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Conference paper

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How the physio-chemical properties of char from the pyrolysis of Automotive Shredder Residue (ASR) influences its future uses

Abstract: Pyrolysis of ASR is an emerging technology which may increase circularity in End-of-Life Vehicle (ELV) waste recycling. To scale up from the current pilot scale, physiochemical characterisation of the by-products is required to determine their utilisation. This paper explored how the physiochemical properties of char from different pyrolysis fractions influence secondary uses. ASR was pyrolysed in a pilot-scale unit capable of processing 100 kg h^{-1} at 900 °C, producing 480 kg of char from which samples were taken for analysis. Three types of pyrolysis char were identified: (i) coarse char (CC) (ii) medium char (MC) and (iii) fine char (FC). Physical (particle size, moisture content and surface analysis) and chemical (calorific value, organic and inorganic elemental analysis) analysis was conducted. Physical and chemical differences were determined between char fractions: CC had the highest particle size (800 μm; mean 353.5 μm) calorific value (14,544 kcal g^{-1}) and metal concentration; the relationship was CC > MC > FC. Organic elemental analysis indicated %C was highest under FC (80.29 %) and %S was highest in CC (1.04 %). Findings from this experiment provided initial insight into the differences in properties of char fractions from ASR pyrolysis. Potential future uses in char commercial markets were evaluated, with upgrading recommendations provided.

Keywords: Automotive Shredder Residue; ICGC-9; pyrolysis; pyrolysis char; thermal processing.

Introduction

The automotive industry currently recycles 85 % of End-of-Life Vehicles (ELVs) and is challenged by European legislation to increase the rate of recycling to 95 % by 2030 [1]. The majority of recycled material of an ELV is achieved through metal recovery (70 % of ELV weight), which is resold to the metallurgical sector [2]. The remaining material which cannot be recovered is classed as Automotive Shredder Residue (ASR). ASR is a heterogenous mixture of organic materials, mainly consisting of foams, plastics, fibres, textiles, glasses, metals and inerts [3]. ASR makes up approximately 25 % of the ELV, so further processing of this material will meet ELV legislative targets [4]. Alongside environmental targets, this is also of economic benefit to waste recycling companies, through a significant reduction in yearly landfill costs. The current rate of vehicles that reach end-of-life in Europe is 6 million per annum [5] and this is expected to grow in the future, posing challenges to waste recycling streams.

The challenges in ASR processing could be met by pyrolysis recovery. Pyrolysis is the thermal processing of a material at a high temperature (400–1000 °C) in the absence of oxygen. Pyrolysis of ASR produces three main

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products: syngas, oil, and char. The type and quality of the end products depends on a range of factors, such as the pyrolysis design, the pyrolyser operating parameters (temperature, residence time) and the feedstock [3, 6–8]. Pyrolysis methodology has been optimised in a pilot scale reactor to produce a high-quality syngas [9], however upon commercialisation challenges remain surrounding the potential contamination within the char and oil by-products [4]. To ensure future circularity of the waste recycling process further information is required on the by-products to determine secondary uses.

Pyrolysis char can be used in a number of different commercial markets. The three most common markets are: (i) a chemical adsorbent for air and water; (ii) a soil modifier to remediate contaminated land; and (iii) a concrete additive. Each product requires different physiochemical specifications of char to create an optimised product which is safe for the environment and human exposure. Many of the products are derived from homogenous pyrolysis feeds such as wood biomass, plastic waste and coal [10–12]. The challenge for char from ASR will be whether as a heterogenous feedstock (main components of plastic, wood and textile materials; [13]) the char fraction will meet the specifications required.

To be utilised in each product, pyrolysis char has to meet certain physiochemical specifications. For a chemical adsorbent, such as activated carbon, there are numerous regulations that are required prior to classification for commercial use. The classification is dependent on the area of application: in water streams or in air filters. Activated carbon is produced by a carbonisation (pyrolysis at 600–900 °C) and activation (addition of an active agent) step. Activation materials range dependant on the feedstock material and the pollutant requiring adsorbing. For example, biomass feedstocks use inorganic catalysts such as KOH as their activation agent [14–17], whereas coal feedstocks use catalysts such as TiO_2 and organic compounds such as ferrocene [18, 19]. Material suitable to be an activated carbon must have a specific surface area and low contamination level. Activated carbon is not classified as a hazardous material, however once the material is spent it has high pollutant concentrations which require reactivation by calcination or safe disposal. The use of pyrolysis char from ASR as an activated carbon has not been tested, the challenges that it may face meeting these markets could be the high levels of calcium and other reactive metals which reduce adsorption capacity.

