

POTENTIAL FOR CONVERTING MSW TO USEFUL FUELS THROUGH PYROLYSIS

NARAYANI MALLYA AND JAMES E. HELT

Argonne National Laboratory
Argonne, Illinois

ABSTRACT

Pyrolysis of municipal solid waste (MSW) has the potential for helping solve two problems: (a) the disposal of the waste generated by our society; and (b) the need for additional sources of energy. Experiments on the pyrolysis of MSW components in a bench-scale reactor are reported. The liquid and solid products formed are analyzed for physical and chemical properties to help determine their potential as useful fuels.

INTRODUCTION

Garbage disposal has been a problem to mankind for centuries. As early as 500 B.C., ancient civilizations were faced with the problem of waste disposal. They handled garbage disposal in a very crude way. Refuse was thrown onto the floor or into the streets, resulting in a deterioration of the living space and the general environment. It was not until 500 B.C. that the Greeks developed "municipal dumps." Ancient Rome had only open dumps to accommodate the refuse from its massive population [1]. In 1400 A.D. mounds of garbage outside the city gates of Paris were so high that they blocked the sighting of potential enemies, thus compromising the defense of the city [2].

In recent years, fluctuations in the price of oil and dependence on the foreign oil supplies have stimulated research in the area of renewable resources. One such

renewable resource is municipal solid waste (MSW), which is rich in cellulosic material and, therefore, represents a potential source of energy or chemical feedstock.

Pyrolysis of MSW (i.e., thermal degradation in the absence of oxygen) produces a solid char, a liquid tar, and a gas—all of which are potentially marketable forms of energy. At the same time, the pyrolysis processing achieves the desired volume reduction of the MSW.

The incentive for producing this type of product depends on local market conditions and on the economic viability and operational reliability of the conversion processes. To date, the pyrolysis of MSW has not been technically or commercially successful [3]. Although many pyrolysis processes have been proposed, the basic mechanisms of thermally degrading MSW to produce a gaseous or liquid fuel that is storable and transportable are not well understood.

The Argonne National Laboratory/Department of Energy (ANL/DOE) program on pyrolysis of municipal solid waste has three overall objectives: (a) to develop a scientific data base and fundamental process information that will support the development of economic engineering processes for the thermochemical conversion of MSW into gaseous and liquid fuels; (b) to understand the basic mechanisms, kinetics, and chemistry involved in the pyrolytic conversion of MSW and its components; and (c) to characterize the prod-

ucts produced in the primary and secondary pyrolysis of MSW and its components.

Argonne National Laboratory is performing closely controlled laboratory-scale tests [4-7]. The goal is to determine how different operating parameters influence the product compositions and the product mix (i.e., yields). As more information is obtained from the experiments, a much better understanding of the basic chemistry will result. This can then be the basis for improved engineering designs for MSW conversion to economical fuels. The work discussed in this paper is ongoing and data reported are preliminary results.

EXPERIMENTAL

Pyrolysis

Municipal solid waste is a highly variable "raw material," by both season and location. Cellulosic materials, including paper, newsprint, packaging materials, wood wastes, and yard clippings typically comprise over 50% of MSW [4]. Investigation of pyrolysis fundamentals using some of these materials, individually or in mixtures, is being undertaken to generate adequate quantities of products in a bench-scale reactor so that the gaseous and liquid products produced and the char remaining can be analyzed. The feedstocks utilized in the experiments ranged from single components of MSW to simple mixtures prepared in the laboratory to represent actual RDF/MSW samples.

Pyrolysis experiments have been performed under non-isothermal conditions in a batch reactor shown in Fig. 1. The quartz reactor, with a 70 mm I.D., was enclosed in a clam-shell furnace. The heating rate for all of the experiments reported in this paper was 20°C/min. A flow of helium purged the reactor as the temperature was raised from ambient to 700°C. Temperatures (centerline of bed, inside reactor wall, outside reactor wall, and ambient air) were recorded on a multipoint recorder to allow indication of existing temperatures and temperature gradients. There was a rotameter on the inlet gas line to measure and control purge gas flow. Cold traps were utilized in the gas outlet downstream of the condenser unit. These traps were filled with ice and dry ice. Downstream of the traps, the gases which did not condense were collected in plastic sampling bags for analysis.

