

## Hydrocarbon generation during the inert gas pyrolysis of automobile shredder waste

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### Abstract

When junked automobiles are shredded to recover the ferrous and non-ferrous metals, a large quantity of non-metallic waste is generated. These waste materials consist mainly of rubber and plastics. In this paper, the product yields and compositions obtained during inert gas pyrolysis of a representative shredder non-metallic waste fraction in three different experimental systems (batch thermogravimetric analyzer, bench scale batch pyrolyzer, and continuous rotary kiln) are compared. Analysis of the products by GC, HPLC, GC-MS, IR spectroscopy,  $H^+$  NMR and GPC show the presence of many hydrocarbon compounds with no single species present in large concentrations. Weight loss kinetics during the pyrolysis are also presented and discussed. The products obtained without additional processing are complex and contain compounds that prevent their direct use as a fuel in many applications. As a result, commercial exploitation of this process must await evaluation of the products obtained and, if necessary, the costs of purification and modification of the products to more useful compositions.

### INTRODUCTION

When junked automobiles are shredded to recover the ferrous and non-ferrous metals, large quantities of non-metallic wastes are generated. These waste materials consist mainly of rubber and plastics. Increasing proportions of these materials in new and future automobiles are likely to increase the non-metallic waste fraction [1–3]. Conversion of these materials to hydrocarbons by inert gas pyrolysis processes would reduce the use of costly landfill sites for disposal and avoid the waste of this potentially valuable resource [4].

In a presentation in 1981, the authors described the effect of operating parameters on the product yield and product composition in batch inert gas pyrolysis experiments [5]. In this paper, the product yields and compositions obtained during pyrolyses in three different experimental systems (batch thermogravimetric analyzer, bench scale batch pyrolyzer, and continuous

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rotary kiln) are presented. The resulting products are evaluated to determine their suitability to replace currently available hydrocarbon fuels in the marketplace.

## EXPERIMENTAL

### *Shredder waste materials*

Automobiles manufactured during the last few years contain a large variety of plastics and rubber components [3,6]. The relative proportions of the major types of non-metallic components in 1980 and 1990 automobiles are listed in Table 1. Rubber and polyurethanes are the largest fractions, followed by polypropylene. PVC, ABS and glass-reinforced sheet-molding compounds are also present in large amounts. As expected, the mixture of non-metallic materials produced by the shredders is highly variable and complex. As shown in Table 1, the quantity of these materials in US-manufactured passenger vehicles has increased both in absolute and relative terms during the past ten years. It is anticipated that these increases will continue in the future [3].

Elemental analyses of the shredder waste products pyrolyzed in the work reported here are shown in Table 2. These samples were provided by the Huron Valley Steel Company, a major automobile shredder operator, and

TABLE 1

Plastics and non-tire rubber composition of U.S.-manufactured passenger vehicles <sup>a</sup>

	(Percent of total)	
	1980	1990
Non-tire rubber	33.8	25.3
Polyurethane	17.6	18.0
Polypropylene	11.6	12.9
Poly(vinyl chloride)	8.3	7.6
ABS	6.1	7.5
Unsaturated polyester (SMC)	13.2	7.3
Nylon	2.6	5.7
Polyethylene	0.6	3.2
Polycarbonate	0.8	3.0
Thermoplastic polyesters	0.8	1.9
Acrylics	1.2	1.1
Acetals	0.7	1.0
Phenolic	1.2	0.7
All other	1.7	4.7
Weight of plastics and non-tire rubber (kg)	145.0	165.7
Average vehicle curb weight (kg)	1528.6	1390.0
Percent plastics and non-tire rubber	9.5	11.9

<sup>a</sup> Sources: Modern Plastics Annual Reviews and Elastomerics Annual Reviews.

TABLE 2

Elemental composition of automobile shredder waste—first dense media reject, Huron Valley Steel Corp. (range for four different samples)

Element	Weight percent
C	57–64
H	5–7
N	0.2–0.4
Cl	3–5
O	5–15
Cu	0.4–1.1
Al	0.4–1.2
Zn	0.2–1.3
ASH	15–20

were subsequently hand-quartered and ground to ensure reasonable homogeneity. The inorganic content of the samples include both loose and imbedded metals due to their incomplete removal during the separation processes, and inorganic fillers in the rubber and plastics. This material is representative of the first non-magnetic float fraction separated from the shredder wastes received by the secondary metals recoverer.

For the batch inert gas pyrolysis experiments discussed here, the waste material was ground cryogenically to particles less than 2 mm in size. The thermogravimetric analyzer samples were further reduced to less than 1 mm in size, while the rotary kiln experiments used particles of 5 mm or less in size.

#### *Batch inert gas pyrolysis*

In the batch inert gas pyrolysis system shown in Fig. 1, a sample weighing approximately 40 grams was placed inside a quartz tube heated by a tube furnace at an initial rate of 60 °C per minute to 300 °C, and then at 25 °C per minute to the final holding temperature, which was varied between 460 and 770 °C. Continuous nitrogen sweep was maintained for the duration of the experiments, with rates varying between 100 and 400 ml min<sup>-1</sup>, to study the effect of gas residence time on the product distribution and composition. The quartz tube used in these experiments had a diameter of 51 mm and a heated length of 914 mm, thus allowing for nominal inert gas residence times (based on the gas density at 20 °C) of between 4.67 and 18.7 minutes in the hot zone.

