POTENTIAL VALORIZATION FOR THE FINEST PARTICLES OF AUTOMOTIVE SHREDDER RESIDUE (ASR)

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POTENCIÁLNE ZHODNOCOVANIA JEMNÝCH ČASTÍC ZO ZVYŠKOV PO ŠRÉDROVANÍ AUTOVRAKOV

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Abstrakt

Výrobcovia automobilov čelia stále tvrdším Európskym opatreniam týkajúcich sa recyklovania autovrakov. V súčasnosti je pozornosť venovaná hrubším frakciám zo šrédrovania autovrakov. Avšak, Európske kritéria môžu byť splnené len ak sa bude uvažovať so spracovaním a zhodnocovaním jemných frakcií (menej ako 2 mm) ktoré obyčajne predstavujú 5-10 hm.% autovraku.

Bolo realizované laboratórne štúdium jemných ľahkých frakcií autovrakov z belgického vrakovišťa. Boli testované rôzne procesy v kombinácií granulometrické triedenie, gravimetrické a magnetické separácie. Optimálny proces viedol k identifikácii štyroch rôznych produktov. Tieto boli charakterizované a bola posúdená možnosť ich využitia. Je doporučované využiť najjemnejšiu frakciou (pod 250 μm) ako plnivo v stavebníctve. Rozdružovanie v ťažkých kvapalinách bolo testované na ostávajúcej frakcií. Bolo posúdené využitie ľahkej frakcie v energetike, pričom sa dosiahli sľubné výsledky. Z ťažšej frakcie bola oddelená magnetická časť, ktoré má potenciálne využitie v oceliarstve. Nemagnetická frakcia, obsahujúca minerály, môže byť využitá ako piesok.

Abstract

Car manufacturers are faced with increasingly severe European regulations concerning End of Live Vehicles (ELV) recycling. Issues for the coarse fractions of Automotive Shredder Residue (ASR) are now quite largely studied. However, the European objectives could only be achieved by considering the processing and valorization of the fine ASR fraction (< 2mm) which usually represent 5 to10 wt.% of shredded ELV.

A laboratory study was carried out on the fine light ASR fraction from a Belgian shredding plant. Different processes were tested by combining granulometric classification, gravimetric and magnetic separations. The optimum one led to the identification of four different products. Characterization and valorization of these four fractions were then investigated.

The use of the finest fraction (< 250 μm) as filler in civil engineering is proposed. A Heavy Liquid Separation (HLS) was done on the remaining fraction. The energetic use of the floating particles was evaluated with promising results. Sinking particles were magnetically

treated. The magnetic fraction has a potential use in the steel industry. The residual non-magnetic mineral fraction can be associated and employed as sand.

Key words : Automotive Shredder Residue (ASR); End of Live Vehicles (ELV); Fluff; Valorization; Fine particles.

1. Introduction

With 170 million vehicles in circulation in the European Union, cars are an important source of waste. Each year, 12-14 million of End-of Live Vehicles (ELV) become unroadworthy and available for recycling. Unfortunately, only ferrous and non-ferrous metals are typically recovered which represent 75 wt.% of total ELV. The non recycled fraction, called Automotive Shredder Residue (ASR), is mainly put into landfill or incinerated. Applying some processes on these ASR, it is still possible to recover plastics or combustible materials that could improve the recovery to 80-85 wt.%.

European directive 2000/53/CE now makes the car manufacturers responsible for the issue of the ELV. They are faced with increasingly severe objectives for reuse and recovery : 85 wt.% for the year 2006 and 95 wt.% for 2015 (with respectively a maximum of 5 wt.% and 10 wt.% in energetic recovery).

The classic procedure of treatment of the ELV could be described as the following main steps. First of all, hazardous materials and components like fluids, batteries, airbags, … should be removed to avoid the contamination of the subsequent shredder fragments. Tyres, glass, catalysts or some large pieces of identifiable plastics or metals should also be separated and sent for their own recycling process. Afterwards, cars are shredded into small pieces which are further available for different physical separations.

An air separator divides the shreds into two fractions. The heavy fraction contains ferrous and non-ferrous scraps which are extracted using magnetic fields and eddy currents. The remaining material is mainly composed of high-density plastics and rubber. The light fraction, called "fluff", contains low-density plastics but also other materials such as glass, wood and fine particles. This fraction is generally disposed of in controlled landfill sites after a possible magnetic separation.

