

Distribution and characteristics of pyrolysis products from automobile shredder residue using an experimental semi-batch reactor

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Abstract—Automobile shredder residue (ASR) generated by end-of-life vehicles, comprises more than 20% of a new vehicle by weight. Significant amounts of polymers in ASR, such as Poly Propylene (PP), Poly Ethylene (PE), Acrylonitrile Butadiene Styrene (ABS), Ethylene Propylene Ethylidene Nobornene (EPDM), rubber, Polyethylene Terephthalate (PET), Poly Amide (PA), and Poly Vinyl Chloride (PVC), can be used as energy or chemical sources, whereas other components, such as tires, rubber, glass, wood, sand/dust, and heavy metals inhibit the recycling of ASR. In many countries, landfill use of ASR is regulated, so landfill costs have increased, as has inappropriate disposal; sending ASR to landfills will be needed to be regulated in Korea. Pyrolysis has been suggested as an economically feasible recycling and recovery technique for ASR in Korea and other advanced countries. Before such technology is implemented, the characteristics of pyrolyzed products should be investigated. Shredded samples from the facility were collected, and calorific value, elemental analysis, and leaching tests were performed to determine ASR characteristics. Pyrolysis experiments were conducted at five different temperatures, 400, 500, 600, 700, and 800 °C, and the product distributions of gas, tar, and char were investigated. The optimal temperature for ASR pyrolysis, in terms of yield efficiency, was found to be 600 °C. The mean calorific value was also found to be higher in this case; thus, ASR can be treated as an auxiliary fuel. During pyrolysis, there were high ignition losses of light and heavy fluff, due to the presence of organic materials. The leaching concentrations of all tested heavy metals were found to be within the Korean guideline values. In terms of carbon number distributions, pyrolysis of ASR at 600 °C was optimal. For further utilization of pyrolysis products as fuel, the characteristics of char, oil, and gas were investigated with an experimental batch reactor.

Key words: Automobile Shredder Residue (ASR), End-of-life Vehicle (ELV), Shredder Dust (SD), Pyrolysis

INTRODUCTION

The Korean automobile industry produced 3.2 million cars, exporting 1.8 million of them, in 2003. Fourteen million cars are currently used in the country, and 0.55 million end-of-life (ELVs) were generated and recycled per year [1]. The collected ELVs are transported to dismantlers to recover usable parts and separate waste fluids, batteries, and tires appropriately. Remaining components are shipped to shredder companies [2,3]. Then, the ELVs are shredded, separated into ferrous and non-ferrous content, and recycled [4-6]. What remains is called automobile shredder residue (ASR) or shredder dust (SD), which accounts for 20% of the total weight of a new car [7,8]. ASR is comprised of various materials, such as plastic, rubber, foam, textiles, glass, and dust, which makes it difficult to develop a thorough recycling process. As a result, most ASRs are dumped into landfills [5,9].

However, the lack of landfill sites and the exhaustion of resources have promoted the reuse of ELVs. In many countries, the landfill use of ASR is regulated; therefore, landfill costs and inappropriate treatment have increased. ASR does not biodegrade easily and includes heavy metals and toxic materials [10]. Therefore, alternative treatments of ASR, including reuse and recycling, are increasingly

considered [11].

The EU and Japan have set a target recycling rate of 95% of new vehicle weight and are experimenting with technologies to meet that target [2-4,12]. Korean regulations indicate that, prior to establishing a target recycling rate, the use of waste-reduction technologies should be implemented by those companies producing or importing 10,000 or more vehicles. Many ELV recycling studies have been conducted by Western vehicle producers [7]. For a vehicle-exporting country, guidelines for treatment and recycling of ELVs are essential. The presence of chloride makes it difficult to incinerate ASR safely. Emitted toxic materials, such as HCl, fly ash, VOC, and dioxin, must also be treated in the process. ASR treatment also poses closely connected environmental and economic problems. In spite of these problems, ASR can be used as an energy and chemical resource; however, energy input is needed to recover or recycle component materials. For these reasons, pyrolysis is preferred [7,8]. Pyrolysis is a notable treatment technology for such materials as wood, residual leather, tire, waste plastics, and biomass wastes [10,13]. Pyrolysis converts organic compounds to byproducts, such as pyrolysis gas, oil, and char. The produced gas can be used as heating fuel [13].

Rausa and Pollesel [14] studied the characteristics of byproducts of ASR pyrolysis at 650, 800, and 850 °C and found that cyclopentadiene production increases with temperature. Day et al. [8] studied the yields of solid, liquid, and gas products of ASR at 500-700 °C,

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using 100 kg/h screw kiln pyrolysis facility. Galvagno et al. [15] evaluated byproduct characteristics and process performance at 550, 600, and 680 °C with a pilot-scale pyrolysis facility. Solid and liquid products were produced, and the highest oil yield ratio was at 600 °C [15]. Roy et al. [13] studied pyrolysis products of North American and European ASR, using vacuum pyrolysis. The material balance and distribution with the development of dry gasification devices was also studied, and the use of this device further reduced dioxin [3,13]. Pyrolysis processes have developed very rapidly, but more research is required to optimize the treatment of shredder dust [16].

