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The pyrolysis and gasification pathways of automotive shredder residue targeting the production of fuels and chemicals

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Abstract. Automotive shredder residue (ASR), also referred to as car fluff, is the 15-25% of end-of-life vehicle's mass remaining after de-pollution, dismantling, shredding of the hulk and removal of metals from the shredded fraction. ASR typically consists of metals, plastics, rubber, textile, wood and glass, and is commonly landfilled. The use of ASR as a fuel in incineration processes is controversial since toxic pollutants can be generated as by-products if operational conditions and gas cleaning systems are not carefully controlled. Thermochemical treatment of ASR consists of advanced technology processes that convert ASR components liable to decomposition under the application of heat into liquids and/or gases and a solid residue containing metals. Within the thermochemical treatment options for ASR, pyrolysis and gasification are generally considered as the emerging technologies. The pyrolysis process uses medium temperatures (400-600°C) and an oxygen-free environment to decompose ASR chemically, thus producing minimum emissions and allowing metals to be recovered. Gasification is operated at higher temperatures (>700-800°C) and typically uses air as a gasification agent, which raises some issues in terms of emissions. Lab and pilot-scale plants fed with ASR have been built using both technologies, also considering a combination of them. The aim of this paper is the identification of the best conversion pathway for the production of transportation fuels, aviation fuels or chemicals (hydrogen, methanol, etc.) from ASR. The intermediate products from gasification and pyrolysis are used as feedstock in secondary processes for the production of the final products. The heterogeneous and complex composition of ASR raises several challenges upon its thermochemical treatment, so that the second step of the conversion process is typically not even addressed. Instead, this further step is fundamental to obtain some valuable products that can directly replace fossil derived fuels or chemicals. The updated picture presented in this work should help identify the main advantages and drawbacks of the pyrolysis and gasification processes when considered part of an overall ASR to fuels or chemicals plant.

1. Introduction

There is a growing concern about the environmental impact of end-of-life vehicles (ELVs) as the amounts of ELVs generated are ever increasing and because the waste generated during the final treatment may contain hazardous components. To date, most of the developed countries have introduced legislations to encourage or make reuse, recovery and recycling of ELVs mandatory [1]. The European Directive 2000/53/CE establishes that a minimum of 95% (in average weight per vehicle and year) of ELVs must be reused or recovered (including energy recovery), and that at least 85% must be reused or recycled, so as to reduce the disposal of this waste in landfills. A review of the ELV European Directive, further fostering circular economy principles, is ongoing and expected to result with a legislative proposal in the fourth quarter of the current year 2022 [2].

Automotive shredder residue (ASR), also sometimes referred to as “car fluff”, is usually defined as the 15–25% of ELV's mass remaining after de-pollution, dismantling, shredding of the hulk, and removal

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of metals from the shredded fraction. ASR is a highly heterogeneous mixture composed of residual ferrous and non-ferrous metals, plastics, rubber, textile and fiber material, wood and glass [1]. It is usually classified based on its origin from the post-shredding scheme into “light fluff”, which is the fraction generated during shredding of the hulk and separated using air classification, and “heavy fluff”, which is the fraction remaining after metal separation from the shredded heavy fraction.

In Europe ASR is mainly landfilled, even though some energy is recovered via incineration in co-combustion with municipal solid waste [3]. Low specific weight, high porosity of large components of ASR with subsequent compactness problems, high calorific values responsible for serious fire hazard, possible chemical reactions, etc. are the major problems associated with the landfilling of ASR. Moreover, landfilling of ASR occupies a large space as well as leads to a waste of potentially valuable materials, together with both soil and air contamination [4].

The use of ASR as a fuel in incineration can present challenges due to the presence of chlorine and metallic species [5]. Toxic pollutants such as polychlorinated dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) can be generated as by-products during the incineration if operational conditions and gas cleaning systems are not carefully controlled [6]. Furthermore, heavy metals, particularly the more volatile ones, concentrate in flue gas or in the finest particulate, requiring efficient, thus expensive, gas cleaning systems. Moreover, non-volatile metals concentrate in bottom ash, which could require additional handling and disposal costs [3].

Thermochemical treatment technologies, such as pyrolysis and gasification, 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 [1]. 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 sent to landfill [1].

The state-of-the-art of research and development of thermochemical conversion and metal recovery from ASR was recently presented in [7]. The present study is a critical review of the experimental studies on pyrolysis and gasification of ASR carried out worldwide in the last two decades, and it is aimed at identifying the most promising conversion pathways for the production of fuels and chemicals from ASR. In this context, the products of both pyrolysis and gasification are considered as the intermediates of a wider process that generates valuable end products for the transportation, chemical or construction sectors. The key aspect here is that the process parameters of pyrolysis and gasification can be adjusted depending on the desired final product/s. Thus, the process design, parameters, and yields are shown in this work in conjunction with the proposed final application. This represents the main novelty of this work in the literature that usually tends to treat the primary conversion process (pyrolysis or gasification) and the upgrading/downstream process as two separate entities. Moreover, this study reports all the options proposed in the literature for valorizing the products of pyrolysis or gasification, which are not obvious considering the contaminated nature of ASR.