The mitigation of contaminated land is a growing challenge in post-industrialised urban areas, where past practices have increased the acidity of soil, increased toxic metal concentration and reduced the carbon concentration. Remediation practices include the addition of pyrolysis char and phytoremediation, where pyrolysis char increased the carbon sequestration [20–22] and the remaining pollution is adsorbed and destabilised by plant growth [23]. Alongside chemical properties the addition of char to soil can improve physical properties such as soil texture and moisture. Utilisation of pyrolysis char from ASR feedstock within this revenue stream will depend on a number of factors: the carbon concentration, the pH, the hydrophilic properties, and the heavy metal concentration. Previous research suggests char from ASR has a high lead concentration (2534 mg kg^{-1}; [24]) which may require further post-treatment.

In the concrete industry a common additive is Pulverised Fly Ash (PFA), sourced from coal fired power stations. PFA is a pozzolanic material containing siliceous and aluminous materials, which in the presence of moisture and CaOH form cementitious properties. PFA mainly composes of Si, Al, Fe and Ca at different compositions [25]. The negative impacts of coal fired power stations on greenhouse gas emissions has caused a reduction in the supply of PFA as global governments seek cleaner energy. This is negatively impacting cement production and increasing the demand for other pozzolanic sources. The optimisation of cement composition to improve performance without reduced amounts of PFA is the main focus of current research, where utilisation of mineral aggregates and chemical admixtures have been used [26]. Addition of pyrolysis char from homogenous feedstocks to concrete has been tested, where the high porosity and surface area has increased the reactivity in cement making and improved concrete strength [27, 28]. If the physio-chemical properties of pyrolysis char from ASR are similar to PFA this could utilise waste from a cleaner energy source and fill the demand for a new concrete additive in the cement industry.

Research surrounding the pyrolysis of ASR has been heavily focussed upon optimising the pyrolysis operating conditions to maximise energy and oil production [29, 30], which is more likely to enhance revenue. Some experiments have recorded the metal concentration of char [13, 24] but no information was provided towards whether the produced material could be utilised in commercial markets. If pyrolysis of ASR is to be commercialised, this would result in large quantities of pyrolysis char being produced, which would require

utilisation to enhance circularity of the waste recycling process and to meet ELV recycling targets (95 % of ELV to be recycled or recovered by 2030; ELV Directive [1]). A research experiment has been designed to physically and chemically characterise pyrolysis char from ASR to define whether they meet the physio-chemical standards to be used in commercial markets. This paper will physically and chemically assess char fractions from a pilot scale pyrolyser to determine whether the char can be reused or requires further processing before recycling.

Methods

Pyrolysis method

ASR was pyrolysed in a pilot scale unit capable of processing 100 kg h^{-1} at 900 °C. This produced 480 kg of char from which samples were taken for analysis. By processing a large amount of ASR, this reduced the sampling error associated with the heterogenous nature of ASR. Char was deposited at 3 points within the system: immediately below the rotary kiln, below the cyclone unit and below the gas scrubber filter (Fig. 1). The masses (% w/w) were determined at a ratio of 80:10:10. To ensure char samples analysed were representative of the whole population, a systematic quasi-random sampling approach was applied. For each subcategory of char, 10 × 0.5 kg samples were collected at different time periods during the pyrolysis period and numerically organised. A 2.5 kg sample of char was developed by mixing a random selection of 5 of the 10 numerical samples and this was used for physical and chemical analysis.

Physical analysis

Particle size of the char fractions was determined by Scanning Electron Microscopy (SEM) analysis. Dry samples were prepared on carbon coated aluminium stubs and analysed in a benchtop Jeol 6000plus SEM. For each fraction, 10 samples were analysed of which 100 particles were size determined. The particle size for each char fraction was presented as a mean average.

The Moisture Content (MC) has a large influence on the amount of energy available within the char, due to the high latent heat of water. The MC of the char fractions was determined by using method BS EN 15414 (2011) where 10 g of sample was weighed using a 3 decimal point analytical balance and subsequently dried in an oven at 105 °C for a 12-h period. Dried samples had their dry mass determined and the MC was calculated.
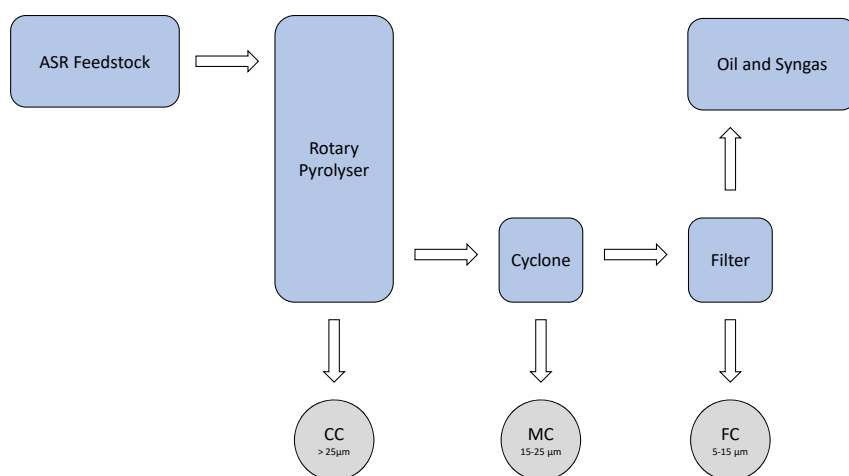

Fig. 1: Diagram of the pilot scale pyrolysis reactor, detailing by-product location within the system.