The vapors generated in these experiments were condensed in a series of cold traps. At the end of each experiment, the liquids collected in the traps were allowed to reach room temperature and the re-volatilized vapors were analyzed along with the uncondensed gaseous products using Fourier-trans-

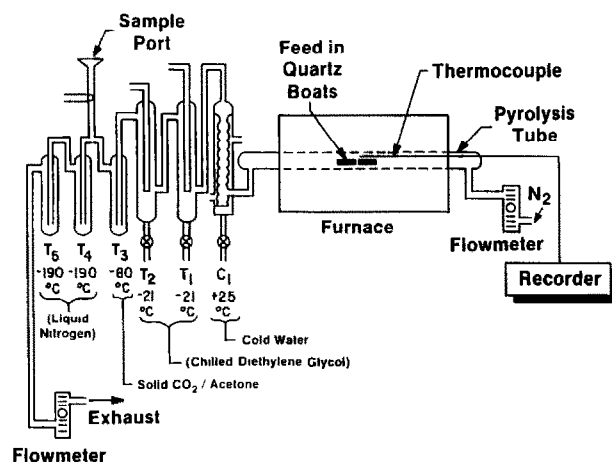


Fig. 1.

form infrared spectroscopy. The remaining condensate (defined here as “oil”) was analyzed using tandem gas chromatography-mass spectroscopy, high performance liquid chromatography, gel permeation chromatography and nuclear magnetic resonance spectroscopy. Elemental analyses were also obtained for the char and liquid products.

### *Thermogravimetric experiments*

A Du Pont Model 951 Thermogravimetric Analyzer was used to obtain the results described. Typically, a 20 mg sample was placed in a platinum pan suspended from the quartz rod of the balance and placed inside a quartz tube heated by a resistance-wound ceramic furnace. For these experiments, the sample was heated from 25 °C to the desired final holding temperature between 500 and 800 °C at heating rates that were varied between 5 and 20 °C min<sup>-1</sup>. Dry argon sweep was maintained during the heating period. In some experiments, the sample was then heated to 800 °C with an air sweep to determine the quantity of ash present in the pyrolysis char.

### *Rotary kiln pyrolysis*

For these experiments, a Pereny Equipment Co. Model RT-472 MT-101 rotary kiln was used. This kiln has a 1830 mm long rotating stainless steel tube, 100 mm in diameter, heated by a three-zone furnace that may be tilted to a maximum of 15 degrees. As shown in Fig. 2, the system consists of the furnace, a Syntron vibratory feeder and feed hopper, a water-cooled char hopper with a 5.1 cm blast gate, a series of glass cold-traps fitted with demisters, and a gas sampling and exhaust system.

A nitrogen inlet was fabricated at the interface between the feeding system and the rotary tube. Temperature inside the furnace was maintained

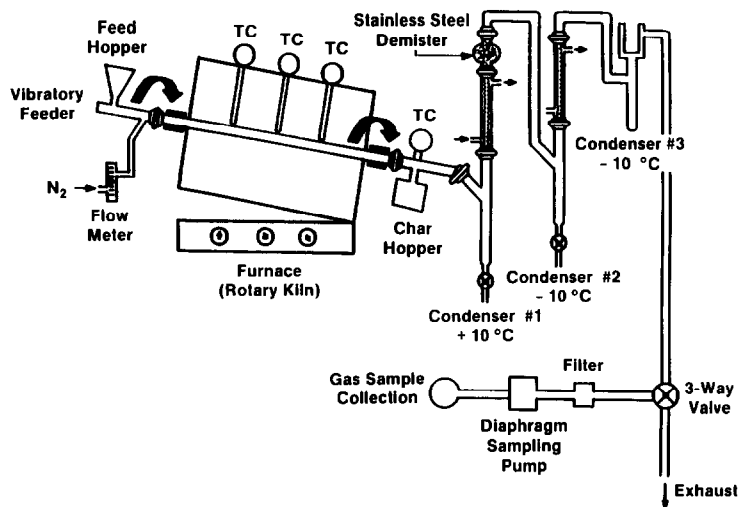


Fig. 2.

by means of three independent Honeywell Dialatrol proportioning temperature controllers driving Halmar thyristor power amplifiers connected to the silicon carbide heating elements of the furnace. Type-J thermocouples mounted outside and just above the rotating tube in the middle of each heated zone were used to monitor each zone temperature.

## RESULTS AND DISCUSSION

### *Batch pyrolysis results*

The results of 12 experiments in the batch pyrolyzer are shown in Table 3. With final holding temperatures in the range of 460 to 770 °C, and nitrogen sweep rates between 100 and 400 ml min<sup>-1</sup>, an average of 53 percent by weight of the feed is volatilized. The liquid produced averaged 34% of the feed, while gaseous product averaged 19.4%. As can be determined from the replicate runs in Table 3, the char/liquid/gas ratios did not appear to vary with the final holding temperature or the inert gas flow rate beyond a 2σ (95%) confidence limit. It appears that variations in feed composition and/or experimental error have a greater effect on yields than the operating conditions examined. The greater variability of the gas yield is caused by the method used to determine this result—by difference, following liquid and char residue weight measurements. The product yields are comparable with those obtained by others [7,8].

