

PRODUCTION AND CHARACTERIZATION OF PYROLYSIS
LIQUIDS FROM MUNICIPAL SOLID WASTE

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INTRODUCTION

Municipal solid waste (MSW) is a highly variable "raw material," by both season and location. However, it is generally accepted to have a composition within the ranges shown in Table 1 (1). Cellulosic materials, including paper, newsprint, packaging materials, wood wastes, and yard clippings, constitute over 50% of MSW.

A basic understanding of the pyrolytic reactions is important and relevant to both combustion and conversion of MSW. As MSW is heated the different components react differently at different temperatures. The volatile species can evaporate without major change, and the rest of the cellulosic components partially break down to volatile components leaving a carbonaceous char that contains the ash and noncombustibles. The volatile pyrolysis products consist of a gaseous fraction containing CO, CO₂, some hydrocarbons, and H₂, which are noncondensables. There is a condensable fraction containing H₂O, volatile hydrocarbons and low molecular weight degradation products such as aldehydes, acids, ketones, and alcohols. Finally, there is a tar fraction containing higher molecular weight sugar residues, furan derivatives, and phenolic compounds. The proportion and composition of these products are highly dependent on the cellulosic composition of the MSW, the pyrolysis temperature and the presence of inorganic compounds that could influence (catalyze) the pyrolysis reactions.

Pyrolysis of cellulose at temperatures below 300°C results mainly in char formation. Any lignin present in the MSW (Kraft paper, cardboard, and wood waste contain significant proportions) has a higher tendency for charring, whereas the cellulose and hemicelluloses readily decompose to volatile products at temperatures above 300°C. Most of the plastics present thermally degrade at a significantly higher temperature (400-450°C) (2).

BASIC MECHANISMS RESEARCH

The ANL/DOE program on pyrolysis of municipal solid waste (MSW) has two overall objectives: (1) to understand the basic thermokinetic mechanisms associated with the pyrolytic conversion of MSW and (2) to seek new processing schemes or methods of producing a liquid or gaseous fuel from MSW feedstock. To meet these objectives, we are performing laboratory experiments with the aim of determining the effects of different operating parameters on the pyrolysis-product compositions and deriving an analytical model of the pyrolytic process that describes the chemical kinetics.

This DOE-sponsored research has both ANL activities and subcontracted work. Argonne is performing closely controlled laboratory-scale parametric tests. The work is being performed on two experimental facilities: (1) a TGA to study the thermal degradation versus temperature, and (2) a bench-scale reactor to produce significant quantities of products to permit characterization. The goal is to determine how different operating parameters influence the product compositions.

Subcontracted activities are being performed at the Solar Energy Research Institute (SERI) and the Chemical Engineering Department at the University of Arizona. SERI has used their direct high-pressure molecular beam mass spectrometric sampling system to collect qualitative "fingerprints" and experimental data on the pyrolysis products generated from components of MSW and various refuse derived fuel (RDF) samples (3). They are also using the same experimental apparatus to distinguish between the primary and secondary reactions leading to the formation of the pyrolysis products (4). This data will be part of an overall data base to describe the influence of sample properties and reaction conditions on the solid phase and gas phase processes of low-temperature (<500°C) MSW pyrolysis to oils. Additionally, SERI has recently started a new task on the development of a rapid method of characterizing the liquid products from pyrolysis based on mass spectrometric data. This new task is composed of three parts: 1) compound class analysis by advanced pattern recognition techniques, 2) liquid product analysis via compound class analysis, and 3) correlation of chemical composition to fuel properties.

The University of Arizona has completed a small research effort on the fundamentals of direct liquefaction of MSW (5). They modified an existing autoclave and a real-time digital microprocessor control system so that it could be operated in a semi-continuous mode. Various components of MSW were studied in order to obtain meaningful data, not confused by the different thermokinetics of more than one distinct MSW component. Feedstocks included wood flour, cardboard, newsprint and rice (starch), as well as the important model compounds alpha cellulose and lignin. It was found that these MSW components could be converted to liquid oils and a high-heating value residual solid at temperatures of 325°C to 400°C and pressures of 1000 psi to 3000 psi.