Potential energetic uses of both light and heavy ASR fractions are now well-studied : pyrolysis (Day et al., 1996), gasification (Iida, 1999), incineration (Lanoir et al., 1997). Those processes could supply oil, gas or heat for energetic valorization causing reduction of the landfill volume. They also permit the recovery of metals in the solid residue that can reach 20 wt.% of the ASR. Literature indicates that the heat value of ASR is comprised between 10.2 and 19.0 MJ/kg (Roy and Chaala, 2001). Ash content is in the range of 38-58 wt.%.

Furthermore, questions still remain about the fine fraction which does not contain high energetic potential. A study carried out on fluff samples with particle size inferior-to-13 mm from a Belgian shredding plant showed that heat value sharply decreases with the particle sizes (Fig. 1). On the other hand, the ash content increases when the particle sizes decrease. Below 2 mm, heat value does not exceed 5 MJ/kg and the ash content raises up to 85 wt.%. For those fine particles, it appears that energy recovery and volume reduction could not be significant. Unfortunately, they are present in a proportion that ranges between 30 and 40 wt.% of the total ASR (until 44.1 wt.% according to Roy and Chaala, 2001), which means that the European objectives could not be achieved without considering that fraction.

This paper summarizes a laboratory study that was undertaken to characterize the fine light ASR fraction (< 2mm). It describes in detail fractions obtained by physical separation in order to evaluate their possible valorization.

2. Experimental

2.1 Sampling

Samples were collected in a Belgian shredding plant that processes together with ELV, Waste of Electrical and Electronic Equipment (WEEE) and other scrap-iron in the proportions given in Table 1.

A sampling procedure was performed according to theoretical considerations (not detailed in this paper). The purpose was to obtain daily representative samples for that kind of material which is heterogeneous in composition, in particle size, in shape, and in time. That was set up by calculation of a minimal representative mass and determination of a sampling scheme. A random stratified scheme was adopted. It consists of gathering random samples within determined periods of time.

ASR was collected directly at the end of the conveyor to avoid segregation into the pile. The fine fraction inferior to 2 mm was obtained by manual screening of the samples.

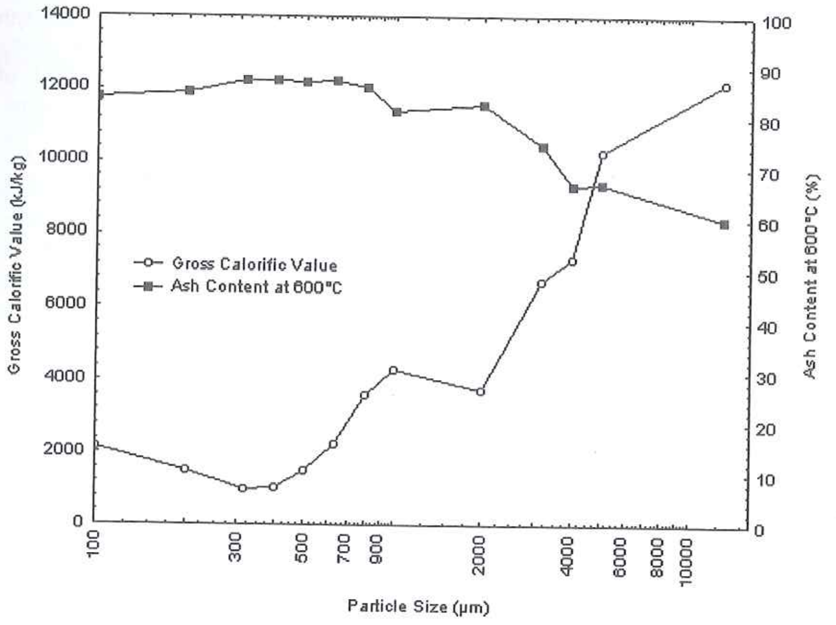

Fig 1 : Gross calorific value and ash content at 600°C vs. particle size for an inferior-to-13 mm ASR sample

2.2 General characteristics

General characteristics were determined on the global fraction. The bulk density was first determined from a known weight of samples placed through a funnel in an adequate cylindrical graduated recipient. A second value of density was obtained after compaction of the sample subject to vibration at 50 Hz with amplitude of 1 mm for 1 minute. Moisture was obtained by the measure of weight loss after heating the samples at 55°C in an air circulated oven for 24 hours. Particle size analyse was performed by hand-screening with standardised screens.

