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Pyrolysis of auto shredder residue: experiments with a laboratory screw kiln reactor[☆]

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Abstract

The pyrolysis of automobile shredder residue (ASR) has been studied using a laboratory scale screw kiln reactor with a feed rate of about 100 g h^{-1}. Pyrolysis at temperatures between 500 and 750°C resulted in the production of gas, liquid and solid fractions with hydrocarbon yields of the organic fraction present in the feed increasing from 60–85% with increasing pyrolysis temperature. While the hydrocarbon pyrolysis product yield increased with pyrolysis temperature, the yield of the oil fraction was higher at the lower pyrolysis temperatures. The composition of the pyrolysis oil also changed with pyrolysis temperature, containing larger quantities of aliphatic compounds at the lower temperatures than at higher temperatures where aromatics were the major compounds. Many of the liquid pyrolysis products have been identified including polycyclic aromatic hydrocarbons as well as organo nitrogen, sulphur and chlorine compounds. The data obtained have been compared with that obtained from a process using short pyrolysis residence times. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; Thermal degradation; Pyrolysis; Screw kiln reactor; Tertiary recycling; Automobile shredder residue; Plastic waste

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1. Introduction

One of the technologies which is receiving a great deal of interest in the recycling of polymeric waste streams is pyrolysis. This technology is particularly applicable to mixed and contaminated plastic wastes which can be converted back to petrochemical feedstocks, along with some carbonaceous char. While incineration with energy recovery may be an attractive process to deal with these waste streams [1,2], public pressure regarding environmental emissions has restricted its universal acceptance. Pyrolysis, on the other hand, is seen as an environmentally attractive alternative for the recovery of hydrocarbon materials from a wide range of polymeric waste streams such as plastic waste [3,4] and tires [3,5], with several processes being investigated by industry [6–9].

Automobile shredder residue (ASR) is a particularly heterogeneous polymeric waste stream for which pyrolysis may represent a viable resource recovery process. This material is a mixture of plastics, rubber, foam, textiles, glass and dirt, the waste produced by shredding operations during the recycling of automobiles [10,11]. In North America alone, over 3 million tonnes of ASR is generated each year [12] with the vast majority destined for landfill disposal. Because ASR is such a heterogeneous material whose composition can be influenced by processing conditions [13–15], pyrolysis appears to offer many advantages as a resource recovery option. Consequently several studies have been reported on the pyrolysis of ASR [3,16–25], including a survey of several pyrolysis processes currently under development [26]. In a previous scientific investigation of the pyrolysis of ASR, we focussed our attention upon a fast pyrolysis process, known as ‘Ultrapyrolysis’ [22]. Subsequently to that study we examined the pyrolysis products produced by a commercial screw kiln process [23]. Although many similarities were noted in the pyrolysis products, significant differences were also noted. Similar quantities of pyro-gas were formed in the two processes but the major difference was in the production of pyro-oil (‘Ultrapyrolysis’ produced no pyro-oil at 700–850°C whereas the commercial screw kiln process produced 21% pyro-oil at 500°C). Because different ASR feeds and pyrolysis temperatures were used in each of these two studies we felt it appropriate to perform some experiments using a laboratory screw kiln pyrolysis unit and the same ASR feed material as that used in the fast ‘Ultrapyrolysis’ process [22]. The data presented in this paper summarizes the results obtained in our laboratory screw kiln pyrolysis unit.

A major concern with pyrolysis processes that employ high pyrolysis temperatures and long residence times is the possible formation of carcinogenic compounds of environmental concern such as polycyclic aromatic hydrocarbons (PAH’s), polychlorinated biphenyls, dioxins and furans [24,27,28]. Rausa and Pollesel [24] pyrolyzed ASR at 650, 800 and 850°C and detected several PAH’s as well as phenol, benzaldehyde, and chlorobenzene as pyrolysis products. At 650°C, the PAH’s accounted for 1.3% of the pyrolyzate while at 800 and 850°C they increased to 32.3 and 55.1%, respectively. Meanwhile the substituted benzene species represented 28.6, 55.0 and 35.8% of the vapours at pyrolysis temperatures of 650, 800 and 850°C, respectively. Williams and Besler [27] also detected PAH’s in the pyrolysis of a variety of biomass material, as well as municipal solid waste (MSW) and have concluded that PAH production mainly occurs through secondary reactions which are favoured by high temperatures (> 700°C) and long gaseous residence times encountered in slow pyrolysis processes. Evans and Milne [29] also found that the fast pyrolysis of wood produced negligible concentrations of PAH's. However, increased concentrations of PAH's were produced when secondary cracking reactions of the primary pyrolysis products occurred at higher temperatures (above 850°C). Diebold et al. [30,31] also found increased quantities of PAH's in the fast pyrolysis of MSW in an entrained flow reactor above 700°C.

2. Experimental

2.1. The ASR feed

The ASR used in this series of tests was the regular ASR material that was used in the 'Ultrapyrolysis' study [22]. This material was collected during a characterization study reported previously [14]. The physical and chemical characterization of this feed material are presented in Table 1. It should be noted that the data reported in Table 1 was for ASR which had been ground cryogenically to produce a material with a particle size less than 1 mm and is comparable to the material previously used in the 'Ultrapyrolysis' experiments [22]. This size reduction was required in order to ensure uniform feed rates through the screw auger used in our experiments.

Table 1
Characteristics of the ASR feed material

Moisture content (wt.%)	2.6
Organic fraction (wt.%)	39.3
Ash content (wt.%)	58.1
Particle size	< 1 mm
Density (kg m^{-3})	438
Calorific value (MJ kg^{-1})	10.18
Elemental analysis (wt.%, dry basis)	
C	27.9
H	4.0
N	0.9
S	0.3
Cl	0.5
Fe	17.6
Si	8.6

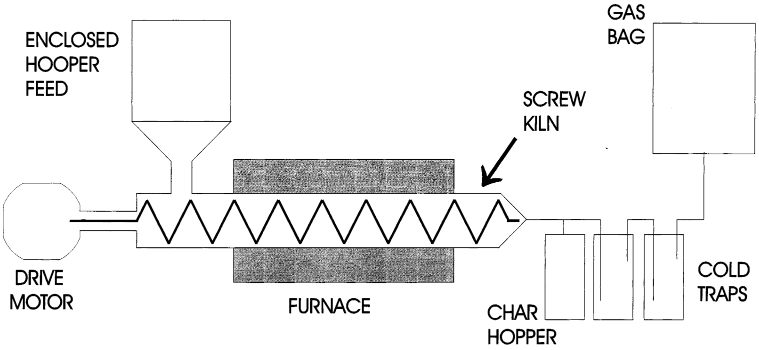

Fig. 1. Schematic of the screw kiln pyrolysis apparatus.

