The Pyrolysis of Refuse Components

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ABSTRACT

During the heating of organic refuse out of contact with air, water, gases and liquids are evolved, leaving a char residue. Ten refuse components from domestic waste were distilled on a laboratory scale, the gaseous products were analyzed and the yields determined. The gases included mainly CO_2, CO, H_2, CH_4, with mixture calorific values of 300 - 400 Btu per standard cu ft. The yield weights were roughly equally divided among water, gas, organic liquids and char.

The rate of heating affected the yields. Increased heating rates decreased the char, water and carbon dioxide, and increased carbon monoxide. The highest gas yields may be expected from flash heating.

The economical disposal of municipal and industrial refuse is a challenge of growing proportions. The quantity of waste paper, wood, textiles, garbage, metal and glass is over 150 million tons a year in the United States alone, and is increasing faster than the population.

The common open dump is being outlawed. Sanitary landfilling requires acreages that are usually not available near large urban centers. Composting reduces the organic matter only partially and is otherwise seldom economical. Incineration is a growing method of disposal, but is an expense.

The conversion of refuse to useful products with economic value is attractive because, 1) the raw material is available at negative cost, 2) it is available in large quantities at urban centers where markets for products and energy also exist, 3) the organic matter can readily be converted by heat to gas, liquids, char, ceramic aggregates and metal. The yields of gas, liquid and char could be varied over a range depending on the method and rate of heating.

This paper reports on exploratory laboratory tests of destructive distillation of organic wastes, and the prospects for complete gasification of the organic matter. The objective is to determine the quantity and quality of the product gas that might be produced for use as a hot, raw boiler fuel, and possibly for chemical manufacture.

COMPOSITION AND ANALYSIS OF REFUSE

The major class of refuse is that from households, and is about 3 lb. per capita day. It consists primarily of paper products, with less than 10 percent each of glass, metal and garbage, and less than 5 percent each of textiles, wood, plastics and dirt.

A fairly typical chemical analysis of mixed refuse:

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Moisture	27.06 percent
Carbon	25.51
Hydrogen	3.37
Oxygen	21.71
Nitrogen	0.47
Sulfur	0.09
Metal	7.25
Glass and ceramics	9.24
Other inerts (ash)	5.30
	100.00 percent

Analyses of refuse components have been published [1].

The organic matter is basically cellulose, but significant amounts of fats, hydrocarbons, proteins and other organics are present. The proportion of plastics is expected to increase and that of food wastes and coal ashes to decrease in future years.

Solid waste from commercial establishments is quite similar to the domestic waste, and is high in paper content. Industrial waste also has a large organic fraction in most instances, but will contain production wastes characteristics of specific industries and processes.

REFUSE PREPARATION

Because the organic matter is the only source of gas from refuse, and because a fourth of the refuse is nonorganic, separation of the organic matter from free metallic, vitreous and other inerts would have advantages. Also, if the organic matter is then dried at, say, 150 F, the organics would be concentrated. Prior to both of these steps, shredding of the refuse could be undertaken to produce a more manageable product and to free organic and nonorganic components. Special shredders for the purpose have been developed.

While prior processing would be helpful, it is not vital. Gasification does not require pure refined feed stock as a residue of ash will be produced anyway, and the product gas will contain much moisture from the dry organics.

ANALYSES OF SAMPLES

As background information the samples tested were analyzed by the ASTM Method D 271 - 64 for coal and coke. The moisture contents were determined by drying to 80° C.

The volatile matter reported in Table 1 is the weight loss by heating a one-gram sample in a closed crucible which is lowered into a furnace at 1742 F (950° C) and held for 10 minutes. The char left ungasified is essentially carbon and ash.

Analyses for bituminous coals and woods are included for comparison. The large loss of volatile matter from refuse indicates a high yield potential of gas and liquids from destructive distillation.