A number of runs were made using kraft paper (KP), kraft paper/polyethylene (KPP), kraft paper/polyethylene/aluminum (KPPA), and kraft paper/polyethylene/aluminum/boric acid (KPPAB). The KPP mixture was 89 wt % kraft paper and 11 wt %

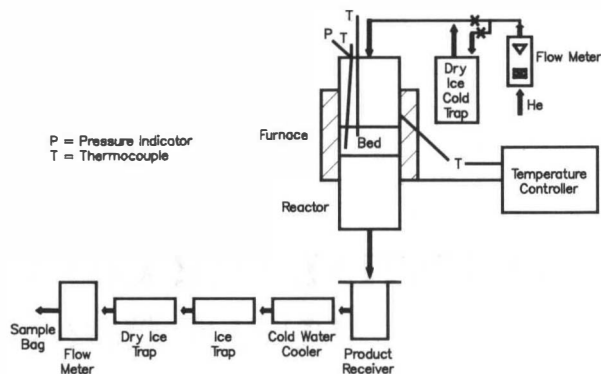


FIG. 1 SCHEMATIC OF A BENCH-SCALE PYROLYSIS UNIT

polyethylene. The KPPA feed was 90 wt % kraft paper, 5 wt % polyethylene, and 5 wt % aluminum. Finally, the KPPAB feed mixture was 82 wt % kraft paper, 4.5 wt % polyethylene, 4.5 wt % aluminum, and 9.0 wt % boric acid. The aluminum, a material often present in MSW mixtures, was added to the cellulosic/plastic mixture to test for catalytic effects. Boric acid was used as a representative weak acid. Weak acids such as sodium hydrogen phosphates are often added to wood and wood products as flame retardants. Also, normal decay of MSW is likely to produce an acidic medium.

The kraft paper and polyethylene samples used as feedstock were prepared by shredding into strips ~0.25 in. wide and ~1.0 in. long. Twenty-five to 30 g of mixture were used in each of the experiments. Condensed liquid vapors accumulated in a graduated cylinder (product receiver) at the bottom of the reactor as well as in the cold traps downstream of the water-cooled condenser. Gases were collected at the end of the trapping train and solid char remained in the static bed.

Physical Measurements of Products

Specific gravity, viscosity and calorific values were determined for the tars produced in the various runs. The tars as collected contained about 50% water. Hence, they had to be dried. The drying procedure was to pass the liquid over a magnesium sulfate (anhydrous) column. A glass column was packed with magnesium sulfate and sea sand in the ratio of 3:1. The sea sand was used to give porosity to the column. The tars were poured over the column and allowed to travel through the column by gravity. As the tar passed

through the column, the anhydrous magnesium sulfate absorbed all of the water and the tar adhered to the hydrated magnesium sulfate. Tetrahydrofuran (THF), a suitable solvent for the tars, was used to elute the tars from the column. Upon elution, the THF/tar solution was collected and the THF was vaporized by blowing nitrogen over the solution. No heat was applied so as to prevent any decomposition or reaction of the tar molecules. There is the possibility that some small, volatile molecules (e.g., CH₃OH) may have been lost during the drying process. However, any such losses, while not quantified, are thought to be minimal.

The specific gravity of the dried tars was measured using a Fisher Scientific Pycnometer made for measuring semi-solid or viscous liquids. It consists of an aluminum container, lid, and a cap which can be screwed down tightly so as to force excess liquid out without leaving any air bubbles entrained in the liquid. The measurement was done at room temperature. The specific gravity was calculated using the density of water at 20°C to be 0.99823.