2. Pyrolysis of automotive shredder residues

2.1. Main features of the pyrolysis process

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 vapors called pyrolytic liquids, and gases. The relative yield of these three 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 [1].

The major constraints which have limited ASR pyrolysis industrial development until now are the high chlorine levels in the ASR, the heavy metals contamination (lead, cadmium, etc.), the disposal of the solid product, the costs of the pretreatment that is required to feed the reactor and the sudden variations in the composition of the feed [3]. However, 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 avoids 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 [1].

2.2. Pyrolysis experiments of automotive shredder residue

This Section describes the main design features, the applied operating conditions and the most important results and findings of a selection of the most significant experiments of ASR pyrolysis, which are also summarized in table 1 for easy comparison. The experimental studies are classified as lab scale or pilot scale, since we could not find evidences of full scale industrial ASR pyrolysis plants to date.

2.2.1. Lab scale pyrolysis of ASR. The peculiar features and results of the lab scale pyrolysis experiments of ASR are described in the following. We have used a chronological order in reporting the different studies in order to identify some kind of evolution from the early studies, which were exclusively focused on the investigation of ASR pyrolysis and its products, to the more recent studies targeting the production of fuels or chemicals, or the recovery of metals:

- A widely reported experimental study of pyrolysis of light and heavy ASR samples is presented in [8]. The pyrolysis experiments were carried out in a non-stirred batch 3.5 dm³ autoclave at 400, 500 and 700°C for 30 min. The authors found pyrolysis as an appropriate technique for treating only the heavy ASR fraction, whereas the light ASR did not yield valuable products. A process temperature of 500°C was deemed adequate to produce total decomposition of the ASR organic matter. All the pyrolysis products were fully characterized. The higher heating value (HHV) of the pyrolysis solid was 16.8 MJ/kg. The HHV of the pyrolysis oil (after separation of the aqueous phase) was 40.9 MJ/kg. The elemental composition (weight percentage) of the pyrolysis oil was carbon (~85%), hydrogen (~10%), and smaller contents of nitrogen (~1%) and sulphur (0.4%). Other elements in the oil were oxygen, chlorine and bromine. The authors found that ASR pyrolysis oils have a great proportion of aromatic compounds (e.g. benzene), and they contain several oxygenated compounds including alcohols, phenols, ketones, aldehydes, etc. and some chlorinated components. The HHV of the pyrolysis gases obtained at 500°C was 32.8 MJ/Nm³. The main gas component was CO followed by CO₂, and then hydrocarbons from C₁ to C₄ and some H₂S. It is noteworthy that no hydrogen was reported among the gas products.
- The study in [3] was aimed at determining whether the European ELV material recycling target of 85% could be achieved by pyrolysis of pretreated ASR. The application of flotation as a pretreatment was effective in increasing the plastic fraction compared to untreated ASR and, ultimately, the oil yield. Indeed, the pyrolysis of untreated ASR samples at 500°C led to a total conversion (sum of the liquid and gas yields) of only 19–26%. Instead, the oil yield raised from 14% to 52% by pretreating the ASR samples with flotation. The authors also found that one sample of pyrolysis oil, obtained after repeated flotation sequences, was made of lighter molecules. This was considered a good starting point for a further refining step to produce gasoline/diesel fuels, or alternatively to obtain chemical products such as olefins or aromatic hydrocarbons.
- In [9] ASR was pyrolysed in a lab scale screw type reactor at moderate to high temperatures, ranging from 550°C to 800°C. The temperature of 550°C was found to be sufficient to achieve total ASR conversion. At higher temperatures an increase in the amount of gases and the consequent decrease in the amount of liquids was observed. ASR pyrolytic gases were mainly composed of light hydrocarbons, hydrogen and methane together with some CO, CO₂ and H₂S. The concentration of hydrogen and CO in the gases increased with the pyrolysis temperature, reaching a maximum H₂ of around 27% (vol.%). Moreover, the temperature of 800°C resulted in the production of high quality char with high carbon and low oxygen contents, making it suitable for use in industrial applications. The heavy metals concentrations in char significantly

decreased with the increasing pyrolysis temperature and were well below the limits of EU legislation. On the other hand, the decrease of the metals content in char implied an increase of the metal content in the gases, which apparently was not of concern for the authors.