2.2. The screw kiln pyrolysis unit

The pyrolysis unit employed in this study is shown schematically in Fig. 1. For the sake of simplicity it can be considered to be composed of three zones: a feed zone, a pyrolysis reaction zone and a product collection zone. The ASR is loaded into a sealed hopper which can be flushed with nitrogen prior to pyrolysis. The ASR in the hopper is fed by gravity into the auger which feeds the material into the reaction zone. The feed rate of material into the reactor is controlled by adjustment to the speed of an electric motor linked directly to the auger. The reaction chamber consists of a stainless steel tube 44.5 cm long with an i.d. of 4.7 cm. This reactor tube is centrally located in a Lindberg tube furnace whose temperature is controlled to ± 2°C of the desired value by a feedback control system. Quoted temperatures are the reactor wall temperature and no attempts were made to measure the actual feed temperature in the reactor. However, it was not anticipated that the feed temperature would be significantly lower than the reactor temperature as the feed was prewarmed as it moved slowly along the screw. On exiting the reactor, solid residue was collected in a catch pot. Hot volatiles, meanwhile, passed through two glass cold traps, in series, maintained at 0 and − 82°C, respectively. The remaining non-condensable gases were collected in a 401 Tedlar sampling bag.

2.3. Operational procedure

With the furnace at room temperature and the auger feed switched off, the feed hopper was loaded with an accurately weighed quantity of ASR (usually about 200 g). The system was then closed and flushed with dry nitrogen for a period of about 15 min, while the furnace was heated to the selected pyrolysis temperature. Once the desired temperature had been reached, the gas and liquid collection systems were connected to the reactor, the feed motor was switched on at the desired feed rate setting and the nitrogen supply closed. The test was then allowed to run for the desired time period, after which the feed motor was stopped and then the collection sections closed off for subsequent analysis. Following the cool down of the reactor, the feed remaining in the hopper was reweighed to determine the weight subjected to pyrolysis. The weight of each pyrolysis fraction was then determined, prior to detailed chemical analysis.

A range of pyrolysis temperatures were evaluated in this study, starting at 500°C and going to a high of 750°C. Most experiments were conducted using a feed rate of about 0.88 g min^{-1} which results in a pyrolysis residence time in the reactor of about 3.2 min. While some variations in total pyrolysis time were employed during the study, a typical run would last for about 100 min. Only one experiment was conducted for each set of conditions. Mass balances were all above 92% except for the 600°C pyrolysis which was 76%.

2.4. Analysis of the pyrolysis gas

The quantity of evolved pyrolysis gas was determined by discharging the gases from the gas bag into two pre-evacuated stainless steel cylinders (500 ml each) and a pre-evacuated tank of known vol. (21.28 l) and measuring the temperature and pressure of the contents. The 500 ml cylinders were pressurized with helium to 1.3 atmospheres and chemical analysis was achieved by gas chromatography using a Hewlett Packard (HP) 5890 Series II gas chromatograph (GC). The analyses were performed by injecting 1 ml gas samples onto a 3.66 m × 3.2 mm Porapak Q (80/100 mesh) packed stainless steel column using a stainless steel injection loop hooked up to a two position rotary Valco valve. The separation was achieved using temperature programming which involved holding at −50°C for 3 min., followed by a ramp of 15°C min^{-1} to 120°C then 30°C min^{-1} to 240°C where it was held for a further 20 min. The separated gases were detected using a thermal conductivity detector (TCD) operated at 280°C. Scott Specialty Gases, Scotty I Can Mixes 219, 221, 234 and 242, with accuracy of analysis ± 2%, were used to create linear calibration curves from which the individual major pyrolysis gases could be identified and quantified.

2.5. Analysis of the pyrolysis liquid

In all cases the pyrolysis liquids collected in both traps were combined and the total reported. The pyrolysis liquid was found to contain both an oil phase and an aqueous phase. The oil phase was subjected to chemical analysis using an HP5890 Series GC coupled to an HP 5972A series mass-selective detector (MSD) both as a neat liquid and diluted with diethyl ether. Separation of the chemical components was achieved using a 30 m × 0.25 mm, 0.25 μm coated HP-5 M.S. (crosslinked 5% phenyl methyl silicone) fused silica capillary column, operated in both the split mode (100:1) and splitless. The column was programmed from 30 to 240°C at 20°C min^{-1} after an initial hold of 3 min at 30°C and a final hold of 60 min at 240°C. Mass spectra peak areas were used for qualitative data comparisons and tentative compound identification was determined by Hewlett Packard's probability-based matching (PBM) library search of the 75 000 compound NIST PBM Library. The GC oven contained both the Porapak Q packed column and the capillary column so maximum oven temperature was limited to 240°C.

2.6. Analysis of the solid residues

The solid residues, produced by the pyrolysis process, were analyzed to determine the organic content, carbonaceous char and ash content by performing weight-loss experiments using a tube furnace. The procedure involved accurately weighing about 1 g of the residual solid into a ceramic boat. The boat was placed in a tube furnace and a flowing inert nitrogen atmosphere (125 ml min^{-1}) was passed over the sample. The sample was heated from room temperature to 640°C at about 40°C min^{-1} and then maintained at this temperature for 3 h. The measured mass loss was assumed to be due to the organic material remaining in the sample. The residual sample was returned to the tube furnace with a 125 ml min^{-1} flow rate of air and the sample was heated to 680°C and maintained there for 3 h. The measured mass loss was assumed to be due to the oxidation of the carbonaceous char. The remaining mass was a measure of the inorganic ash content. Additional samples (10–20 g) of the solid residues were Soxhlet extracted with 750 ml of tetrahydrofuran (THF) for 5 h and the extracted oil was analyzed via GC/MSD as described for the pyrolysis liquids

3. Results and discussion

3.1. Product distribution

As would be anticipated from a feed with a high inorganic content, the solid residue was the major product of the pyrolysis process, ranging from 80% at 500°C to 70% at 750°C. The yield of solid residue was clearly dependent upon pyrolysis