Kinematic viscosity was measured for the dry tar using a Cannon-Fenske routine viscometer. The procedure was taken from ASTM D445 and D446 [8]. The experiments were run in quadruplicate at 40°C. Kinematic viscosity was calculated by taking a product of the efflux time measured in seconds and the viscometer constant provided with the instrument.

Calorific values for both the tar samples and the char were determined using a Parr 1241 bomb calorimeter equipped with a Parr 1710 controller.

Spectroscopic and Analytical Data

Fourier transform infrared spectra were obtained for the tars using a Perkin-Elmer 1500. Approximately 1 mg of tar was ground with 100 mg potassium bromide and pressed into a pellet.

Elemental analyses were obtained from Huffman Laboratories, Golden, Colorado.

RESULTS AND DISCUSSION

Table 1 shows physical properties of tars obtained from the different feed mixtures. For comparison, the properties of No. 2 and No. 6 fuel oil are also included in Table 1. As seen in Table 1, the three mixtures which were pyrolyzed yielded tars that are less dense than the tars obtained from kraft paper only. The KPP mixture and the KPPA mixture produce tars which are less viscous than the kraft paper only tars. The presence of boric acid during pyrolysis of the KPPA

TABLE 1 PHYSICAL PROPERTIES OF PYROLYSIS TARS DRIED OVER MgSO₄

Sample	Specific Gravity	Viscosity (centistokes)	Caloric Value (Btu/lb)
Kraft paper	1.24	257.0	9714.18
KPP	1.03	78.5	9197.88
KPPA	1.08	19.8	9126.12
KPPAB	1.06	287.7	9135.53
No. 2 Fuel Oil ^a	0.887-0.825	1.9-3.0	19,270-19,750
No. 6 Fuel Oil ^a	1.022-0.922	260-750	17,410-18,990

^aReference 11.

mixture produces very viscous tars similar to those from kraft paper only. These observations are consistent with the fact that kraft paper, which is a cellulosic-rich material, produces tars which are rich in hydroxyl groups. The presence of hydroxyl groups is supported by infrared spectrum of the liquid tars (Figs. 2 and 3). (Information on the interpretation of infrared spectra are given in Ref. [9].) If there are significant hydroxyl groups present in the tar, there is likely to be significant intermolecular and intramolecular hydrogen bonding, which in turn makes the molecules less free to move. This causes the increase in viscosity in the liquid.

Addition of polyethylene to the feed mixture may result in aliphatic material being incorporated into the liquid product formed during pyrolysis. Typically, paraffinic materials (aliphatics) are less viscous than any heteroatom-containing functionality since they do not hydrogen bond [10].

The presence of aluminum in the reactor feed, when both kraft paper and polyethylene are present, appears to have a catalytic effect on the reactions between the highly hydrophilic cellulosic radicals and the hydrophobic polyethylene radicals. As observed in Fig. 3, the relative intensities of the hydroxyl band and the aliphatic stretches at 3300 cm⁻¹ and 2900 cm⁻¹ are different in the ternary mixture versus the kraft paper only tars. This increase in the aliphatic band suggests that with the KPPA feed the tars produced have more aliphatic material. As noted earlier, this change in the amount of aliphatics present would also account for the decreased viscosity which has been observed. In short, the addition of polyethylene and aluminum to the kraft paper produces tars containing less hydrogen-bonded constituents. These results suggest that pyrolysis of actual MSW/RDF would lead to tars which are less hydrogen-bonded than the kraft-paper-only tars.