In this study, the thermal characteristics of ASR from ELVs are evaluated at various temperatures in a lab-scale reactor; the toxicities of the pyrolysis byproducts are also analyzed. The characteristic data of pyrolysis products for Korean ASR might be used to minimize waste produced during fuel recovery. These results can then be used for the development of an environmentally friendly process for energy and chemical recovery from ASR.

METHODOLOGY AND MATERIALS

1. Experimental Method

Experimental devices used in this study were divided into three groups: the feeding system, the reactor, and the sampling parts. The feeding system was made of stainless steel (SUS304); after air was removed from the samples by purging them with nitrogen, the samples were dropped into three stages. The reactor, also made of stainless steel (SUS304), was 300 mm in height and 100 mm in inner diameter. Internal temperatures could be adjusted within an accuracy of ± 10 °C. Product gases from the reactor were condensed into 6 impingers, and non-condensable gases were passed over a flow meter and sampled by a Tedlar bag. Pyrolysis experiments were conducted after the air inside the reactor was removed by purging with nitrogen; each ASR sample had a mass of 10 to 20 g and was fed 20 to 40 times (5 min per sample). Yield ratios of pyrolysis tar, oil, gas, and char were calculated by comparing sample masses with total product masses.

2. Analysis Method

Thermogravimetric analysis (TGA, Leco TGA-601) was conducted for combustible components (plastics, spongy, rubbers, woods, papers, etc.), shredding them to less than 2 mm in a reduction atmosphere (N_2 , 6 L/min) with a temperature increase rate of 10 °C/min. The reduction condition was obtained, by using nitrogen as a carrier gas. Calorific values were evaluated with a calorific meter (Leco, AC-350). Gas chromatography (GC: HP-6890) was used to evaluate the components of pyrolysis tar. Table 1 shows the analysis conditions of GC. And the production gases by pyrolysis were

Table 1. GC/FID operating conditions to measure tar composition

| | |
|----------------------|---------------------------------------------------------------------------|
| Column | 60 m × 0.25 mm, DB-1 |
| Film thickness | 0.25 μ m |
| Carrier gas | N_2 |
| Detector | Flame ionization |
| Detector temperature | 300 °C |
| Injector temperature | 250 °C |
| Temperature program | 40 °C, Isothermal 15 min 2 °C min^{-1} to 200 °C, Isothermal 105 min |

analyzed also GC/FID and GC/TCD. A scanning electron microscope (SEM) was used to inspect the detailed structure of the char. Particle and pore sizes were measured with a particle and pore size analysis system (Microtrac, UPA-150). A leaching test to evaluate environmental toxicity was performed by using the Korean standard method [17]. Inductively Coupled Plasma/Mass Spectroscopy (Varian, Ultramass 700) was used to analyze the total amount of heavy metals in the ASR, char, and tar. Samples were shredded to less than 2 mm, and, when needed, pretreatment was conducted according to the EPA 3050B methods [18].

RESULTS AND DISCUSSION

1. Characteristics of ASR

1-1. Composition

Shredder residue is comprised of organic materials, such as plastic, rubber, and urethane foam, inorganic materials, such as glass, steel, wiring (called "harnesses"), and nonferrous metals. ASR is comprised of more than 20 different plastics, several types of rubber, and 12 different metals [19]. Table 2 shows the physical composition and the calorific values of the analyzed ASR. The ferrous material includes metal pieces, springs, iron plates, wires, screws, nuts, bolts, and non-ferrous material includes copper wire, zinc, aluminum, and stainless steel. Other materials include organic components, such as rubber, plastic, textiles, papers, and sponges; the remaining 3.8% was composed of miscellaneous components (Table 2). The calorific values of these ASR components were also measured; the value was 4,000 kcal/kg for rubber, textile, wire, sponge, plastics, and paper excluding that for woods and glass/soil/sand were less. The average calorific value of ASR was about 5,000 kcal/kg; the plastic component had a calorific value of 9,086 kcal/kg, the greatest value of any component [20]. Due to its high calorific value, ASR can thus be thermally treated as auxiliary fuel. Shredder residue has substantial energy, material, and mineral value [20]. Plastic recoveries from SR, as well as the use of SR as a feedstock for pyrolysis and as a supplement for waste combusting and cement manufacturing, have also been implemented [9,22,23].