The gross Calorific Value (CV) determined the amount of energy available within the char for usage in thermal processing. The CV of the char fractions was analysed by using a Bomb Calorimeter (Parr isoperibol: model 6200), method BS EN 15400 (2011).

Chemical analysis

The total C, H, N, and S (%) concentration was analysed using an Organic elemental analyser (ThermoScientific Flash 2000 Series). For each sample, between 2 and 3 mg was weighed into a tin crucible using an analytical balance (Mettler Toledo X6) and sealed. The samples were pyrolysed at 900 °C and the gas was transferred through a capillary column. Prior to samples being analysed, the instrument was calibrated using BBOT (2,5-Bis(5-*tert*-butyl-benzoxazol-2-yl)thiophene) standard. The % C, H, N and S was calculated using FlashSmart software.

Loss on Ignition (LOI) was conducted using standard method BS EN 15935:2021. Prior to analysis, char samples were dried at 105 °C overnight. Approximately 5 g of dried material was measured into crucibles and heated at 525 °C for 6 h then left to cool in a desiccator. Once cooled, samples had their mass determined. LOI was determined using the following formula:

$$LOI = 100 \times (W_2 - W_3 \,/\, W_2 - W_1)$$

W_1 = Crucible mass (g)
W_2 = Crucible + Dry mass (g)
W_3 = Crucible + Ash mass (g)

The total inorganic elemental analysis of char fractions was conducted using a ThermoScientific iCap 7000 series ICPOES (Inductively Coupled Plasma – Mass Spectrometry), method: CEN/TS 15403: 2006. Char samples were prepared for ICPOES analysis by acid digestion in a Milestone Ethos EZ Microwave Digester. Using an analytical balance (3 decimal places), 0.1 g $\pm$ 5 % of char was placed into a microwave vessel. To this, 10 ml of analytical grade nitric acid was added and the microwave vessels were sealed. Prepared samples were placed into the microwave and heated at 0–200 °C over 10 min, with a holding time of 20 min at 200 °C. Following digestion, acid digests were diluted 100× using 18.2 mQ deionised water. The ICP-OES was calibrated using a Fluka ICP Standard Mix 5 at a calibration range between 50 ppb and 1 ppm. The elements analysed for were: Fe, Al, Cu, Na, P, K, Mn, Sr, Cr, Mo, Ni and Co.

In addition to the use of SEM for particle size analysis, an SEM-EDS (Scanning Electron Microscopy – Electron Dispersive X-Ray) was used to determine the total elemental concentration (%) of particles within samples. This technique was conducted to support results determined using the ICP-OES and the Organic Elemental Analyser.

Results

Physical characterisation of the 3 char fractions determined differences in the particle size (Table 1). There were also differences observed in the porosity within the structures of (ii) and (iii) (Fig. 2).

Table 1: The particle size range and mean average for each char fraction derived from pyrolysis of ASR.