- In [10] the ASR light fraction was pyrolysed at moderate to high temperatures (500–800°C) in a bench scale cylindrical quartz reactor. Approximately 6 grams of car fluff were pyrolysed for 30 minutes. The condensable vapours (improperly called tar) and solid residue yields increased with decreasing temperature, and were characterized for their potential use. The HHV of bio-oil was found high, in the range 34–37 MJ/kg, whereas the solid residue showed a negligible residual energy content (<3.5 MJ/kg), regardless of the temperature. The authors analysed the concentrations of dioxins (PCDDs) and furans (PCDFs) in the bio-oil, and the content of metals and polycyclic aromatic hydrocarbons (PAH) in the solid residue. They found that the PCDD/Fs showed maximum concentration at 600–700°C, whereas the maximum concentration of PAHs was detected at 700°C. Accordingly, the lowest pyrolysis temperature of 500°C was found as the most suitable to obtain bio-oil for use as an alternative fuel, and solid residue for use as a filler material.
- Low-temperature pyrolysis of the ASR fraction was investigated in [11] as an effective strategy for recovery of metals (e.g. Cu, Al, Fe). Indeed, using a low temperature and an inert environment the metals would not be further oxidised from their original state, and the organic material could be separated from the metals in the form of volatiles and char. The aim of this study was to obtain from pyrolysis an easy-to-crush residual solid, from which metals could be separated from the carbonaceous char. The authors found that a pyrolysis temperature of 300°C was insufficient for metal liberation, while the char was easier to crush at 400–500°C. The authors suggested an intermediate pyrolysis temperature of 400°C as the most suitable to sufficiently carbonise the organic content, separate the metals, and use the still high HHV of char (~14.5 MJ/kg) for energy recovery.
- The pyrolysis of pretreated ASR was recently investigated in [12], which also demonstrated the feasibility of an integrated production of gasoline and diesel range products. The special pretreatment considered for ASR consisted in heating the sample to 190°C in a furnace, followed by grinding and sieving to ~0.1 mm to bring particulate nature and uniform size. The pyrolysis tests were conducted in a continuous stirred tank reactor, operated as a batch reactor. A moderate pyrolysis temperature of 500°C was chosen to ensure that the ASR metals would not be melt or further oxidized. The products obtained from the pyrolysis process were 9% gases, 29% solid, and 61% pyrolysis oil, which were fully characterized. The pyrolysis gases reached a maximum HHV of 12.7 MJ/m³ and contained up to 30% (vol.%) of hydrogen (nitrogen-free composition). The ASR pyrolysis solid residue was assessed for the recovery of metals (in particular silicon, titanium, aluminium, and iron) by the leaching process. The characterization of ASR pyrolysis oil showed that the carbon atom distribution was in the C₆-C₁₆ range, with benzene and toluene being the main components, and its HHV was 34–35 MJ/kg. The fractional distillation of pyrolysis oil at 220–280°C resulted in 35% of gasoline and diesel-grade products, with the remaining fraction being residual oil.

2.2.2. Pilot scale pyrolysis of ASR. Pyrolysis experimentations of ASR involving major scales are only few and often dated, yet significant, as described in the following:

- A pilot scale experimental ASR pyrolysis plant was built in as early as the late 1990s at the ENEA research centre in south Italy, as reported in [4]. The pyrolysis unit consisted of a rotary kiln reactor (110 dm³ in volume and 0.4 m in diameter), which was heated externally by using electric elements and was operated with ASR feeding rates of 5–7 kg/h. The testing at different temperatures in the range 550–680°C showed that the yield in pyrolysis gases increased from 4.2 to 13% (wt.%) as the process temperature increased. The highest production of pyrolysis oil (32.6%) was obtained at 600°C, whereas the maximum char yield (59.3%) was obtained at the

lowest temperature. The LHV of the pyrolysis gases increased from 19.2 to 30.4 MJ/Nm³ with the temperature. The maximum hydrogen yield of 0.5% (wt.% of the ASR feed) was obtained at a process temperature of 600°C, while it remained nearly constant at higher temperatures. The authors considered the on-site combustion of syngas to fulfil the thermal demand of the process, and the recovery of metals from the solid residue.