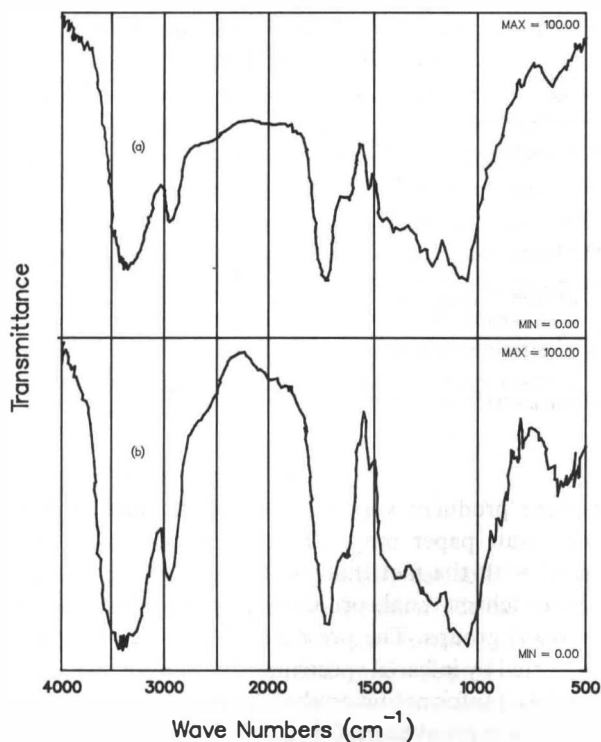


FIG. 2 FTIR SPECTRA OF TARS: (a) KP; (b) KPP

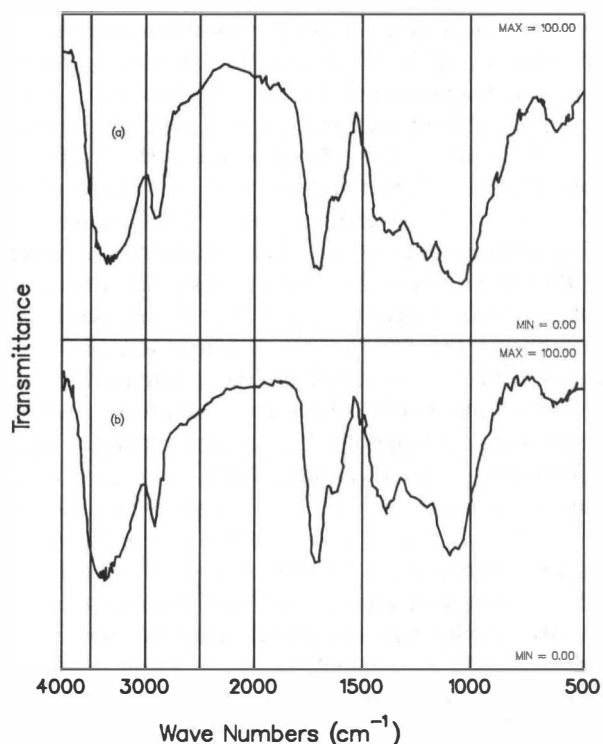


FIG. 3 FTIR SPECTRA OF TARS: (a) KPPA; (b) KPPAB

Addition of a weak acid (boric acid) to the feed increases the viscosity of the tars produced which suggests that an acidic medium retards the reaction between the cellulosic and polyethylene radicals. This is confirmed by the infrared spectra (Fig. 3) which show sharper, better resolved bands at 2900 cm^{-1} in the case of the KPPAB experiments than in the tars obtained from the run made without boric acid. These results suggest that there is very little aliphatic component incorporated into the tars in the presence of the acid.

As seen in Table 2, the calorific values of the chars are much higher than the corresponding tars. The kraft-paper-only pyrolysis leaves behind a char which has a very high heating value. Addition of polyethylene lowers the heating value of the char produced which is difficult to explain at this time. However, if aluminum is added to the mixture of cellulosic and plastic, then the char takes on a heating value similar to that produced from the kraft paper only. Kraft paper with aluminum pyrolysis yields char which is much lower in heating value than chars from the kraft paper only or the ternary mixture. If boric acid is added to the ternary mixture, a significant decrease in calorific value of the char is observed.

The elemental analyses of the chars (shown in Table 3) result in similar compositions for the chars produced from kraft paper only and those produced from the KPPA mixture. The composition of the char remaining when the KPP mixture is pyrolyzed is much higher in oxygen and hydrogen. The reason for this change in char composition is yet to be explained; however, it appears that aluminum may catalyze the reaction between kraft paper and polyethylene.