1-2. Physical and Chemical Characteristics of ASR

Table 3 gives the results of the elemental analysis of ASR. The moisture content of ASR was about 1%, and combustible materials

Table 2. Composition and calorific values of ASR

| Materials | Composition (%) | Calorific value (kcal/kg) |
|---------------|-----------------|---------------------------|
| Metal | 1.1 | - |
| Rubber | 6.3 | 5,526 |
| Textiles | 24.3 | 4,073 |
| Wire | 2.0 | 4,950 |
| Sponge | 16.9 | 4,532 |
| Plastic | 22.6 | 9,086 |
| Wood | 0.6 | 3,757 |
| Paper | 4.6 | 4,043 |
| Soil/sand | 16.0 | 1,378 |
| Glass | 1.8 | - |
| Other | 3.8 | 7,517 |
| Total/Average | 100.0 | 4,970 |

Table 3. Proximate and element analysis of ASR

| wt (%) | Moisture | Combustible | Ash | C | H | O | N | S | Bulk density (kg/m ³) |
|-----------------|----------|-------------|-------|-------|-------|-------|------|------|-----------------------------------|
| Light fluff | 0.14 | 80.80 | 19.06 | 61.68 | 8.96 | 22.48 | 4.74 | 0.00 | 136 |
| Heavy fluff | 1.23 | 76.47 | 22.30 | 64.75 | 10.07 | 12.06 | 0.13 | 0.14 | 263 |
| Glass/soil/sand | 0.89 | 43.68 | 55.43 | 17.23 | 1.94 | 7.56 | 0.63 | 0.00 | 545 |
| Mixed sample | 0.38 | 75.39 | 24.23 | 56.24 | 8.18 | 19.21 | 3.62 | 0.02 | 206 |

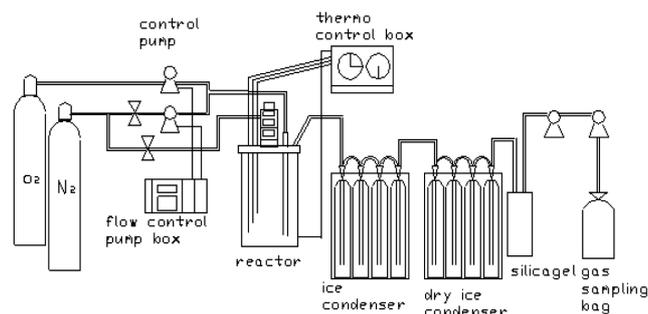


Fig. 1. Schematic diagram of pyrolysis equipment.

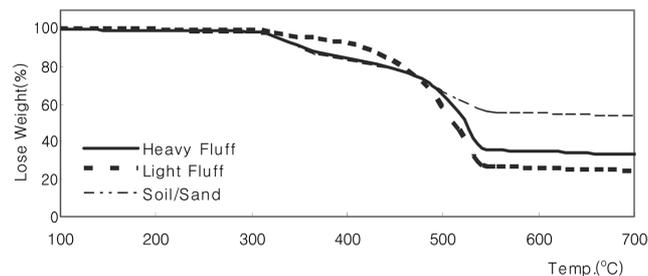


Fig. 2. TGA results of fluffs and soil/sand/glass.

accounted for 80.80%, 76.47%, and 43.68% of light fluff, heavy fluff, and soil/sand/glass, respectively, as measured by an ignition loss test. The high ignition loss was due to the presence of organic materials, which were dominant in light and heavy fluffs. In the soil/sand/glass component, the non-combustible materials resulted in less ignition loss and higher ash content (55.4%). It is notable that, due to their high organic content, ASRs are particularly well-suited for pyrolysis. The ash content of the mixed sample accounts for about 5% of a new vehicle by weight [8].

Furthermore, the measured heavy and light fluffs were 64.75% and 61.68% carbon, respectively, which is a much higher percentage than in the soil/sand/glass sample. Roy et al. [13] also reported high carbon content in the fluffs. The heavy and light fluffs were both about 10% hydrogen and 12.06% and 22.48% oxygen, respectively. Nitrogen and sulfur concentrations were lower due to the low rubber content (6.3%) of ASR.

1-3. Thermal Characteristics of ASR

Fig. 2 gives the results of the thermo-gravimetric analysis of the analyzed light fluff, heavy fluff, and soil/sand/glass. The ash content after thermal treatment of the ASR was 33%; more specifically, it was 17%, 28%, and 53% for light fluff, heavy fluff, and soil/sand/glass, respectively; at higher temperature. The lower solidity of the residue after thermal treatment was attributed to higher organic content in the ASR. Other researchers have obtained a similar range of

Table 4. Results of the leaching test for ASR by the Korean standard method

| (mg/L) | As | Cd | Cr | Cu | Pb | Hg |
|------------------|-------|-------|-------|-------|-------|-------|
| Heavy fluff | 0.014 | N.D. | 0.007 | 0.138 | 0.912 | N.D. |
| Light fluff | N.D. | N.D. | 0.016 | 0.888 | 1.142 | N.D. |
| Glass/soil/sand | N.D. | N.D. | 0.016 | 0.532 | 0.785 | N.D. |
| Korean guideline | 1.500 | 0.300 | 1.500 | 3.000 | 3.000 | 0.005 |

Detection limit 0.001 mg/L

results [8,9,24]. The greater part of ASR decomposition took place between 312 °C and 557 °C.