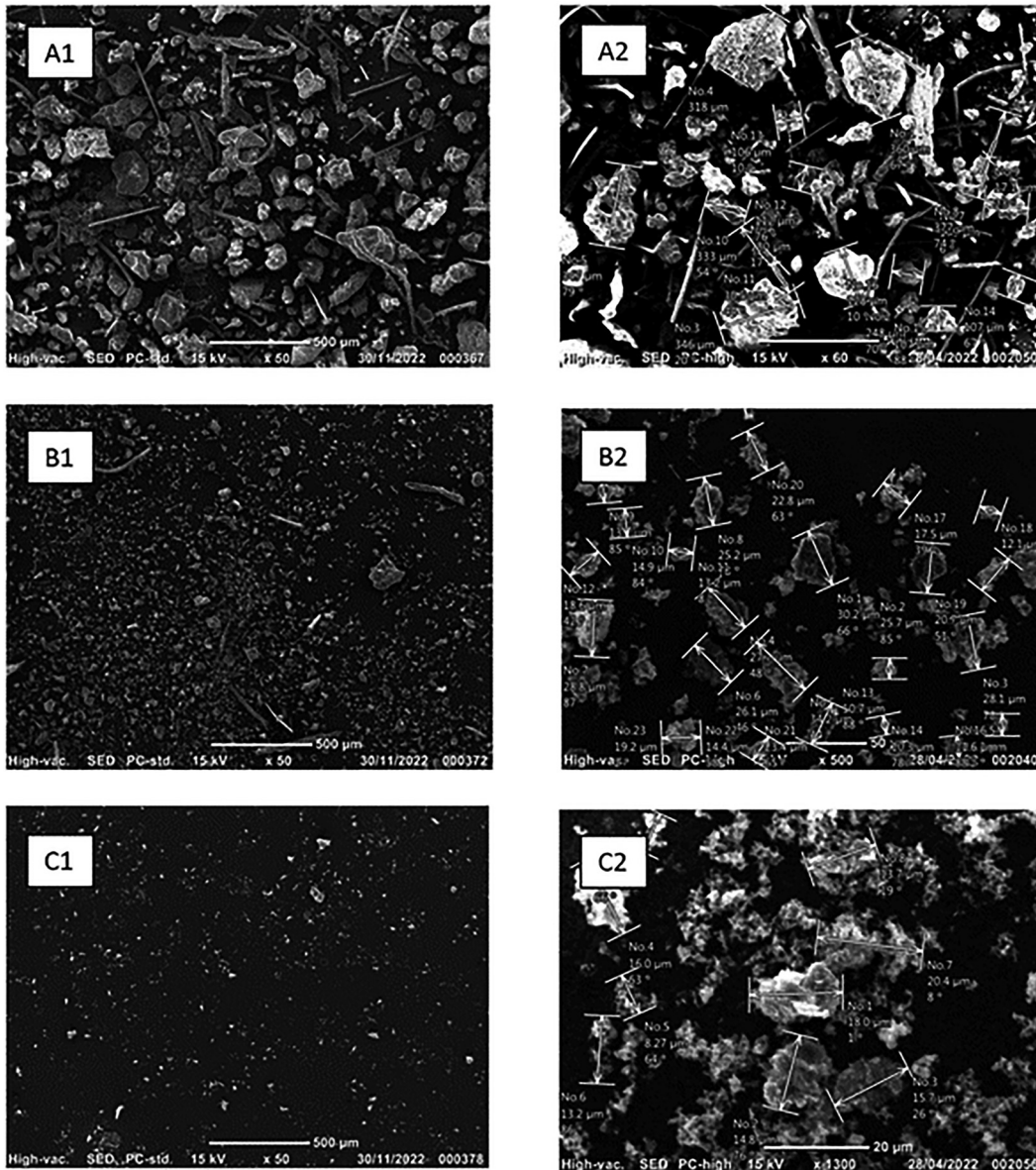| Char fraction	Mean particle size (µm)	Standard error	Maximum particle size (µm)	Minimum particle size (µm)	Modal particle size (µm)
Coarse (CC)	282.4	31.1	856.0	17.1	183
Medium (MC)	21.3	2.0	68.4	8.6	12.5
Fine (FC)	11.9	1.1	25.9	3.7	8

Fig. 2: Scanning Electron Microscope (SEM) images of 3 char fractions (A = CC; B = MC; C = FC). For each fraction. Image 1 presents particles at the same magnification (50×) and image 2 presents the particle size (μm) at relative magnification ranges.

From SEM analysis it was determined that there was a trend in the mean particle size, where Coarse Char > Medium Char > Fine Char. Therefore, for the remainder of the analysis, Coarse char was labelled CC, Medium char was labelled MC and Fine char was labelled FC. In addition to the difference in char particle sizes, there were notable qualitative observations: (i) CC had a larger number of fine fibres within the material (Fig. 2A) (ii) FC had a porous texture (Fig. 2C) (iii) MC had a more regular oval particle shape.
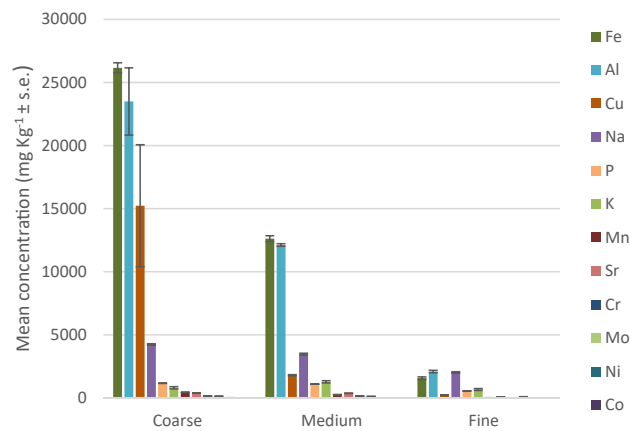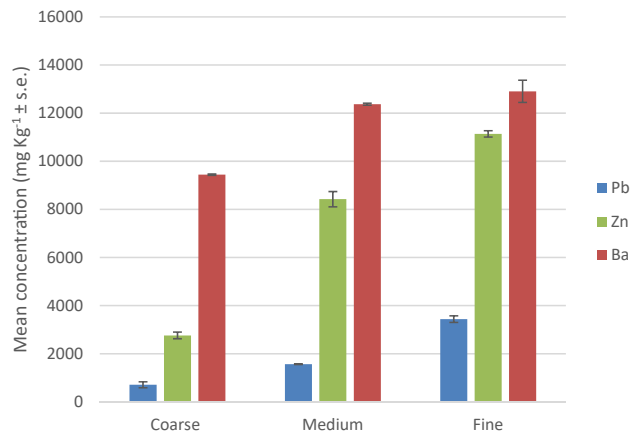
The physical and organic elemental analysis results of CC, MC and FC is presented in Table 2. A larger particle size resulted in a higher calorific value of the char. The mean carbon concentration increased with decreasing particle size (CC < MC < FC), where there was a reduction in mean sulphur (CC > MC > FC).