Of the gases obtained carbon dioxide (28 volume percent) and volatile hydrocarbons are the major components. The average composition and yield of gaseous hydrocarbons are shown in Table 4. Generally, C<sub>1</sub> to C<sub>3</sub> and, on occasion, C<sub>4</sub> hydrocarbons are the major components. The variation in yield

TABLE 3

Effect of operating variables on product distribution in the bench scale experiments

Temp. program <sup>a</sup>	Residence time for nitrogen in hot zone (min)	Final (holding) temp.	Sample weight (g)	Char (percent of feed)	Liquids (percent of feed)	Gases (percent of feed)
<i>Variation of inert gas residence time</i>						
A	9.34	657	40.18	44.9	33.7	21.4
A	6.22	666	40.38	47.0	37.1	15.8
A	6.22	652	41.26	44.8	35.1	20.1
A	6.22	657	39.74	44.4	35.8	19.8
Average of 3 replicates				45.4	36.0	18.6
A	4.67	657	40.71	46.3	35.2	18.5
<i>Variation of holding temperature</i>						
A	4.67	462	41.89	47.0	36.8	16.2
A	4.67	563	41.25	45.7	33.9	20.4
A	4.67	657	40.71	46.3	35.2	18.5
<i>Long nitrogen residence times</i>						
A	12.44	586	50.28	49.2	27.4	23.4
B	6.02	469	14.92	47.2	34.7	18.1
B	> 18.7	660	29.75	48.8	38.1	13.1
B	18.7	700	27.32	47.8	31.5	20.6
B	18.7	770	27.79	45.4	28.5	26.1
Average of all experiments				46.6	34.0	19.4
Range				44.4–49.2	27.4–38.1	13.1–26.0

<sup>a</sup> Temperature programs: A, 60°C min<sup>-1</sup> to 300°C then 25°C min<sup>-1</sup> to hold; B, 100°C steps in an average of 8 min per step to hold.

TABLE 4

Gaseous fraction average composition and yields from bench scale experiments

Hydrocarbon	Volume percent of feed		Weight percent of feed
	Average	Range	
CH <sub>4</sub>	16.3	2.2–24.0	1.2
C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>6</sub>	17.0	12.5–17.3	2.3
C <sub>3</sub> H <sub>6</sub> + C <sub>3</sub> H <sub>8</sub>	9.8	8.9–11.3	2.0
C <sub>4</sub> H <sub>8</sub> + C <sub>4</sub> H <sub>10</sub>	8.0	1.6–18.6	2.2
(Isobutylene) <sup>a</sup>	4.8	0.3–11.4	1.3
C <sub>5</sub> H <sub>12</sub> + C <sub>5</sub> H <sub>10</sub>	3.1	Trace–7.3	1.0
C <sub>6</sub> H <sub>12</sub> (olefins)	3.6	0.6–8.7	1.4
Benzene	1.7	1.0–2.3	0.63
Toluene	1.1	0.7–1.4	0.48
Inorganic gases	40.7		
CO <sub>2</sub> <sup>b</sup>	28.4		

<sup>a</sup> Included in C<sub>4</sub> gases. <sup>b</sup> Included in inorganic gases.

TABLE 5

Effect of inert gas flow-rate on gas-phase composition in bench scale pyrolysis: final gas temperature; 652–660 °C

Compound	Weight percent of feed		
	200 ml min <sup>-1</sup>	300 ml min <sup>-1</sup> <sup>a</sup>	400 ml min <sup>-1</sup>
CH <sub>4</sub>	1.9	1.5	1.2
C <sub>2</sub> s	2.4	2.5	2.2
C <sub>3</sub> s	2.5	1.9	2.0
<i>n</i> -Butane	Trace	0.7	Not detected
1- and 2-Butane	0.2	0.2	0.2
Isobutylene	3.4	1.1	1.9
C <sub>5</sub> s	0.4	0.6	0.5
C <sub>6</sub> s (olefins)	0.3	1.3	1.9
Benzene	0.9	0.7	0.4
Toluene	0.4	0.4	0.4
Total gas <sup>b</sup>	21.4	18.6	18.5

<sup>a</sup> Average of 3 experiments. <sup>b</sup> Including inorganic compounds not listed.

of gaseous hydrocarbons with inert gas flow rate and final holding temperature are shown in Tables 5 and 6 respectively. The concentrations of many of the components vary widely over the operating ranges examined. However, in many cases, variations in the concentration of individual components in replicate experiments (Table 7) are as great or greater than the variations observed with changes in the inert gas flow rate or the final temperature. Hence, the variations cannot necessarily be attributed to these

TABLE 6

Effect of final holding temperature on gas-phase composition in bench scale pyrolysis: inert gas flow-rate, 400 ml min<sup>-1</sup>

Compound	Weight percent of feed		
	657 °C	563 °C	462 °C
CH <sub>4</sub>	1.2	1.1	0.1
C <sub>2</sub> s	2.2	2.7	1.5
C <sub>3</sub> s	2.0	2.4	1.5
<i>n</i> -Butane	Not detected	Trace	0.6
1- and 2-Butane	0.2	0.2	1.0
Isobutylene	1.9	0.2	0.6
C <sub>5</sub> s	0.5	2.7	1.8
C <sub>6</sub> s (olefins)	1.9	0.8	3.0
Benzene	0.4	0.8	0.3
Toluene	0.4	0.4	0.3
Total gas <sup>a</sup>	18.5	20.4	16.2

<sup>a</sup> Including inorganic compounds.