A task which is related to the basic mechanisms work is also being performed by ANL (2). This task explores the possibility of using catalytic hydrotreating to upgrade the liquid products produced during conventional pyrolysis of MSW. The liquid products obtained from MSW pyrolysis processes are generally unsuitable for use as liquid fuels. Heating values are low and the liquids are very corrosive, viscous and unstable during storage. A major reason for these problems is the extremely high oxygen content of the pyrolysis products. The kinetics of catalytic reactions that remove oxygen-containing compounds from the pyrolysis liquids is being experimentally determined in a high-pressure, fixed-bed microreactor of the trickle-bed type. The reactions of interest involve the reduction of the oxygen-containing hydrocarbon with high pressure hydrogen using a solid catalyst. The catalysts which have been used are primarily commercially available hydrodesulfurization (HDS) catalysts containing molybdenum oxide with either cobalt or nickel oxide, supported on high surface area alumina matrix.

ANL BENCH-SCALE STUDIES

The emphasis of this paper will be on the bench-scale studies being performed at ANL and on the associated activities in characterizing the liquids produced in the pyrolysis reactions.

The reactor is a fixed bed contained inside a quartz tube (70-mm ID) and placed between two glass frits. The outside of the tube is enclosed in a furnace. The reactor tube can be purged from top to bottom with the desired gas(es). The reactor is operated in the nonisothermal mode with heatup rates as high as 30°C/min. Temperatures are recorded on a multipoint recorder to allow indication of existing temperatures and temperature gradients. There is a rotameter on the inlet gas line and a dry gas meter on the outlet. Cold traps are in the gas outlet downstream of the condenser unit. These traps are filled with ice or dry ice. Downstream of the traps, the gases that do not condense are collected in plastic sampling bags for analysis by gas chromatography (GC).

Experimental results on the thermal decomposition of typical MSW components (Whatman #1, newsprint, kraft paper, cardboard, aspen, and pine) over a temperature range of 275-475°C have been gathered. The details of these experimental runs may be found elsewhere (6). Also, information on the TGA runs used in support of this bench-scale work is available elsewhere (7,8).

CHARACTERIZATION OF LIQUIDS

Various liquid samples produced in the bench-scale apparatus have been analyzed with GC and GC/MS. The chromatograms were qualitatively compared to each other by both measurement of peak retention times and by observation of the patterns present. As a result, six different groups were identified:

- Group A - Most components elute early in the chromatogram as many sharp peaks within a small retention window.
- Group B - Bulk of components elute across a 6- to 20-min retention window and are a mix of both sharp and broad peaks.
- Group C - Many peaks are observed; the bulk of components elute across a 4- to 30-min retention window.
- Group D - Similar to C, but most components elute across a 4- to 20-min retention window.
- Group E - A few early peaks are observed, especially in the 5- to 7-min retention window.
- Group F - Similar to D, but many peaks are observed in the 9- to 11-min retention window.

The mass spectrum obtained from a typical tar sample is shown in Fig. 1. This tar sample was produced from a newsprint feedstock pyrolyzed in an inert atmosphere of helium. A computer search was performed using the 31,000 component NIH/EPA library in addition to a library of compounds from Battelle Pacific Northwest Laboratory (9). The results of the computer search and from interpretation of various standard spectra yielded tentative identification of numerous compounds. It is apparent that many compounds of homologous series are present. Recognition of just one of the compounds in a series leads to identification of all since they will most likely differ only by 14 amu (a CH₂ group) or by 31 amu (a CH₃O group). In some cases the same identification is made for more than one compound. Actually, different isomers of the compound are probably being found. The percent found was estimated by dividing the response of the most abundant ion for a compound by the total of the responses of the most abundant ions for all compounds.

In general, the classes of compounds included furfurals (9.4%), phenols (2.5%), methoxyphenols (16.9%), cyclic compounds such as methyl cyclopentanones (10.8%), methoxy benzenes (3.8%), and the substituted propane tentatively identified for the peak at scan number 1207 (36.8%). Although the compound eluting at scan 1207 is by far in the highest concentration, insufficient information is available from its spectrum to allow a reasonable identification. The base peak observed is 75amu, and a 115 amu ion is also present at 40% abundance.

With the computerized mass spectral matching capability, a substituted propane with a molecular weight of 192 g/mol (propane, 1,3-dimethoxy-2,2-bis(methoxymethyl)) was selected as the most probable compound. The sample was submitted for gas chromatograph/matrix isolation/Fourier transform infrared (GC/MI/FTIR) analysis to add to the information necessary for better identification.

