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Ultrapyrolysis of Automobile Shredder Residue¹

Z. SHEN, M. DAY* and J. D. COONEY

*Institute for Environmental Research and Technology, National Research Council Canada, Montreal Road,
Ottawa, Ontario, Canada K1A 0R6*

and

G. LU, C. L. BRIENS AND M. A. BERGOUGNOU

*Department of Chemical and Biochemical Engineering, Faculty of Engineering Science, The University of Western Ontario,
London, Ontario, Canada N6A 5B9*

A fast pyrolysis (Ultrapyrolysis) process was employed to convert automobile shredder residue (ASR) into chemical products. Experiments were conducted at atmospheric pressure and temperatures between 700 and 850°C with residence times between 0.3 and 1.4 seconds. Pyrolysis products included 59 to 68 mass% solid residue, 13 to 23 mass% pyrolysis gas (dry) and 4 to 12 mass% pyrolytic water from a feed containing 39 mass% organic matter and 2 mass% moisture. No measurable amounts of liquid pyrolysis oil were produced. The five most abundant pyrolysis gases, in vol%, were CO (18-29), CO₂ (20-23), CH₄ (17-22), C₂H₄ (20-22) and C₃H₆ (1-11), accounting for more than 90% of the total volume. The use of a higher organic content ASR feed (58 mass%) resulted in less solid residue and more pyrolysis gas. However, no significant changes were noted in the composition of the pyrolysis gas.

On a utilisé un procédé de pyrolyse rapide (ultrapyrolyse) pour convertir les résidus des déchiqueteuses d'automobiles (ASR) en produits chimiques. Des expériences ont été menées à des pressions proches de la pression atmosphérique et à des températures comprises entre 700 et 850°C, les temps de séjour variant de 0,3 à 1,4 secondes. Les produits de pyrolyse comprennent de 59 à 68% en masse de résidus solides, de 13 à 23% en masse de gaz de pyrolyse (sec) et de 4 à 12% en masse d'eau pyrolytique, à partir d'une alimentation contenant 39% en masse de matière organique et 2% en masse d'humidité. On n'a pas produit de quantités mesurables d'huile de pyrolyse liquide. Les cinq gaz de pyrolyse les plus abondants, en pourcentage volumique, sont le CO (18-29), le CO₂ (20-23), le CH₄ (17-22), le C₂H₄ (20-22) et le C₃H₆ (1-11), qui comptent pour plus de 90% du volume total. L'utilisation d'une alimentation en ASR à forte teneur organique (58% en masse) donne moins de résidus solides et davantage de gaz pyrolytique. Cependant, aucun changement significatif n'est noté dans la composition du gaz de pyrolyse.

Keywords: ultrapyrolysis, pyrolysis, tertiary recycling, automobile shredder residue, plastic waste.

Automobile shredder residue (ASR), commonly known as auto fluff, is a waste stream generated from the shredding of scrap vehicles in the recovery of metals (Dean et al., 1985). An automobile is generally scrapped after an average life time of 10 years. It is often sold to an automobile dismantler where saleable items, such as batteries, radiators, gas tanks and catalytic converters, are removed. The remaining hulk is then sold to a shredding plant for scrap processing. In the shredding process, automobile hulks are fed into a large hammer mill where they are broken up into small pieces, typically 20 cm or less in size. Pneumatic and magnetic separation processes are then used to produce separated streams of ferrous products, non-ferrous metals, and a waste stream, known as ASR. Both ferrous and non-ferrous metal streams are sold for further processing and recycling, while the ASR is currently landfilled at a cost to the shredding operation.

ASR is a complex mix that contains plastics, foams, rubber, glass, moisture, dirt and small fragments of unrecovered metals (Hubble et al., 1987). It is also contaminated with fluids and lubricants. The composition of ASR varies greatly, depending on the make, model and year of the vehicles being shredded. Typically, ASR contains approximately 40 to 50 mass% combustible materials, which are essentially hydrocarbon-based compounds, with the remainder being non-combustible.

In recent years concerns have been raised regarding the potential hazardous nature of the waste (Nieto, 1989). These concerns have arisen because of the fact that toxic metals, such as lead, could leach out into the groundwater. This has resulted in ASR being classified as a regulated waste in a certain number of regions of North America. In the meantime, declining landfill capacity and difficulties in obtaining permits for new landfill sites have created a major problem for the shredding industry (Repa and Sheets, 1992). These factors, along with more stringent government regulations and public pressure for recycling, have made landfilling an increasingly unsatisfactory disposal option for ASR.