The TGA results for heavy fluff exhibit multiple decomposition stages (Fig. 2) due to the high content of rubber and plastics. The result agrees with the findings [25]. This result also shows that the measured residual content agrees well with the results of proximate analysis. After thermal treatment, ash content will account for about 7%, whereas, in direct landfilling, the content will account for 25% to 30% of a new car. Based on volume reduction, then, thermal treatment is a better method than direct landfilling.

1-4. Assessment of the Environmental Toxicity of ASR

Many heavy metals are used in the manufacturing of vehicles, such as lead or bronzed silver in bearing shells, Cr(IV) in anti-sound coating material, and mercury in indicator lights on the display [2,8, 26]. The leaching concentrations of all the tested heavy metals were found within the Korean guideline values (Table 4). The leaching concentrations of Pb and Cu were 0.785-1.142 mg/L and 0.138-0.888 mg/L, respectively, higher than those of the others. Cd and Hg were not detectable in the sample, and As was detected only in the heavy fluff sample. This shows that further processing for heavy metal removal is not required to meet the Korean guideline values and, thus, the waste was safe to dump in a landfill. Nevertheless, it is notable that EU countries require that such heavy metals not be used at all, which might prompt investigation of any further treatment, like a thermal melting technology, for the final residue.

1-5. Heavy Metal Content of ASR

Table 5 shows the metal content of three streams of ASR. Even after magnetic separation and non-ferrous metal separation, Al, Cu, Fe, and Zn were all significantly present in the ASR samples. Similar results were also obtained by Schmitt [25], and Roy and Chala [13]. Generally, more metals were found in glass/soil/sand, heavy fluff, and light fluff, in decreasing order. This result shows that some metals could be recovered, by using appropriate chemical or physical means, as in the copper smelting industry. The total concentrations of those elements were different between soil/sand/glass and light fluff; however, the ratios of the materials were similar.

2. Characteristics of Pyrolysis and Byproducts by Pyrolysis of ASR

2-1. Characteristics of Pyrolysis at Various Temperatures

Table 5. Metal content (mg/kg) of ASR

| Metal | Light fluff | Heavy fluff | Glass/soil/sand |
|-------|-------------|-------------|-----------------|
| Al | 2,208.2 | 568.7 | 4,893.9 |
| As | 8.2 | N.D. | N.D. |
| Cd | 1.5 | 2.7 | 5.2 |
| Cr | 28.3 | 5.0 | 204.3 |
| Cu | 10,889.7 | 17.7 | 69,131.8 |
| Fe | 11,815.3 | 804.1 | 51,411.3 |
| Mn | 137.4 | 43.5 | 534.0 |
| Ni | 32.7 | 2.9 | 68.4 |
| Pb | 673.9 | 456.5 | 2,160.0 |
| Ti | 75.5 | 17.0 | 413.3 |
| V | N.D. | 1.4 | N.D. |
| Zn | 2,375.7 | 2,895.8 | 16,812.0 |
| Si | N.D. | N.D. | 1,700.7 |
| Ca | 4,444.7 | 17,150.2 | 29,726.2 |
| K | 368.8 | 134.4 | 666.6 |
| Mg | 663.1 | 642.5 | 3,822.6 |
| Na | 1,087.7 | 325.1 | 1,095.0 |

N.D.=Not detected.

Detection limit 0.1 mg/L

Table 6. Composition of products of pyrolysis reactions at various temperatures

| (%) | 400 °C | 500 °C | 600 °C | 700 °C | 800 °C |
|------|--------|--------|--------|--------|--------|
| Gas | 38.7 | 42.2 | 45.8 | 47.4 | 44.6 |
| Tar | 12.3 | 13.6 | 18.2 | 13.4 | 14.4 |
| Char | 49.0 | 44.2 | 36.0 | 39.2 | 41.0 |

The yield percentages of gas and tar were calculated by dividing the weight of each product by the total weight. The pyrolysis of ASR is complex and occurs in a series of reactions. Therefore, reaction conditions affect the production ratios and the compositions of byproducts. Variables that affect the byproduct yield ratio include reaction time, temperature, and pressure. In addition, byproduct compositions also vary with yield ratios [6,10,14].