The mean inorganic elemental analysis indicated that there were increased concentration of elements, notably Fe, Al and Cu within CC (Fe = 26 159 mg kg^{-1}, Al = 23 496 mg kg^{-1}, Cu = 15 237 mg kg^{-1}). There was a general relationship within results that indicated contamination reduced with char particle size CC > MC > FC (Fig. 3).

Table 2: Physical and chemical composition of pyrolytic char from ASR feedstock.

	CC	MC	FC
Moisture content (%)	0.60	1.64	0.95
Calorific value (kcal g^{-1})	14 544	10 489	10 012
Loss on ignition (%)	21.83	48.89	98.28
%C	31.83	48.36	78.04
%H	0.43	0.71	1.42
%N	0.39	0.46	0.61
%S	1.04	0.87	0.27
%O[*]	66.30	49.60	19.65

[*]%O calculated from subtraction.

Fig. 3: Mean inorganic elemental concentration of pyrolytic char derived from ASR feedstock. CC = coarse char; MC = medium char; FC = fine Char.

Fig. 4: Mean inorganic elemental concentration of pyrolytic char derived from ASR feedstock. CC = coarse char; MC = medium char; FC = fine Char.

Of the 15 inorganic elements analysed, 3 analytes had the opposite relationship between concentration and particle size (Fig. 4: CC < MC < FC). The lead concentration for all samples was high (708–3441 mg kg^{-1}).

Elemental analysis of char on the EDS highlighted the increase in carbon concentration within the fine char (Table 3). An increase in carbon concentration under FC resulted in lower numbers of elements within the chemical composition. The chlorine concentration, not detected by ICPOES, reduced in char with lower particle size (CC > MC > FC).

Table 3: Mean concentration (%) of elements in char fractions (CC, MC and FC) following SEM-EDS analysis. n.d. = not detected.

Element	Mean concentration (%)		
	CC	MC	FC
C	60.8	53.5	87.0
O	18.4	12.6	7.8
F	0.2	n.d.	n.d.
Na	0.4	0.5	0.2
Mg	0.4	1.1	0.6
Al	2.8	0.6	0.2
Si	3.3	7.1	1.4
P	0.03	0.1	n.d.
S	0.4	0.6	0.2
Cl	3.2	2.5	0.8
K	n.d.	0.3	n.d.
Ca	7.9	10.7	1.5
Fe	0.3	7.8	0.1
Cu	n.d.	0.8	n.d.
Zn	0.09	0.8	0.1
Ba	1.3	0.4	n.d.
Ti	0.3	0.4	0.06

Table 4: A comparison of the recommended concentration of dissolved elements in freshwater ecosystems with actual element concentration determined for pyrolysis chars from ASR feedstock (Data source: UK Government, [31, 32]).

Element	Recommended concentration (mg L^{-1})	ICP-OES result (mg kg^{-1})		
		Coarse	Medium	Fine
Chromium (III)	4.7	165	146	0
Chromium (IV)	3.4	165	146	0
Copper (dissolved)	1	15 237	1801	225
Iron (dissolved)	1000	26 159	12 625	1570
Lead	10	708	1564	3441
Manganese	123	439	260	20
Zinc (dissolved)	10.9	2760	8423	11 139

Table 5: Limit values for concentrations of trace heavy metals in soil when organic matter is applied.

Element	SSV (mg kg^{-1})	Source	Char Result (mg kg^{-1})		
			Coarse	Medium	Fine
Co	4.2	Environmental agency [33]	22	9	0
Cu	35.1	Environmental agency [33]	15 237	1801	225
Mo	5.1	Environmental agency [33]	123	113	95
Ni	28.2	Environmental agency [33]	85	61	24
Zn	35.6	Environmental agency [33]	2760	8423	11 139
Cr	400	European union [34]	165	146	0
Pb	300	European union [34]	708	1564	3441

The ICP-OES data was compared with recommended concentrations set by the UK government for freshwater ecosystems of classified pollutant elements (Table 4). FC had the closest levels to the recommended concentrations.