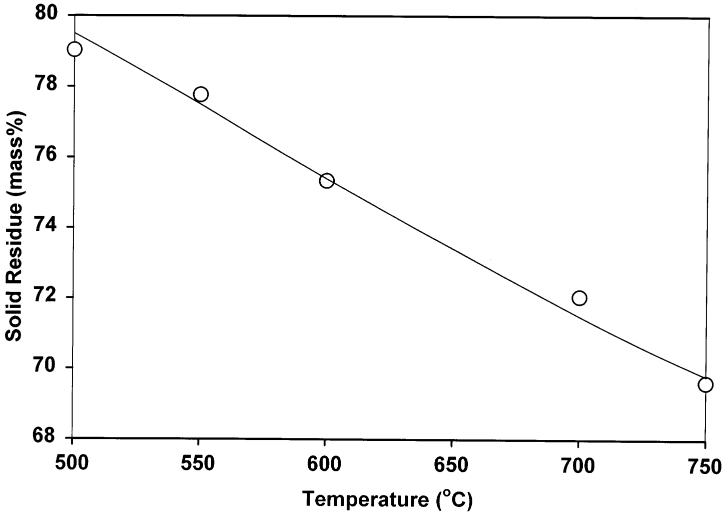

Fig. 2. Yield of solid residue fraction as a function of pyrolysis temperature.

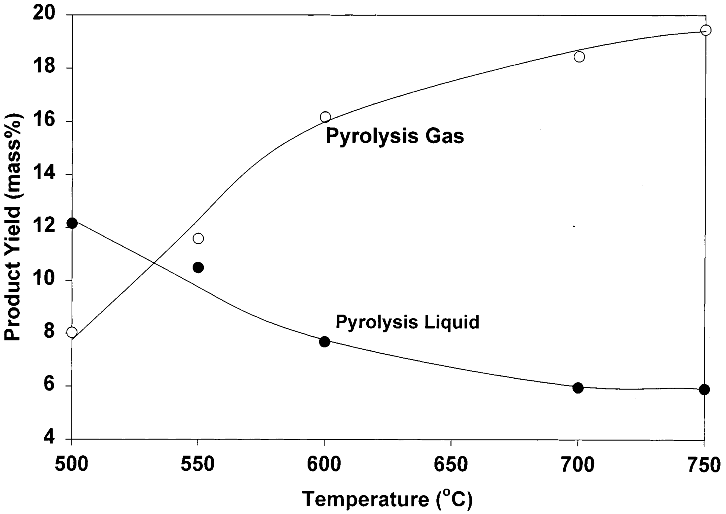

Fig. 3. Yields of pyrolysis gas [○] and pyrolysis liquids [●] as a function of pyrolysis temperature.

temperature as can be seen from the data presented in Fig. 2. High pyrolysis temperatures caused greater degradation of the organic matter in the ASR and lowered the yield of the solid residue. This observation was similar to that reported in the 'Ultrapyrolysis' study [22] at a 700°C pyrolysis temperature. At 750°C the 'Ultrapyrolysis' process yielded approximately 10% less solid residue than was obtained in the screw kiln experiment.

Yields of the pyrolysis liquid and pyrolysis gas as a function of pyrolysis temperature are presented in Fig. 3. It will be noted that the yield of pyrolysis gas shows a steady increase from about 8% at 500°C up to about 20% at 750°C, although there appears to be a leveling off in the gas yield at temperatures above 700°C. These pyro-gas quantities are similar to those observed in the 'Ultrapyrolysis' experiments [22]. The screw kiln pyrolysis liquid yield appears to be highest at the lower pyrolysis temperatures, and decreases as the pyrolysis temperature increases. This arises because the higher pyrolysis temperatures causes greater chain scission reactions to occur, resulting in higher yields of the lower molecular weight gaseous products. While the yields of the pyrolysis liquid in the screw kiln pyrolysis experiments were not high, they were at least measurable. In the case of the 'Ultrapyrolysis' experiments [22], no measurable quantities of pyrolysis liquid were obtained.

Although only one experiment was performed to determine the effect of residence time on pyrolysis product distribution, the results are summarized in Table 2. At a pyrolysis temperature of 550°C, increased residence time of the ASR in the kiln caused a slight increase in the material pyrolyzed. The yield of pyrolysis gas also increased while the yield of the pyrolysis liquid decreased.

Table 2
Influence of residence time on pyrolysis product distribution

Residence time (min)	Reactor temperature (°C)	Solid (mass.%)	% Liquid	% Gas
3.2	550	77.8	10.5	11.6
11.6	550	75.4	8.5	14.9

The yields of pyrolysis liquid obtained in this study are lower than those reported by Braslaw et al. [17] for his bench scale experiments (33.9–36.8 mass.%), but close to those obtained with the commercial screw kiln process (9.4 ± 4.2 mass.%) at pyrolysis temperatures of 610–650°C [23].

3.2. Composition of the pyrolysis gas

Analysis of the ASR pyrolysis gas indicated that the major chemical species were hydrogen, carbon dioxide, carbon monoxide and low molecular weight hydrocarbons. The product yield of these major compounds in the pyrolysis gas as a function of pyrolysis temperature is presented in Figs. 4 and 5. These values were calculated based upon the 18 major compounds detected while correcting for any nitrogen, oxygen and water that may have entered the system. From Fig. 4 it can be seen that the composition of hydrogen in the gas mixture remains relatively constant over the range of pyrolysis conditions employed.

From both Figs. 4 and 5 it can be seen that the yields of all the major gases increase with pyrolysis temperature. However at the higher pyrolysis temperatures,

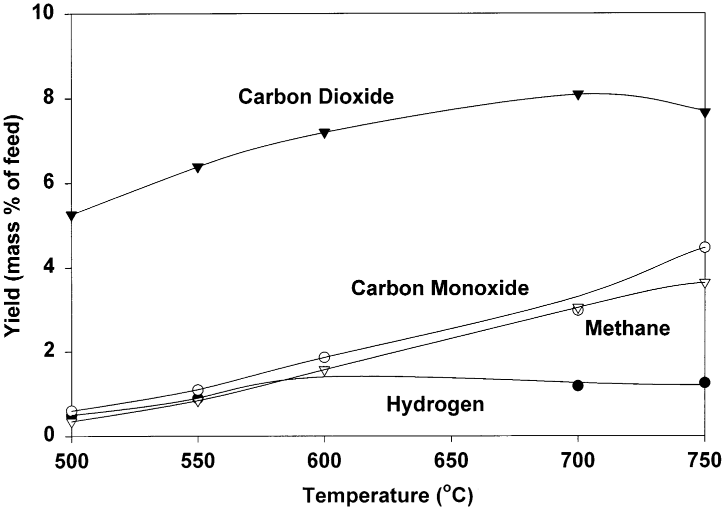

Fig. 4. Mass yields of hydrogen [●], carbon dioxide [▼], carbon monoxide [○] and methane [▽] expressed as a percentage of ASR feed, plotted as a function of pyrolysis temperature.