To find the optimal reaction temperature (600 °C) in a lab scale pyrolysis reactor, experiments were performed at 400, 500, 600, 700, and 800 °C; measured yield ratios are shown in Table 6. The tar production rates were 12.3%, 13.6%, 18.2%, 13.4%, and 14.4%, respectively; in particular, the highest rate occurred at 600 °C. Previous research suggests that, as temperature increases, char yield decreases [10,14]. This result agreed with ours obtained for tem-

Table 7. Major compounds in gas produced by pyrolysis reactions at various temperatures (vol%)

| Items | 400 °C | 500 °C | 600 °C | 700 °C | 800 °C |
|-----------|--------|--------|--------|--------|--------|
| Hydrogen | 1.24 | 2.79 | 5.35 | 7.69 | 11.03 |
| Methane | 4.04 | 8.86 | 10.50 | 29.97 | 33.53 |
| Ethylene | 2.04 | 3.95 | 3.02 | 4.79 | 3.81 |
| Propane | 1.99 | 0.62 | 3.37 | 9.61 | 18.65 |
| Propylene | 0.92 | 1.15 | 0.59 | 0.22 | 0.03 |
| n-Butane | 2.67 | 1.78 | 3.40 | 3.59 | 1.13 |
| Acetylene | 0.30 | 0.36 | 0.05 | 0.04 | 0.00 |
| Others | 86.80 | 80.49 | 73.72 | 44.09 | 10.26 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

peratures between 400 and 600 °C; char yield increased at 700 °C and 800 °C. Galvagno et al. [15] also reported a decreasing trend of char yield at 550, 600, and 680 °C. At higher reaction temperatures, the production of decomposable organic compounds and gases both increased. As reaction temperature increased past 700 °C, tar production decreased.

2-2. Characteristics of Production Gas as gaseous Byproducts

Non-condensable pyrolysis byproduct gas is called "production gas." The composition of product gas was analyzed by GC/FID, for hydrocarbon compounds and by GC/TCD for non-hydrocarbon compounds, and the results of the analysis are given in Table 7. A major component was CH₄, the production (or generation) of which increased with temperature, from 4.04-33.53% by volume. As reaction temperature increases, the portions of hydrogen and methane increase rapidly. At 800 °C the proportions are 11.03% and 33.53%, respectively. The concentrations of propylene and acetylene decreased, although not sharply, but the other components of the product decreased sharply with increasing temperature. These noncondensable gases have high energy content and can be safely used for a make-up heat source for the process [13].

2-3. Characteristics of Tar Byproducts

Pyrolysis tar has many uses. Table 8 shows the moisture, specific gravity, and calorific value of tar. An ASTM D-95 was used to analyze moisture content. Moisture content was lower than 1%, and specific gravity ranged from 0.8 to 1.0. The calorific values decreased as reaction temperature increased, but the values were still greater than 9,000 kcal/kg, similar to that of fuel oils.

The area percentage of BTX in tar produced at various reaction temperatures can be analyzed. The area of benzene increases with reaction time. Xylene production peaked at 600 °C; the decrease at higher temperatures was due to a xylene synthesis polymer with a

Table 8. BTX peak area percents of tars from pyrolysis reactions at various temperatures

| (°C) | Moisture (%) | Specific gravity | Benzene (%) | Toluene (%) | Xylene (%) | Calorific value (kcal/kg) |
|------|--------------|------------------|-------------|-------------|------------|---------------------------|
| 400 | 0.7 | 1.00 | 1.01 | 1.23 | 0.00 | 9,436 |
| 500 | 0.2 | 0.97 | 3.10 | 4.06 | 3.40 | 9,492 |
| 600 | 0.2 | 0.88 | 1.06 | 12.02 | 5.50 | 9,257 |
| 700 | 0.2 | 0.98 | 26.45 | 20.51 | 4.20 | 9,192 |
| 800 | 0.3 | 0.80 | 29.62 | 13.80 | 1.71 | 9,149 |

BTX=Benzene, Toluene, Xylene.

