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Pyrolysis of automobile shredder residue: an analysis of the products of a commercial screw kiln process¹

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Abstract

The products from the pyrolysis of automobile shredder residue, the waste produced in the recycling of old automobiles, have been studied. The pyrolysis process employed in the study was a commercial screw kiln unit. The chemical composition of the gas, liquid and solid fractions have been analyzed using a variety of techniques. The results of these analyses suggest that, while pyrolysis may represent a viable process for separating the organic materials from the inorganics, a full commercialization of the process must await a more detailed evaluation of the marketability of the products and their acceptance as feeds for full resource recovery.

Keywords: Automobile shredder residue; Pyrolysis; Screw kiln pyrolysis

1. Introduction

Automobile shredder residue (ASR), commonly referred to as “auto fluff”, is produced as a waste stream when scrap vehicles are shredded to recover metals. The material is a complex mix composed of plastics, foams, rubber, glass, moisture, dirt and small fragments of unrecovered metals contaminated with fluids and lubricants [1]. In North America there are 204 shredding operations which together produce about 3 million tons of ASR each year [2]. Although ASR is not considered a hazardous material in the majority of the US and Canada, it is a regulated material in most states and provinces due to concerns regarding the presence of heavy metals such as cadmium and lead, along with PCBs [3]. Consequently, there has been a

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great deal of interest in various recycling/recovery options for ASR as opposed to the current practice of landfilling the material [4].

One of those options which is receiving a great deal of attention is pyrolysis. The rationale for favoring pyrolysis as a disposal option lies in the complex nature of the waste material which may inhibit the economics of other processes. Because ASR is a complex mixture of numerous polymeric organic materials [5] these macromolecular hydrocarbons can be thermally degraded by heat to produce smaller fragments [6,7] which can be used as fuels or petrochemical feedstocks. Although many pyrolysis processes have been developed over the years to deal with a wide variety of feed materials such as biomass, used tires and plastic wastes [8], data on the pyrolysis of ASR in the open scientific literature is still scarce [9–15].

In this paper, the chemical composition of the various fractions obtained from the pyrolysis of ASR using a screw kiln reactor are presented. Based upon a detailed chemical analysis of the products of pyrolysis it is possible to get a better understanding of the commercial viability of the process for the production of hydrocarbon fuels and chemical feedstocks.

2. Experimental

2.1. The pyrolysis process

The pyrolysis unit employed in this study of ASR was a commercial screw kiln system located at the facilities of NATRL Inc. in Wind Gap, PA, USA. The process was designed for the pyrolysis of scrap tires to produce carbon black, oil and combustible gases. The unit, which is shown schematically in Fig. 1, consists of a heated reactor zone, located within a combustion chamber. The ASR feed was fed to the screw via a double lock feed hopper. The feed rate used in this study was approximately 200 kg h^{-1} which corresponded to a residence time of about 15 min. The residual solids after pyrolysis were discharged from the reactor into a catch pot. The catch pot was fitted with a screen separator in order to separate the solids into two streams: a fines portion and a coarse portion. In addition, magnetic separation was performed on the solids residue fractions in order to isolate the magnetic fraction. The hot gases subsequently flowed through a condenser to condense the pyrolytic liquid fraction. The remaining non-condensable gases were then either flared or recycled to be burnt in the combustion chamber as a replacement for the natural gas fuel.

Although the temperature inside the combustion furnace was maintained at $700\text{--}760^\circ\text{C}$ during the 4 day experiment, the average temperature reached by the solid product in the pyrolysis unit was estimated to be about 500°C , at the exit of the reactor. This estimate was based upon a measured exit gas temperature of 450°C .

2.2. The ASR feed material

The ASR material used in this study was prepared in Ontario, Canada, and shipped to the pyrolysis site by truck. This ASR material was produced using a conventional dry shredding process in which the ASR was removed from the metals by an air classification system. The stream was then hand picked to remove any large metallic fractions that were carried over, prior to being passed through a second stage shredding operation to reduce the size such that the material passed through a 50 mm screen. This second stage shredding of the ASR was introduced in order to ensure a more uniform sized material for the reactor.

Although this particular waste stream was not characterized prior to pyrolysis, it could be anticipated to have properties similar to material characterized in an earlier study [16].

This characterization study indicates that the ASR produced in North America can contain from 1% to 25% moisture, although a value of about 6% is typical. In terms of organic content 45% represents an average value, although values from 60% to 30% have been reported. In terms of elemental composition the following analysis is typical of material being produced in Ontario by operations such as the one that provided the material for this study: C 30%; H 3.7%; O 7%; N 1.7%; S 0.3%; Cl 1.4%; Fe 13%; Si 9.5%.

Fig. 1. Schematic of the screw kiln pyrolysis unit.

2.3. Sampling procedures

The gaseous, liquid and solid samples analyzed in this study were collected approximately 18 h after the commencement of the pyrolysis trial. Gas samples were collected in two pre-evacuated stainless steel cylinders (500 ml each). The collection point was located between the condenser and the gas splitter. The pyrolysis liquid was collected in three glass jars (350 ml each) at the exit of the discharge pipe. Samples of both the fines and coarse solids were each scooped into 350 ml glass jars from the collection bins. It should be noted that the gaseous, liquid and solid samples so collected were only grab samples and their composition, reported in this study, only reflect those at the time of sampling and might not be representative of the average pyrolysis products during the complete 4 day trial. However, these samples do provide some valuable information about the nature of the products of ASR pyrolysis. These grab samples were then brought to the laboratories of the Institute for Chemical Process and Environmental Technology of the National Research Council Canada for subsequent analysis.

