredded fuels such as MSW, ASR and up to 50% post-consumer plastics at 500–550 °C in 100,000 ton/year rotary kilns supplied by *TECHNIP* and combusts the gas directly in a pulverised coal (PC)-fired boiler [153]. Residues from the process are screened and sorted to recover materials, mainly metals. A coal mill is attached to the main processing line to treat the char fraction.

The PKA process, described previously by PKA [154] and Malkow [153], comprises a modular pyrolysis and gasification concept. The pyrolysis step was developed by Kiener and modified by PKA. A pre-processing involves separation, screening and shredding of the different feedstock (MSW, ASR, spent tires, plastic waste, contaminated soil). Pyrolysis proceeds at 500–550 °C for about 45–60 min in an indirectly heated rotary kiln. The main product is a CO/H_2 rich fuel gas. Char and ashes are treated by separating ferrous and non-ferrous metals, then dried to below 10 wt% moisture and milled to <2 mm before being used as a fuel, as activated carbon or a raw material in brick plants [153].

The PyroMelt process, developed by ML Entsorgungs und Energieanlagen GmbH, combines pyrolysis and slagging combustion in a sequential mode, yielding a vitrified granular slag [155]. The feedstock consists of MSW, hazardous waste, ASR and post consumer plastic waste. The process gas (500–600 °C) is subjected to multiple scrubbing steps using pyrolysis oil, cooling the gas to 120–150 °C. The char is cooled to 50 °C and jointly burnt with a slurry of dust and heavy pyrolysis oils in a melt furnace (Kubota-Surface-Melt).

The pyrolysis Kanemura plant [156] uses of a rotary pyrolysis reactor to treat 90 ton/day of ASR, generating 20 ton/h of 48 bar saturated steam and nearly 2 MWh of electricity. The emission data of the exhaust gas (dioxins, HCl, NO_x, SO_x, dust and CO), and leaching test results of both slag and flue gas cleaning residue (Cr(VI), Cd, Pb, As, Hg and Se) comply with the corresponding Japanese standards, and the results are detailed in the publication.

The occurrence of dioxins, furans and dioxin-like PCBs in the solid residue from a pyrolysis and melting process, as well as the fate of brominated flame retardants and heavy metals in such a process were reported respectively by Joung et al. [149] and by Osada et al. [157]. Both studies confirm that the pyrolysis-melting process is efficient in the reduction and/or fly ash recovery of possible toxic chemicals.

6.3. ASR gasification

Gasification is commonly operated at high temperatures (>700–800 °C). Air is used as a gasification agent, and the air factor is generally 30% or 40% of the amount of air needed for the combustion of the organic fraction of the feedstock. Gasification produces mostly a gas phase and a solid residue (char and ashes). The use of air introduces N_2 in the gases, thereby considerably reducing the calorific value of the syngas because of the dilution.

Gasification has been widely studied and applied for biomass, coal and plastic solid waste, with results reported and published in literature. The application for the treatment of ASR is less documented. The study of Harder and Forton [18] describes the process developed by Schwarze Pumpe (SVZ; Global Energy), producing methanol as a fuel. Sequential gasification and incineration tests were reported by Mancini et al. [31] and make use of a rotary kiln,

operated between 850 and 1120 °C with an air factor <1. Combustion of the gases is completed in a secondary afterburner chamber. The system is completed with a boiler (steam at 43 bar, 430 °C) and turbine. The capacity was on average 2400 kg/h during the tests. The paper fully describes the characteristics of the ASR used, the combustion properties, the ash analyses, the composition of the exhaust gases, the process operational problems, the residue management, and the energy efficiency. It was concluded that the process requires minor modifications. Atmospheric emissions were invariably considerably below the legal limits.

A similar full report of a sequential gasification and combustion unit to treat ASR, using a fluidized bed gasifier (590 °C) followed by a cyclonic afterburner (1400 °C) is described by Viganò et al. [152] and by Cho et al. [158]. All operational details and properties of the different process streams are included in the publications. Operation of the afterburner at 1400 °C moreover produces a vitrified (and hence inert) slag. It is concluded that the sequential gasification and combustion system reaches appealing energy and environmental performances, despite the unfavourable characteristics of ASR.