- Almost twenty years after the previous study, the pyrolysis of ASR in a similar rotary kiln was investigated within the same research centre in [13] at temperatures in the range 450–650°C, mainly targeting the recovery of metals. At 550°C pyrolysis oil reached its maximum production, whereas the char production reached a minimum. The LHV of the pyrolysis oil ranged between 12.5 and 14.5 MJ/kg, with water contents around 10%. Only small amounts of metals (<0.1g/kg) were detected in the pyrolysis oil, especially the lightest ones (Na, Cu, Al, Mg) due to the metal thermal devolatilization. The LHV of the chars were found in the range 12.2–18.2 MJ/kg, with the highest values obtained at the lowest pyrolysis temperatures. The authors highlighted that any energetic valorisation of the char must address its high ash content (~50%). The specific surface area of chars was found comparable to that of low cost sorbents, hence suggesting a further application. The most abundant metals in the char were copper, iron, calcium, zinc, aluminium, magnesium and barium, which were the most abundant also in the original ASR.
- In [14] ASR was processed through a pilot-scale high temperature rotary kiln pyrolyser, targeting the production of char as potential commercial product. Chars were produced from two processing temperatures of 800°C and 1000°C. These high temperatures maximized gas production and produced the best quality char in terms of low organic contamination. The maximum total PAHs concentration in char was found in the fine fraction (≤ 0.1 mm) produced at 800°C, whereas the coarse fraction (≥ 0.1 mm) was shown to be non-hazardous. Indeed, the fine fraction had a shorter residence time within the pyrolyser, which resulted in organic material residing within the char. The same research group, formed by University of Central Lancashire and a UK recycling firm (called “Recycling Lives”), has recently announced the development of an advanced process, where the char from ASR pyrolysis is used for hydrogen production [15]. No further details about this process were disclosed, which apparently might be based on high temperature pyrolysis followed by steam gasification of the coarse char fraction.

Table 1. Lab scale and pilot scale experiments of pyrolysis of automotive shredder residues: design parameters and performance.

ASR type/ pretreatment	Type of pyrolysis reactor	Operation mode	Volume of the reactor (dm ³)	ASR feed rate (g/min)	ASR input per run (g)	Temperature (°C)	Solid (%wt.)	Liquid (%wt.)	Gas (%wt.)	Reference
Constant material granulometry	Rotary kiln	Continuous	110	80–120	/	550–680	43.6–59.3	19.5–32.6	4.2–13	[4]
Crushed and sieved to 5 mm	Tubular reactor	Batch, pyrolysis	2.3	/	30	500–800	37–55	21.8–30	5.8–34	[16]
		Batch, fast pyrolysis	0.4	/	25	500–800	25–47.5	35–58	5.8–12.2	
Heavy fraction/ Ground	Unstirred autoclave	Batch	3.5	/	100	400–700	38.3–54.1	20.2–29.0	20.4–41.5	[8]
Light fraction/ Sieving and flotation	Reactor with a helicooidal stirrer	Batch	0.1	/	10–15	500	<60	14–52	5–10	[3]
Separated from inorganics and fines/ Ground to 4 mm	Screw reactor	Batch	N.A.	/	200	550–800	28–34	7–28	42–65	[9]
Light fraction/ Ground to < 4 mm	Tubular reactor	Batch	0.6	/	6	500–800	39–48	15–37	15–46	[10]
Coarse fraction (>30 mm)/ Ground and pelletized	Rotary kiln	Continuous	110	200– 350	/	450–650	32.9–47.6	13.9–35.3	28.1–40.4	[13]
Fine fraction (<30 mm)/ Ground and pelletized							28.1–52.8	15.5–33.7	18.2–44.1	
Removal of metals, plastics and fines from ASR/	Vertical fixed- bed tube reactor	Batch	N.A.	/	10	300–500	55–82	13–32	0.6–1.2	[11]
Ground and pelletized Crushed and screened to ≤20 mm	Rotary kiln	Continuous	400	167	/	800–1000	30–32	N.A.	N.A.	[14],[17]
Heated at 190°C, then ground and sieved to ~ 0.1 mm	Continuous stirred tank reactor	Batch	5.3	/	2000	500	29.1	61.6	9.3	[12],[18]

3. Gasification of automotive shredder residues

3.1. Main features of the gasification process

Gasification is typically operated at high temperatures (>700 – 800°C). Air is commonly used as a gasification agent, and the air factor is generally 30–40% 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 nitrogen in the gases, thereby considerably reducing the calorific value of the syngas [1].

Gasification has been widely studied and applied for biomass, coal and plastic solid waste, whereas its application for the treatment of ASR is less documented. Gasification is achieved in a partially oxidizing atmosphere, thus partly omitting the advantages of pyrolysis [1]. ASR gasification has some challenges that need to be resolved when dealing with contaminants, such as tar, HCl, H_2S , heavy metals, and other compounds in the syngas [19].

3.2. Gasification experiments of automotive shredder residues

Gasification experiments of ASR have been conducted both at lab scale and demonstration/semi-commercial scale, whose main features and results are described in the following and summarized in table 2 for easy comparison:

3.2.1. Lab scale gasification of ASR. The lab scale gasification of ASR was investigated using both fixed bed and fluidized bed gasifiers, with or without the addition of catalysts to enhance syngas yield and quality:

- The catalytic gasification of ASR in a lab-scale fixed-bed downdraft gasifier targeting the generation of high-purity hydrogen was presented in [20]. The experimental data obtained using $\text{NiO}/\text{Al}_2\text{O}_3$ as a catalyst were used to design the scale-up of this technology. The principal operational units proposed for inclusion in the devised pilot plant included a pressurized downdraft gasifier operating at a moderate temperature (900 K), a hydrogen purification section composed of pressure swing adsorption (PSA) and Pd membrane purifier, and a PEM fuel cell. A concentration of 54% (mol%) of hydrogen in the syngas at the outlet of the gasifier was estimated. Simulated data indicated that approximately 220 kg/h of ASR would be catalytically gasified for the generation of 100 kW_e using an internal combustion engine, or alternatively 175 kW_e using the purified stream of hydrogen in a PEM fuel cell. The authors mentioned in the paper that a 10 ton per day pilot plant was under construction in Taiwan to prove the viability of this concept, however no reference to such plant was found in the literature or on the web.
- The ASR catalytic gasification was also examined in [19], using lab scale fixed bed and fluidized bed gasifiers, while paying particular attention to the trace contaminants. The waste material oyster shell was used as a calcium-based catalyst to enhance the hydrogen production and, possibly, to reduce the partitioning of the contaminants in the syngas. For the fixed bed gasification, the authors showed that a gasification temperature of 900°C increased the syngas yield, the LHV and the cold gas efficiency (CGE) and decreased the tar content compared to a gasification at 800°C . They also showed that a 10% (wt.%) oyster shell catalyst addition could increase the content of H_2 , CO, and CH_4 in the syngas compared to a non-catalytic gasification. A positive effect of the catalyst was also found for the fluidized bed gasification at 900°C , which could achieve a better performance in terms of syngas LHV and CGE compared to the fixed bed gasification. As for the trace contaminants, the catalyst addition was effective in increasing the sulfur content partitioning in the solid phase, yet rather ineffective in reducing the chloride content partitioning in the syngas.
- The gasification of the light fraction of ASR for syngas generation and the concurrent production of a recycling material from melting the solid residue was firstly investigated in the late 2000s in [22] by a research group in South Korea. Temperatures in the range 600 – 1000°C

for gasification and equal to 1200°C for melting were tested in the two chambers of the shaft-type gasification unit. It was found that the concentration of CO, H₂ and CH₄ and the LHV of the syngas increased at higher temperatures and lower equivalence ratios (ER). On the other hand, the carbon conversion efficiency and the dry gas yield markedly increased with the ER. Also, tar yield and solid residue yield both decreased with increasing ER and temperatures. The tar yield was below 0.10% and the residual yield was below 30%. The authors highlighted that the residual yield was higher than other wastes (like municipal solid waste), due to various metal contents in ASR waste. Therefore, the solid residue was melted to produce a slag solid portion that could be used as recycled material. The leaching test conducted on the slag showed that the concentration of metals fulfilled the Korean standard, resulting in appropriateness to recycle.

- More than ten years later, the gasification and melting process of ASR was investigated in [21] within the same research group. ASR gasification was conducted in a fixed-bed reactor at high temperatures in the range 800–1200°C and ER between 0.1–0.5. The solid residue was melted at high temperatures around 1300°C to produce a slag for use in clay bricks manufacturing. The authors showed that the hydrogen content in the syngas increased with the gasification temperature, reaching values higher than 40% at 1200°C and ER lower than 0.3. They selected a temperature of 1200°C and an ER of 0.5 as the optimum conditions for ASR gasification, which maximized the syngas yield and minimized the tar content. Even though the clay bricks produced using the melting slag showed similar properties (e.g. compressive strength, absorption) to the standard material, the authors warned about the high content of heavy metals (e.g. copper) in melting slag.

3.2.2. *Demonstration/semi-commercial scale gasification of ASR.* There are only a limited number of studies reporting ASR gasification at the demonstration/semi-commercial scale, and they all share the use of non-conventional gasification systems:

- The viability of an advanced thermal treatment technology (called Gasplasma[®]), comprising fluidized bed oxy-steam gasification followed by plasma treatment, was demonstrated in [5] for ASR, refuse derived fuel (RDF) and blends of ASR and RDF wastes. This technology consisted of a bubbling fluidized bed gasifier with a bed temperature of 700–800°C, followed by a plasma converter with a syngas exit temperature of 1100–1200°C. The function of the plasma converter was to reduce the impurities in syngas (and therefore the load on downstream gas clean-up technologies), by both transforming tars, chars and large organic molecules into syngas components (mainly H₂, CO, CO₂, H₂O and CH₄), and immobilizing inorganic materials (particulates and heavy metals components) into the vitrified material generated within the plasma converter. The experimental data reported in the paper referred to a demonstration plant located in Swindon (UK), where the cooled syngas, after further cleaning to remove fine particulate and acid gases, was used for power generation in a gas engine. When only ASR was used as the feedstock, the authors recorded a CGE equal to 87%. The estimated net electrical efficiency was 25% using gas engines having a conversion efficiency of 35%, and accounting for the parasitic loads associated with the plasma power.
- The application of the dual fluidized bed (DFB) gasification technology as a recycling/valorization method of ASR was investigated at a semi-industrial scale in [23], targeting the production of fuels or chemicals from the produced gas. The authors investigated the impact of the high content of ash in the ASR (46% of the ASR mass) on the operation of the DFB gasifier, compared to the operation with woody biomass. They showed that the presence of ASR ash in the system decreased the yield of hydrogen. Moreover, the catalytic activity of the olivine bed material was shaded/masked by the accumulation of ASR ash, so that olivine could not confer any benefits to the gasification of ASR. The gasification of ASR resulted in a lower percentage of syngas components (CO and H₂) and a higher fraction of hydrocarbons compared to the gasification of wood. Accordingly, they proposed the recovery of aromatic and