The economics of the shredding industry have an influence on other industries, the iron and steel industry in particular. Prior to the mid-1960s the majority of scrap automobiles were processed by hand dismantling and sorting (Curlee, 1985). The remaining hulks were then baled into compact bundles to facilitate transportation and handling. The resulting bundles contained a relatively large percentage of contaminants, especially copper which caused them to be unacceptable as quality scrap and consequently could only be used to produce low quality products. The introduction of automobile shredders in the mid-1960s made it possible not only to reduce the contaminants and to produce a higher quality ferrous scrap, but also to facilitate the recovery of non-ferrous metals. The development of shredders represented vertical integration of the scrap market into a processing area that had been performed by the steel industry. Today, obsolete vehicles form the single largest source of recycled ferrous scrap for the iron and steel industry, although other

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*Author to whom correspondence should be addressed.

sources of materials (such as refrigerators, washing machines, and household appliances, commonly referred to as "white goods") also contribute to the supply of recycled metals. In 1988, the U.S. automobile shredding industry supplied more than 10 million tons of recovered ferrous scrap to the iron and steel industry, while at the same time, generating approximately 2.5 million tons of ASR that had to be landfilled (Jody et al., 1990; Jody and Daniels, 1991). A rise in landfill tipping fees for the disposal of ASR causes an increased cost for the shredding industry which could affect the supply and price of high-quality ferrous scrap. In addition to rising disposal costs, the situation is further exacerbated by the increasing quantities of ASR per vehicle due to the use of more plastics for lighter weight vehicles in order to achieve better fuel economy.

Various non-thermochemical alternatives to landfilling ASR have been investigated (Voyer, 1992). Although efforts have been made to convert ASR into composite materials, the economics of these processes have been questioned (DeAngelis et al., 1985). Other attempts involving compression, injection and specialty molding (Spaak, 1986), as well as low- and high-pressure molding (Deanin and Nadkarni, 1984; Deanin and Yniguez, 1984) have had limited success. The possibility of incorporating ASR into acrylic polymer concretes has been investigated by Crawford and Manson (1983), but the experiment was preliminary. It is clear that more research in this area is required if conventional plastics processing equipment is to be used (Deanin et al., 1985).

Pyrolysis has long been recognized as an effective method for decomposing organic wastes to recover valuable resources. Most of the early investigations to develop an industrially viable process have focussed on the pyrolysis of municipal solid waste (MSW), or refuse derived fuel (RDF). For example, in the late 1960's, the US Bureau of Mines tested the feasibility of converting municipal solid waste, in a sealed tank pyrolyzer, into solid, liquid, and gaseous fuels (Sanner et al., 1970). Furue et al. (1983) investigated the production of liquid fuel oil from MSW in a fluidized bed process, while Agra and Soehendro (1983) investigated the production of charcoal from MSW in a descending bed process. In the meantime, Ishii et al. (1984) used MSW and Suzuki and Yakowitz (1983) used RDF to generate electric power in a dual fluidized bed reactor system which incorporates pyrolysis and combustion in two separate units.

In recent investigations, many pyrolysis processes and processing conditions have been evaluated to recover resources from a variety of organic waste streams. Maschio et al. (1992) found that charcoal was the principal product when conventional (slow heating) pyrolysis was used with biomass as a feed in a moving bed reactor. However, when fast heating pyrolysis was used in an entrained bed reactor the charcoal production was low and a medium BTU gas was the main product. Williams and Besler (1992a, b) also studied the effect of heating rate on pyrolysis product distribution. They observed that when the heating rate was increased from 5 to 80°C/min, char formation was reduced and oil production increased when both rice husk and municipal solid waste were pyrolyzed in a static batch tube reactor. Diebold and Scahill (1984, 1988), using a vortex reactor, in which heat fluxes were rapidly transmitted from the reactor wall to entrained biomass particles, obtained high oil yields (70 mass%). In a theoretical study, Lédé (1994) further pointed out the importance of heating rate on the

selectivity of the pyrolysis of biomass which is generally recognized to involve competing reaction processes.

Williams and co-workers at the University of Leeds, UK, have conducted extensive studies of a two-step pyrolysis of a variety of organic wastes. The approach involves thermal cracking of a waste material and subsequent catalytic or non-catalytic cracking of the thermally cracked vapor products. Besler et al. (1992) found that the oils produced by the two-step pyrolysis of wood and rice husk using zeolite ZSM-5 as a catalyst had significantly higher calorific values than the oils produced by the thermal cracking only. Williams et al. (1993), using the same catalyst in the two-step pyrolysis of polystyrene, reduced the concentration of styrene oligomers and increased the concentration of polycyclic aromatic hydrocarbons, as compared to the single step thermal cracking. Williams and Taylor (1993), on the other hand, found that the non-catalytic two-step pyrolysis of tires simply produced more gas and less oil.

Evans and Milne (1987a, b) and Milne et al. (1988) employed a free-jet molecular beam mass spectrometric sampling technique to study the two-step pyrolysis of biomass. The principal advantage of the technique was its capability of direct, simultaneous sampling, in real time, of light gases, reactive intermediates, and condensable vapors. Using this technique, Evans and Milne (1988) also studied the pyrolysis of RDF and Evans et al. (1992) further studied the pyrolysis of waste plastics.