A catalytic gasification of ASR with hydrogen generation is presented by Lin et al. [159], using a lab-scale fixed-bed downdraft gasification process. A 15 wt% NiO/Al_2O_3 catalyst is used at 760–900 °C. It is predicted that such a process, conducted at 46.2 atm would yield 87% of syngas, with a 0.27 m^3 reactor allowing to ultimately produce 100 kW of electricity starting from 220 kg/h of ASR. Further tests are however needed.

Sequential microwave pyrolysis and high temperature agent gasification (HTAG) experiments were performed by Donaj et al. [139,140]. The research suggests using the liquid and solid residue from the microwave pyrolysis as fuel for the HTAG process. In this process a gasifying agent (steam, air or an air/steam mixture) is heated to temperatures above 900 °C, providing all the heat needed for gasification. The use of HTAG can lead to higher conversion of fuel to gas, higher hydrogen yields and lower tar content in comparison to conventional gasification [139],[140]. Although the results are fairly supportive for the gasification of the liquid pyrolysis residue, additional process optimization is required towards the pyrolysis of the solid residue.

6.4. Major environmental concerns when pyrolysing or gasifying ASR

It is generally believed that pyrolysis reduces the environmental burden of a thermal process, by operating at low temperature and in the absence of oxygen. The reducing atmosphere avoid the formation of products of incomplete combustion or post-combustion synthesis (such as PCDD/F), whereas the low temperature operation avoids the volatilization of heavy metals and/or their oxides or salts.

The main problems remaining relate to both the difficulty of pyrolysing some of the ASR components, and the difficulty in handling products being formed: PUR is difficult to crack, PVC can contaminate the pyrolysis gas with methylchloride, rubbers form tars and major quantities of carbonaceous residue, whereas PE and PP tend to form waxes.

The literature data of Takuma [156] give evidence of the fact that the emission data of the exhaust gas (dioxins, HCl, NO$_x$, SO$_x$, dust and CO), and leaching test results of both slag and flue gas cleaning residue (Cr(VI), Cd, Pb, As, Hg and Se) comply with the corresponding Japanese standards. The occurrence of dioxins, furans and dioxin-like PCBs in the solid residue from a pyrolysis and melting process, as well as the fate of brominated flame retardants and heavy metals in such a process were reported respectively by Joung et al. [149] and by Osada et al. [157]. Both studies confirm that the pyrolysis-melting process is efficient in the reduction and/or fly ash recovery of possible toxic chemicals.

Gasification is on the contrary achieved in a partially oxidizing atmosphere, thus partly omitting the advantages of pyrolysis. Unfortunately, the application for the treatment of ASR is less documented. The use of a sequential gasification and combustion system (at very high temperatures) as reported by Mancini et al. [31], by Viganò et al. [152] and by Cho et al. [158] demonstrates that atmospheric emissions were considerably below the legal limits. In the specific Japanese case, the operation of the afterburner at 1400 °C moreover produces a vitrified (and hence inert) slag. It is concluded that the sequential gasification and combustion system reaches appealing energy and environmental performances, despite the unfavourable characteristics of ASR.

7. Environmental assessment of the different ASR treatment methods

Despite the past decade developments with respect to the treatment of ASR and the various levels of commercialisation achieved, as reported in Sections 4–6, landfill of ASR is still common practice. The different alternatives to the current disposal practice of ASR can be assessed and compared by using financial and life cycle assessment models to quantify both the economical and ecological benefits of the various methods. To date literature is scarce and only very few papers have addressed this topic: depending on their basic assumptions and system boundaries, general conclusions can slightly differ [37,160,161]. Agreement exists on the fact that landfill should be the least preferred option.

The life cycle assessment (LCA) approach of Boughton and Horvath [37] considered hydrolysis to light fuel oil (thermo-chemical treatment), co-combustion in a cement kiln and material recovery for recycling as alternatives to landfill of ASR. They concluded that the co-combustion of ASR in a cement kiln is the most advantageous and practical short term option, assuming that co-combustion of ASR does not affect the net release of emissions, product quality or kiln operation. Sections 5.1.4 and 5.1.5 of the present review however give evidence of the environmental concern to be taken into consideration. The environmental benefits of material recovery appeared to be the lowest, but they were found to be very sensitive to assumptions on process energy requirements and recovery yield.