nonaromatic hydrocarbons from the produced gas for the chemical industry, and the utilization of the syngas components for the synthesis of methanol.

- An Australian recycling company (Sims Limited) has recently reported to the media the development of a pilot plant in Rocklea (near Brisbane), which will be operational during the current year 2022, to conduct research and assess the commercial viability of a proprietary ASR-to-syngas technology [24]. The process schematic, communicated by the same company, includes a plasma gasifier, which produces a syngas and a vitrified inorganic product. The syngas is then converted into olefins that can be transformed in recycled plastic or, alternatively, it can be converted into alternative fuels such as hydrogen. The glass-like solid fraction was portrayed as being suitable as a paving material aggregate. Unfortunately, no further details about the process were disclosed.

Table 2. Lab scale and demonstration scale experiments of gasification of automotive shredder residues: design parameters and performance.

ASR type/ pretreatment	Gasifier type	Gasification agent	Catalytic gasifier	Gasifier volume (dm ³)	Feed rate (kg/h)	Temperature (°C)	Tar yield (%)	Cold gas efficiency (%)	H ₂ (vol.%)	CO (vol.%)	Reference
Light fluff/ Crushed to ≤1cm	Shaft-type	Air	No	N.A.	0.9	600–1000	<0.1	N.A.	<10 ^a	<10 ^a	[22]
Light or heavy fraction	Fixed bed (downdraft)	Oxygen and steam	Yes (NiO/Al ₂ O ₃)	0.3	N.A. ^b	487–627 (557 avg.) 700–800 (Fluidized bed)	N.A.	76–85	54.2	32.8	[20]
N.A.	Gasplasma® (bubbling fluidized bed and plasma converter)	Oxygen and steam	No	N.A.	40– 100	1100–1200 (Plasma converter)	~0	87	N.A.	N.A.	[5]
Pelletized	Dual fluidized bed	Steam	Yes (olivine/ash)	N.A.	370– 375	775–840	8.2–8.5	N.A.	N.A.	N.A.	[23]
Crushed to 2.4 mm	Fixed bed (horizontal tubular) Fluidized bed (bubbling)	Air	Yes (Ca based)	1 1.25	/ 0.3	900	<3.5	18 ^c	6.6 ^c	6.0 ^c	[19]
Mixture of light and heavy fluff/ Cut into pieces ≤1cm	Fixed bed (downdraft)	Oxygen	No	12	0.6	800–1200	<10 ^d	30–50	15–45	25–38	[21]

^a evaluated at an equivalence ratio of 0.3.^b the value of 100 kg/h reported in the referenced paper does not seem to be correct, due to the small size of the lab-scale gasifier.^c maximum values.^d evaluated at an equivalence ratio of 0.5.

4. Production of transportation fuels and chemicals from the products of ASR pyrolysis and ASR gasification

4.1. Proposed applications for the pyrolysis products of automotive shredder residues

Table 3 shows the proposed applications for the solid, liquid and gas products of ASR pyrolysis, as suggested in the literature. It clearly appears that the end uses are different depending on the process conditions, in particular the pyrolysis temperature:

- *Solid char.* The recovery of metals by the leaching process and the use of the residual char as a fuel appear the main uses of char when ASR pyrolysis is carried out at moderate temperatures ($\leq 500^{\circ}\text{C}$). Instead, the production of a high quality and saleable inert char appears the target when pyrolysis is carried out at higher temperatures ($\sim 800^{\circ}\text{C}$). A recent demonstration plant even implements hydrogen production from the pyrolytic char.
- *Pyrolysis oil.* The proposed applications have evolved from its direct use as a fuel in a furnace to the production of more valuable products, such as transportation fuels and chemicals through refining and distillation. In particular, the lab scale production of gasoline and diesel-range fuels from ASR bio-oil has been recently reported. Moreover, the refining to obtain chemical products such as olefins or aromatic hydrocarbons has been suggested. The pyrolysis temperature considered for these applications is in the range $500\text{--}600^{\circ}\text{C}$, which maximizes the yield in bio-oil.
- *Pyrolysis gases.* The most obvious application is their use as a fuel to provide the thermal energy required by the pyrolysis reactor. However, their peculiar composition, containing e.g. propylene, has recently led to consider them as a raw material to synthesize chemicals. Since the gas yield and hydrogen concentration both increase at higher pyrolysis temperatures, the hydrogen production has also been considered.

