Low temperature pyrolysis of the Automotive Shredder Residues (ASR) for energy recovery and metal recycling

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Technical topic: Energy from Waste

Abstract

Automotive Shredder Residues (ASR) is the remaining fraction from metal recovery of end-of-life vehicle (ELV). While the processes for recovery metal from ELV are well developed, the process for recovery metal from ASR remains a challenging problem. In this work, low temperature pyrolysis of ASR is investigated with the speculation that low temperature and inert environment would benefit the metal property i.e. metal will not be oxidized and enhance the separation of the organic part from the metals. The pyrolysis experiments were done in a tube reactor at 300 - 500°C. The gas and oil were analyzed by micro GC and GC/MS accordingly. It is found that the gas contains high amount of CO₂ and the energy recovery is limited. The oil contains high phenolic and aromatic compounds. The solid residue was crushed and fractionated by different particle sizes. It was found that temperature of 400°C seem to be suitable for liberating metal fractions with a particle size greater than 0.5mm.

1. Introduction

End-of-life vehicles (ELV) has become a global concern the recent years not only because of their challenging composition but also because of their increasing rate which is related to the growing population. A lot of effort has been put in to recycling of this fraction, mostly because of its high value, as it consists of more than 68% of iron and high percentages of non-ferrous (NF) metals [4]. The recycling most of the base metals is already established by employing magnetic separators and eddy current separators [5]. On the other hand, 15 – 25% of ELV is small particle size shredder residues which is referred to as Automotive Shredder Residues (ASR) or Shredder Light Fraction (SLF) or Shredder Residues (SR). This fraction has drawn scientific community’s attention since if it is further recycled, it can increase the overall percentage of the total ELV recycling.

The ASR’s composition varies a lot because every recycling company uses different systems and separation techniques and the economic market drivers varies over time [6]. In general, ASR or SLF is a highly heterogeneous material which can include metals, plastics, ceramic materials, textiles, glass, sand, dust, rocks and rubbers. Sometimes the ASR can be blended with other waste fractions in order to reach composition requirements for specific industrial applications, like replacing virgin carbon as reduction material in metallurgical applications or as fuel [5].

The inhomogeneity of ASR fraction can also result in contaminant concentrations which can limit recycling and other applications. The chlorine content derived from PVC plastic and rubbers is a vital parameter for all the thermal treatment processes since during its decomposition HCl is produced which can corrode the process facility. Moreover, plastics with brominated flame retardants can end up in this fraction. These halogenated materials can lead to the production of persistent organic pollutants (POP) when they are thermally decomposed. Lastly, this fraction

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usually contains high concentration of heavy metals such as zinc and lead which has low boiling points and might migrate to the gas phase influencing the entire process’s feasibility [7].

Pyrolysis of ASR or SR has been extensively investigated in the past decades since it is a promising option for recovering materials from the ASR. Zolezzi et al. investigated the effect of heating rate on pyrolysis of ASR by comparing the results of conventional and fast pyrolysis at four different temperatures (500, 600, 700 and 800°C), and concluded that more that 80% of the initial mass can be transferred to either the gas or the liquid phase. One of the main findings is that the lower pyrolysis temperature, the higher the heating value of the acquired solid residue and liquid fraction [8]. Anzano et al. has recently published a study on pyrolysis of ASR on the same temperature range focusing on the possibilities of metal recycling present in the solid residue and the formation of persistent organic pollutants (POP), such as polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The outcome of this study was that the ASR considered a precious secondary source of metals since high amount of metals have been found on the solid residue, which emphasizes the potential economic benefit of this fraction of waste [9]. Donaj et a l. has done experiments both on pretreating this fraction with microwave pyrolysis followed by gasification experiments in order to propose a holistic approach of ASR treatment to produce gas with a high heating value [2]. From these reviews, not so many work have been done on pyrolysis. Considering that ASR contains high metal fractions, low temperature pyrolysis might be an interesting option. Since this process is done at low temperature and inert atmosphere, less metal will be oxidized which might enhance metals qualities. Moreover, most of the organic part will be removed which might aid the liberation of metals.

This study investigates the possibility of using low temperature pyrolysis for metal recoveries where the process should assist in separating non-volatile fractions (including char and metals e.g. Cu, Al and Fe) from volatile fractions and in liberating metals from carbonaceous char. The metal can then be recovered and the char can be further utilized as reduction agent in replacement of coal or as a fuel.