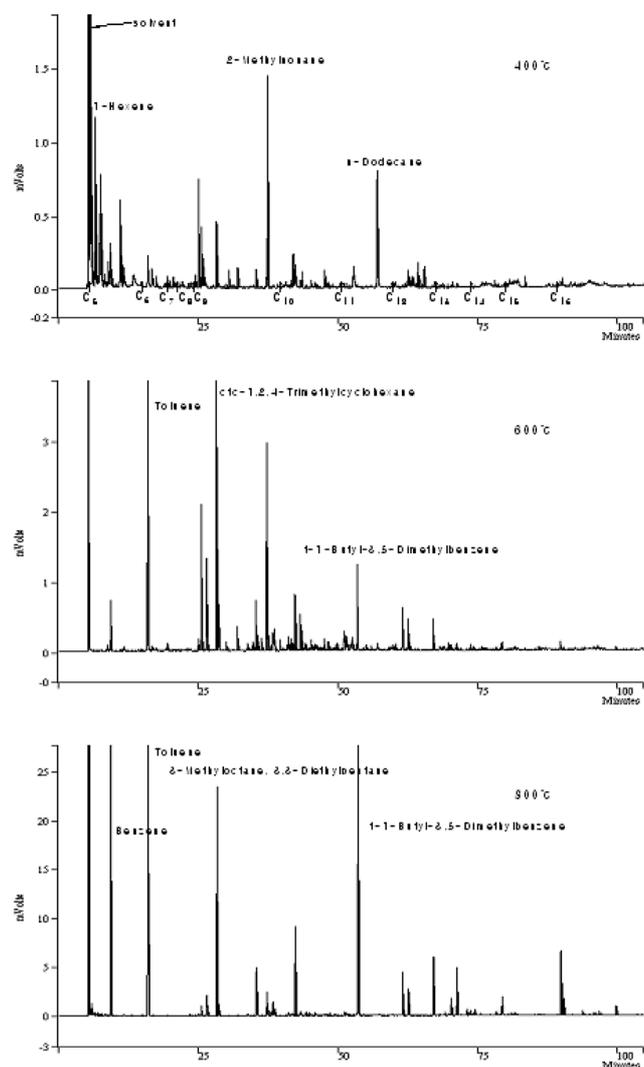


Fig. 3. Major compounds in tar produced by pyrolysis reactions at various temperatures, as measured by GC/FID.

high molecular weight. The distributions of major compounds in tar from pyrolysis are reported for various temperatures in Fig. 3. The relative distributions of carbon numbers were $C_9 > C_5 > C_{12} > C_{10} > C_6$ at 400 °C, $C_9 > C_8 > C_{11} > C_{12} > C_7$ at 500 °C, $C_9 > C_{11} > C_8 > C_{10} > C_{12}$ at 600 °C, $C_7 > C_8 > C_9 > C_{11} > C_{10}$ at 700 °C, and $C_7 > C_{11} > C_9 > C_8 > C_{13}$ at 800 °C. As temperature increased, so did the proportion of compounds with higher carbon number. Most of these compounds were aromatic compounds because low molecular weight compounds tend to be of higher molecular weight compounds through cationic and radical polymerization of aromatic compounds, rather than aliphatic compounds. The decomposition rates of C_9 compounds also show peak values of around 40% at 600 °C, in agreement with previous studies [8,10]. From analyzing the carbon number distributions, 600 °C was found to be optimal for ASR pyrolysis.

2-4. Characteristics of Char as Solid Byproducts

The solid byproducts of pyrolysis are organic compounds, such as fixed carbon and ash. Table 9 gives the characteristics of solid byproducts at various temperatures. As temperature increases, the portion of ash increased, but the portion of organic material decreased. The portion of fixed carbon increased with temperature at temperatures higher than 600 °C, however, and reached about 30% at 800 °C.

The compositions of solid products are significantly affected by temperature and residence time, as well as by initial moisture content, heat transfer coefficient, and sample composition. The calorific

Table 9. Proximate analysis and calorific value of char produced from pyrolysis reactions (%)

| (°C) | Moisture | Volatile | Fix-carbon | Ash | Calorific value (kcal/kg) |
|------|----------|----------|------------|-------|---------------------------|
| 400 | 5.12 | 19.40 | 19.97 | 55.53 | 2,824 |
| 500 | 3.94 | 11.45 | 15.91 | 68.71 | 2,420 |
| 600 | 3.59 | 6.70 | 17.15 | 72.57 | 2,364 |
| 700 | 3.83 | 4.91 | 18.94 | 72.34 | 2,045 |
| 800 | 4.78 | 4.82 | 29.88 | 60.54 | 2,072 |