Canada is one of a few countries in the world with leading technologies in pyrolysis of organic wastes, especially in the use of biomass as the feed. Hayes (1988) reviewed the history and development of these technologies. Included in these technologies, three processes are particularly noteworthy. Scott and co-workers at the University of Waterloo have developed a fluidized bed flash pyrolysis process which features short vapor residence times (Scott and Piskorz, 1981, 1982). Scott and Piskorz (1984) and Scott et al. (1985) achieved high organic liquid yields of 60 to 70 mass% from wood and of 40 to 50 mass% from agriculture residues. Scott et al. (1990, 1991) also studied the pyrolysis of waste plastics using this process. Roy and co-workers at the Laval University have conducted extensive developmental work on a vacuum pyrolysis process (Roy et al., 1988). The process, employing a six-hearth furnace, features stepwise heating of feed and rapid removal of evolved vapor products under vacuum conditions. A wide variety of materials have been tested using this process, including scrap tires (Roy et al., 1990; Pakdel et al., 1991a), wood (Pakdel and Roy, 1988, 1991), petroleum residues (Pakdel et al., 1991b), bituminous coal (Kalkreuth et al., 1986), etc. Bergougnou and co-workers at the University of Western Ontario have developed an ultra-fast pyrolysis process, termed "Ultrapyrolysis" (Graham et al., 1985, 1987; Vogiatzis et al., 1989). The process incorporates a jet impact mixer into a tubular transport-bed reactor and achieves fast heating rates by rapidly mixing the feed with a heat carrier. The process has been mainly investigated for the pyrolysis of biomass, achieving liquid yields as high as 88 mass% from cellulose (Graham et al., 1988).

Although many pyrolysis processes exist, only a few have been applied to ASR. These include the vacuum pyrolysis process developed at the University Laval (Roy et al., 1992) and the fluidized bed pyrolysis process developed at the University of Hamburg (Kaminsky, 1992). Both processes produced approximately 20 mass% of liquid oils which required further upgrading to produce a conventional fuel.

Figure 1 — Ultrapyrolysis pilot plant.

ASR can also be upgraded to produce a solid fuel by the use of mild pyrolysis conditions incorporating an intense mixing operation using a screw kiln process (Jones, 1991), while a rotary kiln process at higher temperatures employed by Braslaw et al. (1991) resulted in a high yield of gas.

In order to further understand the process chemistry and to provide design data for emerging technologies, we have conducted research on the pyrolysis of ASR using a fast pyrolysis process, known as Ultrapyrolysis. The data presented in this paper summarizes the results of this study.

Experimental

THE ULTRAPYROLYSIS PROCESS

The Ultrapyrolysis process, shown schematically in Figure 1, is composed of four sections: feeding, preheating, reaction and product collection. In the feeding section ASR feed and sand were loaded into sealed hoppers. The material from each hopper was delivered to the reactor at a constant rate using a mechanical table feeder. Nitrogen was employed to facilitate the flow of ASR through a transport pipe. The transport pipe was maintained at 7°C by a water cooling jacket to prevent possible melting of thermoplastic materials before entering the hot reaction zone. A nitrogen stream was used as a heat carrier, which could be loaded with the sand, and heated by passing through a double helix coil in the preheating section. In the mixer of the reaction section, the heat carrier gas and ASR were mixed to maximize heat transfer. The mixer was a conical vessel which had two opposing tangential inlets to introduce streams of heated nitrogen. One tangential stream essentially destroyed the momentum of the other, resulting in severe turbulence. ASR was fed from the top of the mixer and rapidly heated via turbulent mixing (of the order of 30 milliseconds based on data given by Graham et al. (1986)). The pyrolysis was initiated in the mixer and continued in the tubular reactor (2.2 cm i.d. and 111 cm long) which was maintained under isothermal conditions. The output stream from the tubular reactor was rapidly quenched by a nitrogen stream to stop further reactions and discharged into a catch-pot where solids were collected. A cyclonic condenser in an ice-water bath

and a liquid trap in a dry ice-acetone bath were employed to recover condensable liquid products. Non-condensable gases exiting the liquid trap were passed through a glass-wool filled filter to remove solid and liquid particulates. Four gas bags (170 L capacity each) were used to collect the gaseous products.

Temperature and residence time are the two principal control parameters for the Ultrapyrolysis process. In this study the pyrolysis temperature, measured at the outer wall of the tubular reactor, was varied in the range of 700 to 850°C, while residence times in the range of 0.3 to 1.4 seconds were employed. The mixer and the tubular reactor were maintained at the same temperature during each test. The residence time in the reactor was controlled by the flow rate of nitrogen used as the heat carrier stream. In all experiments the nitrogen flow used to transport the ASR feed to the reactor was fixed and the Ultrapyrolysis system was operated at slightly above atmospheric pressure. A constant feed rate, ranging from 1 to 3 g/min, was used in each experiment which lasted approximately 30 minutes. All pyrolysis runs employed only nitrogen as the heat carrier stream, except for one run conducted to investigate the effect of sand as a heat carrier.