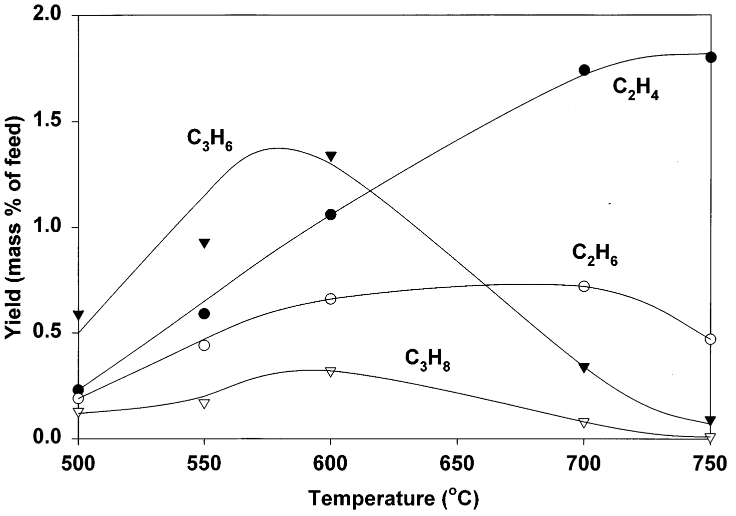

Fig. 5. Mass yields of ethylene [●], ethane [○], propylene [▼] and propane [▽] expressed as a percentage of ASR feed, plotted as a function of pyrolysis temperature.

the yields of the C_3 hydrocarbons show noticeable decreases while the yield of CO and methane continue to increase. In the case of the hydrocarbons, it would appear that peak quantities are formed at specific temperatures above which there is a steady decline. In the case of methane and ethylene this maximizing appears to occur around 750°C, while in the case of ethane, propane and propylene it occurs at a lower temperature, around 600°C.

The effect of residence time on the composition of the pyrolysis gas at a pyrolysis temperature of 550°C is summarized in Table 3. From this data it appears that the quantities of hydrogen decrease with increased residence time while the quantities of the small hydrocarbon molecules increase. This suggests that cracking of the primary pyrolysis products may be occurring at longer residence times.

At first glance the levels of CO_2 appear to be high considering that the pyrolysis was conducted in an inert atmosphere. However, it should be noted that automotive plastics such as polyesters [32] and polycarbonates [33] can yield relatively high yields of CO_2 under pyrolysis conditions. Carbonate fillers are also present in automotive plastics and can also contribute to CO_2 production [17]. At 700°C

Table 3
Influence of residence time on composition of pyrolysis gas (vol.%)[a]

Residence time (min)	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}
3.2	59.50	5.20	7.04	19.46	2.80	1.94	2.97	0.53	0.52	0.02
11.6	53.74	5.25	10.12	19.56	3.16	2.83	3.50	0.79	0.94	0.05

[a] All values are averages of two GC/TCD injections. Pyrolysis temperature = 550°C.

pyrolyses, CO_2 production was higher in the screw kiln experiment than in 'Ultrapyrolysis' (residence time = 1.4 s) [22], i.e. 8.1 versus 4.2 mass.% of feed, respectively. Similarly, CH_4 was double, whereas CO and C_2H_4 were the same and C_3H_6 was one-sixth of that observed in 'Ultrapyrolysis'.

The calculated high heating values of the gases obtained at pyrolysis temperatures of 600–750°C were fairly constant at 28.1–29.0 MJ kg^{-1}. However, at lower pyrolysis temperatures of 500 and 550°C lower values of 20.0 and 26.1 MJ kg^{-1}, respectively were obtained.

The average molecular weight of the pyrolysis gas decreased as the pyrolysis temperature increased (Av. MW = 18 at 500°C and 14 at 750°C).

3.3. Composition of the pyrolysis liquid

The pyrolysis liquid not only condensed out in the two cold traps but was also present in the tubing from the reactor to the traps. The oil fractions were collected both as neat liquids and diluted with diethyl ether (solvent used to wash the traps and tubing). Both neat liquids and the resulting ether solutions were then analyzed using GC/MSD to determine the chemical composition of the mixture. Pyrolysis liquid quantities were determined by weighing all sections of the screw kiln and its traps before and after each pyrolysis.

Based upon the data presented in Fig. 3, it can be clearly seen that as the pyrolysis temperature increased the yield of pyrolysis liquid decreased. Thus although the extent of degradation was increasing (see Fig. 2), the higher pyrolysis temperatures were responsible for secondary degradation reactions leading to lower molecular weight compounds, causing increased yields of pyrolysis gases as has been observed in the literature [28]. The composition of the pyrolysis liquid was also significantly different at the lower temperatures than was obtained at the highest temperature (750°C).

At a pyrolysis temperature of 500°C, when the highest yield of pyrolysis liquid was obtained, over 100 organic compounds were detected. Table 4 provides a partial listing of some of the compounds present in the liquid with peak areas over 2%. From this data it can be seen that 16 compounds have peak areas over 2%. At the 1% cut-off level, this number would double to 32 compounds. It is interesting to note that while the aromatic compounds, benzene and toluene, are the compounds with the largest peak areas, it is the aliphatics which dominate the pyrolysis liquid at this temperature, with a peak area ratio of aliphatics to aromatics of about 4 to 1, see Table 10.

The 15 major compounds of both 550°C pyrolysis experiments are listed in Tables 5 and 6. Once again, over 100 compounds were detected in each experiment. The 550°C product lists are similar to that observed at 500°C. Increasing the ASR residence time at 550°C from 3.2 to 11.6 min appears to increase the quantities of benzene and toluene. It also appears that the quantities of PAH's increased on increasing the pyrolysis temperature from 500°C to 550°C as shown in Table 10. The longer 550°C pyrolysis residence time of 11.6 min further increased both the mono-aromatic and PAH production over that of the 3.2 min residence time in

Table 4
Major compounds detected in pyrolysis liquid from pyrolysis at 500°C

Compound	Area (%)
Benzene	5.75
Toluene	5.54
1-Hexene	5.50
Pentane	5.26
Styrene	4.47
2-Butanone	4.24
2,4-Dimethyl-1-heptene	3.81
1-Propene, 2-methyl-	3.45
1-Heptene	2.85
Ethylbenzene	2.82
2,3-Pentadiene	2.71
2-Methylfuran	2.68
Cyclopentene	2.65
1-Pentene	2.59
1-Octene	2.40
3-Pentanone	2.08

keeping with the observations of Williams and Besler [27] for slow biomass pyrolysis processes.