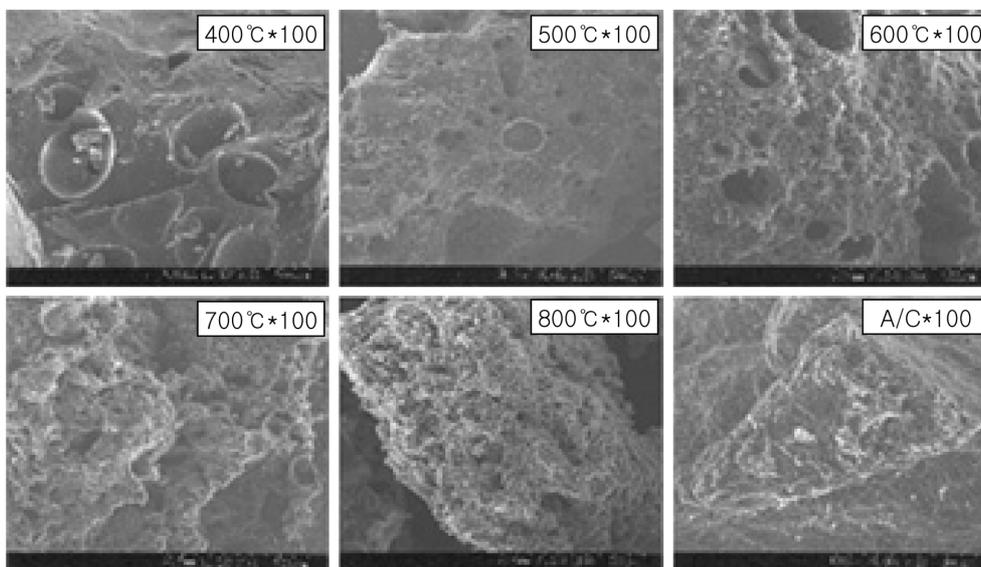


Fig. 4. SEM images of chars, generated by pyrolysis reactions, at various temperatures ($\times 100$).

value of char was 2,000-2,800 kcal/kg and decreased with increasing temperature; this trend was related to the organic material contained in char. Roy et al. [13] also reported a higher correlation between organic content and calorific value.

Fig. 4 depicts the detailed structure of char at various temperatures, as pictured by a SEM. Pores were detected in chars when reaction temperatures were greater than 500 °C. The biggest pore size was detected at 600 °C. Above that temperature, pore size decreased, yet greater numbers of fine pores were formed. At lower temperatures, isolated scissions and β scissions of C-C bonds of lower polymers decomposed into higher molecular weight compounds, generating pores. At higher temperatures, instantaneous, isolated scissions of C-H bonds occurred, tending to produce smaller but more pore char which exhibits more fine pores than commercialized carbon does [9,10,14].

Table 10 and Fig. 5 gives the analyzed results of a particle and pore size analysis (microtrac, UPA-150). The largest measured pore size was 21.718 nm at 500 °C; at higher temperatures, the largest measured pore size decreased as temperature increased. The BET surface area ranged from 3.089 to 6.399 m²/g. BJH pore volume values also increased with temperature. These results also supported the SEM observation.

3. Characteristics of Heavy Metal Contents in Byproducts by Pyrolysis

3-1. Heavy Metal Contents in Tar

Table 10. Characteristics of char produced by pyrolysis reactions at various temperatures

| | 400 °C | 500 °C | 600 °C | 700 °C | 800 °C |
|--------------------------------------|--------|--------|--------|--------|--------|
| Pore size avg. (nm) | 15.150 | 21.718 | 18.469 | 17.420 | 15.526 |
| BET surface area (m ² /g) | 3.089 | 3.305 | 3.682 | 4.287 | 6.399 |
| BJH pore volume (cm ³ /g) | 0.010 | 0.018 | 0.016 | 0.023 | 0.032 |

Surface Area and Pore Volume: Desorption.

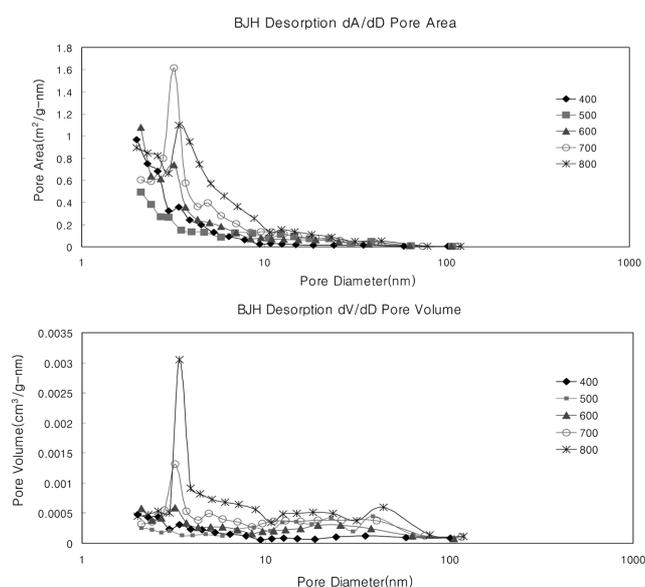


Fig. 5. Pore size distribution of char generated by pyrolysis reactions at various temperatures.

Pyrolysis tar contains many chemicals, including metals. Table 11 gives the metal content of the measured pyrolysis tar. The Fe, Zn, and Al contents of tar are relatively greater than the other metals, which existed in greater quantities in ASR prior to pyrolysis. The metal composition of tar was affected by the initial composition in ASR. However, the metal content of tar exhibited no dependencies on pyrolysis temperature. Metal in tar seems to be produced when fine particulate matter, emitted with gas, is trapped by tar condensation.