2.4. Analysis of the pyrolysis gas

The chemical analysis of the components of the pyrolysis gas was conducted using a Hewlett Packard (HP) 5890 Series II gas chromatograph (GC). Two different analytical procedures were employed to separate and identify the chemical species. In the first procedure the analytical approach was to use a 3.6 m $\times$ 3 mm Porapak Q (80/100 mesh) packed stainless steel column, programmed with an isothermal hold at -80°C for 7 min, followed by a ramp of $40^{\circ}\text{C min}^{-1}$ to 230°C where it was held for a further 20 min. The separated gases were detected using a thermal conductivity detector (TCD) operated at 250°C . Gas samples (1 ml) were injected into the system using a stainless steel gas injection loop hooked up to a two position rotary Valco valve.

Gas samples were also analyzed using a HP 5970B Series mass-selective detector. In this analysis the separation was achieved using a J&W Scientific 30 m $\times$ 0.25 mm, 0.25 μm DB-5 coated capillary column programmed with an isothermal hold at -50°C for 3 min, followed by a $15^{\circ}\text{C min}^{-1}$ ramp to 120°C , a $30^{\circ}\text{C min}^{-1}$ ramp to 240°C and a final hold of 20 min at 240°C . The mass spectrometer, which was interfaced to the GC at a temperature of 240°C , was operated at a vacuum of 3×10^{-5} Torr with an electron impact energy of 70 eV. Once again a 1 ml gas sample loop was used but a split ratio of 83:1 was employed for the analysis.

2.5. Analysis of the pyrolysis liquid

The pyrolysis liquid was found to contain oil, water and sediment. Analysis of these components was achieved using a two-step approach. First the liquid was centrifuged at 2100 rev min^{-1} for 2 h to isolate the sediment. The Dean and Stark procedure [17] was then used to determine the water content.

Table 1
Material balance for the pyrolysis of the ASR

	Mass (kg)	Mass (%)
Input of ASR	18350	
<i>Material output:</i>		
Pyrolysis gas	4660	26
Pyrolysis oil	3840	21
Pyrolysis water	1890	10
Total pyrolysis liquids	5730	31
Magnetic material	2090	11
Fines	4640	25
Coarse	1230	7
Total residual solids	7960	43

The isolated oil fraction was then subjected to further analysis. The elemental carbon, hydrogen and nitrogen composition in the oil sample was determined by a combustion method using a Perkin–Elmer 240C elemental analyzer. A 2 mg oil sample was weighed into a platinum boat which was then introduced into the cool end of the combustion tube. The entrance to the tube was sealed and the tube was flushed with helium for 2 min. Oxygen was then introduced into the helium carrier gas stream and the sample in the boat was moved into the combustion zone of the tube where the temperature was approximately 1000°C. All organic materials were completely burnt at this temperature producing CO₂, H₂O, NO and NO₂. The products of the combustion were flushed with helium through the remaining part of the tube which contained various silver salts to absorb any products formed due to the presence of sulfur or halogens in the sample. The gases then passed through a tube containing copper at 650°C, where NO and NO₂ were reduced to N₂. After this, the mixture of CO₂, H₂O, N₂ and the helium gas was passed through three pairs of thermal conductivity cells and traps. Between the first and second cells there was a trap containing magnesium perchlorate to absorb H₂O, and a trap with “Ascarite” was in between the second and third cells for CO₂ absorption. The concentrations of CO₂, H₂O and N₂, which were related to the C, H and N content in the sample, were determined based on the three thermal conductivities of the gas mixture.

The concentration of organic oxygen in the sample was determined based on the method of Unterzaucher [18]. Essentially in this technique 2–10 mg samples were pyrolyzed in a nitrogen stream with the products being swept over a bed of carbon at 1000–1135°C which converts the organic oxygen into CO₂ which is adsorbed and measured by coulometric titration.

Sulfur in the oil was determined using a LECO SC-32 sulfur determinator according to the procedure outlined in the manufacturer’s manual (LECO Corporation) [19]. Chlorine in the sample was determined in accordance with ASTM test method E442-74 [20].