TABLE 1. PROXIMATE ANALYSES OF REFUSE COMPONENTS, PERCENT ON MOISTURE BASIS GIVEN

	Moisture	Volatile Matter	Fixed Carbon	Ash	Btu/lb.	Ratio: $\frac{VM}{VM + FC}$
Low-vol. bituminous coal (2)	3.61	17.41	74.84	4.14	14,587	0.189
High-vol. bituminous coal (2)	3.56	37.18	56.55	2.71	14,220	0.397
Hardwood maple (3)	0.0	76.1	19.6	4.3	8,190	0.795
Western Hemlock (3)	0.0	74.2	23.6	2.2	8,620	0.759
White pine sawdust	7.0	78.76	14.10	0.14	8,260	0.848
Pine sawdust (3)	0.0	79.4	20.1	0.5	9,130	0.798
Balsam spruce	3.67	77.75	15.52	3.06	9,196	0.835
Hardwood leaf mixture	9.97	66.92	19.29	3.82	7,984	0.776
Newspaper	5.97	81.12	11.48	1.43	7,974	0.877
Corrug. box paper	5.20	77.47	12.27	5.06	7,043	0.864
Brown paper	5.83	83.92	9.24	1.01	7,256	0.900
Magazine paper	4.11	66.39	7.03	22.47	5,254	0.905
Lawn grass	5.47	71.16	17.18	6.19	7,858	0.835
Citrus fruit waste	8.02	71.46	17.34	3.18	7,372	0.804
Vegetable food waste	5.43	73.31	16.37	4.89	7,820	0.818

TABLE 2. ULTIMATE ANALYSES OF REFUSE COMPONENTS, PERCENT

	Moisture	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
Low-vol. Bitum. coal (2)	0.0	83.68	4.57	5.73	1.12	0.76	4.14
High-vol. Bitum. Coal (2)	0.0	79.61	5.54	9.83	1.61	0.70	2.71
Ford hardwood (4)	0.0	51.03	6.60	41.68	0.15	0.06	0.48
Hardwood maple (3)	0.0	50.40	5.90	39.10	0.50	0.0	4.10
Western hemlock (3)	0.0	50.40	5.80	41.40	0.10	0.10	2.20
White pine sawdust	7.0	48.90	5.65	37.43	0.52	0.36	0.14
Pine sawdust (3)	0.0	51.80	6.30	41.30	0.10	0.0	0.50
Balsum spruce	3.67	51.41	6.41	33.81	1.44	0.19	3.07
Hardwood leaf mixture	9.97	46.95	5.50	27.32	6.29	0.15	3.82
Newspaper	5.97	46.21	5.74	40.46	0.05	0.14	1.43
Corrug. box paper	5.20	41.46	5.42	42.57	0.09	0.20	5.06
Brown paper	5.83	42.28	5.73	45.05	0.00	0.10	1.01
Magazine paper	4.11	31.56	4.74	36.96	0.07	0.09	22.47
Lawn grass	5.47	43.65	6.74	33.33	4.22	0.40	6.19
*Citrus fruit waste	8.02	44.11	5.22	38.34	1.02	0.11	3.18
Vegetable food waste	5.43	44.33	5.92	37.55	1.68	0.20	4.89
Cellulose ($C_6H_{10}O_5$)		44.44	6.22	49.34			

Fats, rubber, polyethylene plastic, and waste oils distill almost 100 percent of the ash-free organic matter on rapid heating away from air.

The cellulosic matter, VM + FC, is distilled 75 to 90 percent in the rapid heating of the ASTM crucible.

The ultimate analyses for the same refuse fractions, and for coals, woods, and pure cellulose are reported in Table 2.

DISTILLATION TESTS

The laboratory apparatus used to explore the destructive distillation phase of gasification and to determine yields from typical refuse components is shown in Figure 1.

The test lots were shredded, air dried, sampled for chemical analysis, and sealed. Test samples of about 5 gm each were weighed and loosely packed in a 21 mm I.D. Vicor retort and around a central, shielded chromelalumel thermocouple of 1/8 inch diameter. From ambient temperature and pressure, the sample was heated to 1500 F (816 C) at a controlled rate. Exploratory heating above 1500 F indicated that all of the gas had been driven off at 1500 F.

A typical time-temperature and time-volume log is shown in Figure 2.

The liquids evolved were trapped in U-tubes immersed in ice water. The fixed gases were collected over saturated NaCl brine, and analyzed by a combustion Orsat apparatus.

Gasification took place at atmospheric pressure. The volume of the air initially present in the system was deducted from the gas yield, as was the water vapor present in the gas. The volume of gas was measured by liquid displacement. The volumes were corrected to 30 inches Hg and 60 F.

The yields under the conditions of relatively slow heating of Figure 2 are given in Table 3. The reproducibility of the tests can be judged by comparing Test I and II of newspaper and of magazine paper.

The mixture of gases has approximately the heating value of 100 percent hydrogen or carbon monoxide. Refuse gases compared favorably with the gases from hardwood distillation.