Analyses were performed on the solids, liquid and gaseous products of pyrolysis. The analyses included the determination of the product distribution between the three product fractions and the composition of the pyrolysis gases. Total solids collected in the catch-pot were weighed, while the quantity of the pyrolysis gases was determined by discharging the gases from the gas bags into a pre-evacuated tank of a known volume with pressure and temperature being measured. The composition of the pyrolysis gases was determined by gas chromatography employing both thermal conductivity and flame ionization detectors. In most experiments little or no liquid products were produced, except for small quantities of water.

AUTOMOBILE SHREDDER RESIDUE FEED

The ASR used for the Ultrapyrolysis tests was obtained from an automobile shredder in Quebec, Canada. The material was collected using a standard cone and quartering procedure (Day, 1991). Two types of ASR feed were prepared for this study from the original waste. One was a regular feed obtained through cryogenic grinding of the original waste to less than 1 mm. The other was an organic-rich fraction prepared by a two-stage beneficiation process. In the first stage, a polymer enriched fraction was obtained from the original waste through a series of density and size separation operations and the resulting fraction was cryogenically ground to less than 1 mm in the second stage.

Prior to use in the pyrolysis study, the physical and chemical characteristics of the ASR feed were determined. The physical properties measured included ash content, moisture, density, and calorific value (dry basis). The chemical analyses included determination of the elements C, H, N, O, S and Cl and the two oxides Fe₂O₃ and SiO₂. The results of these analyses are presented in Table 1. The organic or combustible content was 39.3 mass% for the regular feed, compared to 58.2 mass% for the organic-rich feed, based upon the ash contents of 58.1 mass% and 39.8 mass% and the respective moisture contents. Because of its higher organic material content, the organic-rich feed had a calorific value of 16.5 MJ/kg, much higher than the value

TABLE 1
Characteristics of Automobile Shredder Residue Feed

	Regular	Organic-Rich
Physical Properties:		
organics	39.3 mass%	58.2 mass%
ash	58.1 mass%	39.8 mass%
moisture	2.6 mass%	2.0 mass%
density	438 kg/m ³	262 kg/m ³
size	< 1 mm	< 1 mm
calorific value (dry)	10.18 MJ/kg	16.51 MJ/kg
Chemical Analysis (mass%, dry basis):		
C	27.9	46.2
H	4.0	6.3
N	0.9	1.9
O	17.0	22.0
S	0.3	0.3
Cl	0.5	0.7
Fe ₂ O ₃	25.2	3.3
SiO ₂	18.5	8.7

10.2 MJ/kg of the regular feed. Meanwhile the bulk density of the organic-rich fraction was much lower at 262 kg/m³, compared with 438 kg/m³ for the regular feed. Both types of feed had similar moisture contents, 2.6 mass% for the regular feed and 2.0 mass% for the organic-rich feed. The organic-rich fraction also had higher carbon, hydrogen and nitrogen percentages associated with its higher polymeric content. The chlorine in the feed is assumed to be associated with the polyvinyl chloride in ASR and flame retardants in the ASR polymers. Road salt used during Canadian winters might also contribute to the total chlorine measured. The oxygen content was determined by coulometric titration of CO₂ formed during the thermal decomposition of the sample at 1100°C in nitrogen and attributed to two sources. One was the organic source including polyurethanes, polyesters, nylon, polycarbonate, wood, etc., all of which decomposed to give CO₂ and CO which was in turn converted into CO₂ over a carbon bed in the analysis. The other was the inorganic source including metal carbonates, like calcium carbonate (CaCO₃) widely used as a plastic filler, which decomposed to CO₂ and stable oxides (CaO in the case of calcium carbonate). On the other hand, oxides such as Fe₂O₃ and SiO₂ were stable during the analysis and did not contribute to the oxygen content. The major sulfur source in ASR is rubber. The two inorganic compounds, Fe₂O₃ (chemical compound for rust) and SiO₂ (principal component of dirt and glass), constituted the major ash components.

Results and discussion

PRODUCT DISTRIBUTION

The major product from the Ultrapyrolysis of the regular ASR feed was the solid residue. Employing pyrolysis temperatures of 700 to 850°C and residence times of 0.3 to 1.4 seconds, the solid residue accounted for 59 to 68 mass% of the feed. A very obvious reason for this high solid residue yield is the high ash content of the feed (58 mass%) which cannot be pyrolyzed and hence must contribute to the solid residue. Meanwhile more than 32 mass% of the feed, or 82 mass% of the organic matter, was converted into steam or gaseous products. In all experiments little or no oil was produced. This was attributed to the high pyrolysis temperatures employed (700–850°C), which results in the

Figure 2 — Product distribution vs. temperature.