TABLE 7

FTIR analyses of gases in replicate experiments in bench scale pyrolysis: inert gas flow-rate, 300 ml min<sup>-1</sup>; final holding temperature, 652–666 °C

Compound	Weight percent of feed			
	Run R1	Run R2	Run R3	Avg. (std. dev.)
CO <sub>2</sub>	4.7	5.3	6.1	5.4 (0.7)
H <sub>2</sub> O	0.3	0.3	0.3	0.3 (0.02)
HCl	N.D. <sup>a</sup>	0.9	1.2	1.1 (0.2)
CH <sub>4</sub>	1.3	1.9	1.2	1.5 (0.4)
C <sub>2</sub> s	2.0	2.8	2.7	2.5 (0.4)
C <sub>3</sub> s	1.5	2.0	2.1	1.9 (0.3)
<i>n</i> -Butane	1.2	0.7	0.7	0.9 (0.3)
1- and 2-Butane	0.6	N.D. <sup>a</sup>	N.D. <sup>a</sup>	0.2 (0.3)
Isobutylene	2.2	0.4	0.7	1.1 (1.0)
C <sub>5</sub> s	0.8	Trace	0.9	0.6 (0.5)
C <sub>6</sub> s (olefins)	0.2	2.1	1.7	1.0 (0.8)
Benzene	0.5	0.8	0.9	0.7 (0.2)
Toluene	0.5	0.4	0.4	0.4 (0.1)
Total gas	15.8	20.1	19.8	18.6 (2.4)

<sup>a</sup> Not detected.

operating variables. A striking example is the yield of isobutylene, which ranges from 0.4 to 2.2% of the feed (Table 7). One possible explanation is that the HCl concentration in the gas could change the rate of polymerization of the isobutylene. Decreased levels of isobutylene are observed when the concentration of HCl increases. This change in HCl level may be due to sample-to-sample variation of the poly(vinyl chloride) present in the feed.

The high CO<sub>2</sub> levels measured in these experiments caused concern as to whether unwanted combustion was occurring in parallel with the pyrolysis process. However, experiments with model compounds in the same system and under similar conditions produced significantly lower yields of CO<sub>2</sub>, giving evidence that little or no combustion was occurring. These results are shown in Table 8. It is likely that the CO<sub>2</sub> evolved is the result of the degradation of polymers and fillers present in the waste. The results of Straus and Wall [9] indicate that ester and urethane linkages or carbonate fillers are the likely sources of CO<sub>2</sub>. Similarly, polymers containing acrylonitrile are the likely source of the HCN observed.

The HCl evolved can be traced to the presence of poly(vinyl chloride) in the feed [7,10,11]. The concentration of HCl in the volatile products is a source of concern. Control of this compound is necessary both to minimize acid-catalyzed reactions that reduce the concentration of valuable olefins and to minimize corrosion of the reactors used were the process to be commercialized.



TABLE 8

Inorganic gas composition from bench scale experiments: comparative study with synthetic mixtures

Product gas	Shredder waste <sup>a</sup>	Weight percent of feed recovered				
		NR/PBD <sup>b</sup>	NR <sup>c</sup>	PP <sup>d</sup>	ABS <sup>e</sup>	ABS/PP
CO	0.5	2.5	3.1	0.7	0.2	0.2
CO <sub>2</sub>	28.4	4.7	7.2	0.2	2.0	1.1
HCN	0.4	0.2	< 0.1	–	7.9	1.0
HCl	6.4	–	–	–	–	–
H <sub>2</sub> O	4.8	48.8	35.4	7.4	37.2	53.3
NH <sub>3</sub>	0.1	–	2.8	–	7.6	0.3

<sup>a</sup> Average of 12 experiments. <sup>b</sup> NR/PBD, natural rubber/polybutadiene/carbon black filler. <sup>c</sup> natural rubber. <sup>d</sup> PP, polypropylene. <sup>e</sup> ABS, acrylonitrile/butadiene/styrene.