Table 2
Composition of the ASR pyrolysis gas

Compound	Formula	Molecular weight	Vol. %
<i>Components detected by GC/TCD</i>			85
Methane	CH ₄	16	25
Hydrogen	H ₂	2	18
Carbon monoxide	CO	28	18
Ethylene/acetylene	C ₂ H ₄ /C ₂ H ₂	28/26	13
Carbon dioxide	CO ₂	44	7
Ethane	C ₂ H ₆	30	4
<i>Components detected by GC/MS</i>			
Propylene	C ₃ H ₆	42	2.26
Benzene	C ₆ H ₆	78	1.55
2-Methyl-1-propene	C ₄ H ₈	56	1.43
1,3-Butadiene	C ₄ H ₆	54	0.73
Methylbenzene (toluene)	C ₇ H ₈	92	0.71
3-Pentene-1-yne	C ₅ H ₆	66	0.51
Pentane	C ₅ H ₁₂	72	0.39
Styrene	C ₈ H ₈	104	0.37
Isocyanomethane	C ₂ H ₃ N	41	0.33
2-Methylpentene	C ₆ H ₁₂	84	0.31
2-Methyl-1,3-butadiene	C ₅ H ₁₀	70	0.28
1-Butene	C ₄ H ₈	56	0.21
1-Pentene	C ₅ H ₁₀	70	0.19
1-Chloro-3-methylbutane	C ₅ H ₁₁ Cl	127	0.18
Ethylbenzene	C ₈ H ₁₀	106	0.14
Methyl 2-methyl-2-propenoate	C ₅ H ₈ O ₂	100	0.12
1,2-Dimethylbenzene (o-xylene)	C ₈ H ₁₀	106	0.11
Others			5.17
Total			100.00

In addition to measuring the elemental chemical composition of the oil fraction, several physical properties were also measured, including density, viscosity, heating value and ash content.

Table 3
Composition of pyrolysis liquid

Component	Wt. %
Sediment	9.2
Water	55.4
Oil	35.4
Total	100

Table 4
Elemental analysis of a grab sample of ASR pyrolysis oil

Element	Wt.%	Mol%	Comparative literature data [10]		
				Tube reactor (wt.%)	Rotary kiln (wt.%)
C	86.21	44.33	C	83.45	85.42
H	8.70	53.68	H	10.44	9.65
N	2.41	1.06	N	1.45	0.13
O	2.15	0.83	O	3.34	1.70
S	0.36	0.07	S	0.81	0.77
Cl	0.18	0.03	Cl	1.80	0.31
Total	100.0	100.0			

The density of the oil was determined at 22°C using a standard 10 ml pycnometer. The viscosity was determined according to the standard ASTM test method D445 [21] using a Cannon–Ubbelohde capillary viscometer. The heating value of the oil was determined with a LECO A.C. 300 automatic calorimeter using the procedure outlined by the manufacturer [22]. The ash content was determined from the residue of the proximate analyzer when heated at 750°C using the LECO MAC 400 proximate analyzer.

The boiling range of the oil product was determined according to the ASTM distillation simulation procedure described in Test Method D2887 [23]. In this method the oil sample was analyzed using temperature-programmed gas chromatography which elutes the components according to boiling point. A Varian VISTA 600 gas chromatograph equipped with a 10 m × 0.536 mm Megabore DB 2887 column and a flame ionization detector was used for the analysis using a 0.5 µl sample. The column was programmed from 35 to 350°C at 8°C min⁻¹ followed by a 15 min hold at 350°C. Based upon calibration curves for standard hydrocarbon mixtures the boiling range distribution of the oil sample was calculated.

The chemical composition of the oil was analyzed both by nuclear magnetic resonance (NMR) spectroscopy and gas chromatography. NMR analysis of the pyrolysis oil was performed using a Varian VXR-200 according to the method of Glavincevski and Burton [24]. This method gives some insight into the aromaticity of the pyro-oil as well as providing some indication of the various types of hydrocarbon species present. The proton NMR spectra were obtained using 200.057 MHz while that employed for the carbon-13 analysis was 50.309 MHz.

Gas chromatography/mass spectrometry (GC/MS) was used to determine the chemical composition of the pyrolysis oil by performing both head space analysis and liquid sample injection. Both analyses were performed using an HP 5890 Series GC coupled to an HP 5970B Series mass-selective detector. Separation of the chemical components was achieved using a 30 m × 0.25 mm, 0.25 µm coated

HP-5MS fused silica capillary column, operated in the split mode. In the case of the head space analysis, a 200 μl injection volume was used with a 82:1 split ratio, with the column temperature programmed with a hold at -50°C for 3 min, followed by a $15^\circ\text{C min}^{-1}$ ramp to 240°C , and then a 20 min hold at 240°C .

Pyrolysis oil samples were first diluted 1:2 with tetrahydrofuran (THF) and then 0.3 μl was injected onto the column using a 35:1 split ratio. The column was programmed from 30 to 240°C at 5°C min^{-1} after an initial hold of 5 min at 30°C and a final hold of 60 min at 240°C .