ASR undergoing severe thermal cracking during the Ultrapyrolysis process. The yield of dry pyrolysis gas or pyrogas was found to be in the range of 13 to 23 mass% of the feed. Meanwhile, the yield of pyrolysis water or pyrowater was in the range of 4 to 12 mass% of the feed. The pyrowater was the total water measured in the collection system and assumed to be derived both from the thermal cracking of the feed organic matter as well as the feed moisture.

Pyrolysis temperature and residence time have both been shown to have significant effects on product distribution. Figure 2 shows the product distribution as a function of temperature (residence time = 1.2 to 1.4 s). The yield of solid residue dropped from 68 to 59 mass% of the feed as the temperature increased from 700 to 800°C. A further increase in temperature from 800 to 850°C, however, did not cause further reduction in solid residue. This suggests that the organic matter in the feed was completely pyrolyzed at 800°C. Coupled with the decrease in solid residue were increases in dry pyrogas from 14 to 23 mass% of the feed and pyrowater from 4 to 10 mass% of the feed as a result of increasing the temperature from 700 to 800°C. The effect of residence time on product distribution is shown in Figure 3 for experiments conducted at a pyrolysis temperature of 800°C. An increase in residence time reduced the production of solid residue and resulted in more dry pyrogas and pyrowater. The amount of solid residue was reduced from 64 to 59 mass% of the feed as residence time increased from 0.3 to 1.4 seconds. Meanwhile the amounts of dry pyrogas and pyrowater increased from 13 to 23 mass% and from 7 to 12 mass% of the feed, respectively.

At this point it may be appropriate to compare the product distribution in our study with those reported by Roy et al. (1992) for a vacuum pyrolysis process. The Ultrapyrolysis process is a fast process with high temperatures (700–850°C) and short residence times (0.3–1.4 s), while the vacuum pyrolysis process has longer residence times and lower temperatures (450–530°C). Although the ASR materials used in both processes came from different sources, they basically had the same composition (i.e., organic content = 40 mass%, inorganic content = 58 mass% and moisture = 2 mass%). While both processes gave similar total conversion of the organic matter in the ASR (i.e., 84 mass% for the

Figure 3 — Product distribution vs. residence time.

vacuum pyrolysis and more than 82 mass% for Ultrapyrolysis), the yields of oil and pyrogas were significantly different, 14 mass% oil and 4 mass% pyrogas (dry) for the vacuum pyrolysis versus little oil and 13–23 mass% pyrogas (dry) for Ultrapyrolysis. The fact of little oil production in this study may suggest that the combination of the Ultrapyrolysis process' high temperature and high metal content of the waste material promotes severe cracking of the pyrolytic vapors formed. The pyrowater yield from the vacuum pyrolysis at 17 mass% was also higher than that of 4–12 mass% from the Ultrapyrolysis process.

PYROLYSIS GAS COMPOSITION

The major chemical species found in the pyrogas were CO, CO₂, CH₄, C₂H₄ and C₃H₆, accounting for more than 90 vol% and more than 70 mass% of the total gas. Other chemical compounds detected included ethane (C₂H₆), propane (C₃H₈), butenes (C₄H₈), butane (C₄H₁₀), pentenes (C₅H₁₀), pentane (C₅H₁₂), benzene (C₆H₆), toluene (C₇H₈) and styrene (C₈H₈). Kaminsky (1992), using a fluidized bed process, also reported that CO, CO₂, CH₄, C₂H₄ and C₃H₆ were the five most abundant chemical species in pyrogas. It is interesting to note that no hydrogen (H₂) was found in both the Ultrapyrolysis process and the fluidized bed process. Experiments by Vogiatzis et al. (1989) showed that no significant amounts of molecular hydrogen (< 0.5 mass% of the total gas) in the Ultrapyrolysis of a bitumen feedstock were obtained until the temperature reached 750°C for an average residence time of approximately 0.4 seconds. The study of Vogiatzis et al. (1989) showed that increasing the reaction temperature from 750 to 900°C resulted in an increased production of H₂ from 0.5 to 2 mass% of the total gas, indicating that high pyrolysis temperatures favored H₂ formation. This may suggest that the temperatures of 700 to 850°C used in our study and the temperature of 700°C used in the fluidized bed process by Kaminsky (1992) for ASR pyrolysis are not high enough to produce significant amounts of molecular hydrogen.

Both temperature and residence time affect pyrogas composition, as shown by the results in Figures 4 and 5, respectively. Employing a residence time of 1.2 to 1.4 seconds, CO increased from 18 to 29 vol%, while C₃H₆

Figure 4 — Pyrolysis gas composition vs. temperature.