The boiling range of the oil produced is shown in Fig. 3. This figure indicates that the liquid will require at least some fractionation to make it suitable to replace currently available transportation fuels. About one half or more of the liquid boils between 300 and 600 °C. As shown in Table 9, this amount depends on the final holding temperature. The higher yields of liquids with boiling temperatures less than 315 °C that result as the final holding temperature increases is encouraging, since the overall oil yield did not appear to change substantially. This result indicates the possibility of additional cracking to produce more valuable liquid mixtures without reducing the overall liquid yields. Elemental analyses and compositions of the lower boiling fraction (B.P. less than 240 °C) are shown in Table 10. This table shows a significant amount of sulfur, nitrogen and chlorine that cannot be removed with a simple alkaline aqueous wash. Also, the low boiling

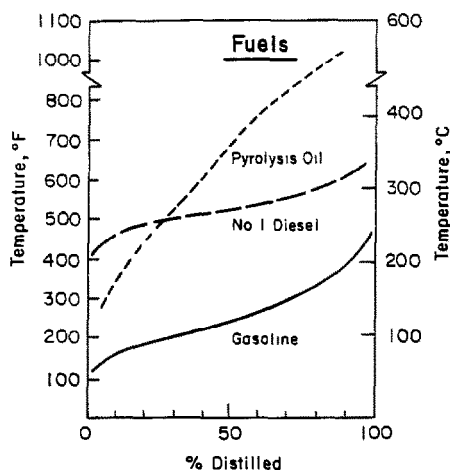


Fig. 3.

TABLE 9

Influence of holding temperature on oil recovered from bench pyrolysis experiments

	Final temperature (°C)		
	657	563	472
Total oil (wt.% of feed)	35.2	33.5	36.8
C <sub>5</sub> s to C <sub>11</sub> s (wt.% of oil)	28.9	44.1	38.3
Boiling below 315°C (wt.% of oil)	51.0	44.1	38.3

TABLE 10

Comparison of pyrolysis oil and diesel fuel

Element	Pyrolysis oil <sup>a</sup> (wt.%) (std. dev.)	Diesel no. 1 (wt.%)
C	83.45 (1.9)	86.61
H	10.44 (0.22)	13.26
N	1.05 (0.17)	0.022
S	0.81 (0.13)	<1.0
Cl	1.80 (0.78)	—
H/C ratio	1.5	1.8

<sup>a</sup> Average of seven experiments.

fraction contains a large number of components, each present in small fractions (see Table 11). Only alkylbenzenes are present in excess of 9 wt.%. Semi-quantitative analyses of the fraction boiling above 240°C are shown in

TABLE 11

Average composition of pyrolysis oil—fraction boiling below 240°C

Compounds	Weight percent of oil	
	Average	Range <sup>a</sup>
C <sub>5</sub> and C <sub>6</sub> aliphatic	1.57	0.3–4.1
Benzene	0.96	0.7–1.2
C <sub>7</sub> paraffins	0.69	0.5–0.9
Toluene	1.96	1.6–2.7
Styrene, xylene and ethylbenzene	3.53	0.8–5.9
C <sub>9</sub> s <sup>b</sup>	3.83	3.1–5.1
C <sub>10</sub> s <sup>b</sup>	4.69	3.2–4.7
C <sub>11</sub> s <sup>b</sup>	4.34	1.9–6.2
Naphthalene	2.54	1.5–3.1
Methyl naphthalene	4.14	3.5–4.7

<sup>a</sup> Seven experiments. <sup>b</sup> Includes aromatic and paraffinic compounds.

TABLE 12

Semi-quantitative analysis of pyrolysis oil by HPLC/GC/MS—fraction boiling above 240 °C

Compounds identified	Concentration in ppm ( $\pm 25\%$ )
C <sub>2</sub> –C <sub>3</sub> alkyl-substituted	
Naphthalene	1900
Anthracene	1700
C <sub>1</sub> –C <sub>3</sub> alkyl-substituted	
anthracene	10900
Pyrene and isomers	3100
Benzopyrene and isomers	2500
C <sub>1</sub> –C <sub>3</sub> alkyl-substituted	
biphenyl	1800
Terphenyl	3800
Chrysene	600
N-O species	4400
Phthalates	45000
Phenylbenzothiazole	400
Quinolinol	500
Methyl quinoline	1500

Table 12; alkylated polycyclic aromatic hydrocarbons and phthalates are present in the largest concentration, with significant concentrations of nitrogen- and sulfur-containing heterocyclic compounds detected. These compounds are undesirable if the liquid product is to be used directly as a fuel.

The concentration of aromatic compounds in the liquid fraction, Table 12, indicates that a significant degree of aromization occurs during the pyrolysis process with the conditions of the experiments. Control of this aromization is desirable in order to achieve the desired octane or cetane numbers and to obtain a boiling point range for the product liquids that is more desirable for fuel and feedstock applications.

TABLE 13

Composition of bench scale pyrolysis char

Element	Weight percent	
	Average <sup>a</sup>	Std. dev.
C	59.9	4.0
H	1.28	0.13
N	0.11	0.10
Cl	3.33	0.31
Cu	0.50	0.35
Zn	2.05	0.11
S	1.38	0.25

<sup>a</sup> Seven experiments.

TABLE 14  
Effect of holding temperature on extent of reaction

	Final pyrolysis temperature (°C)		
	462	563	652-666
<i>Char yield</i>			
Wt.% of feed	47.0	45.7	45.5
<i>Char composition</i>			
Wt.% carbon	57.7	59.7	60.3
Wt.% hydrogen	1.53	1.36	1.22
<i>Percent of element volatilized<sup>b</sup></i>			
Carbon	57.2	56.9	56.7
Hydrogen	85.6	87.6	88.9

<sup>a</sup> Average of five experiments. <sup>b</sup> Feed composition: 63.4 wt.% C, 5.0 wt.% H.