Soil Screening Values (SSVs) have been determined by international governments as maximum limits of pollutants obtained within soil. Some limits for heavy metals are presented in Table 5 and compared with the concentrations recorded in this experiment. Cu and Zn are a factor of 100× higher than the recommended SSVs, which may limit applications.

Discussion

The results from this experiment identified notable differences in the particle sizes (mean and modal) and texture of the 3 char fractions. These differences could suggest that upgrading of the material could be focussed on three separate products. In this section, the physiochemical results from char fractions from ASR feedstock will be evaluated against the aforementioned products to determine whether they can enter these commercial markets or require upgrading. If upgrading is required, potential methods will be discussed.

Pyrolysis char as a chemical adsorbent

Research findings suggest that char of lower particle size can be more irregular in shape [35], which along with increased microporosity has higher adsorbent properties more useful in environmental applications such as water purification [36, 37]. The findings from this experiment suggest that char of lower particle size (FC) was more regular in shape, due to the standard error within the mean particle size being lower within CC and MC fractions (Table 1). Further testing would be required to determine whether this has an effect on water purification systems. The porosity observed in FC (Fig. 2: C2) could also imply this would be better suited to a chemical adsorbent [38, 39]. Further investigations on the activation properties within FC would be required to determine what pollutants are effectively adsorbed.

In water-based systems, phosphate is a pollution of significant concern due to the damages caused to the aquatic ecosystem from eutrophication. The EU Water Framework Directive (WFD) (2000/60/EC) legislates that the mean amount of phosphate in rivers should not exceed 0.1 mg L^{-1} [40]. High concentrations of P detected was in all char fractions (554–1160 mg kg^{-1}: Fig. 3). Therefore, to utilise pyrolysis char as a chemical adsorbent for water systems, a reduction in P would be required. Further investigation of the char at a molecular level is required to determine how much of the P is in the form of phosphate, and how much forms other P compounds. Phosphorus could be sourced in the foam of the ASR feedstock, where it is often used as a component within flame retardants [41]. Removal of the foam from the feedstock could result in P elimination from the char.

To meet water quality standards required of the WFD, the UK government has introduced predicted no-effect concentrations (PNECs) for metal elements of environmental concern [33]. Of the analytes analysed by ICP-OES, chromium, copper, iron, lead, manganese and zinc have PNEC limitations set for freshwaters (Table 4). The concentrations of toxic metals determined in the ICPOES analysis are higher than the PNEC requirements, where concentration values for the selected elements were up to a factor of 10 higher (Figs. 3 and 4). Therefore, it is likely that pyrolysis char from ASR is not suitable for water adsorption practices in freshwater ecosystems. The limitations set are for dissolvable fractions of metals, in this analysis the total concentration in char solid residue was recorded. Not all the metal compounds within the solid fraction will be dissolvable and further analysis of the dissolvable fraction of elements is required to confirm this.

In addition to the concentration of heavy metals, the presence of sulphur within pyrolysis feedstock can cause significant problems through the production SO$_x$ gasses, which are environmental pollutants causing damage to human health [42]. Sulphur present in the feedstock being transformed into char could be a method of diverting pollutants into this by-product and reducing impact to other areas of the system. However, presence of sulphur in char limits the potential to be utilised. Pyrolysed char with high sulphur concentration can be utilised within flue

gas depollution, where sulphide presence can reduce Hg concentrations [43]. However, following mercury adsorption, char would become a toxic waste difficult to depollute. Rubber, which is known to have a high S concentration [44, 45] is a component within ASR fractions [13]. Further removal of this component from the feedstock through optimisation of upstream processes could reduce S from the system. Overall, the S concentration within all chars was low (<1.1 %). If cost-effective, post-treatment desulphurisation steps could further reduce the concentration to meet market requirements for gasification and soil conditioning.

Pyrolysis char as a soil modifier

Utilisation of char as a soil conditioner is significantly impacted by the particle size, where coarse biochar (>2 mm) can increase soil water retention due to hydrophilic surfaces and increased porosity [46]. Although a lower particle size may inhibit the adsorbent properties of char within soil, there are positive effects of its application by increasing nutrient availability in soil effective for plant growth [47]. Due to the differences in particle sizes recorded between fractions (Table 1), it could be suggested that the pyrolysis chars are suitable for different applications, dependant on the requirements of soil modification [48]. For example, the larger particle size determined in CC may be more effective applied to soils with poor physical structure and FC with a small porous structure may be more effective in soils with drought to enhance adsorbent properties of moisture and nutrients for plant selection. Further analysis of the soil type and information on soil health could influence which char fraction would be suitable for specific applications.