Figure 5 — Pyrolysis gas composition vs. residence time.

decreased from 11 to 1 vol% as the temperature increased from 700 to 850°C. The other three compounds (CO₂, CH₄ and C₂H₄) did not appear to be affected by temperature as their concentrations remained approximately constant at about 21 vol%. The effect of residence time on pyrogas composition at a temperature of 800°C is summarized in Figure 5. The C₃H₆ concentration in the pyrogas decreased from 8 to 4 vol% as the residence time increased from 0.3 to 1.4 seconds. The CH₄ concentration, on the other hand, increased from 14 to 21 vol%. Meanwhile only slight changes in CO, CO₂ and C₂H₄ were observed as a function of the residence time. The dependence of pyrogas composition on residence time indicates that pyrolysis of ASR involves complex reaction mechanisms. These results suggest that plug flow reactors such as the downer of the Ultrapyrolysis process may be desirable to obtain controlled and desired products.

In addition to measuring pyrogas composition, the yields of gaseous species were calculated and the results are presented in Figures 6 and 7 as a function of temperature and residence time, respectively. It is noted that the yields of CO₂, CO, C₂H₄ and CH₄ all approximately double on increasing reaction temperature from 700 to 850°C with major changes occurring between 700 and 800°C, reflecting the overall pyrogas yield shown in Figure 2. The C₃H₆

TABLE 2
Comparison of Pyrolysis Products from Regular and Organic-Rich Feed

ASR Feed			
Type		Regular	Organic-Rich
Organics	mass %	39.3	58.2
Ash	mass %	58.1	39.8
Moisture	mass %	2.6	2.0
Operating Conditions			
Temperature	°C	753	754
Residence Time	s	1.255	1.158
Feed Rate	g/min	2.03	0.87
Yield (mass % of Feed)			
Pyrogas (dry)		16.4	27.1
Pyrowater		9.4	19.8
Liquid Oil		nil	nil
Solid Residue			
combustible:		8.2	15.4
non-combustible:		55.0	37.7
Total		89.0	100.0
Composition of Pyrogas (dry)			
CO	vol %	24.4	28.1
CO ₂	vol %	21.0	24.3
CH ₄	vol %	19.2	16.4
C ₂ H ₄	vol %	19.6	19.1
C ₃ H ₆	vol %	7.4	5.8
Others*	vol %	8.4	6.3
CO	mass %	21.1	24.5
CO ₂	mass %	28.4	33.1
CH ₄	mass %	9.5	8.1
C ₂ H ₄	mass %	16.9	16.6
C ₃ H ₆	mass %	9.5	7.5
Others*	mass %	14.7	10.2

*Others: ethane (C₂H₆), 1,2-propadiene (C₃H₄), 1-propyne (C₃H₂), propane (C₃H₈), 2-methyl-1-propene (C₄H₈), 1,3-butadiene (C₄H₆), 1-butene-3-yne (C₄H₂), 1,3-pentadiene (C₅H₆), 3-pentene-1-yne (C₅H₄), propenenitrile (C₃H₃N), benzene (C₆H₆), toluene (C₇H₈), styrene (C₈H₈).

organic content in ASR on the pyrolysis products. The operating conditions are summarized in Table 2. The pyrolysis temperature was 750°C and the residence time was 1.2 seconds. The only difference in the operating conditions was the feed rate (0.87 g/min for the run with the organic-rich feed and 2.03 g/min for the run with the regular feed), resulting from the difference in the feed density.

Both pyrolysis runs showed high conversions of the organic matter in the ASR feed. The yield of the solid residue was 63.2 mass% for the regular feed and 53.1 mass% for the organic-rich feed, which translated into 87 mass% and 81 mass% conversions, respectively, of the organic matter. The pyrogas yield (27.1 mass%) and the pyrowater yield (19.8 mass%) for the organic-rich feed were higher in comparison with 16.4 mass% and 9.4 mass%, respectively, as would be expected based upon the higher organic content. Neither of the two pyrolysis runs showed a measurable amount of liquid oil.

Pyrogas composition data from the two types of ASR feed (Table 2) showed remarkable similarities. The five major gases, CO, CO₂, CH₄, C₂H₄ and C₃H₆, represented 92 vol% of the pyrogas (dry) for the regular feed and 94 vol% for the organic-rich feed. Furthermore, the individual concentrations of CO, CO₂, CH₄, C₂H₄ and C₃H₆ were similar between the two types of feed.

Figure 6 — Yield of gaseous species vs. temperature.

Figure 7 — Yield of gaseous species vs. residence time.

yield, on the other hand, showed a continuous decline from 2 to 0.5 mass% of the feed over the temperature range of 700 to 850°C. The yields of the four major chemical components also showed similar increases on increasing the residence time from 0.3 to 1.4 seconds when a pyrolysis temperature of 800°C was employed (Figure 7). Once again these results reflect the role of residence time on pyrogas yield (Figure 3). In the case of C₃H₆, residence time did not seem to have any effect on the C₃H₆ yield which remained relatively constant at about 1 mass% of the feed.