3-2. Heavy Metal Content of Char

At higher temperatures, the distribution of metals remaining in char after ASR pyrolysis was related to both the initial metal content and the boiling points of various metal compounds. Table 12 shows the distributions of various metals in char. The amounts of Al, Fe, and Ni increased with temperature due to the decreasing amounts of produced char; these metals could not be evaporated and thus were concentrated. The amounts of Cd, Cr, Cu, Pb, and Zn decreased with increasing temperature. The ranges of metal contents were 4,291.3-12,635.9 mg Al/kg, 8,203.2-22,197.2 mg Cu/kg, 39,214.2-89,432.2 mg Fe/kg, and 5,234.8-5,560.6 mg Zn/kg; these distributions resemble the initial content levels. Similar results were also noted earlier [13]. In char, Hg is quite concentrated, with distributions varying from 0.020 to 0.084 mg/kg. The metal content of char was related to both the composition of the original ASR

Table 11. Metal contents (mg/L) in pyrolysis tar at various reaction temperatures

| Metal | 400 °C | 500 °C | 600 °C | 700 °C | 800 °C |
|-------|--------|--------|--------|--------|--------|
| Al | 5.547 | 7.203 | N.D. | 7.484 | N.D. |
| Cd | 0.004 | 0.014 | 0.020 | N.D. | 0.030 |
| Cr | 2.667 | 1.713 | 1.093 | 0.380 | 0.233 |
| Cu | 0.259 | 1.021 | N.D. | N.D. | 2.795 |
| Fe | 27.177 | 61.266 | 8.622 | 6.916 | 7.216 |
| Ni | 2.877 | 6.672 | 0.641 | N.D. | N.D. |
| Pb | 1.969 | 5.252 | 6.417 | 0.982 | 2.500 |
| V | 0.005 | 0.103 | 0.013 | 0.032 | N.D. |
| Zn | 20.543 | 22.742 | N.D. | 32.094 | N.D. |

N.D.=Not detected.

Detection limit 0.001 mg/L

Table 12. Metal contents (mg/kg) in pyrolysis char at various reaction temperatures

| Metal | 400 °C | 500 °C | 600 °C | 700 °C | 800 °C |
|-------|----------|----------|----------|----------|----------|
| Al | 4,291.3 | 6,127.2 | 8,303.8 | 9,508.8 | 12,635.9 |
| Cd | 10.2 | 13.1 | 19.7 | 8.5 | 4.8 |
| Cr | 135.1 | 195.1 | 143.4 | 122.5 | 90.3 |
| Cu | 15,450.3 | 22,197.9 | 14,338.9 | 8,203.2 | 8,983.4 |
| Fe | 71,604.1 | 39,214.2 | 47,823.8 | 65,025.2 | 89,432.4 |
| Ni | 129.4 | 161.5 | 217.4 | 205.7 | 205.2 |
| Pb | 2,028.1 | 3,069.1 | 2,249.9 | 2,109.8 | 1,533.1 |
| V | 12.7 | 14.1 | 15.6 | 16.5 | 19.0 |
| Zn | 7,335.9 | 6,221.7 | 8,560.6 | 7,621.9 | 5,234.8 |
| Hg | 0.084 | 0.033 | 0.022 | 0.020 | 0.081 |

N.D.=Not detected.

and the corresponding boiling points.

CONCLUSIONS

The results of the study of SASR characteristics and the pyrolysis experiments can be summarized as follows:

1. ASR contains combustible materials. The average calorific value was about 5,000 kcal/kg, which is appropriate for energy recovery by thermal treatment.

2. The tar yield ratio was 12.3 to 18.3%, that of gas was 38.7 to 45.8%, and that of char was 36.0 to 49.0%. In terms of tar yield, 600 °C was the optimal pyrolysis temperature for ASR.

3. Gas composition analysis revealed that hydrogen, methane, propane, acetylene, and butane were major products. The mass fraction of methane and propane increased from 4.04 to 33.53% and from 1.99 to 18.65%, respectively, as pyrolysis temperature increased from 400 °C to 800 °C. These noncondensable gases have high energy content and can be safely used for a make-up heat source for the process.

4. The calorific value of tar was about 9,000 kcal/kg; the content of tar increased with temperature. The carbon distribution of tar at 600 °C was in the vicinity of C₉.

5. Scanning electron microscope images of char products showed that pore size decreased and pore count increased with temperature. The surface area and pore volumes exhibited similar trends by temperature changes. This might be due to scission processes that varied with temperature.

6. Leaching concentrations of the heavy metals tested were found to be within the range of Korean guideline values. Cd and Hg were not detectable in the sample, and As was detected only in the heavy fluff sample. This shows that further processing for the heavy metal removal is not required to meet the Korean guideline, and in particular, that the material can be stored in a landfill relatively safely.

7. Al, Fe, Zn, and Cu occurred in relatively large proportions in ASR; the distribution of these metals in char produced by pyrolysis was similar to that of raw ASR. The concentrations of metals in tar and char were similar to that of raw ASR, regardless of the metal boiling points.

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