The 18 major compounds, out of a total of 34, observed for the 600°C pyrolysis are listed in Table 7. Based upon this data it would appear that results obtained with the 600°C experiment could be an anomaly in that no detectable quantities of benzene were found in the liquid fraction while benzene was the major liquid

Table 5
Major compounds detected in pyrolysis liquid from pyrolysis at 550°C[a]

Compounds	Area (%)
Benzene	6.19
1-Hexene	5.02
Toluene	4.79
Cyclopropane	4.38
1,3-Butadiene	4.10
1,3-Butadiene, 2-methyl-	3.71
Styrene	3.38
1-Pentene	3.03
2-Butanone	2.77
Ethylbenzene	2.62
1-Heptene	2.55
Cyclopentene, 1-methyl-	2.37
Cyclopentene	2.36
Cyclopropane, 1,2-dimethyl-, *cis*-	2.07
1-Buten-3-yne, 2-methyl-	2.03

[a] Residence time = 3.2 min.

Table 6
Major compounds detected in pyrolysis liquid from pyrolysis at 550°C[a]

Compounds	Area (%)
Benzene	9.34
Toluene	7.96
1-Pentene	5.56
Ethylbenzene	4.11
Styrene	3.80
1-Hexene	3.57
2-Butanone	2.83
1-Propene, 2-methyl-	2.75
1,3-Pentadiene	2.63
Cyclopropane, 1,2-dimethyl-, *cis*-	2.58
Cyclopentene, 1-methyl-	2.39
p-Xylene	2.23
1-Heptene	2.18
1-Octene	1.74
1,3-Cyclopentadiene	1.70

[a] Residence time = 11.6 min.

product in all the other pyrolyses. It should also be noted that the mass balance for this experiment was also inconsistent with the other experiments, suggesting that the results obtained at 600°C should be interpreted with care. However, of the compounds detected, methylstyrene and styrene had the largest peak areas. The

Table 7
Major compounds detected in pyrolysis liquid at 600°C

Compounds	Area (%)
.alpha. -Methylstyrene	12.96
Styrene	10.64
1H-Indene, 1-methyl-	10.59
Benzene, 1-propenyl-, (*E*)-	5.89
Acetophenone	5.43
Naphthalene	4.10
Ethylbenzene	3.93
Indene	3.53
Benzene, 2-butenyl-	3.32
p-Xylene	3.10
Phenol, 2-methyl-	2.64
Phenol, 4-methyl-	2.59
Benzene, 1-propenyl-, (*E*)-	2.46
1H-Indene, 1,1-dimethyl-	2.44
Naphthalene, 1-methyl-	2.39
Naphthalene, 2-methyl-	2.23
4,7-Methano-1H-indene, 3a,4,7,7a-tetrahydro-	2.16
Benzonitrile, 2-methyl-	2.03

Table 8
Major compounds detected in pyrolysis liquid from pyrolysis at 700°C

Compounds	Area (%)
Benzene	30.37
Toluene	17.25
Styrene	10.55
Naphthalene	4.72
Benzene, 1,3-dimethyl-	3.98
Acetone	3.24
Indene	2.32
1,3-Butadiene	2.07
Thiophene	1.97
2-Norbornene	1.78
1,3-Cyclopentadiene	1.66
Ethylbenzene	1.58
Bicyclo [2.2.1] hept-5-ene-2-carbonitrile	1.55
Phenol	1.43
Naphthalene, 2-methyl-	1.30
Benzonitrile	1.10
Benzene, 1-propenyl-	1.08
Anthracene	1.04

600°C pyrolysis liquid also had very few aliphatics (4% peak area) and large portions of mono-aromatics (59% peak area) and PAH's (37% peak area) as listed in Table 10.

The major 18 compounds of the 45 detected in the 700°C pyrolysis liquid are listed in Table 8. Benzene was the compound with the largest peak area response. The increase in mono-aromatics also continued as the pyrolysis temperature was increased (see Table 10), however, the PAH content dropped with respect to the questionably very high values observed at 600°C.

All 14 detected compounds in the 750°C pyrolysis liquid are listed in Table 9. In this case the mono-aromatics (see Table 10) were the most dominant organic compounds identified in the pyrolysis liquid, with benzene, toluene, naphthalene and styrene being the major components. However, it should be noted that the yield of the pyrolysis liquid produced at this pyrolysis temperature, 750°C, was one half of that obtained at the lower pyrolysis temperature of 500°C (see Fig. 3). The PAH's were maintained at the 700°C pyrolysis level but the aliphatics content almost disappeared (see Table 10).

The product yields of several of the major liquid compounds are presented, in Figs. 6 and 7, as a function of pyrolysis temperature, for the major aromatic and aliphatic compounds, respectively. From this data it can be seen that the yield of the aliphatic compounds fall off rapidly as the pyrolysis temperature increases while that of the aromatic compounds remain relatively constant.

Although the compounds listed in Tables 4–9 represent the major compounds produced; from an environmental point of view, it is interesting to know what organo sulphur, nitrogen, and chlorine compounds are produced. In terms of

Table 9
Major compounds detected in pyrolysis liquid from pyrolysis at 750°C

Compound	Area (%)
Benzene	52.77
Toluene	19.92
Naphthalene	8.71
Styrene	6.33
Phenanthrene	2.48
Indene	1.96
p-Xylene	1.32
Acenaphthylene	1.16
Benzonitrile	1.02
Naphthalene, 2-methyl-	0.80
Naphthalene, 2-ethenyl-	0.77
Aniline	0.76
Fluorene	0.67
Acetonitrile	0.46

nitrogen containing compounds, the following were detected: propanenitrile, butanenitrile, 1-butylpyrolidine, 2-methylbenzonitrile, benzonitrile, pyridine, 2-methylpyridine, pyrrole, *p*-aminotoluene, aniline, indole, quinoline, and isoquinoline. Only two organo-sulfur compounds were detected, i.e. 1-dodecane thiol, and thiophene. Several organo-chloride compounds were also detected, including: 1-chloro-1-propene, 1-chlorooctadecane, 5-chloro-2-methylbenzofuran, and 1-chlorohexadecane. Other species of possible concern included: 2-methylfuran, 2,5-dimethylfuran, benzofuran, acetophenone, 2,2′-oxybisethanol, phenol, 2-methylphenol, and 4-methylphenol.