Complete mass balances have not been obtained for all of the experimental mixtures. However, analytical results from the kraft paper only feedstock showed a tar product yield of 24.5 wt. % and a char yield of 23.7 wt. %, both on a dry, ash-free basis. The remaining feed material produced water and permanent gases in almost equal amounts (approximately 25–30 wt. % each).

Figure 4 shows the infrared spectra of kraft paper tars produced at 450°C and 700°C . Comparison of the two spectra show very interesting differences. The secondary tars obtained at 700°C contain strong, sharp bands of aromatic C-H stretches at 3011 cm^{-1} , 3022 cm^{-1} , and 3045 cm^{-1} . Bands in the 900 cm^{-1} to 800 cm^{-1} region, which can be assigned to the out-of-plane

TABLE 2 CALORIFIC VALUES OF THE CHARS

Sample	Calorific Value (Btu/lb)
Kraft paper	14,290
KPP	12,847
Kraft paper/aluminum	12,271
KPPA	13,966
KPPAB	12,702
Lignite ^a	7,020-9,720
Subbituminous Coal ^a	9,900
Bituminous Coal ^a	12,060-15,840

^aReference 12.

TABLE 3 ELEMENTAL COMPOSITION OF CHARS

Kraft paper	88.03	1.57	6.04
Kraft paper/polyethylene	84.13	3.05	8.21
Kraft paper/polyethylene/ aluminum	88.87	1.52	5.38

bending modes of aromatic C-H concur with the higher frequency bands. These bands do not appear in the tars obtained at 450°C, suggesting the absence of aromatic species in the tar produced at the lower temperature. These results suggest that either the kraft paper radicals formed at higher temperatures undergo aromatization, or perhaps the lignin component of the kraft paper decomposes at a higher temperature. The other major difference between these two spectra is the disappearance of the 1725 cm⁻¹ band in the high temperature tars, suggesting the absence of carbonyl in these tars. Investigation to determine which of the above reasons is leading to the highly aromatic nature is underway. The production of aromatics from MSW may be a useful process.

The tars analyzed by gas chromatography-mass spectrometry and infrared spectra show the presence of 2-furaldehydes. This is consistent with published literature which shows that pyrolysis of 1,6-anhydro-β-d-glucopyranose is known to yield 2-furaldehyde [13]. The 2-furaldehydes are convertible to aromatics via a series of catalytic reductions similar to the catalytic reforming applied in the petroleum industry.

CONCLUSIONS

The preliminary data indicate the tars produced by pyrolysis may offer the possibility of being converted