Table 5

Major components in head space vapour of the ASR pyrolysis liquid

Compound (15 major components ^b)	Formula	Molecular	Concentration ^a		P_v (mmHg)	T_b ($^\circ\text{C}$)
			Wt.%	Mol%		
Benzene	C_6H_6	78	16.8	16.8	95.0	80.1
Toluene	C_7H_8	92	9.2	7.7	28.2	110.8
2-Methyl-1-propene	C_4H_8	56	8.3	11.4	N/A ^c	-6.9
Propylene	C_3H_6	42	7.0	13.0	N/A	-47.4
Styrene	C_8H_8	104	4.2	3.2	7.3	145.1
2-Methyl-1,3-butadiene	C_5H_8	68	3.2	3.7	577.6	34.1
1,3-Butadiene	C_4H_6	54	3.0	4.4	N/A	-4.4
Pentane	C_5H_{12}	72	2.7	2.9	511.5	36.1
3-Pentene-1-yne	C_5H_6	66	1.6	1.9	170.0 ^d	59.0
2-Methyl-2-butene	C_5H_{10}	70	1.5	1.7	457.8	38.6
1,2-Dimethylbenzene	C_8H_{10}	106	1.5	1.1	6.6	144.4
2-Methyl-1-pentene	C_6H_{12}	84	1.4	1.3	170.0 ^d	60.7
1-Pentene	C_5H_{10}	70	1.3	1.4	511.5	30.0
Naphthalene	C_{10}H_8	128	1.3	0.8	0.0	217.9
1-Hexene	C_6H_{12}	84	1.2	1.1	169.6	63.3
Sum of the above 15 components			64.3	72.3		
Others (130 minor components ^e)		100 ^f	35.7	27.7		
Total			100.0	100.0		

MW, molecular weight; P_v , vapour pressure at 25°C ; T_b , boiling point at 1 atm.

^aThe concentration (wt.% or mol%) of a given component in the head space vapour was calculated with respect to a total of 145 hydrocarbon compounds separated and detected.

^bMajor components have a concentration of >1.0 wt.%.

^cNot applicable.

^dThe vapour pressures of 3-pentene-1-yne and 2-methyl-1-pentene are assumed to be 170.0 mmHg, close to that of 1-hexene, because of their similar boiling points.

^eMinor components have a concentration of <1.0 wt.%.

^fThe average molecular weight of the 130 minor components in the head space vapour was estimated to equal to that of the 75 identified minor components.

2.6. Analysis of the residual solids

The residual solids produced by the pyrolysis process were also subjected to a series of characterizing analyses. These included the determination of particle size distribution by the use of a series of Tyler screens and elemental analysis for the six elements C, H, N, O, S and Cl according to the procedures outlined previously for the pyrolysis oil. The residual solids were also analyzed for the following elements: Si, Fe, Al, Ca, Ti, P and K using X-ray fluorescence spectrometry.

Quantification of the organic fraction, carbonaceous char and ash content of the residual solids were determined by a series of weight loss experiments using a tube furnace and TA Instruments Model 951 thermogravimetric analyzer (TGA). In the case of the tube furnace experiments, 4–7 g of the residual solids were accurately weighed into a ceramic boat which was heated from 25 to 640°C over a 20 min period in an inert nitrogen atmosphere and maintained at 640°C for a total of 160 min. The observed weight loss was assumed to be due to the decomposition of the organic material remaining in the sample. The residual sample from the tube furnace was then placed in a muffle furnace operating in an air environment at 500°C for 2 h and the resulting weight loss was determined. This measured weight loss was assumed to be due to the oxidation of the carbonaceous char, while the weight left was due to the inorganic ash.

Several thermogravimetric weight loss experiments was also performed on the residual solids. In these experiments approximately 60 mg of material was accurately weighed into a platform pan of a TGA thermobalance. The balance unit was then closed and purged with nitrogen at a flow rate of 50 ml min⁻¹. The sample was then heated from 25 to 500°C at 10°C min⁻¹ and held at this temperature for 90 min. During the first 45 min of this hold period the nitrogen purge gas flow rate was 50 ml min⁻¹. At the 45 min mark the nitrogen purge gas was stopped and replaced with an air flow for the remaining 45 min period while the temperature was maintained at 500°C.

The concentration and leachability of heavy metals present in ASR has always been an area of concern when dealing with this material [25–27]. The residual solids were therefore analyzed for the total concentration of the five heavy metals: zinc (Zn), lead (Pb), cadmium (Cd), chromium (Cr) and copper (Cu). These metals were determined by first ashing 5 g samples of the material for 3 h at 500°C in a muffle furnace. A 100 mg sample of the ash was then digested in 5 ml of aqua regia solution (3 parts concentrated hydrochloric acid to 1 part concentrated nitric acid) for 24 h at 100°C according to the procedure outlined by Kolthoff and Elving [28]. The dissolved metal ions were then separated from the residue and the concentration of the heavy metals determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The leachability of these five heavy metals from the residual solids was determined according to the “Quebec Procedure for Assessing the Characteristics of Solid Wastes and Pumpable Sludges” [29], a test very similar to the US Environmental Protection Agency (EPA) TCLP test [30]. Essentially the test employs 100 g of material which was placed in a 1250 ml plastic leaching bottle. To the sample

were added 900 ml of distilled water and 100 ml of a sodium acetate buffer solution to give a pH of 4.5 ± 0.1 . Following a 24 h agitation period the leachate was decanted and filtered and the concentration of the heavy metals in the leachate was determined using ICP-AES.