The char produced (Table 13) has a high carbon and significant metal content. Note that the hydrogen, nitrogen and chloride have not been totally volatilized. The nitrogen and chlorine content would make direct use of the char as fuel less desirable than coal in many cases.

It is interesting to note the effect of final holding temperature on the carbon to hydrogen ratio in the char; this is shown in Table 14. This ratio increases somewhat as the final holding temperature was increased from 462 to 666°C. However, even at the lower temperature, 85.6% of the feed hydrogen is found in the volatile products. These results indicate that char yield cannot be substantially reduced in the absence of other sources of hydrogen or oxygen, since most of the intrinsic hydrogen has already left the solid phase.

#### *Thermogravimetric reaction studies*

Weight-loss data obtained using thermogravimetric analyzers can be used to obtain kinetic rate expressions necessary for the scale-up of pyrolysis reactions. The data obtained with the automobile shredder waste material using the DuPont thermal analyzer at heating rates of 5, 10 and 20°C per minute are shown in Fig. 4 which shows that weight losses in excess of 1 wt.% of the sample occur as the temperature increases above 150°C. However, most of the weight loss occurs between 200 and 500°C. Between 500 and 650°C weight loss rates become negligible, with the residual char weighing 47.5 (±0.7) wt.% of the original sample. Continuing the heating above 600°C causes an additional weight loss of about 2% at temperatures between 650 and 750°C. The weight loss at these temperatures is more likely to be the result of decomposition or reduction of the inorganic compounds in the char than of pyrolysis of organic matter.

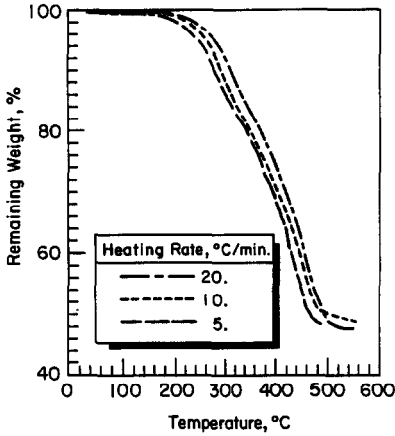


Fig. 4.

For the pyrolysis of pure compounds, a number of methods to obtain kinetic rate parameters from weight loss data at constant heating rate are available [12–17]. Given a starting temperature,  $T_0$ , if the weight loss can be assumed to follow first-order Arrhenius-type kinetics, solution of the macroscopic material balance yields [14]

$$\ln\left(\frac{W - W_0}{W_0 - W_c}\right) = \frac{k_0 \Delta E}{\beta R} [\Psi_0(\eta) - \Psi_1(\eta) - \Psi_0(\eta_0) + \Psi_1(\eta_0)] \quad (1)$$

where  $W$ ,  $W_c$  and  $W_0$  are the weights of the sample at temperature  $T$ , of the char residue, and of the sample before pyrolysis, respectively. In the above equation,  $\beta$  is the programmed heating rate in degrees per unit time,  $k_0$  is the Arrhenius pre-exponential factor (in reciprocal time units),  $\Delta E$  is the activation energy of the reaction and  $R$  is the gas constant.

The terms inside the brackets are functions of the dimensionless reciprocal temperature  $\eta$  defined as

$$\eta = \frac{\Delta E}{RT} \quad (2)$$

while  $\eta_0$  is the value of the dimensionless reciprocal temperature at time zero (usually room temperature). The functions  $\Psi_0$  and  $\Psi_1$  are defined as

$$\Psi_0(\eta) = \frac{\exp(-\eta)}{\eta} \quad (3)$$

and

$$\Psi_1(\eta) = \int_{\eta}^{\infty} \left[ \frac{\exp(-t)}{t} \right] dt \quad (4)$$

Tables as well as polynomial and rational approximations for  $\Psi_1(\eta)$ , the exponential integral, are available in the literature [18].

Equations (1)–(4) may be used to obtain least-squares values of  $k_0$  and  $\Delta E$  from the weight-loss curves obtained during the pyrolysis of pure compounds. However, given the complexity of the mixtures collected by automobile shredders, the assumption that the material pyrolyzes as if it were a single compound leads to gross errors. For the experimental data in Fig. 4, a non-linear least-squares fit for  $k_0$ ,  $\Delta E$ , and  $(W_0 - W_c)$  yields “best” values of  $3.03 \times 10^{17} \text{ min}^{-1}$ ,  $224.8 \text{ kJ g}^{-1} \text{ mol}^{-1}$  ( $53.7 \text{ kcal g}^{-1} \text{ mol}^{-1}$ ), and 39.3 wt.%, respectively. The standard error of the residues, however, is large (9.43 wt.%), and the maximum error of the predicted value is 17.5 wt.%.

When more than one component is present in the mixture, the assumption that pyrolysis proceeds independently for each compound allows eqn. (1) to be rewritten in the form

$$\ln \frac{V_i}{V_T} = - \frac{k_0 \Delta E_i}{\beta R} [\Psi_0(\eta_i) - \Psi_1(\eta_i) - \Psi_0(\eta_0) + \Psi_1(\eta_0)] \quad (5)$$

where the subscript  $i$  refers to a given component in the mixture, and  $V_i$  and  $V_T$  are the weight of volatiles remaining in the sample and the total weight of volatiles produced during the pyrolysis of a given compound, respectively.