A GC/MI/FTIR run provided useful information on the bulk of the material present in the sample at scan number 1207. Data from the GC/MI/FTIR analysis indicated that the computerized mass spectral identification of the component eluting at scan number 1207 is not far off. The compound does not contain phenyl groups, and computerized IR searches came up with compounds with an ethanol/ethane or propanol/propane backbone substituted with methoxy or ethoxy groups. In particular, three close matches are dimethyl acetaldehyde, $(\text{CH}_3\text{O})_2\text{-CH-CHO}$; 1-methoxy-2-propanol, $\text{CH}_3\text{O-CH}_2\text{-CH(OH)-CH}_3$; and 1,3-diethoxy-2-propanol, $\text{CH}_3\text{CH}_2\text{O-CH}_2\text{-CH(OH)-CH}_2\text{-OCH}_2\text{CH}_3$. The presence of methoxy or ethoxy groups is consistent with the tentative identification given for the compound.

Another compound present in a relatively large concentration but which cannot be identified is that eluting at scan number 1343. This compound has an apparent molecular weight of 110 amu, with ions at 71, 89, and 110 amu. It appears to be neither a methyl furfuryl, benzenediol, nor dimethyl cyclopentanone. The 71-amu ion probably results from a $\text{CH}_3\text{-CH}_2\text{-C=O}$ group, which can come from a tetrahydrofurfuryl structure or from a butyl ester. The compound's real molecular weight may be above 110 amu.

YIELDS AND ANALYTICAL RESULTS

With the Whatman No. 1 filter paper, the yields at 475°C of water vapor and gases were in the ranges 5-13 wt % and 26-34 wt %, respectively, of the original cellulose. The hydrogen balance suggests the higher water content (13%), whereas both the carbon and oxygen contents suggest a lower water yield (5 wt %).

Efforts have been made to analyze the gases collected in the sample bags. A Hewlett-Packard Gas Chromatograph is being used to identify major gas components. The preliminary GC analyses show that, for the Whatman No. 1 paper at 475°C, the gases produced are 56.6 vol% CO_2 and 43.4 vol% CO . No other gases were detected in significant quantities. The yield of CO_2 is, therefore, in the range of 18-23 wt % of the original cellulose and the yield of CO is 8-11 wt %. Roughly 25% of the energy in the feedstock is released in the gaseous products. These pyrolysis gases can be considered a low-Btu fuel.

The Whatman No. 1 paper (as received) contained 4.1 vol % moisture and 0.074 wt % ash. All results reported here are on a moisture-ash-free basis unless otherwise specified. Table 3 summarizes some analytical results of cellulose and condensed-phase cellulose pyrolysis products. A comparison of the results in Table 2 for cellulose and cellulose tars indicates that the elemental composition of these two materials is very similar. (The heating value of cellulose tars reported here may be low due to the loss of lower-molecular-weight products during the drying step.) Tars seem to have a slightly higher heating value than that of cellulose. These results strongly suggest that the nature of cellulose tars is similar to that of its parent cellulose.

As can be seen from Table 2, the cellulose chars are very different from the parent cellulose. When compared with the original cellulose, the cellulose chars have a carbon content that is roughly double, and H_2 and O_2 contents that are about one-half and one-third respectively. The richness in carbon content of the chars is indicated by their high heating value (7566 cal/g). Unfortunately, the low H_2 content of the chars make them an unlikely candidate for use as transportation fuels. Because of the high carbon content and low H_2 and O_2 content, the cellulosic chars are comparable to a low-volatile bituminous coal or a low-grade anthracite coal. However, since the chars contain no sulfur or nitrogen compounds that could form potential air pollutants upon combustion, they do have potential as a solid fuel. Tables 3 and 4 give the analytical results for newsprint and Kraft paper feedstock.

The atomic ratios (H/C and O/C) and the heating value of cellulosic chars indicate that they are very similar to coal. The H/C ratio of cellulose tars (1.73) is comparable to that of No. 2 fuel oil (1.84). Unfortunately, the high oxygen content indicated by the O/C ratio (0.91 compared to 0.01 for fuel oil) significantly reduces the heating value of the tars.

DISCUSSION

It should be noted that the tar analysis results of this study are very similar to those obtained from vacuum pyrolysis of small cellulose samples conducted by Agrawal et al (10). Also the tar yields are comparable to those obtained by Shafizadeh (11) using small samples of Whatman No. 1 paper under vacuum conditions. These findings support the assumption that negligible tar decomposition takes place in the reaction bed.