The distribution of phenols in the pyrolysis liquids, as a function of pyrolysis temperature, is listed in Table 11. Only two methylphenols were detected in the 600°C experiment while phenol was detected in the 500, 550 and 700°C liquids. Much smaller quantities of phenol were detected in the 500 and 550°C pyrolysis liquids. Phenolic compound production dropped off above 600°C pyrolysis temperatures. This contrasts sharply with the data observed by Rausa and Pollesel [24] who observed maximum phenol production at 800°C. These differences are indica-

Table 10
Peak area percentages of classes of compounds found in the pyrolysis liquid

Pyrolysis temperature (°C)	Residence time (min)	Aliphatics	Mono-aromatics	PAH's
500	3.2	77.28	22.55	0.18
550	3.2	77.58	20.79	1.61
550	11.6	65.55	31.81	2.65
600	3.2	3.86	58.78	37.36
700	3.2	13.00	69.53	17.47
750	3.2	1.32	82.12	16.55

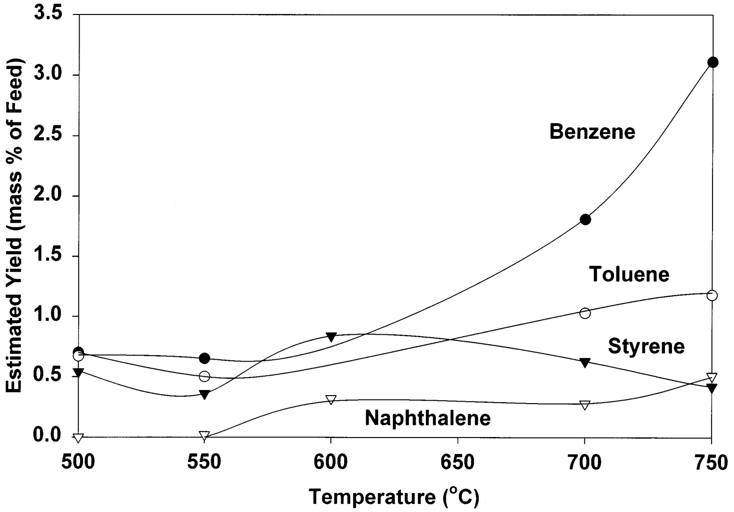

Fig. 6. Mass yields of the pyrolysis liquids benzene [●], toluene [○], styrene [▼] and naphthalene [▽] expressed as a function of ASR feed, plotted as a function of pyrolysis temperature.

tive of the two pyrolysis processes. The PAH formation data is listed in Table 12. This data on PAH formation is similar to that observed by Rausa and Pollesel [24] using Italian ASR and by Williams and Besler [27] pyrolysing shredded municipal solid waste, wood waste and rice husks. No PAH's were observed in the 500°C and 550°C pyrolysis liquids. Naphthalene and its methyl derivatives were the com-

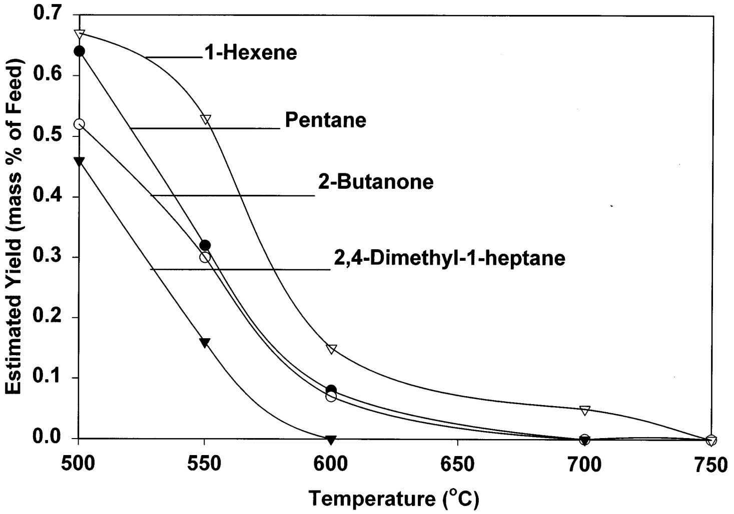

Fig. 7. Mass yields of the pyrolysis liquids pentane [●], 2-butanone [○], 2,4-dimethyl-1-heptane [▼] and 1-hexane [▽] expressed as a percentage of ASR feed, plotted as a function of pyrolysis temperature.

Table 11
Phenols present in ASR pyrolysis liquids

Pyrolysis temperature (°C) Residence time (min)	500 3.2	550 3.2	550 11.6	600 3.2	700 3.2	750 3.2
Compounds						
Phenol	<0.01	<0.05	<0.05		1.43	
2-methylphenol				2.70		
4-methylphenol				2.65		
Total peak areas	<0.01	<0.05	<0.05	5.35	1.43	0.00

pounds with the largest peak area percentages at the 600°C pyrolysis temperature. Naphthalene was also the compound exhibiting the largest peak area percentage at 700°C, with its concentration increasing as the pyrolysis temperature increased, similar to the flash-pyrolysis results of Rausa et al. [24]. Clearly many of the PAH organo-chlorine compounds are undesirable if the oil is to be used as a fuel. This situation could be exaggerated by the presence of PVC in the feed under certain pyrolysis conditions as has been reported elsewhere [34].