3. Results and discussion

3.1. Pyrolysis product distribution

The pyrolysis trial was conducted over a 4 day period and during that time a total of 18 350 kg of material was fed through the unit. The resulting material balance achieved during this 4 day period is presented in Table 1. The product yield distribution expressed in this table is comparable to the data obtained by Braslaw et al. [10] using a batch, bench scale tube pyrolyzer and by Kaminsky [15] using a fluidized bed unit. However, based upon a previous characterization study of ASR [16], the low yield of residual solids was a little surprising in view of the anticipated typical inorganic concentration of about 55% found in other ASR samples characterized in Canada [11,16]. In terms of the product distribution between the gas and liquid phases, the value of 0.8 for the gas to liquid ratio is in keeping with several studies reviewed previously [31] such as the value of 4.7 reported by Braslaw et al. for a screw kiln unit [10] and the value of 0.13 observed by Roy and Malette [11] with a vacuum pyrolysis system.

3.2. The pyrolysis gas

Analysis of the gas sample by GC/TCD revealed a total of 50 compounds, while a total of 150 compounds were detected using GC/MS. Of the gases detected, however, the major compounds were methane, hydrogen, carbon monoxide, ethylene/acetylene and carbon dioxide which represented about 80% of the total gas volume as can be seen from the data presented in Table 2. All the gases listed in this table have concentrations greater than 0.1 vol.%, while other gases detected, but not listed, had concentrations less than 0.1 vol.%. Based upon the chemical gas composition presented in this table, the heating value of the pyrolysis gas was calculated to be 37.0 MJ m^{-3} , which is in good agreement with the measured value of 44.7 MJ m^{-3} and comparable to that of natural gas, 35.4 MJ m^{-3} . Consequently, the pyrolysis gas was mixed with the natural gas and used to heat the pyrolysis reactor.

3.3. The pyrolysis liquid

The pyrolysis liquid sample was found to contain water and sediment in addition to the pyrolysis oil (see Table 3). While the weight of water in the pyrolysis liquid was high it is not unrealistic when it is realized that ASR can contain as much as 20–30% moisture [16] and that the particular sample used in this evaluation had been exposed to some rainy weather in the week before the tests were performed.

Table 6
GC/MS analysis of pyrolysis oil

Area (%)	R. time (min)	Formula	Compound	Molecular weight	Q. fit	Six most intense peaks
11.23	22.08	C ₁₀ H ₈	Naphthalene	128	9925	128, 51, 129, 64, 127, 63
8.61	11.35	C ₈ H ₈	Ethenylbenzene (styrene)	104	9783	104, 78, 103, 51, 77, 50
4.70	6.27	C ₇ H ₈	Methylbenzene (toluene)	92	9894	91, 92, 39, 65, 63, 51
3.53	25.39	C ₁₁ H ₁₀	1-Methylnaphthalene	142	9897	142, 141, 115, 139, 143, 63
2.95	17.23	C ₉ H ₈	1-Propynylbenzene	116	9800	115, 116, 63, 89, 51, 62
2.55	10.37	C ₈ H ₁₀	1,2-Dimethylbenzene	106	9938	91, 106, 105, 39, 51, 77
2.28	14.96	C ₉ H ₁₀	1-Propenylbenzene	118	9716	118, 117, 103, 78, 51, 77
2.18	10.02	C ₈ H ₁₀	Ethylbenzene	106	9956	91, 106, 51, 65, 39, 77
2.16	25.89	C ₁₁ H ₁₀	2-Methylnaphthalene	142	9916	142, 141, 115, 139, 71, 63
2.00	27.81	C ₁₂ H ₁₀	1,1'-Biphenyl	154	9933	154, 153, 152, 76, 155, 51
1.91	29.74	C ₁₂ H ₈	Acenaphthylene	152	9777	152, 151, 76, 150, 153, 63
1.90	15.06	C ₇ H ₅ N	Benzonitrile	103	9631	103, 76, 50, 75, 51, 104
1.66	16.69	C ₁₀ H ₁₆	1-Methyl-4-(1-methylethenyl) cyclohexene	136	9846	68, 67, 93, 39, 79, 94
1.56	15.16	C ₆ H ₆ O	Phenol	94	9775	94, 66, 39, 65, 40, 38
1.46	9.25	C ₁₀ H ₁₈ O	2-Decenal	154	9389	43, 70, 55, 41, 29, 39
1.29	15.41	C ₉ H ₁₀	2,3-Dihydro-[1H]-indene	118	9715	117, 118, 115, 91, 39, 51
1.28	20.82	C ₁₀ H ₁₀	1-Methyl-2-cyclopropen-1-ylbenzene	130	9925	130, 115, 129, 128, 127, 51
1.17	21.01	C ₁₀ H ₁₀	1-Methyl-[1H]-indene	130	9965	130, 115, 129, 128, 51, 127
1.15	30.65	C ₁₃ H ₁₂	1-(2-Propenyl)naphthalene	168	8925	168, 153, 167, 152, 154, 165
1.13	15.36	C ₉ H ₁₂	1,2,4-Trimethylbenzene	120	9500	105, 120, 41, 39, 55, 56
1.03	25.65		Saturated aliphatic			43, 69, 41, 55, 57, 71
0.94	29.17	C ₁₂ H ₁₀	1,2-Dihydroacenaphthylene	154	9757	154, 153, 152, 76, 155, 151
0.91	26.54	C ₁₀ H ₁₁ N	Benzenebutanenitrile	145	9807	91, 145, 104, 105, 65, 92
0.82	14.80	C ₆ H ₇ N	Benzenamine	93	9675	93, 66, 65, 39, 57, 38
0.80	17.72	C ₇ H ₈ O	3-Methylphenol	108	9300	108, 107, 77, 79, 39, 51
0.76	18.50		Unsaturated aliphatic			43, 69, 57, 41, 55, 70
0.75	11.39	C ₈ H ₁₀	1,3-Dimethylbenzene	106	9500	91, 106, 105, 39, 51, 77
0.73	28.91	C ₁₂ H ₁₂	2,3-Dimethylnaphthalene	156	9726	156, 141, 155, 115, 157, 76
0.73	16.77	C ₈ H ₁₈ O	2-Ethyl-1-hexanol	130	9461	57, 41, 43, 55, 56, 70
0.70	30.90		Aromatic hydrocarbon			168, 167, 57, 153, 43, 165
0.69	18.02	C ₈ H ₈ O	Acetophenone	120	9500	105, 77, 51, 120, 43, 50