Ciacci et al. [161] compared five ASR management strategies: (i) landfilling, (ii) increased metal recovery before landfilling, (iii) increased metal recovery before thermal treatment with energy recovery,(iv) advanced material recovery (by PSTs) followed by energy recovery and (v) feedstock recycling. The LCA methodology was again applied to characterize and quantify the environmental impact of the different scenarios. It was found that scenario (iv) and (v) resulted in the highest environmental benefits compared to the present practice, with a slight advantage for feedstock recycling. As advanced material recovery followed by energy recovery achieved the highest ASR recycling rate, this was considered the best solution.

Both studies point out that environmental considerations should however be completed with economical considerations. Duval et al. [160] clearly demonstrate that market conditions still need to be improved in order to facilitate profitable recycling of automotive plastics. These economic barriers or market uncertainties often hamper the full-scale application of several alternative ASR treatment methods [24,37,160].

8. Conclusions

The automotive industry is facing significant challenges as vehicles have a considerable environmental impact at all stages of their life cycle. In the mid-1990s and under increasing pres-

sure from national governments, the automotive industry signed voluntary agreements to achieve higher recycling and recovery rates and to accept responsibility for the treatment of ELVs. To date, most of the developed countries introduced legislations to encourage or make reuse, recovery and recycling of ELVs mandatory. EU member states must meet the targets of "reuse and recovery" and of "reuse and recycling" of 95% and 85% respectively by the 1st of January 2015. Similar targets were set in Japan.

Primary recovery techniques, mostly of mechanical or physical nature, are capable of recycling up to 75% of the ELV components, leaving a residual 25%, called automotive shredder residue (ASR). ASR is classified as an hazardous waste, but is still largely landfilled. The present review paper assessed the complete ELV and ASR fate. The available literature was used to fully define the characteristics of ASR, with special emphasis on contaminants. Additional post shredder technologies, isolating pure plastics, allow to meet the European reuse and recycling targets of 85%. ASR can moreover be split up into fractions of sufficient quality for direct use as fuel or for integration into manufactured products, such as composites, concrete or asphalt, however with limitations as to product quality and characteristics.

A further reduction in ASR to be disposed of therefore calls upon either incineration (waste-to-energy plant, cement kiln, metallurgical process) or the use of thermo-chemical processes, such as pyrolysis or gasification. This will also allow to meet the European reuse and recovery targets of 95%.

For the *incineration* of ASR in grate-furnaces, fluidized beds or rotary kilns, most of the literature data point towards co-incineration together with e.g. MSW, WWT sludge, etc. In the *cement industry*, generally only low percentages of ASR can be used, unless ASR is previously upgraded and despite remaining problems of increased ash formation, clogging of the fuel injection zone, volatilization of mercury and increased concentrations of hazardous elements in the cement clinker en cement kiln dust. It was demonstrated that the energy-applications of ASR need to address issues of environmental impact due to emissions, using currently available abatement techniques applied in many countries throughout Europe and abroad. The application of ASR in *metallurgical processes* has been found troublesome, due to variable quality and quantity of ASR production, along with the presence of certain contaminants. Pyrolysis and gasification are often presented as the emerging technologies. Although the sole use of ASR is debatable, its mixing with other waste streams, such as municipal solid waste, tires or biomass is gradually being applied in commercial processes. Recent developments of sequential gasification/combustion, often with vitrification of the solid residue, is expected to produce atmospheric emissions well below the legal limits. Unfortunately, the application of pyrolysis/gasification to treat ASR is less documented, so that research is certainly required and the practical advantages compared to (co-)incineration remain to be demonstrated.

In conclusion, the review demonstrated that enhanced recycling and recovery of ELVs, possibly in combination with incorporation of ASR into products, will allow to meet the European 85% target for reuse and recycling. Moreover, the 95% reuse and recovery target can be met by applying in addition thermal incineration techniques or emerging technologies such as pyrolysis or gasification. All these treatment methods were found to result in environmental benefits compared to present landfill practice.

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