Equation (5) may be used to calculate the remaining weight of a mixture of compounds pyrolyzing independently as a function of temperature by means of the expression

$$W = W_0 + \sum_{i=1}^n (V_i - V_{T_i}) \quad (6)$$

Expressions (5) and (6) contain 3 adjustable parameters for each component assumed to be present in the mixture:  $V_{T_i}$ ,  $k_0$ , and  $\Delta E_i$ . Non-linear least-squares estimates for these parameters when the shredder mixture is assumed to contain from 1 to 4 components that pyrolyze independently are listed in Table 15. Standard error of the sample weights predicted by the models for 345 data points (115 for each heating rate) obtained from the experimental weight-loss curves shown in Fig. 4 between 200 and 500 °C are also shown in the table. Since errors in digitizing the TGA weight-loss curves are approximately 1 wt.%, the results in Table 15 indicate that even postulating the existence of as many as 4 different groups of compounds that pyrolyze at similar rates as a function of temperature, a 12-parameter model is not capable of reproducing the data within the experimental error. This is not surprising since, in addition to pyrolysis, there is likely to be some boiling of the oils and plasticizers present in automobile shredder waste mixtures. The addition of one more parameter in the weight-loss models to account for the weight loss caused by evaporation of these compounds below 200 °C improves the standard error of the model predictions. However, it does not substantially reduce the maximum error when

TABLE 15

Comparison of kinetic models—TGA weight-loss experiments

Number of components	Volatiles due to component (wt.% of feed)	Kinetic parameters		Std. deviation (wt.% of feed) <sup>1</sup>	Maximum error (wt.% of feed)
		$k_0$ ( $\text{min}^{-1}$ )	$\Delta E$ ( $\text{kJ g mol}^{-1}$ )		
1	39.3	3.03E+17	224.8	9.43	17.53
2	28.9	3.63E+16	208.1		
	21.7	6.04E+18	262.5	5.23	12.53
2+ volatiles	7.9	—	—		
	23.2	2.53E+18	232.0	4.16	9.32
	20.8	5.16E+19	278.9		
3	13.2	3.25E+11	130.2		
	13.6	1.91E+16	211.4	1.72	3.89
	20.7	5.83E+13	197.6		
3+ volatiles	2.6	—	—		
	16.8	5.88E+13	146.5		
	13.5	1.78E+17	226.0	1.53	3.82
	19.5	1.28E+14	202.6		
4	5.5	5.68E+19	200.1		
	15.2	6.97E+12	149.0	1.41	2.91
	15.3	2.27E+17	230.7		
	15.6	6.68E+13	199.7		
4+ volatiles	3.2	—	—		
	10.4	6.74E+19	215.2		
	13.9	2.20E+14	180.5	1.16	2.91
	12.1	1.11E+18	247.5		
	12.6	1.66E+14	206.8		

the same number of compounds are assumed to be present in the mixture. These maximum errors occur, for all three heating rates studied, at temperatures between 250 and 350°C. At these temperatures, reactions such as rubber devulcanization and polymer chain scission, which produce non-volatile intermediates that then pyrolyze further, are likely to occur. Thus, the simplified first-order models described here are not likely to fit the data below 350°C much better than the four-compounds-with-volatiles model (13 parameters) shown in Table 15. Above 350°C, however, the predictions of this model are in excellent agreement with the experimental weight-loss data. This is shown in Fig. 5.

The parameters obtained from this model may be used to estimate reasonable residence times in isothermal reactors required for near complete volatilization. For rotary kilns with solid residence times of less than 10 minutes in the reaction zone, the model indicates that the waste must reach temperatures in excess of 450°C in order to ensure 95% volatilization. If heat transfer is not limiting, 8 minutes at this temperature should be

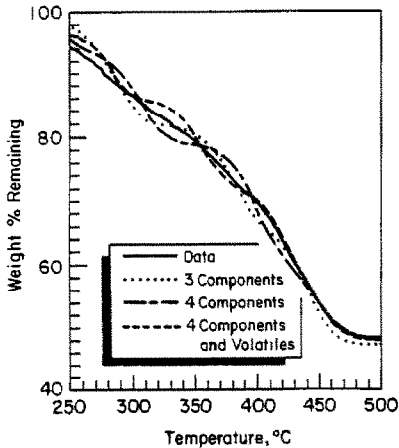


Fig. 5.

sufficient. These results were used in the design of initial rotary kiln experiments described below.