Table 6 (Continued).

Area (%)	R. time (min)	Formula	Compound	Molecular weight	Q. fit	Six most intense peaks
0.67	15.53	C ₉ H ₁₀	2-Propenylbenzene	118	9847	117, 118, 115, 91, 39, 51
0.67	26.14		Saturated aliphatic			43, 69, 41, 55, 57, 85
0.62	28.49	C ₁₂ H ₁₂	1,3-Dimethylnaphthalene	156	9844	156, 141, 155, 115, 128, 157
0.61	7.00	C ₅ H ₈ O	Cyclopentanone	84	9100	28, 55, 27, 41, 84, 56
0.56	31.57	C ₁₁ H ₇ N	1-Naphthalenecarbonitrile	153	9854	153, 126, 63, 154, 76, 91
0.55	23.34	C ₉ H ₁₂ O	3-(1-Methylethyl)phenol	136	9958	121, 136, 77, 91, 103, 39
0.53	37.71	C ₁₄ H ₁₀	9-Methylene-[9H]-fluorene	178	9925	178, 176, 179, 76, 89, 152
0.50	18.91	C ₁₁ H ₂₄ S	1-Undecanethiol	188	9958	41, 43, 55, 56, 69, 70
0.50	24.48	C ₁₁ H ₁₂	1,2-Dihydro-3-methylnaphthalene	144	9164	129, 128, 144, 141, 142, 115
0.49	23.61	C ₉ H ₇ N	Isoquinoline	129	9913	129, 102, 128, 51, 76, 50
0.48	22.24	C ₈ H ₆ S	Benzo(b)thiophene	134	9300	134, 89, 90, 69, 63, 45
0.47	14.13	C ₉ H ₁₂	1-Ethyl-2-methylbenzene	120	9888	105, 120, 77, 79, 91, 51
0.42	16.41		Benzene derivative			105, 120, 39, 77, 91, 119
0.41	29.87	C ₁₂ H ₁₂	2,6-Dimethylnaphthalene	156	9300	156, 141, 155, 115, 157, 76
0.41	18.83	C ₁₀ H ₁₂	Methyl(1-methylethyl)benzene	132	9633	117, 132, 91, 115, 116, 92
0.40	20.53	C ₈ H ₇ N	Benzeneacetonitrile	117	9500	117, 90, 116, 89, 51, 39
0.40	16.88	C ₉ H ₁₀	1-Ethenyl-2-methylbenzene	118	9672	117, 118, 115, 39, 91, 58
0.40	18.23		Two compounds			41, 55, 56, 106, 43, 107
0.39	29.00	C ₁₂ H ₁₂	1,7-Dimethylnaphthalene	156	9896	156, 141, 155, 115, 153, 152
0.38	24.64	C ₁₂ H ₂₄	(Z)-3-Dodecene	168	9756	43, 55, 41, 56, 70, 69
0.38	28.05	C ₁₂ H ₂₆ S	1-Dodecanethiol	202	9770	41, 43, 55, 56, 57, 83

3.4. The pyrolysis oil

The pyrolysis oil was separated from the pyrolysis liquid and subjected to a series of analyses and characterization studies.

Elemental analyses of the pyrolysis oil are shown in Table 4. Although this analysis was conducted on just one of the grab samples, the results are the same order of magnitude as the values reported by Braslaw et al. [10] which are also listed in Table 4 for comparative purposes.

In terms of the chemical composition of the pyrolysis oil the analysis was carried out in two stages. Analysis of the head space vapours resulted in 145 hydrocarbons being separated and 90 being tentatively identified. However, it was found that the 15 compounds listed in Table 5 accounted for over 64% of the total hydrocarbons separated, with these compounds having concentrations of over 1 wt.%. Also provided in the table are vapour pressures of these compounds calculated using the data of Lide and Frederikse [32] along with their boiling points as reported by Dean [33]. Based upon this analysis it can be seen that the major volatile hydrocarbons in the pyrolysis liquid are alkyl benzenes and C_3 – C_6 alkenes.

Meanwhile, analysis of the pyrolysis oil directly by liquid injection resulted in a total of 269 chemical compounds being separated and detected following the elution of the THF solvent peak. Of these compounds 108 have been tentatively identified using the NIST/EPA/NIH mass spectral database. The major compounds are identified in Table 6 according to peak area. Based upon a semiquantitative analysis of the data contained in Tables 5 and 6 and using the vapour pressure data, the approximate composition of the pyrolysis oil can be calculated.