COMPARISON OF PYROLYSIS PRODUCTS FROM REGULAR AND ORGANIC-RICH FEED

A pyrolysis run was conducted with the organic-rich feed at the same temperature and residence time as those for a run with the regular feed in order to examine the effect of

External energy must be provided to maintain a pyrolysis process at a constant temperature due to thermodynamic considerations. The energy for the Ultraprolysis of ASR is achieved from two sources. One is supplied by the heat carrier, which can be either a pure nitrogen stream or a sand-loaded nitrogen stream. Heat stored in the preheated carrier stream is transferred to the ASR feed through the intensive mixing in the mixer. Sand is frequently used because it has a large heat capacity and is readily obtainable in large quantities at low cost. The other source of energy is radiative heating from the walls of both the mixer and the tubular reactor. The obvious purpose of using a heat carrier is to rapidly transfer heat to the ASR feed from room temperature to the required pyrolysis temperature within a very short time, typically less than 30 ms (Graham et al., 1986). The pyrolysis process is then maintained at this temperature through radiative heating from the walls of the reactor.

To determine the effect of the nature of the heat carrier on the pyrolysis of ASR, two pyrolysis runs were performed, one using pure nitrogen and the other using sand-loaded nitrogen. The experiments were conducted under the same operating conditions with the exception of the incorporation of sand in the heat carrier stream. Table 3 summarizes the operating conditions and the experimental results. The regular feed was used at a feed rate of 2 g/min. The reactor temperature was set at 850°C and the pyrolysis residence time was 0.6 seconds. The nitrogen flowrate was set at 11.8 g/min for the pyrolysis run using only nitrogen as the heat carrier, while in the other run sand at a delivery rate of 5.5 g/min was loaded into the nitrogen stream flowing at 11.8 g/min. It should be noted that the temperature of the heat carrier at the two tangential inlets of the mixer was 732°C for the pure nitrogen and 702°C for the sand-loaded nitrogen, while the reactor temperature was maintained at 850°C. The implication of these conditions is that the heating of the ASR feed from room temperature to the pyrolysis temperature of 850°C was realized through both heat stored in the heat carrier and radiation from the walls of the mixer.

The results from the two runs presented in Table 3 indicate that the addition of sand to the heat carrier had little effect on pyrolysis products. For example, the yield of pyrogas (dry) was 19 mass% with a solid residue yield of 63 mass% for the pure nitrogen and remained essentially unchanged when sand was added. In both cases no measurable amounts of liquid oil were detected. No data on pyrowater was available for the pyrolysis run using the pure nitrogen heat carrier. However, a similar experiment at the same temperature and residence time gave a pyrowater yield of 13.9 mass%, which was very similar to the 14.6 mass% from the run with the sand-loaded nitrogen heat carrier. The two pyrolysis runs also gave similar pyrogas compositions. For the five major components CO, CO₂, CH₄, C₂H₄ and C₃H₆, which accounted for more than 95 vol% of the measured gases, CO at a concentration of over 30 vol% was the major component, while C₃H₆ at 3 vol% was the lowest. The concentrations of the other three major components were all close to 20 vol%.

PROCESS FEASIBILITY

A conceptual commercial ASR fast pyrolysis process has been proposed based on the Ultraprolysis results. For this

TABLE 3
Comparison of Pyrolysis Products for N₂ Heat Carrier With and Without Sand

Case		No Sand	Sand
Heat Carrier Stream			
Temperature	°C	732	702
N ₂	g/min	11.80	11.80
Sand	g/min	0	5.45
ASR Feed			
Type		regular	regular
Organics	mass%	39.3	39.3
Ash	mass%	58.1	58.1
Moisture	mass%	2.6	2.6
Operating Conditions			
Temperature	°C	849	855
Residence Time	s	0.610	0.610
Feed Rate	g/min	2.22	2.01
Yield (mass% of Feed)			
Pyrogas (dry)		19.2	18.4
Pyrowater		(13.9)	14.6
Liquid Oil		nil	nil
Solid Residue			
combustible:		7.4	4.7
non-combustible:		55.4	56.0
Total		95.9	93.7
Composition of Pyrogas (dry)			
CO	vol%	34.6	31.0
CO ₂	vol%	16.6	16.4
CH ₄	vol%	20.8	20.0
C ₂ H ₄	vol%	22.4	23.4
C ₃ H ₆	vol%	3.2	3.7
Others*	vol%	2.4	5.5
CO	mass%	33.1	28.3
CO ₂	mass%	24.9	23.5
CH ₄	mass%	11.4	10.4
C ₂ H ₄	mass%	21.5	21.4
C ₃ H ₆	mass%	4.5	5.1
Others*	mass%	4.6	11.3