2. Materials and Methods

The tested sample was provided by Stena Recycling AB. The examined ASR fraction has been extensively homogenized and then pelletized for acquiring representative samples, increasing density and for easier handling as shown in Figure 1.
2.1. Sample characterization

The ASR material was sent for analysis to an external company in order to determine important parameters prior to the experiments. The material was analyzed for moisture, ash content, volatile matter and fixed carbon for the proximate analysis, as well as the basic elements for a fuel analysis including chlorine and bromine. Moreover, AC600 Semi-Automatic Isoperibol Calorimeter was used for gross calorific value and the net calorific value determination according to EN-15408:20011 standard. Finally, the trace minerals and metals were also analyzed.

2.2. Pyrolysis experiments

The pyrolysis experiments were performed on a fix bed tube reactor (Figure 2). The reactor consists of a 1 inch stainless steel tube inserted in a 1 kW electrically heated furnace. Flow of N\textsubscript{2} was controlled by a flow meter. Approximately ~10g of ASR pellets as received was loaded in a glass tube. This glass tube would minimize the risk of melting sample falling to the bottom of the furnace and clogging the outlet. So the entire sample was subject to the thermal stress during the entire experiment. Moreover, a thermocouple was placed inside the glass tube with the sample in order to accurately measure the temperature of the sample both during the heating up phase and during the pyrolysis at the target temperature. Three temperatures were selected for the experiments, 300°C, 400°C and 500°C in order to evaluate the possibility of liberation the metal fraction by carbonization of the organic matter. Moreover, the produced vapors are cooled in cold traps which were submerged in liquid bath maintained at ±1°C. Then, the condensed products were analyzed by GC/MS liquid analysis while the composition of the gases produced were analyzed by a micro GC.
2.3. Metal fraction separation

The solid residue was collected and its mass was measured. The solid fraction was crushed with a mortar and a pestle to pulverize residual carbon. The chars obtained from the pyrolysis experiments were separated with 1, 0.5 and 0.25mm sieves. The finest fractions (0.5mm>x>0.25mm and x<0.25mm) of the solid residue was analyzed by SEM-EDS in order to evaluate the degree of separation.

3. Results and Discussion

3.1. Material characterization

Compared with similar waste fractions such as refuse derived fuels (RDF) [10], the tested fraction has high energy potential but also high ash content. The proximate, ultimate and elemental analysis is illustrated on the table below (Table 1). The moisture of the sample (3.4%) is reasonable for a pre-dried mixture of waste.

The halogenated compounds are a vital parameter since it will limit the application of the pyrolysis products. The bromine content is relatively low compared with flame retardants fractions of waste such as plastics derived from e-waste. Moreover, sulphur content is rather low compared with sulphur content of coal. This indicates possibility for clean fuel. Finally, the chlorine content, which probably derives from PVC plastic is rather high and it can be classified as class 2 according to the BS EN 15359:2011 since it contains lower than 0.6% [11]. The oxygen content is rather high which implies that there is high quantity of plastic material contained oxygen such as polycarbonates.

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>Ultimate Analysis</th>
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<tbody>
<tr>
<td>Moisture 105°C</td>
<td>Carbon (C) 35.40%</td>
</tr>
<tr>
<td>Ash 550°C</td>
<td>Hydrogen (H) 4.60%</td>
</tr>
<tr>
<td>Volatile</td>
<td>Nitrogen (N) 1.65%</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>Oxygen (O) 12.60%</td>
</tr>
<tr>
<td>Elemental analysis</td>
<td>Heating value (as received)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------------</td>
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<tr>
<td></td>
<td>Heating value (dried)</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica (Si)</td>
<td>54600 mg/kg ts</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>19600 mg/kg ts</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>27700 mg/kg ts</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>103000 mg/kg ts</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>3880 mg/kg ts</td>
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<tr>
<td>Magnesium (Mg)</td>
<td>5760 mg/kg ts</td>
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<tr>
<td>Manganese (Mn)</td>
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<tr>
<td>Sodium (Na)</td>
<td>6830 mg/kg ts</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>948 mg/kg ts</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>3720 mg/kg ts</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>173 mg/kg ts</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>15.5 mg/kg ts</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>3600 mg/kg ts</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>1560 mg/kg ts</td>
</tr>
<tr>
<td>Boron (B)</td>
<td>354 mg/kg ts</td>
</tr>
</tbody>
</table>

The elemental composition shows which materials could potentially be recovered from this fraction of waste. The high ash content can be explained by the high quantities of metals such as iron and aluminum, minerals and ceramic materials that do not react during combustion. These metals composition are reasonable as all can be found in the automobile products.