Although CC had the lowest C (%), it also had the lowest LOI (26 %), meaning it had a low organic C content (Table 2). This means that the carbon within the material is more stable and the carbon added to soil would retain within the ecosystem longer and degrade at a slower rate [49]. A carbon level of char lower in carbon concentration could be an effective soil conditioner for soils of poor structure soils, such as in brownfield sites or reclaimed mining areas. Soil conditioners have different specifications dependant upon the requirement of the soil requiring improvement. For example, soils of drought areas require a conditioner that would retain moisture in the soil and acquire available nutrients for plant uptake [50], whereas clay soils may require a soil conditioner to loosen the structure and increase soil porosity to improve drainage. Further information on the hydrophilic properties of the char would determine which soil improvement market each char fraction would be suitable for.

The concentration of H within the organic structure (Table 2) provided initial information in the differences in carbon structures within the char fractions. An increase in H (%) concentration in the FC fraction could indicate a lower aromaticity within the char structure, however further analysis would be required to confirm this. The H% concentration also increased with increasing C (%) in each fraction, so the compounds could be the same at a higher concentration. Further chemical analysis using GCMS or FTIR would confirm whether there were any changes in the organic molecular structure between char fractions. A higher aromaticity would suggest a higher level of PAHs, which would limit opportunities certain markets such as soil conditioners. High levels of Persistent Organic Pollutants (POPs) in char produced from ASR has been determined in a study by Williams and Khodier [4]; further information on the differences in PAH levels between char fractions could identify what upgrading is required before reuse.

What may limit utilisation of CC in biochar markets is the potential pollutants in the plastic components of the waste [4] and the high metal concentration which may need to be reduced to avoid leaching of pollutants [51]. Of the high metal concentrations determined, Fe and Al are in abundant concentrations in soil, therefore this would not limit applications to reclaimed land sites. However, the concentration of heavy metals in pyrolysis char is higher than the maximum SSVs. Therefore, when applying char to soil, it is essential that the application rate does not increase the pollutant levels over the SSV limits. Chemical analysis of the background concentration of the pollutants in soil must be analysed prior to application to determine an acceptable dosage for char applications. The two elements which require a significant reduction in concentration before a potential application in soil is Cu and Zn. Further upgrading of char via acid digestion may reduce these values.

The EDS analysis confirmed that there were higher concentrations of inorganic elements in the CC char fraction (Table 4). Low levels of chlorine were determined in EDS analysis, which would require further investigation prior to product development. It is likely that Poly Vinyl Chloride (PVC) within car plastics is the source of this analyte. In soil, Cl is an essential nutrient for crops vital for crop growth, therefore may be a better storage for Cl which can be a pollutant when used in other systems such as flue gas cleaning, where increased production of HCl can corrode the internal components of a gasification system [52]. However, excessive anthropogenic applications of Cl- can lead to saturation and phytotoxicity [53]. Soil testing prior to application would be required to reduce negative overapplication effects.

Pyrolysis char as a concrete filler

Char added to civil engineering products such as concrete and epoxy resins can significantly improve the tensile strength of the material whilst reducing demand for raw materials. General physical requirements of these products are char with a regulated particle size and structure [28]. Of the three char fractions, MC had the most regulated structure with low porosity, which could be a better match for these products. In addition to physical size and structure, the compressive strength of chars can impact its use. Research findings suggest that pyrolysis temperature conditions can have an impact on char physical structure and compressive strength, however this is feedstock dependant [54]. Findings suggest that optimum temperature conditions for char from coal feedstock is 800 °C [54]; plastic and construction waste wood is 500 °C [55, 56] and sewage sludge is 300 °C [57]. Although 900 °C has been determined as the optimum pyrolysis temperature for syngas production [13], to improve CC characteristics, which largest fraction of char a lower pyrolysis temperature could be required. The utilisation of char in civil engineering products is also limited by char leachate properties and the concentration of any pollutants within it. Although addition of char with stable pollutants to concrete or epoxy resins could be a sink for pollutants from the pyrolysis process, further information on upgrading would be required.

The main components of PFA, aluminium, iron and silica were detected in all three pyrolysis chars (Fig. 3, Table 3). Of the metal analysis, Fe and Al were the most abundant metals in the char composition, indicating a potential for use as a concrete filler. However, the % composition of Fe, Al and Si conducted using EDS analysis was lower than that of other studies of PFA [25, 58, 59]. This is potentially caused by the high carbon concentration. A high carbon concentration may limit the reactivity of the char with the cementitious material and reduce the tensile strength of the concrete. The high carbon concentration within the char makes the material above the LOI limit set by British Standards Index (BSI) EN 450-1 for addition to concrete as an ash material [60]. Further trials of char addition to concrete with co-products would be required to test this and the effects of dosage on concrete stability. However, of the three product types discussed, the addition of char to concrete may be the most effective market due to the high demand for an alternative to PFA and the large abundance of material following commercialisation. The high concentrations of pollutants detected could be stored in concrete and protected from environmental damage without further post-treatment.