For this purpose, the concentration of each hydrocarbon compound was computed using the molar fraction in the head space vapour analysis, vapour pressure data at 25°C, along with the use of styrene as the reference compound which was detected in both the head space vapour and the pyrolysis oil. The results of these calculations are presented on Table 7. From this table it can be seen that the principal pyrolysis products contained in the pyrolysis oil are all aromatic, which raises the issue of the suitability of the oil as a fuel or for petrochemical feedstock applications.

Listed in Table 6 are several nitrogen and sulfur compounds. Altogether a total of 17 nitrogen compounds and six sulfur compounds were detected in the pyrolysis oil. Typical nitrogen compounds detected included nitriles, isocyanates, amines and pyridine compounds which together represented 6.3 wt.% of the oil fraction. Meanwhile the principal sulfur compounds were aliphatic thiol compounds and substituted thiophenes which in total contributed approximately 1.4 wt.% to the total oil fraction. Clearly these compounds, along with any organo chlorides, are undesirable if the pyrolysis oil is to be used directly as a fuel.

Confirmation of the high concentration of aromatic compounds in the pyrolysis oil was obtained from the NMR analysis [24]. The results of this analysis suggested that the pyrolysis oil contained 66.1 wt.% aromatics and 33.9 wt.% aliphatics, very much in keeping with the C/H ratio calculated from the elemental analysis presented in Table 5. In addition to providing information on the aromaticity of the

Table 7

Composition of the ASR pyrolysis oil from combined GC/MS analysis of pyrolysis liquid head space vapour and pyrolysis oil

Compound (13 major components)	Formula	Molecular weight	Concentration	
			Wt.%	Mol%
Naphthalene	C ₁₀ H ₈	128	10.9	11.7
Styrene	C ₈ H ₈	104	8.3	11.0
Toluene	C ₇ H ₈	92	4.5	6.7
1-Methylnaphthalene	C ₁₁ H ₁₀	142	3.5	3.4
1-Propynylbenzene	C ₉ H ₈	116	2.8	3.4
Benzene	C ₆ H ₆	78	2.5	4.5
1,2-Dimethylbenzene (<i>o</i> -Xylene)	C ₈ H ₁₀	106	2.5	3.3
1-Propenylbenzene	C ₉ H ₁₀	118	2.2	2.6
Ethylbenzene	C ₈ H ₁₀	106	2.0	2.7
2-Methylnaphthalene	C ₁₁ H ₁₀	142	2.0	2.0
Acenaphthylene	C ₁₂ H ₈	152	1.9	1.7
Benzonitrile	C ₇ H ₅ N	103	1.9	2.5
1,1'-Biphenyl	C ₁₂ H ₁₀	154	1.9	1.7
Sum of the above compounds		47.0	57.0	
Others			53.0	43.0
Total			100.0	100.0

pyrolysis oil, the NMR analysis was also able to give some indication of the types of the other hydrocarbon groups present. This analysis suggested that there was 12.5 mol% olefins, 14.5 mol% naphthalenes and 15.4 mol% vinylaromatics.

The boiling range of the pyrolysis oil, as determined by ASTM Method D2887 [23], is shown in Fig. 2. Also provided in Fig. 2 is the distillation profile of a diesel fuel for comparative purposes. It will be noted that the pyrolysis oil has a lower initial boiling temperature of 76.3°C than does the diesel fuel, and a higher distillation yield up to a boiling temperature of 275°C. Above this temperature, however, the distillation rate for the pyrolysis oil is less than that of diesel fuel. Clearly, therefore, the pyrolysis oil has a wider boiling range and a higher average boiling temperature (279°C compared with 258°C) than the diesel fuel. However, the pyrolysis oil was found to have a similar distillation curve to the oil produced by Braslaw et al. [10] from ASR.

In terms of the physical properties of the pyrolysis oil, these values are summarized in Table 8. It is interesting to note that the viscosity of the pyrolysis oil lies between the $(2-5) \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ range of No. 2 fuel oil and the $(15-20) \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ range of No. 4 fuel oil [34]. However, in comparison with the pyrolysis oil obtained by Roy and Malette [11] the density is slightly higher and the viscosity is significantly less. The heating value of the oil, however, at 41 MJ kg⁻¹ is significantly higher than that of No. 2 fuel oil with a reported value of about 31 MJ kg⁻¹.

Simulated Distillation of ASR Pyrolysis Oil

Fig. 2. Simulated distillation curve for the ASR pyrolysis oil as determined by ASTM-D2887 [23].

3.5. The residual solids

The particle size distribution of the non-magnetic fractions of the residual solids are presented in Table 9. Interestingly, while over 56% of the coarse fraction is greater than 1 mm in size, this corresponds to less than 12% of the total non-magnetic residual solids. On the other hand, 44% of the fines fraction or 34% of the total non-magnetic residual solids is less than 0.1 mm in size. This means that the majority of the non-magnetic residual solids (24%) has a size between 0.1 and 1 mm.