Table 1 Input material in the shredder plant

Materials	Content (wt.%)
ELV	25
WEEE (mainly washing machine and cooking stove)	15
Other iron scraps	60

2.3 *Physical separations*

Physical separations were conducted on samples of 600 g in order to identify and characterize the different constituents of the fine ASR. Because they disturb the further treatments, particles under 250 μm (35.1 wt.%) were separated by screening. They were characterized separately (see section 3.3). Samples free of fine particles were then screened into several fractions on which magnetic and gravimetric separations were carrier out.

Magnetic separations were carried out with a light magnet over the spread out materials. Different Heavy Liquid Separations (HLS) were investigated to divide particles into categories with similar characteristics. Density properties of main ASR components are given in Table 2. In order to isolate organic fractions, saline solutions were preferred to organic liquids which could react with polymers and modify their gross calorific value. Two saline solutions were used. Solutions of density up to 1.20 kg/dm^3 were obtained with sodium chloride (NaCl). These solutions were used to separate the light products (wood, rubber, foam, low density polymers). Additional separations were carried out using zinc chloride ($ZnCl_2$) solutions with density up to 2.0 kg/dm^3. These solutions allow the separation of the remaining polymers from the heavy fractions which also contain mineral and metallic components. Floating and sinking particles were suitably rinsed and dried before further separations or characterizations.

Table 2 Density of main ASR components

Component		Density (kg/dm^3)
Polyurethane foam	PUF	less than 0.5
Wood	PP	0.5 – 1.0
Polypropylene		0.90 – 0.91
Rubber		0.91 – 0.95
Low-density polyethylene	LDPE	0,91 – 0,93
High-density polyethylene	HDPE	0.95 – 0.96
Acrylonitrile butadiene styrene	ABS	1.05 – 1.07
Polyurethanes	PU	1.11 – 0.25
Polycarbonate	PC	1.2
Polyvinyl chloride	PVC	1.30 – 1.35
Polyethylene terephtalate	PET	1.37
Concrete-mortar-cement		2.3 – 3.1
Ceramic		2.0 – 3.0
Glass		2.4 – 2.8
Aluminium	Al	2.70
Zinc	Zn	7.19
Steel		7.83
Copper	Cu	8.89
Lead	Pb	11.34

2.4 *Analysis of the different fractions*

Once the separations were carried out, characterization methods were defined for each sorted fraction in order to determine possibilities for further valorization.

Organic fractions were analysed in order to investigate a possible energetic valorization. Gross calorific values were measured by combustion in a IKA C 5000 bomb calorimeter. Ash content was determined by weight measurement on the residue obtained after incineration of 2 g samples in porcelain crucibles using an electric furnace which was gradually heated to 550°C, 875°C and 1100°C. These temperatures were maintained for 30 minutes.

Metal contents were quantitatively measured by atomic absorption. Silica and alumina of the mineral fraction were determined by gravimetric method from the solution from the pulverized fraction.

Morphological characterization of the very fine fraction (< 250 μm) was carried out using a scanning electronic microscope Jéol JSM-5800.

3. Results and discussion

3.1 *General characteristics*

Results of the general characteristics of ASR light fraction under 2 mm are presented in Table 3. It is a dark brown powder with a bulk density ranging from 970 (uncompacted state) to 1 312 kg/dm^3 (compacted state). These values are higher than the density of the total ASR fraction which is in the range of 358 to 495 kg/dm^3 (Roy and Chaala , 2001).

Moisture largely depends on the weather conditions. The lowest value (2.7 wt.%) was found after a large period of dry weather conditions but 17.0 wt.% moisture could be obtained under wet weather shredding conditions. The mean moisture of 6 samples gave a higher value (11.4 wt.%) than the typical moisture of 6 wt.% mentioned by Day et al. (1996) for the total ASR fraction. The difference could be explained by the water retention capacity caused by the high specific surface of the fine components (oxidized particles, foams, fibres,…).

3.2 *Physical separations*

Parameters in the separation processes were chosen with the goal of being able to be applied on an industrial scale.

When magnetic separations are first conducted on the several particle size fractions over 250 μm, the magnetic recovered products are strongly contaminated by undesirable particles like foam and wood. This contamination is due to fine iron particles that are caught in these porous materials. To avoid that problem, gravimetric separations were conducted before magnetic separations.