Recommended upgrading requirements

Following an evaluation of the physiochemical characteristics of pyrolysis char and an assessment of the capability of the fractions to be utilised within commercial markets, a number of upgrading requirements have been identified. Of the three commercial applications assessed, the most accessible market pyrolysis char fractions could be utilised within is concrete additives. Due to the contamination levels of heavy metals, to be utilised within other markets a post treatment to reduce the concentration would be required. This creates another waste stream to find a market for, which does not enhance circularity of the automotive industry and still creates challenges to meet the targets of the ELV directive. However, to meet chemical specifications similar to

PFA products, the LOI concentration of the char needs to be significantly lower [60] or a co-feed may be required. Further testing of the effects of char addition on concrete strength parameters is required to determine whether char is an effective additive.

Within activated carbon markets, further testing of the char porosity and activation agent is required to determine the correct product. Pyrolysis char from other waste feedstock sources such as wood, sewage sludge and plastics have been used as an activated carbon, but the activation chemical used and target pollutant differs between feedstocks, where there is no common trend between applications [11, 61, 62]. An extensive review on activated carbons, with reference the effect of feedstock, pyrolysis (carbonisation) and activation (catalyst, calcination, or steam activation) conditions would provide vital information to enhance methodology design of the production of activated carbons from waste heterogenous products such as ASR. With the highest carbon concentration (Table 2) and porous structure (Fig. 2), FC could be an effective activated carbon, but further steps will be required to remove metal contamination.

Within biochar application markets, further information would be required on the leachate concentration in soil, the char hydrophilic properties and the phytotoxicity before a product could be optimised. The utilisation of char from ASR feedstock in its current form is limited to specific soil markets such as contaminated land, due to the presence of plastics and foam fractions. This experiment indicated that pyrolysis char fractions were above the SSVs for a number of heavy metals, however further analysis of the available metal concentration may be of lower concentration and within range of SSV legislation. Further lab scale testing is required to determine the metal availability when applied to soil. The high aromaticity of carbon compounds within ASR feedstocks previously detected [4] could imply that addition to soil could enhance carbon sequestration in low carbon soils, however further tests of char *in-situ* is required to determine the volatility of the pyrolysis char in soil systems to determine whether total carbon is increased over time. Further testing on the hydrophilic properties of the char could provide insight into the adsorbent properties to determine what soil conditions the char is most suitable for. The carbon concentration within char produced from ASR could be upgraded through addition to organic matter such as compost as an alternative to peat [63], however it is uncertain whether char from heterogenous material will be an effective additive due to potential inconsistent properties.

A common theme within all products is the high metal concentration within the CC limiting its access to many markets. Metal makes a large percentage (75–80 % w/w; [3]) of all car products. Although many upstream processes occur to remove the valuable material [9], much could remain in processed ASR as metal fibres in wood and in smaller electrical products, which are growing components of newer ELVs [4]. Pre-treatment of ASR through acid washing could remove the metal contaminants of the char prior to pyrolysis. This method has been applied to pyrolysis of coal and biomass feedstocks but has not trialled with ASR [64, 65]. If successful, there could be challenges in upscaling this method, due to the large amounts of acid required. Further economic and environmental assessments of these approaches would be required with increased trials at a pilot-scale.

Identification of the fractions of ASR which have the most pollutants within them could be a useful solution to remove these components from the pyrolysis feedstock and recycle using a different process. This would remove the contamination from the feedstock at source, at a potential lower cost. There is currently limited detailed chemical analysis of the ASR fractions within cars and the difference in components between car manufacturers makes this difficult. However, trial tests of the metal concentrations within ASR fractions could be a simple method to eliminate contamination if the pollutant in question is only sourced within a single fraction. The change in ELV waste expected over the coming years as an increase in electrical components of cars would require a continued monitoring of ASR fractions to meet a changing feedstock.

One area of pyrolysis char upgrading that has not been explored is metal extraction through refining [66]. The increased amount of WEEE products within cars could result in a higher concentration of precious metal within char. Although a large amount of energy is required through the refining process due to the high temperatures required, the high metal concentration indicated within this experiment could result in a large profit. It would also increase the carbon concentration within the char making it a better product to fit within the commercial markets discussed within this project.

Conclusion

This paper highlights that pyrolysis char from ASR feedstock has differing physiochemical properties dependant upon the location deposited within the system. There are opportunities to separate these products into different commercial markets, however, a number of modifications to the products are required before the products can meet specifications to be sold in these markets, notably a reduction in the high metal concentration and desulphurisation. Further chemical analysis on the POPs contained within the char will determine whether they can meet specific commercial markets. Modifications to upstream processing of ASR feedstock to remove fractions containing more polluting materials such as plastics may improve the char quality. Investigations into post-treatment methods could remove the metal concentration. To ensure a smooth transition to a commercial market, future investigations into char post-treatment methods would benefit the pyrolysis of ASR.

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