3.2. Thermal decomposition

Thermal decomposition of the material has been investigated through Thermogravimetric analysis (TGA) experiments with the heating rate of 20°C/min under oxygen and nitrogen atmospheres prior to the pyrolysis experiments (Figure 3). The material’s decomposition starts at 250°C in both the nitrogen and oxygen atmosphere.

The TGA has been performed to determine ash and volatile content. On the other hand, those results were useful for setting up the experimental cases. Three temperatures of pyrolysis were chosen, 300, 400 and 500°C based on the decomposition curve. At 300°C, the decomposition of the material has been initiated and it seems that the mass loss is expected to be between 10-20%. At 400°C the mass of the material is expected to be close to 70% while at 500°C the volatile matter conversion is expected to be at its maximum among the examine cases.
3.3. Pyrolysis experiments

The ASR material has been pyrolyzed in a nitrogen atmosphere for the temperatures 300, 400 and 500°C. The Figure 4 summarizes the distribution of the mass after the pyrolysis experiments. The three different fractions are the solid residue (char) mainly consists of inorganic material and unreacted carbon, the liquid fraction which consists of light and heavy condensable organic compounds and gases (H₂, CO, CH₄, CO₂, C₂H₂, C₂H₄ and C₂H₆) that has been produced during the decomposition process.

The pyrolysis experiments show high influence on the distribution of the mass among the pyrolysis products. The final temperature of the pyrolysis plays an important role since the higher the temperature, the more organic fraction is transformed into gas and liquid products.

i. Gas composition

The gas composition changes according to the temperature conditions. The higher the temperature, the more gas is being produced since more organic matter is being transformed into gas. Furthermore, the production of CO₂ is rather high compared with the other gases, which shows that the heating value of the produced gas mixture might be low due to the high oxygen content.

Figure 5 a & b summarize the production of gas according to the temperature conditions of pyrolysis. The volume of the gas produced is more than double by increasing the temperature conditions from 300°C to 500°C. On the other hand, minor increase of CO has been observed, which shows that the energy potential of the produced gas is low.
High gas yield are not expected for the chosen low temperature conditions, nevertheless the mass conversion to gas phase is evaluated. The gas conversion does not play a significant role on the results since only a low amount (0.6-1.2%) of organic fraction is being transferred to the gas phase.

![Mass of gas produced at different pyrolysis temperatures normalized by the mass of sample](image1.png)

![Volumetric gas yield per gram of tested sample](image2.png)

**Figure 5**

### ii. Oil yield and composition

The oil yields differ a lot according to the temperature conditions of the pyrolysis since the ASR mixture consists of a variety of organic materials that decompose at different temperature. More of the liquid fraction is collected from the 500°C pyrolysis (~32%). The oil consists of two immiscible phases as can be seen from Figure 6b-c, the heavy fraction and the light fraction. Those two fractions can be distinguished from their color, since the light fraction has clear light yellowish color while the heavy fraction has dark brown. The amount of heavy fraction was observed to be higher when the temperature was increased from 300°C to 500°C. This has been also observed on previous studies [12] which found that at low temperature (300°C) only light molecular weight compounds are being produced, while at higher temperatures conditions (500°C), more materials are decomposed e.g. plastics which produce heavier fraction such as wax and tar.

![Pyrolysis oil at 300°C](image3.png)  
![Pyrolysis oil at 400°C](image4.png)  
![Pyrolysis oil at 500°C](image5.png)

**Figure 6 Pyrolysis oil produced at the different temperature conditions**
The compounds detected by the GC/MS analysis is presented in the Figure 7 as well as their intensities (areas from total ion chromatogram). The volatile products expected from plastic fractions of the material are oxygenated compounds e.g. phenolic compounds and hydrocarbons e.g. aromatic compounds.

Toluene and benzene has been found only on the high temperature experiments at 500°C since they require higher temperatures to be produced from the decomposition of the polymers. Those compounds can increase the heating value of the oil fraction, which can be used for energy utilization. Moreover, separation of the products can enhance feedstock recycling of the separated materials for producing new plastics. On the other hand, phthalates that are present at all the examined cases are derived from soft plastic and it decompose at low temperatures. This compound is a well-known environmental contaminant that is mainly used during the manufacturing process of rubber as plasticizer [13]. Since one of the main contaminants on the oil fraction is being released at low temperature (300°C) case, lower temperature can be used as removal technique prior to any other recycling for removing this compound.