Efforts are also in progress to ascertain some of the possible heat and mass transfer limitations of the pyrolysis process. Fig. 2 depicts the residue and tar yields of 5-g and 15-g cellulose samples at a heating rate of 5°C/min. Increased sample weight shifts the weight-loss curve to a higher temperature by about 10°C. Fig. 2 also shows that increased sample weight decreases the tar yields. Efforts to explain this effect of sample weight on product yield are in progress.

Figures 3 and 4 summarize the data for the influence of heating rate on product yields from Whatman No. 1 paper. It is seen from Figs. 3 and 4 that increasing the heating rate or sample weight has a similar effect in shifting the weight-loss curve to a higher peak temperature. However, the shift in the weight-loss curve along the peak-temperature axis in the case of increased sample weight is due to mass transfer limitations, whereas, in the case of increased heating rate, this shift is due to combined effects of kinetics and heat transfer resulting in delayed decomposition. At a peak temperature of about 370°C, the product yields are essentially independent of the heating rates (Fig. 4).

The results in Table 6 illustrate the influence of sample weight and heating rate on product yields. The data show that increasing sample size reduces the tar yields and increases the char yields. The drastic decrease in tar yields is primarily due to increased vapor residence time in the reaction bed. If the vapor residence time is reduced in the reaction bed by using a fluidized bed or an entrained flow reactor, then secondary decomposition can be significantly reduced, and the effects of sample weight will not be as drastic. Thus, data collected in the loosely packed fixed-bed reactor of the present study may represent an extreme for an operating industrial reactor.

Increasing the heating rate appears to decrease the char yields but has little influence on tar yields. This implies that gas yields increase at the expense of char yields.

Table 7 summarizes elemental analyses of chars formed under various pyrolysis conditions. The elemental analyses of cellulosic chars suggest that the composition of chars is not strongly influenced by either the heating rate or sample weight.

Results to date strongly imply that, depending on the residence time, the tar yields for final pyrolysis temperatures above 300°C will be independent of heating rates. This observation is strengthened by the finding from TGA data analysis (7,8) that the apparent activation energy for cellulose decomposition is similar to that for tar formation.

Olefins and other hydrocarbon gases were not detected in the pyrolysis gases. This is not surprising since these fuels are not products of primary cellulose pyrolysis (12,13). The significant yields of olefins and hydrocarbon gases from flash pyrolysis studies are most likely a result of secondary tar decomposition. Cellulose tars start to decompose at about 550°C, and most of these studies were carried out over the temperature range of about 600-800°C. These observations suggest that results from flash pyrolysis studies are dominated by secondary tar decomposition reactions.

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Table 1. Composition Ranges for Several MSW Samples^a

Component	Composition Range, wt %
Paper	30-50
Glass	8-10
Metals	7-10
Plastics	1-5
Rubber-Leather	1-3
Wood	1-4
Textiles	1-5
Food Wastes	10-20
Yard Wastes	5-20
Other	1-4

^aReference 1.

Table 2. Analytical Results of Feedstock, Tars, and Chars from Whatman No. 1 Paper (heating rate, 5°C/min; final temp., 475°C)

	Feedstock	Tar Product	Char Product
Heating Value, ^a cal/g	4170	4330	7566
Ash Content, wt %	0.074	-0.075	0.63
Moisture Content, wt %	4.1	--	--
Elemental Analysis, ^a wt %			
Carbon	44.7	42.3(43.6) ^b	81.0(27.3)
Hydrogen	5.9	6.1(47.5)	3.6(10.0)
Oxygen ^c	49.4	51.6(48.0)	15.4(4.7)
Yield, wt %	--	-46	-15

^aDry basis.

^bNumbers in parentheses give percent of original material (based on the reported yields).

^cDetermined by adding together the carbon and hydrogen contents and subtracting them from 100%.

Table 3. Analytical Results of Feedstock, Tars, and Chars from Newsprint (heating rate, 5°C/min; final temp., 475°C)

	Feedstock	Tar Product	Char Product
Heating Value, ^a cal/g	4722	5573	7866
Ash Content, wt %	.95	--	4.1
Moisture Content, wt %	8.3	--	--
Elemental Analysis, ^a wt %			
Carbon	48.0	47.5(45.5) ^b	78.0(24.4)
Hydrogen	5.4	5.6(47.7)	3.7(10.3)
Oxygen ^c	46.6	46.9(46.3)	18.3(5.9)
Yield, wt %	--	-46	-15

^aDry basis.