3.4. Composition of the pyrolysis solid residues

The solid residues can be considered to be composed of three components. An organic fraction composed of organic material (not fully degraded polymeric

Table 12
Peak area percentages of some polycyclic aromatic hydrocarbons (PAH's) in ASR pyrolysis liquids

Pyrolysis temperature (°C) Resdence time (min)	500 3.2	550 3.2	550 11.6	600 3.2	700 3.2	750 3.2
Compounds						
Indene				3.53	2.32	1.96
Naphthalene				4.10	4.72	8.71
Acenaphthylene				1.07	0.61	1.16
Fluorene					0.23	0.67
Phenanthrene/anthracene					1.42	1.39
Fluoranthene					0.25	
Pyrene					0.45	
Derivatives						
Naphthalene, methyl				4.62	2.18	0.80
Naphthalene, 2-ethenyl				1.35	0.91	0.77
Naphthalene, dimethyl				1.56		
Anthracene, methyl					0.13	
Naphthalene, 2-phenyl					0.23	
Total peak areas	0.00	0.00	0.00	16.23	13.45	15.46

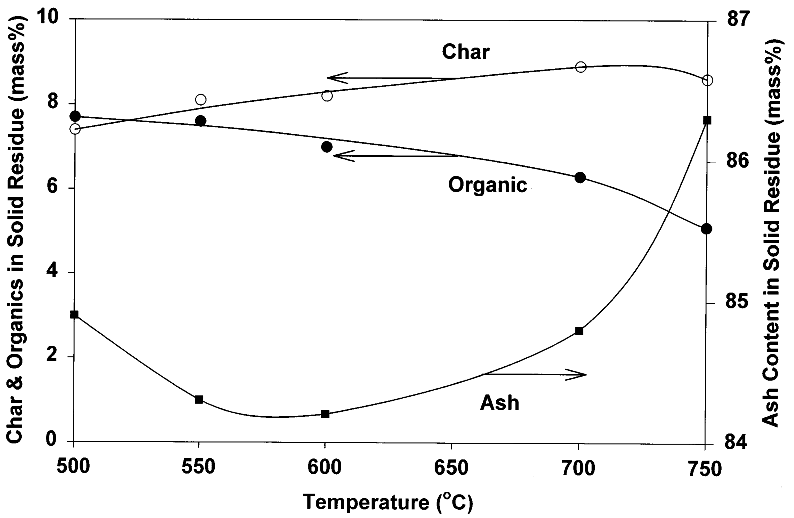

Fig. 8. Weight distribution of organic [●], char [○] and inorganic [■] ash fractions in the solid residue product as a function of pyrolysis temperature.

species and high molecular weight products), a carbonaceous char and inorganic ash. The composition of these three components in the solid residues is presented in Fig. 8 as a function of pyrolysis temperature.

From this data it can be seen that the organic fraction decreases while the inorganic content increases as the pyrolysis temperature increases. The carbonaceous char yield, however, was found to remain relatively constant between 7 and 9% over the whole range of pyrolysis temperature conditions explored.

From the quantities of pyro-gas, pyro-oil and residue-extracted oil it would appear that a relatively high conversion rate of between 60 and 85% was achieved for the organic material in the ASR at the temperatures used in this study.

In terms of the variable residence time experiments at 550°C, it would appear that increasing the residence time from 3.2 to 11.6 min had little influence on the ash content of the solid residue (Table 13). However, the increased residence time did result in a reduction in the organic content, and an increase in the carbonaceous char produced in the solid residue.

Table 13
Composition of solid residues of samples pyrolyzed at 550°C

Residence time (min)	Total solids (%)	Organic fraction (%)	Carbonaceous char (%)	Ash contents (%)
3.2	77.8	7.6	8.1	84.3
11.6	75.4	5.9	9.9	84.2

Table 14
Phenols present in ASR pyrolysis residue extracts

Pyrolysis temperature (°C)	500	550	550	600	700	750
Residence time (min)	3.2	3.2	11.6	3.2	3.2	3.2
Compounds						
2-methylphenol	1.27	0.59	0.98			
4-methylphenol	1.42	0.96	1.28			
2,5-dimethylphenol	0.77	0.65	0.51			
3-(1-methylethyl)phenol	1.07	0.35				
2,4,6-tris(1,1-dimethylethyl)phenol	0.74	0.87	0.86	1.94		
2,6-bis(1,1-dimethylethyl)-4-ethylphenol	2.64	2.47	1.83	3.18	0.29	0.29
Total peak areas	7.91	5.89	5.46	5.12	0.29	0.29

GC/MSD analysis of the THF residue extracts from the solid residues indicated the presence of between 32 (600°C pyrolysis) and 90 (500°C pyrolysis) organic species. The occurrence of phenols in the pyrolysis residue extracts is presented in Table 14. The quantities of phenols drop off dramatically above pyrolysis temperatures of 600°C which is consistent with the observations for the pyrolysis liquids. Some of the tentatively identified polycyclic aromatic hydrocarbons (PAH's) are listed in Table 15. A few PAH's were detected in the 500 and 550°C pyrolysis residue extracts while none were detected in the corresponding liquids (Table 12). The 600°C pyrolysis residue extract however indicated the presence of phenanthrene/anthracene only, while no other PAH's were detected. When the pyrolysis temperature was increased to 700°C the variety and quantities of PAH's increased dramatically. An increase in PAH content was observed with increased residence time (3.2 vs. 11.6 min), at a 550°C pyrolysis temperature, see Table 15.

The THF extracts obtained from the 700 and 750°C pyrolysis residues also yielded some compounds not observed in the pyrolysis liquids, namely, the nitrogen compounds: benzothiazole, carbazole, 9-anthracenecarbonitrile, 2-naphthalenecarbonitrile, 5-methylquinoline, the sulfur compounds: benzothiozole, dibenzothiophene as well as dibenzofuran, and butyrolactone.

4. Conclusions

Pyrolysis of ASR offers an alternative process for the recovery of hydrocarbon resources from an otherwise waste material. However, while the use of the screw kiln technology may be relatively easy to perform and control, the value of the hydrocarbon products obtained still needs to be fully evaluated. Clearly, based upon the information provided in this paper, the gaseous and liquid hydrocarbon products of pyrolysis are a complex mixture of organic compounds in which the quantities obtained are very much dependent upon the pyrolysis conditions employed (i.e. temperature and residence time). While the gas fraction may be acceptable as a fuel for most applications, it would appear that the pyrolysis liquid may need further processing to achieve a marketable product. The fate of chlorine associated with poly(vinyl chloride) and flame retardants present in the ASR still remains a major concern which is the focus of a separate paper [34]. The pyrolysis residue could be separated into heavier organic compounds, recyclable metals and a waste stream for disposal. The pyrolysis technique, its temperature and both the material and gaseous product residence times can be varied in an attempt to maximize the yield of the desired products (types and quantities gases or liquids). Low screw-kiln pyrolysis temperatures (500°C) favoured the production of liquids and these liquids contained mainly akanes, alkenes and mono-aromatics with undetected polycyclic aromatic hydrocarbons but some PAH's were extractable from the solid residue.