Heavy liquid separations with a 1.19 kg/dm^3 density sodium chloride (NaCl) solution were allowed to recover a light fraction which represents 7.3 wt.% of the total. These floating particles are mainly composed of wood, foam, textiles and some pieces of low density polymers (PP, LDPE, HDPE, ABS, PU, …). Second separations using a zinc chloride ($ZnCl_2$) solution with a density of 1.83 kg/dm^3 were allowed to float 8.8 wt.% of residual polymers (PVC, PET) without inorganic materials. The sinking fractions were magnetically treated. The final laboratory separation scheme is given on Fig 3.

Non-magnetic fractions represent 31.4 wt.% of the fine ASR. It contains almost only mineral materials like glass, ceramic and concrete. Metal contents were too low to consider their separation with industrial objectives. Only a few particles of copper from electric wires could be observed. Some aggregates composed of very fine particles coated in bituminous matrix were also identified. The magnetic fraction corresponds to 17.4 wt.%. It is mainly composed of oxidised iron which is now clean of foam and wood. Painting flakes are recovered in all floating and sinking fractions due to their surfaces properties and their large density range.

Table 3 General characteristics

Bulk density		
- uncompacted	kg/m³	970
- compacted	kg/m³	1 312
Moisture		
- min. after 15 days of sun (April)	wt.%	2.7
- max. after 15 days of rain (November)	wt.%	17.0
- mean on 6 samples	wt.%	11.4
Particle size		
- $d_{80\%}$	µm	1 000
- $d_{50\%}$	µm	425
- $d_{25\%}$	µm	165

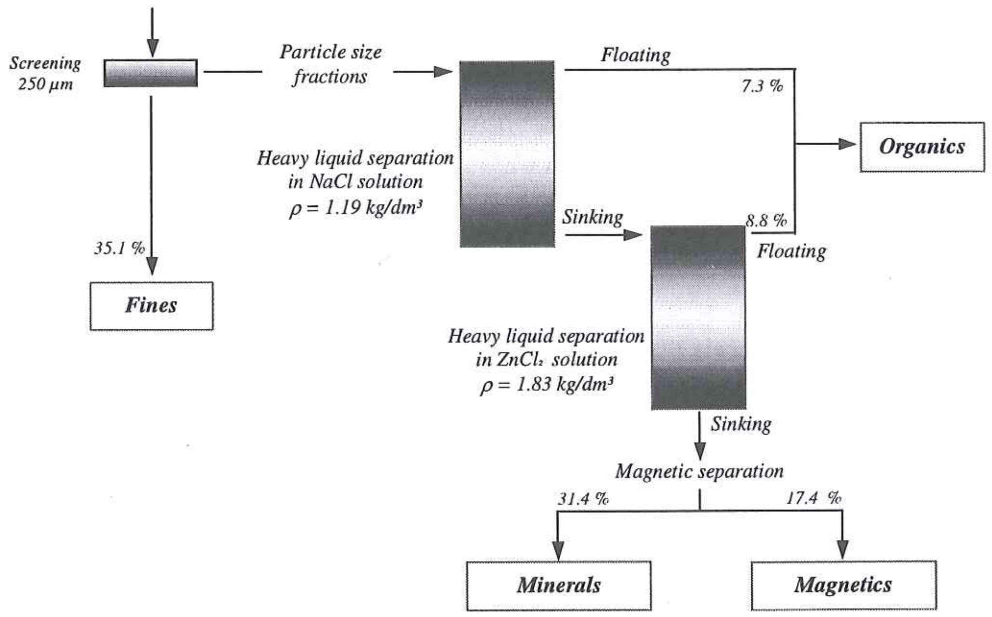

Fig. 3 : Final laboratory separation scheme

3.3 Characteristics of the recovered fractions and their possible valorization

The results of the analysis for each fraction are presented in Table 4. Based on these analysis, potential valorizations are discussed.

With 50.7 wt.% of iron, magnetic fraction could be considered as a low grade iron ore. Valorization in steel industry could be considered. A first possibility is introduction into an electric arc furnace (EAF) which already valorizes magnetic fraction from automotive shredders. However, feeding could be a problem if the EAF is fed by grapnel. Contamination by other metals could be acceptable depending on the application of the resulting steel. Oxidized iron particles could require reducing agent. Blast furnace (BF) is a second possibility. Magnetic particles could be introduced together with iron ore after pelletizing, sintering or other agglomeration processes. Direct injection in blast injection tuyeres could be the best option. It offers a high temperature treatment (2100 °C) of the potential organic pollutants.