*Others: ethane (C₂H₆), 1,2-propadiene (C₃H₄), 1-propyne (C₃H₄), propane (C₃H₈), 2-methyl-1-propene (C₄H₈), 1,3-butadiene (C₄H₆), 1-butene-3-yne (C₄H₄), 1,3-pentadiene (C₅H₈), 3-pentene-1-yne (C₅H₈), propenenitrile (C₃H₃N), benzene (C₆H₆), toluene (C₇H₈), styrene (C₈H₈).

exercise the process was designed to be an integrated part of an ethylene plant and for simplicity was divided into four process sections: size reduction, fast pyrolysis, quenching, and gas separation. The process would deliver a mixture of low molecular weight hydrocarbons (primarily CH₄, C₂H₄ and C₃H₆) to an ethylene plant for further processing. The solid residue produced from the pyrolysis process, which consists principally of iron oxide (Fe₂O₃), silica (SiO₂), alumina (Al₂O₃) and calcium oxide (CaO), could potentially be used in cement production.

A preliminary economic analysis of the process indicated that the quenching and gas separation process sections would account for a large portion (about 85%) of the capital investment. This is due to the fact that large quantities of heat carrier gas are required to achieve fast pyrolysis. This carrier gas has subsequently to be quenched and separated from the gaseous products, prior to being recycled to the pyrolysis process. In our study nitrogen (N₂) was employed as the carrier gas. However, other gases could be used, including those which could be more easily separated from the gaseous products. However, the selection of carrier gas will have a dramatic impact on the process economics. For example, 60% of the capital investment and the operation

cost is associated with the quenching, separation and recycling of the nitrogen (N_2) carrier gas. However, if the pyrolysis gas was used as a carrier gas, there would be a 30% reduction in processing costs.

The proposed system that we examined required a capital investment similar to conventional chemical plants with returns being dependent upon the economic climate. The construction of an 11 t/h fast pyrolysis plant using internally recycled pyrolysis gas as the carrier gas would require a \$10 million investment. This appears to be in line with other analyses such as a 10 t/h waste plastics pyrolysis plant (Dieffenbach et al., 1993) and a 4 t/h ASR vacuum pyrolysis plant which required \$5 million to be built (Roy et al., 1993). Both these pyrolysis plants were designed to produce saleable products (pyrolysis oil, pyrolysis gas, etc.) at break-even operations of \$10/t to \$20/t tipping fee revenue. Our analysis is also based on a tipping fee to generate income. Based on our analysis the proposed ASR fast pyrolysis process would require a \$50/t fee to offset the operation cost while contributing an additional annual saving of 6 million gallons of naphtha, a common raw material for the production of ethylene produced by steam cracking.

Conclusions

The Ultrapyrolysis of ASR at temperatures of 700–850°C and residence times between 0.3–1.4 seconds can be expected to yield 59–68 mass% solid residue, 13–23 mass% pyrolysis gases (dry) and 4–12 mass% pyrolytic water from a regular feed containing 39 mass% organic matter. No measurable amounts of pyrolytic liquid oil fraction were produced. The high yields of solid residue were due to the high ash content (58 mass%) of the feed.

The five major components detected in the pyrolysis gas obtained from regular ASR feed were CO , CO_2 , CH_4 , C_2H_4 and C_3H_6 , accounting for more than 90 vol% of the total gas. The concentrations of CO_2 and C_2H_4 in the total gases were relatively stable at approximately 20 vol% over the temperature range of 700–850°C and the residence time range of 0.3–1.4 seconds. Meanwhile the CO concentration varied between 18 and 29 vol%, increasing with temperature and decreasing with residence time. The CH_4 concentration showed only small changes with temperature but registered a rise from 14 to 20 vol% with increase in residence time from 0.3 to 1.4 seconds. The measured C_3H_6 concentrations were the lowest of these five gases with concentrations varying between 1 and 11 vol%.

Increasing the organic content from 39 mass% (the regular feed) to 58 mass% (the organic-rich feed) resulted in less solid residue and more pyrolysis gas. However, the percentage (80–90 mass%) of organics pyrolyzed was not significantly affected with the composition of the pyrolysis gases remaining basically the same.

The inclusion of sand in the nitrogen heat carrier stream had little impact on pyrolysis product distribution and composition of pyrolysis gas.

The experimental data has shown that the Ultrapyrolysis process is a possible, technologically feasible process for converting ASR into basic chemical feedstocks, such as ethylene, propylene, etc. The economics of the process would greatly depend upon the tipping fee charged and markets for the solid residue. Based upon a quick economic analysis of an 11 t/h Ultrapyrolysis-based plant, integrated with an ethylene plant, it appears that a \$50/t tipping fee may offset the operation cost, while producing annual savings of

6 million gallons of naphtha produced from non-renewable resources.

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