### *Rotary kiln pyrolysis*

Rotary kiln experiments were conducted using shredder waste cryogenically ground to pass through a 5 mm opening screen. Solids feed rates in the range of 200 to 400 g h<sup>-1</sup> were employed, with the kiln angled to provide an average (based on room temperature measurements) residence time for the solids of 5.5–7 min in the heated zone of the furnace (8–10 min total). A 100–160 °C difference between the external skin temperature of the stainless steel rotating tube and the internal vapor space temperature was measured in preliminary experiments. As a result, the Dialatrol controllers were set to maintain skin temperatures of between 740 and 810 °C in order to have a vapor space temperature between 610 and 650 °C. At these vapor space temperatures, near complete volatilization of the feed would be expected. This appears to have been the case. Material balances indicate that 48.2 (±5.3)% of the feed material appears in the product as char, not very different from the 46.6% char recovered in the batch pyrolysis experiments. The ratio of liquid to gas recovered in the rotary kiln experiments, on the other hand, was quite different. In the kiln, liquid yield was 9.4 (±4.1) wt.% of the feed, while gases contained the remaining 42.4 (±7.5) wt.%.

Elemental analyses of composite batches of the pyrolysis liquids obtained during the batch and rotary kiln experiments are shown in Table 16. The kiln liquids contain somewhat less nitrogen, chlorine, sulfur and oxygen and have a lower hydrogen to carbon ratio. Approximate IR and NMR analyses of the liquids are also shown in the table. It is also evident from the table that substantial additional aromatization of the products has occurred in the



TABLE 16

Comparative analysis of pyrolysis liquids—bench scale and rotary kiln composites

	Weight percent of oil	
	Bench scale	Rotary kiln
<i>Elemental analysis</i>		
Carbon	83.45	85.42
Hydrogen	10.44	9.65
Nitrogen	1.45	0.13
Chlorine	1.80	0.31
Sulfur	0.81	0.77
Oxygen	3.34	1.70
<i>Hydrocarbon type</i>		
Aromatic		
by IR	33.8	47.3
by C-NMR	33.0	47.1
by H <sup>+</sup> NMR	33.5	42.9
Olefinic	11.4	5.5
Paraffinic	55.1	50.5
Carboxylic	—	4.0

kiln. These results, as well as the high wall temperatures required in the kiln experiments to ensure complete volatilization, indicate that the product vapors may be undergoing additional pyrolysis in the kiln, and that liquid yields may be improved by reducing the vapor residence time in the hot zone. This could be accomplished by using faster nitrogen sweep rates or by recirculating into the kiln the non-condensable gases produced during the pyrolysis. The effect of reduced gas residence time in the hot zone of the rotary kiln on product distribution remains to be investigated.

## CONCLUSIONS

Inert gas pyrolysis of automobile shredder non-metallic waste materials has the potential to yield valuable hydrocarbon products. This process is very attractive because the technology is relatively simple and well established. However, as discussed in this paper, the mixtures obtained are complex and contain compounds that may prevent their direct use as a fuel in many applications. Further processing of the products may be desirable to obtain more readily marketable materials. As a result, commercial exploitation of this process must await an evaluation of these purification and modification costs. To conduct the necessary studies, long-term operation of a pilot scale pyrolysis facility is desirable. It is hoped that this paper will encourage such a study.

## REFERENCES

- 1 Ward's Auto World, December 1979.
- 2 L.R. Mahoney, J. Braslaw and J.J. Harwood, Society of Automotive Engineers Paper 790299, February 1979.
- 3 J. Braslaw, S.S. Labana and P.C. Killgoar, Recycling Plastics from the Automobile of the Future, *Plast. Rubber Proc. Appl.*, 13 (1990) 229–235.
- 4 J. Milgrom, Incentives for the Recycling and Reuse of Plastics, A.D. Little, Inc., Cambridge, MA, 1971.
- 5 R.C. Wingfield, J. Braslaw and R.L. Gealer, Pyrolytic Conversion of Polymeric Automobile Shredder Waste to Hydrocarbons, Presented at Central and Great Lakes Regional American Chemical Society Meeting, Dayton, OH, May 20–22, 1981.
- 6 Anon, Modern Plastics, *Annu. Rev.*, January 1981 and January 1990.
- 7 H. Sinn, W. Kaminsky and J. Jannig, *Angew. Chem. Int. Ed. Engl.*, 15 (1976) 660.
- 8 G. Collin, G. Grigolet and G.P. Bracker, *Chem. Ing. Tech.*, 50 (1978) 836.
- 9 S. Straus and L.A. Wall, *J. Res. Nat. Bur. Std.*, 60 (1958) 39.
- 10 L.A. Wall, The Mechanism of Pyrolysis Oxidation and Burning of Organic Materials, NBS Special Publication 357, 1972, pp. 47–60.
- 11 G. Collin, G. Grigolet and E. Michel, *Chem. Ing. Tech.*, 51(3) (1979) 220–224.
- 12 H.E. Kissinger, *Anal. Chem.*, 29(11) (1957) 1702–1706.
- 13 J.H. Flynn, *Polym. Lett.*, 4 (1966) 323–328.
- 14 A. Murty Kanury, *Combustion and Flame*, 18 (1972) 75–83.
- 15 K. Akita and M. Kase, *J. Polym. Sci. Part A-1*, 5 (1967) 833–848.
- 16 Z.D. Zivkovic and B. Dobovisek, *Thermochim. Acta*, 32 (1979) 205–211.
- 17 J. Zsako and J. Zsako, Jr., *J. Therm. Anal.*, 19 (1980) 333–345.
- 18 M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions*, Dover Publications, New York, 1964, pp. 228–251.