![Figure 7 GC/MS analysis on the oil fraction for 300, 400 and 500°C pyrolysis experiments](image)

iii. Char yield

The higher solid residue yield (~80%) was expected at the lowest temperature of the pyrolysis experiments (300°C), which is confirmed by the experimental data (81.66%) (Figure 4). Since the material consist of high amount of thermoset plastics that when they are subject to heat, hydrogen and oxygen are removed and the unreacted carbon forms the char. The tested material contains several metals in either oxidized or unoxidized form. Due to the low temperature they remain unaltered in the solid residue. Lower solid residue yield have been found at the temperatures of 400°C and 500°C, (66.77% and 54.89% accordingly) which shows that at higher temperature, more organic fraction is decomposing and it is transferred to either the liquid or the gas fractions.
The pulverization of the char from the low temperature of 300°C showed that the material was not fragile and the carbonization has not completely achieved. This indicates that the temperature of 300°C was not sufficient for the entire decomposition of the material. The char from the pyrolysis experiment of 400°C was much more carbonized and fragile. So the liberation of the metals was much easier. Similar behavior has been observed also on the char fraction of the 500°C pyrolysis experiment.

The pictures on the Figure 8 shows the different char fractions obtained at different temperature conditions of pyrolysis. Most of the metallic components stayed on the higher particle size at the cases of 400°C and 500°C fractions since the separation of the carbonized material with the metallic pieces was more efficient. Furthermore, the particle size distribution of the obtained char is illustrated in Figure 9. The fact that more mass in terms of percentage can be pulverized to smaller particle size, verifies the highest degree of carbonization which happens at higher temperatures.

SEM-EDS analysis performed on the two smaller fractions at the different temperatures. The results illustrated on the Figure 10 are the average of four measurements. The results are also normalized based on the initial material.

<table>
<thead>
<tr>
<th></th>
<th>X&gt;1mm</th>
<th>1mm&gt;X&gt;0.5mm</th>
<th>0.5mm&gt;X&gt;0.25mm</th>
<th>X&lt;0.25mm</th>
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</thead>
<tbody>
<tr>
<td>Char at 300°C</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Char at 400°C</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Char at 500°C</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
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*Figure 8 Char separation on different particle sizes*
Based on the results acquired by SEM-EDS (Figure 10), the fraction of 0.5mm>x>0.25mm seems to have a stable percentage of iron, which indicates that the temperature does not play an important role on its separation for this particle size. On the other hand, the iron percentage is higher on the smallest fraction in the case of 500°C experiment compared to the rest low temperature experiments. This shows that the higher the temperature the higher portion of iron goes to the smaller particle size fraction. This implies that the quantity of iron left on bigger particle sizes (x>0.5mm) is higher at low temperatures. Moreover, the carbon detected seems to decrease on the 0.5mm>X>0.25mm fraction, which is as expected because of the low degree of pulverization, while on the smaller fraction of char (X<0.25mm), the carbon content seems to have a maximum percentage on the 400°C, which is a combination of the degree of separation of the material and the low amount of carbon left on the char. The higher percentages on the smaller particle size fraction are strongly related to the high degree of carbonization of the material, which is in accordance with the particle size distribution of the char.

<table>
<thead>
<tr>
<th>Char 0.5mm&gt;x&gt;0.25mm</th>
<th>Char x&lt;0.25mm</th>
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<tbody>
<tr>
<td>Figure 10Metals detected based on the SEM EDS analysis</td>
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</table>

### 4. Conclusions

The ASR has been pyrolyzed at three different temperatures, 300°C, 400°C and 500°C in order to evaluate the degree of separation of valuable materials and to evaluate the potential of utilizing the char as a solid fuel. The pyrolysis experiments indicated that the produced gas at the chosen temperature range does not play a significant role, since its energy potential is limited.

Benzene and Toluene has been detected on the oil produced at 500°C pyrolysis experiments, which both can increase the heating value of the oil. On the other hand, they are also valuable products that can be utilized for feedstock recycling if they are separated.

The low temperature experiment (300°C) indicated that the obtained char was not fragile in order to separate the valuable metals only by the size. Furthermore, the higher the temperature conditions, the lower the char could be obtained, since more organic mass was transferred to the liquid and gas phase. Finally, the medium temperature of 400°C seem to be suitable for pyrolyzing this material.
in order to carbonize part of the organic content and separate metal fractions with a particle size greater than 0.5mm.

5. Acknowledgements
The authors would like to acknowledge the fruitful cooperation with Stena Metall AB and Jernkontoret for the financial support.

6. References