Elemental analysis of the residual solids was performed only on the fines fraction and the results of these analyses are presented in Table 10. Clearly carbon at a

Table 8
Physical properties of the ASR pyrolysis oil

Property	Value	Temperature (°C)
Density (g cm^{-3})	0.95	22.0
Viscosity ($\text{m}^2 \text{s}^{-1}$)	8.06×10^{-6}	22.8
Heating value (MJ kg^{-1})	41.0	25.0
Ash (wt.%)	<0.01	750

Table 9

Particle size distribution of the ASR pyrolysis residual solids

Size range (Tyler mesh)	Size range (mm)	Size (mm)	Percentage (wt.%)
<i>Coarse fraction</i>			
+9	7.00–2.00	4.50	6.0
9–20	2.00–0.84	1.42	51.1
20–28	0.84–0.60	0.72	23.1
–28	0.60–0.00	0.30	19.8
		1.22 (Ave.)	100.0 (Total)
<i>Fines fraction</i>			
+80	0.21–0.18	0.20	42.2
80–100	0.18–0.15	0.17	5.2
100–150	0.15–0.11	0.13	8.8
–150	0.11–0.00	0.03	43.8
		0.12 (Ave.)	100.0 (Total)

concentration of 38% is the major element present, although there are also appreciable concentrations of iron, silica and aluminum present. The concentration of calcium in the residual solids is also high, no doubt due to calcium carbonate which is widely used as a filler for thermoplastic components. The high chloride content of the residues is obviously a reflection on the formation of hydrochloric acid during the dehydrochlorination of organo chlorides such as PVC, which

Table 10

		fluid reactor	vacuum unit data
C	37.8	59.9	11.3
H	0.48	1.3	NR
N	0.3	0.1	NR
S	0.9	1.4	NR
Cl	1.4	3.3	NR
Fe ₂ O ₃	8.5	NR	22.0
SiO ₂	20.8	NR	NR
Al ₂ O ₃	8.1	NR	4.3
P ₂ O ₅	0.1	NR	NR
K ₂ O	<0.1	NR	NR
CaO	7.6	NR	NR
TiO ₂	0.7	NR	NR

NR, not reported.

Table 11
Weight loss analysis for the ASR pyrolysis residual solids

	Organics (wt.%)	Char (wt.%)	Ash (wt.%)	Total (wt.%)
<i>Fines fraction</i>				
Tube furnace (640°C in N ₂ , 500°C in air)	5.0	30.3	64.7	100.0
Thermogravimetry (500°C in N ₂ , 500°C in air)	5.3	32.6	62.1	100.0
<i>Coarse fraction</i>				
Tube furnace (640°C in N ₂ , 500°C in air)	9.3	14.6	76.1	100.0

subsequently reacts with cations in the ASR to give inorganic chlorides which ultimately are found in the residues.

The carbon content of the residual solids produced in this study are in keeping with the values reported by others [10,11]. However, by performing a series of controlled weight-loss experiments the weights of organic carbon and carbonaceous char can be differentiated. The results of these weight-loss experiments are summarized in Table 11. Clearly these results suggest that a relatively high conversion of the organic material in the ASR has been achieved during the pyrolysis process; however, the fines still contain a relatively high concentration of carbonaceous char with potential for recovery should economics be worthwhile.

In terms of heavy metal content, both the fines and coarse fractions showed relatively high concentrations of zinc, lead, and copper (Table 12). The level of copper was particularly high in the coarse fraction due to a preponderance of electrical copper wire in this fraction. Also presented in Table 12 are the results of

Table 12
Heavy metal concentrations and leachability results for ASR pyrolysis residual solids

	Total concentration (wt.%)	Leachability value (mg l ⁻¹)	Regulation limits (mg l ⁻¹)
<i>Fines portion</i>			
Zn	1.62	<1	10
Pb	0.25	<2	5
Cd	0.003	<0.05	2
Cr	0.02	<0.2	5
Cu	0.27	<0.1	10
<i>Coarse portion</i>			
Zn	0.61	20	10
Pb	0.56	<2	5
Cd	0.006	<0.05	2
Cr	0.05	<0.2	5
Cu	6.78	<0.1	10

leachability tests performed using the Quebec test protocol [29]. These leachate test results clearly indicate that, although heavy metals are still present in the residual solids, the pyrolysis process does not cause any problems regarding their leachability.

4. Conclusions

The pyrolysis of ASR to produce liquid aromatic hydrocarbons and other petrochemicals appears to be a possible option for the recovery of materials. While it has been demonstrated that the pyro-gas is sufficiently high in energy content and large enough in quantity to maintain the energy requirements of the pyrolysis process, more work is required to demonstrate the economics of recovering the magnetic and non-magnetic material from the residual solids. However, while the pyrolysis oil contains many valuable hydrocarbons, it is a very complex mixture of chemical compounds and it does contain measurable quantities of sulfur-, nitrogen- and chlorine-containing compounds, which could prevent its direct use as a fuel in many applications and locations. The choice of appropriate pyrolysis conditions could be an important factor in obtaining saleable products suitable for subsequent resource recovery processes.

Further studies are therefore required in order to optimize the process to ensure that commercially exploitable products are obtainable at a reasonable economic cost.

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