Table 15
Peak area percentages of some polycyclic aromatic hydrocarbons (PAH's) in ASR pyrolysis residue extracts

Pyrolysis temperature (°C)	500	550	550	600	700	750
Residence time (min)	3.2	3.2	11.6	3.2	3.2	3.2
Compounds						
Indene		0.68	0.93		1.63	0.43
Naphthalene	2.98	1.71	2.30		10.59	8.25
Acenaphthylene					3.79	2.89
Acenaphthene					0.66	0.34
Fluorene			0.32	1	3.64	1.69
Phenanthrene/anthracene	2.02	0.30	0.58	0.90	5.41	6.91
Fluoranthene					1.47	2.82
Pyrene	0.43	0.38	0.43		1.69	2.68
Benzo(a)anthracene					0.75	0.74
Chrysene					0.54	0.64
Derivatives						
1H-Indene, 1-methyl		1.27	1.90		0.35	
Naphthalene, methyl		1.57	2.83		6.85	2.42
Naphthalene, 2-ethenyl		0.53	0.61		2.00	1.35
Naphthalene, dimethyl					3.05	
1,1′-Biphenyl, 3-methyl					0.59	0.22
2-Naphthalenecarbonitrile					0.60	0.31
9H-Fluorene, 1-methyl					1.43	0.16
Naphthalene, 1-phenyl					0.84	0.69
Anthracene, methyl					3.06	1.02
Naphthalene, 2-phenyl			0.44		1.03	1.05
11H-Benzo[b]fluorene					0.84	0.81
Pyrene, 2-methyl					0.22	
Total areas	5.43	4.49	7.51	0.90	48.46	34.77

References

[1] R.J. Rowatt, Chemtech 23 (1993) 56.
[2] R. Higgs, Plastic News 9 (April 28) (1997) 17.
[3] W. Kaminsky, Makromol. Chem., Macromol., Symp. 57 (1992) 145–160.
[4] H. Bockhorn, A. Hornung, V. Hornung, J. Anal. Appl., Pyrolysis 46 (1998) 1–13.
[5] A. Napoli, Y. Soudais, D. Lecomte, S. Castillo, J. Anal. Appl., Pyrolysis 40–41 (1997) 373–382.
[6] Anon. Modern Plastics 71 (1) (1994) 93.
[7] M. Lee, Chem. Britain 31 (7) (1995) 515.
[8] M.G. Leuna, Kunststoffe 85 (1995) 214.
[9] P. Mapleston, Mod. Plast. 70 (11) (1993) 58.
[10] S.X. Liu, G.R. Winslow, S. Yester, G.P. Gromek, A. Crouch, V. Sendijarevic, Automotive Eng. Intl. 106, No. 9 (1998) 78–81.
[11] G.R. Winslow, S.X. Liu, S.G. Yester, Automotive Eng. Intl. 106, No. 9 (1998) 83–87.
[12] American Iron and Steel Institute Report, Recycling: state of the art for scrapped automobiles, prepared by Arthur D. Little Inc. Ref. 67110, January 10th, 1992
[13] R.J. Schmitt, Automobile Shredder Residue—the Problem and Potential Solution, CMP Report #90–1, Centre for Material Production, Pittsburgh, PA, 1990.
[14] M. Day, J. Graham, R. Lachmansing, E. Chen, Res. Conserv., Recycl. 9 (1993) 255.
[15] D. Lanoir, G. Trouve, L. Delfosse, D. Froelich, A. Kassamaly, Waste Manag. Res. 15 (1997) 267.
[16] A.G. Van Stolk, A.C. Lewis, C.A. Snavely, Proc. 49th Annu. Tech. Conf. (Antec 91), Society of Plastic Engineers, Brockfield, CT, (1991), 2142
[17] J. Braslaw, D.J. Melotik, R.L. Gealer, R.C. Wingfield, Thermochim., Acta 186 (1991) 1–18.
[18] C. Roy, P. Malette, Vacuum pyrolysis of automobile shredder residue, presented at IGT Conference: Energy from Biomass and Wastes, XVI, Chicago, IL, March, 1992.
[19] S.C. Arrington, Pyrolyis conversion of commingled solid waste including auto shredder residue, presented at Auto Recycle 92, November, 1992, p. 155–172
[20] A. Pierce, Gasification of heterogeneous polymers via catalytic extraction processing: auto shredder residue—case study, presented at Auto Recycle (November) 92 (1992) 203–213.
[21] L.L. Sharp, R.O. Ness, Gasification-Pyrolysis of Waste Plastics for the Production of Fuel Grade Gas, ACS Symp. Ser. 513, American Chemical Society, Washington, DC (1993), 129.
[22] Z. Shen, M. Day, J.D. Cooney, G. Lu, C.L. Briens, M.A. Bergougnou, Can. J. Chem., Eng. 73 (1995) 357.
[23] M. Day, J.D. Cooney, Z. Shen, J. Anal. Appl., Pyrolysis 37 (1996) 49.
[24] R. Rausa, P. Pollesel, J. Anal. Appl., Pyrolysis 40–41 (1997) 383–401.
[25] O. Patierno, P. Cipriani, F. Pochetti, M. Giona, Chem. Eng. J. (Lausanne) 70, No. 2 (1998) 157–163.
[26] M. Day, J. Shen, Automobile Shredder Residue—An Assessment of Thermal Recycling as a Recovery Option, ISBN 0-660-16732–8 (1997).
[27] P.T. Williams, S. Besler, J. Anal. Appl. Pyrolysis 30 (1994) 17–33.
[28] D.C. Elliott, in: J. Soltes, T.A. Milne (Eds.), Pyrolysis Oils from Biomass; Producing, Analyzing and Upgrading, ACS Symposium Series 376, , Washington, DC 1988, Chapter 6, 55–65.
[29] R.J. Evans, T.A. Milne, Energy Fuels 1 (1987) 125.
[30] J.P. Diebold, in: J.L. Jones and S.B. Radding (Eds), Thermal Conversion of Solid Wastes and Biomass, ACS Symposium Series 130, Washington, DC, 1980, pp. 209–226.
[31] J.P. Diebold, R. Evans, J. Scahill, Energy, Biomass Wastes 13 (1990) 851–878.
[32] M.E. Bednas, M. Day, K. Ho, R. Sanders, D.M. Wiles, J. Appl. Polym., Sci. 26 (1981) 277.
[33] S. Tsuge, T. Okumoto, Y. Sugimura, T. Takeuchi, J. Chromatogr., Sci. 7 (1969) 253.
[34] M. Day, L. Shabnavard, J.D. Cooney, SAE International Congress & Exposition, Cobo Center, Detroit, MI, USA, March 1–4, 1999.