^bNumbers in parentheses give percent of original material (based on the reported yields).

^cDetermined by adding together the carbon and hydrogen contents and subtracting them from 100%.

Table 4. Analytical Results of Feedstock, Tars, and Chars from Kraft Paper (heating rate, 5°C/min; final temp., 475°C)

	Feedstock	Tar Product	Char Product
Heating Value, ^a cal/g	4445	5272	7333
Ash Content, wt %	1.3	--	4.3
Moisture Content, wt %	6.1	--	--
Elemental Analysis, ^a wt %			
Carbon	47.5	46.9(24.7) ^b	75.5(38.2)
Hydrogen	5.5	5.3(24.1)	3.9(17.0)
Oxygen ^c	47.0	47.8(25.4)	20.6(10.5)
Yield, wt %	--	-25	-24

^aDry basis.

^bNumbers in parentheses give percent of original material (based on the reported yields).

^cDetermined by adding together the carbon and hydrogen contents and subtracting them from 100%.

Table 5. Effect of Sample Weight and Heating Rate on Ultimate Product Yields from Whatman No. 1 Paper

Sample No.	Pyrolysis Sample Weight, g	Heating Rate, °C/min	Yields, %	
			Tar ^b	Char
FPLO8	5	5	46.14	14.55
FFL15	10	5	42.13	15.26
FFL13	15	5	38.54	15.66
FPMD3	5	20	47.18	12.65
FPMD5	5	30	47.76	11.93

^aProduct yields are given for a peak temperature of 475°C.

^bBased on weight percent Whatman No. 1 paper (dry basis).

Table 6. Effect of Sample Weight and Heating Rate on the Composition of Chars from Whatman No. 1 Paper

Sample No.	Pyrolysis Sample Weight, g	Heating Rate, °C/min	Ultimate Char Yield ^a at 475°C, wt %	Chars, wt %		
				C	H	O ^b
PFL08	5	5	14.55	81.80	3.75	13.45
PFL15	10	5	15.26	81.00	3.55	15.45
PFL13	15	5	15.66	81.90	3.45	14.65
PPH03	5	20	12.65	81.30	3.45	15.15
PPH05	5	30	11.93	80.30	3.55	16.15

^aYield from original Whatman No. 1 (dry basis).

^bDerived by adding together C and H contents and subtracting from 100%.

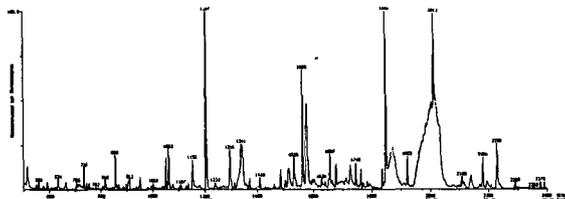


Fig. 1. Mass Spectrum Obtained from Sample 06298402

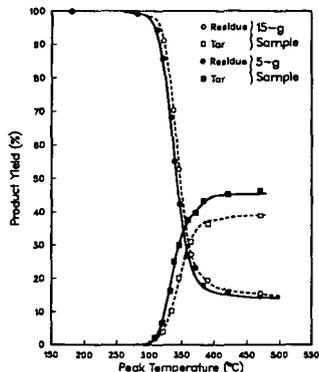


Fig. 2. Effect of Sample Weight on Product Yield for Whatman No. 1 Paper (heating rate, 5°C/min).

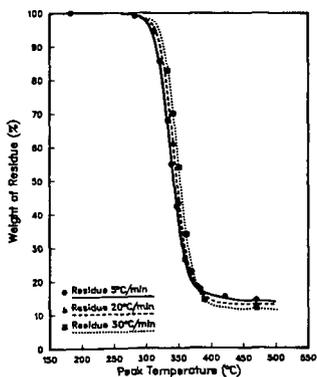


Fig. 3. Effect of Heating Rate on Weight Loss for Whatman No. 1 Paper

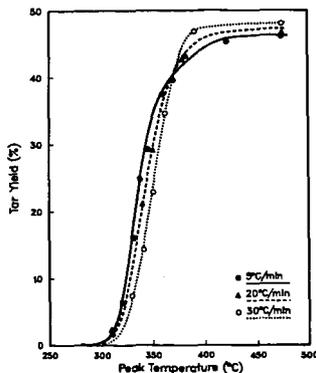


Fig. 4. Effect of Heating Rate on Tar Yields for Whatman No. 1 Paper