4.2. Proposed applications for the gasification products of automotive shredder residues

Table 4 shows the proposed applications for the syngas, tar and solid residue of ASR gasification, as suggested in the literature, where some common trends can be identified:

- *Syngas.* The proposed applications have evolved from its direct utilization in internal combustion engines or gas turbines for power generation, to the production of transportation fuels or chemicals. In particular, the recovery of hydrogen using a purification unit, the synthesis of methanol, the recovery of olefins (e.g. ethylene) already contained in the syngas or the production of olefins that can be used as recycled plastic.
- *Solid char/ash.* The most recurrent proposed use consists in high temperature melting for the production of an inert slag to be used as recycle material or as construction aggregate. The recovery of metals has also been proposed in one study.
- *Tar.* Due to the high tar content in the produced gas obtained from ASR gasification, the recovery of aromatic hydrocarbons for the chemical industry has also been proposed.

Table 3. Proposed applications for the solid, liquid and gas products of pyrolysis of automotive shredder residues.

Solid product (char)	Liquid product (bio-oil)	Gas product (permanent gases)	Suggested pyrolysis temperature (°C)	Reference
a) Recovery of metals; b) Use as a fuel; c) Use as an inert additive	Use as a fuel in a conventional furnace	Use as a fuel to heat the pyrolysis reactor	600	[4]
a) Separation of metals; b) Use as a fuel; c) Pigment, component of asphalt fabric	a) Use as liquid fuel, provided that the potential pollutants are controlled; b) Use as source of chemicals	Use as a fuel to provide the energy requirements of the process plant	500	[8]
Recovery of metals	a) Production of gasoline/diesel fuel; b) Production of chemical products such as olefins or aromatic hydrocarbons	Refined and exploited as chemicals (propylene)	500	[3]
High quality char for use in metallurgical, chemical or food industry	/	/	800	[9]
a) Filler in construction materials; b) Secondary source for metals	a) Use as alternative fuel; b) Use as a feedstock for the chemical industry	/	500	[10]
a) Metal recycling; b) Energy recovery	/	/	400	[11]
Production of a non-hazardous inert saleable char	/	/	800–1000	[14]
/	/	Hydrogen production due to favorable H ₂ :CO ratio	600	[27]
/	/	A fuel with desirable combustion properties (adiabatic flame temperature, laminar flame speed)	700–800 or higher	[28]
Recovery of metals (silicon, titanium, aluminum, iron) by the leaching process	Production of gasoline and diesel-grade products through distillation	a) Fuel for heating the pyrolyser via combustion; b) Raw material to synthesize chemicals	350–500	[12]
a) Use of char for hydrogen production; b) Use of residual char as soil modifier	/	/	N.A.	[15]

Table 4. Proposed applications for the syngas, tar and solid products of gasification of automotive shredder residues.

Gas product (clean syngas)	Tar	Solid (char/ash)	Reference
a) Use as fuel gas; b) Use as raw chemicals	/	Melting at high temperatures and production of slag to be used as recycle material or as construction aggregate	[22]
a) Utilization in an internal combustion engine for power generation; b) Production of hydrogen and utilization in a PEM fuel cell	/	/	[20]
a) Use for power generation via gas engine or gas turbine; b) Use as a source of hydrogen; c) Use as a chemical or biochemical precursor for the production of chemicals and liquid fuels	/	a) Recovery of metals (copper, iron, aluminum) and glass/ceramic; b) Use of molten slag produced within plasma converter as an aggregate	[5]
a) Methanol synthesis due to the favorable H ₂ /CO ratio; b) Recovery of olefins from the nonaromatic hydrocarbon fraction	a) Production of aromatic hydrocarbons (benzene, toluene, styrene, and naphthalene) for the chemical industry; b) Use as a fuel in the DFB gasifier	/	[23]
Use in internal combustion engines and gas turbines	/	/	[19]
Use for power generation	/	Melted to produce slag and used as an aggregate (as a substitute for kaolin) for the manufacturing of clay bricks	[21]
a) Use for olefins production that can be transformed into recycled plastic; b) Use for the production of alternative fuels such as hydrogen	/	Use of the vitrified solid product as a paving material aggregate	[24]

5. Discussion and critical remarks

This work has highlighted several interesting ASR valorization options enabled by pyrolysis and gasification, which are summarized and discussed here below:

- 1) The results of the pyrolysis experimentations reported in the literature in terms of yields have shown that it is possible to convert up to 50% of the shredding residue in pyrolysis oil, while limiting the residual solid fraction to 30–50%. The yield is mainly dependent on the type of ASR, the pretreatment, the process temperature and the type of pyrolysis reactor. Bio-oil has been obtained not only from the heavy ASR fraction, but also from the light fraction that is typically landfilled. Typical pretreatments consist in crushing and sieving, or grinding and pelletization. However, other pretreatments like flotation to separate the lighter fraction, or preheating and grinding have resulted in higher yields of bio-oil. The maximum yield in bio-oil is obtained at temperatures centered around 550°C, yet process temperatures in the range 400–1000°C have been used targeting different applications for the ASR pyrolysis products.
- 2) The results of the gasification experimentations have shown that cold gas efficiencies up to 85% can be achieved using both fixed bed and fluidized bed gasifiers. This shows that the heating value of the shredding residue can be effectively converted into syngas, a more convenient

energy vector. Both the light and heavy ASR fractions have been gasified using crushing or pelletization as typical pretreatments. Depending on the type of gasifier and the end uses of syngas, air, oxygen and/or steam have been considered as gasification agents. Different types of catalysts (nickel or calcium based) have been tested to improve the yield and quality of the syngas produced. The typical gasification temperatures are in the range 750–900°C, however temperatures in the wider range 500–1200°C have been used, depending on the type of gasifier, the use of catalysts and the end uses of syngas. A hydrogen content as high as 50% in volume has been reported using oxygen and/or steam as gasification agents.

- 3) Various applications have been proposed to date in the literature for the main products of ASR pyrolysis and gasification, namely bio-oil and syngas, respectively. Besides the traditional ones, where bio-oil and syngas are used as fuels in furnaces or stationary thermal engines for power production, newer pathways have been proposed targeting the production of transportation fuels or chemicals, which would greatly enhance the commercial value of this waste material. In particular, gasoline and diesel grade fuels have been obtained from the ASR pyrolytic oil through distillation, and a very high interest in olefins and aromatic hydrocarbons extraction from the bio-oil is noticeable. With regards to ASR gasification, the high hydrogen content in the syngas has naturally led to consider syngas purification and pure hydrogen production. However, methanol synthesis has also been proposed due to the favorable H₂/CO ratio. Also, a significant interest has been found for direct olefins extraction from syngas or olefin production from the syngas components.
- 4) There is a high interest in taking advantage also of the co-products of pyrolysis and gasification. Due to the high amount of solid residue produced in pyrolysis, many studies have focused on potential ways to valorize it. Thanks to the moderate pyrolysis temperatures and oxygen-free environment most of the metals contained in the ASR remain in their original state and can be easily separated from the carbonaceous char. In some studies, the pyrolysis temperature is intentionally reduced to favor the metal recovery to the detriment of energy recovery. Conversely, very high pyrolysis temperatures are desired in other studies to obtain a non-hazardous and saleable char and/or increase the yield in pyrolysis gases. Very recently, hydrogen production from ASR pyrolytic char has also been proposed in an industrial scale process. The solid residual fraction from gasification is in a lesser amount and has a negligible heating value compared to that from pyrolysis, hence its proposed use is melting to produce an inert vitrified product that can be used as construction material.

6. Conclusions

Pyrolysis and gasification have been considered in this work as promising thermochemical conversion methods of automotive shredder residues, which enable the reduction and, possibly, the elimination of the waste to be landfilled, the energy recovery from the organic material, a lower environmental impact compared to incineration, and the production of valuable fuels, chemicals and solid products. The literature review has highlighted that there is much interest in developing and implementing both these technologies for automotive shredding residues, due to the wide availability of this waste material and the specific legislative directives existing in most countries fostering its reuse, recycling and energy recovery.

When dealing with such heterogeneous and complex waste material, the analysis of the fate of the contaminants (e.g. metals, chlorides, etc.) contained in the shredding residues and the reduction/elimination of their partitioning in the desired product/s shall take precedence over the maximization of the product yields. Indeed, the presence of contaminants in bio-oil or syngas can hinder or even preclude their direct utilization as fuels or any subsequent conversion into transportation fuels or chemicals. In this context, the choice of the design of the gasifier and the processing conditions play a primary role. The present work has drawn the attention to some pathways to obtain fuels or chemicals from automotive shredder residues, which have been recently suggested in the literature. It must be noticed that only a few of them have been tested to date, while most of the experimentations have limited their scope to the characterization of the products of ASR pyrolysis and ASR gasification.

In conclusion, more theoretical and experimental research is needed to check the viability of the proposed pathways when using such a difficult waste material. Fundamental research for the development of new conversion technologies of automotive shredder residues should go hand in hand with applied research for the development of industrial plants that implement the existing technologies. This twofold approach appears the key strategy for a sustainable green transition, where the principles of circular economy appear increasingly important to contain its high cost.

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