An alternative to the steel industry is injection through cement kiln lances as a ferrous material contribution to the cement. However, the heavy metal content could limit that possibility.

Mineral fraction could be considered for and developed as sand in civil engineering. Applications using concrete or bituminous agents could be preferred because they inert the low heavy metal content.

Table 4 Characteristics of the fractions[a]

Fraction	Magnetic	Mineral	Organic	Fine
Proportion (wt.%)	17.4	31.4	16.1	35.1
Gross calorific value (Mj/kg)	ND[c]	ND	10.8	ND
Ash content at 550°C (wt.%)	ND	ND	54.7	ND
Ash content at 875°C (wt.%)	ND	ND	50.1	ND
Ash content at 1100°C (wt.%)	ND	ND	48.5	ND
Iron (wt.%)	50.69	5.84	9.68[b]	16.50
Copper (wt.%)	0.21	0.95	0.13[b]	0.43
Zinc (wt.%)	1.30	2.33	1.85[b]	1.76
Lead (wt.%)	0.36	1.27	0.54[b]	1.41
Chromium (mg/kg)	7344	3070	2684[b]	4174
Nickel (mg/kg)	3138	1390	478[b]	1210
Manganese (mg/kg)	3817	1390	802[b]	1803
Cobalt (mg/kg)	741	446	555[b]	617
Silica (wt.%)	ND	38.86	ND	16.5
Alumina (wt.%)	ND	10.12	ND	4.05

[a] All results are reported on dry material.
[b] Analysed on the ash at 550°C and reported on the total fraction.
[c] ND = not determined

Energetic potential of the organic fraction is quite promising. The gross calorific value of 10.8 Mj/kg was obtained. That value is below the typical value of 20.0 Mj/kg found in literature for the total ASR (Roy and Chaala, 2001). However, energetic issues which are proposed for the total ASR could be investigated for the organic fraction. Furthermore, its fine granulometry offers possibility of injection through lances, for example in blast furnace or cement kiln. Ash content (48.5 to 54.7 wt.%) is close to the 50 wt.% mentioned in literature for the total ASR (Roy and Chaala, 2001). The metal content is quite high (12.7 wt.% versus 9.7 wt.% of iron).

Particles of minus 250 μm are composed of mineral, metallic and organic fragments in proportion similar to the coarse fraction (according to chemical analysis). That kind of fine particles could be valorized as filler in plastics, concrete, asphalt, … Images from electronic microscope analysis show that a lot of fibres are present in the very fine fraction. These fibres could offer interesting properties in the case of valorization as filler substitute.

4. Conclusion

This proposed study improves the knowledge of the very fine particles from light ASR which are generally studied together with the coarse fraction despite the difference in their properties. A laboratory scheme of treatment is suggested in order to recover four valuable products. An industrial scaling up could be investigated. Several possibilities for valorization were proposed for each recovered fraction. Further studies must determine which are the best

However, a total valorisation of ASR particles below 2 mm could improve the recovery of End of Live Vehicles from 5 to 10 wt.% which represents an important step to achieving European Union objectives.

References

[1] Day, M., Cooney, J.D. and Shen, Z. 1996 : Pyrolysis of automobile shredder residue : an analysis of the products of a commercial screw kiln process. Journal of Analytical and Applied Pyrolysis 37, 49-67.

[2] Ferrara, G. and Meloy T.P. 1999 : Low dense media process: a new process for low-density solid separation. Powder technology 103, 151-155.

[3] Iida, S. 1999 : Development of batch-type distillation/gasification technology for ASR (automotive shredder residue). Technical Notes JSAE 20, 259-279.

[4] Lanoir, D.,Trouvé, G., Delfosse, L., Froelich, D., and Kassamaly, A. 1997 : Physical and chemical characterization of automotive shredder residues. Waste Management & Research 15, 267-276.

[5] Mirabile, D., Pistelli, M., Marchesini, M., Falciani, R. and Chiappelli, L. 2002 : Thermal valorisation of automobile shredder residue : injection in blast furnace. Waste Management 22, 841-851.

[6] Mutz, S., Pretz, T., Weingart, A. and van Looy, E. 2002 : Possibilities and use automatic picking within the automobile recycling industry. Fundamental of Advanced Materials for Energy Conversion EDP Congress 2002, 657-667.

[7] Roy, C. and Chaala, A. 2001 : Vacuum pyrolysis of automobile shredder residues. Resources Conservation & Recycling 32, 1-27.