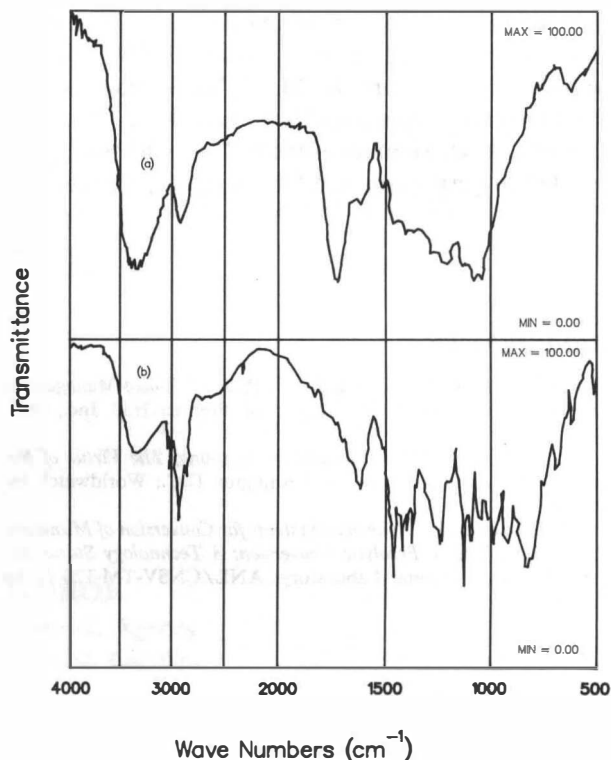


FIG. 4 FTIR SPECTRA OF KRAFT PAPER TARS: (a) OBTAINED AT 450°C; (b) OBTAINED AT 700°C

to aromatics, which in turn have found use in making higher grade fuels. The route to obtain these aromatics could be via pyrolysis at high temperatures or via 2-furaldehyde formations. The chars, with calorific values in the 12,000 to 14,000 Btu/lb range, have heating values close to that of lignites. They may find use in hydrogasification. Since the presence of polyethylene and aluminum do not significantly affect the heating values of the chars produced, the as-received MSW may also produce chars of similar heating value. In fact, the presence of polyethylene and aluminum in garbage may be beneficial to the tar formation since the material left behind is less viscous and less prone to hydrogen bonding. If left standing, these tars may not easily undergo coupling. Since acidic medium is not favorable, as observed from the boric acid experiments, the pH of the feedstock is a variable of interest in MSW pyrolysis.

ACKNOWLEDGEMENTS

This work was funded by the U. S. Department of Energy (DOE), Biofuels and Municipal Waste Tech-

nology Division. The authors wish to acknowledge the support and guidance of J. Lazar, EMW Program Manager at ANL, and K. M. Myles, Section Head in the Chemical Technology Division of ANL. Benny A. Esposito, ANL Summer Student Research Participant, assisted in performing the laboratory experiments.

REFERENCES

- [1] Neal, H. A., and Schubel, J. R. *Solid Waste Management and the Environment*, B. M. Webber, ed. Prentice-Hall, Inc., 1987, 14.
- [2] Chandler, W. V. "Materials Recycling: The Virtue of Necessity" Worldwatch Paper 56, Washington D.C.: Worldwatch Institute, 1983, 52.
- [3] Kuester, J. L. *Thermal Systems for Conversion of Municipal Solid Waste*, Vol. 5, *Pyrolytic Conversion: A Technology Status Report*. Argonne National Laboratory, ANL/CNSV-TM-120 (June 1983).
- [4] Helt, J. E., et al. "Pyrolysis of Municipal Solid Waste" Argonne National Laboratory, ANL/CNSV-45 (December 1984).
- [5] Helt, J. E., et al. "Pyrolysis of Municipal Solid Waste: Annual Report July 1984-June 1985." Argonne National Laboratory, ANL/CNSV-54 (July 1986).
- [6] Helt, J. E., and Agrawal, R. K. *Pyrolysis of Municipal Solid Waste Components*, AIChE Mtg., Chicago, Illinois (November 1985).
- [7] Agrawal, R. K. and Helt, J. E. "Applications of Thermogravimetry in Energy from Solid Waste Research." 15th Annual North American Thermal Analysis Society Conference, Cincinnati, Ohio (September 1986).
- [8] *Annual Book of ASTM Standards*. 1985, D445-446.
- [9] Silverstein, R. M., Bassler, G. C., and Morrill, T. C. *Spectrometric Identification of Organic Compounds*. New York: John Wiley & Sons, 1981.
- [10] Vinogradov, S. N., and Linnell, R. H. *Hydrogen Bonding*. Van Nostrand Reinhold Company, eds. 1971, 31.
- [11] *Steam/Its Generation and Use*, New York: Babcock & Wilcox, 1975.
- [12] Rider, D. K. *Energy: Hydrocarbon Fuels and Chemical Resources*. New York: John Wiley & Sons, 1981.
- [13] Shafizadeh, F., and Lai, Y. Z. "Thermal Degradation of 1,6-Anhydro- β -D-Glucopyranose." *J. Org. Chem.* 37 (no. 2, 1972): 278.