Table 3 shows the following range of gas analyses for the materials tested:

	Volume percent, dry basis
CO_2	20.3 - 43.1
CO	15.7 - 45.1
O_2	0.0 - 2.0
H_2	2.8 - 22.2
CH_4+CnHm	16.9 - 28.2
N_2	2.0 - 11.7
Btu/cf	284 - 423

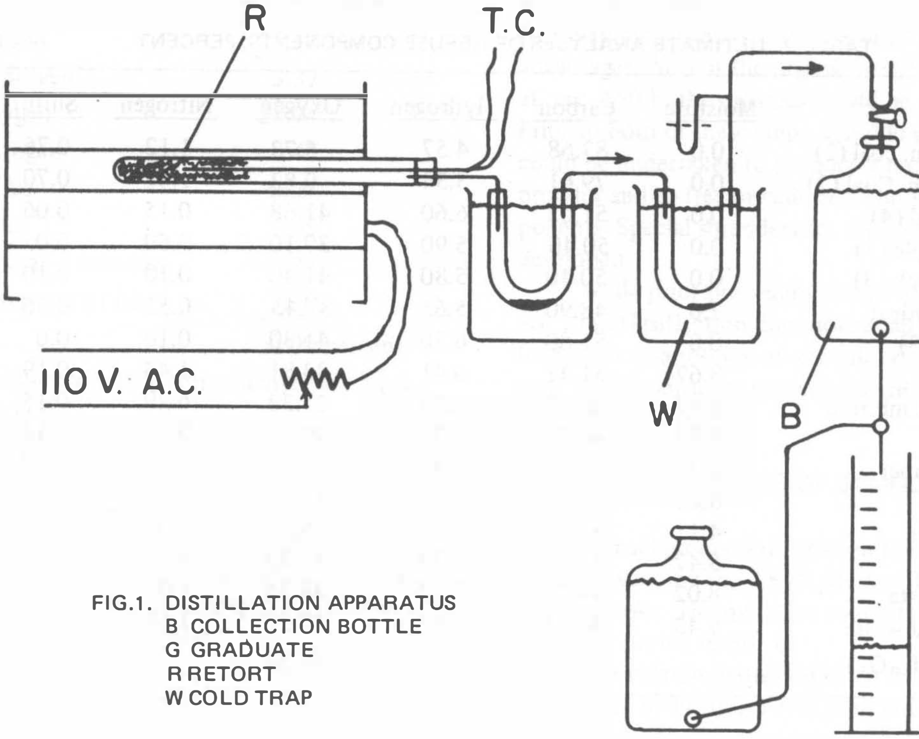

FIG.1. DISTILLATION APPARATUS
B COLLECTION BOTTLE
G GRADUATE
R RETORT
W COLD TRAP

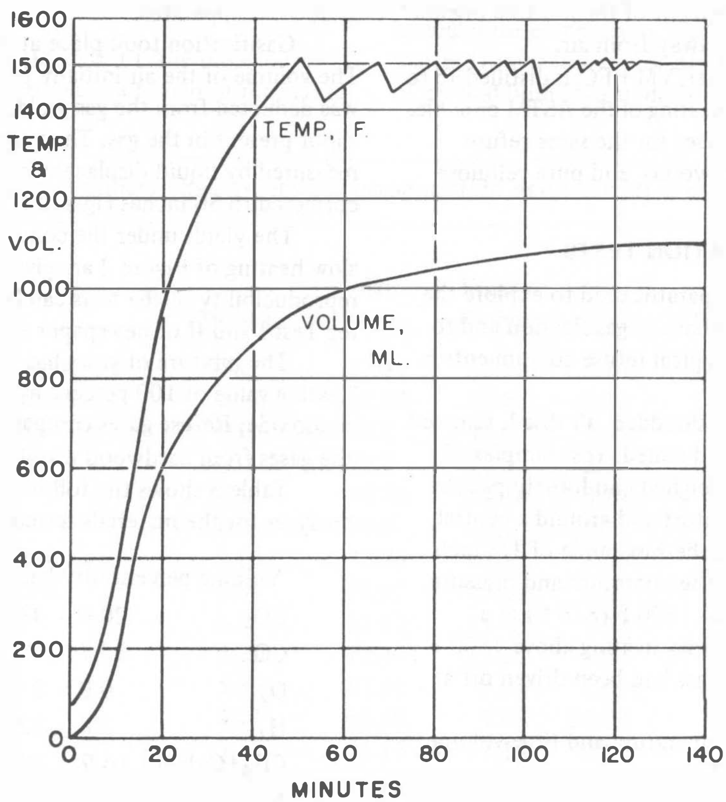

FIG. 2. TYPICAL GAS VOLUME VS. TEMPERATURE

TABLE 3. ANALYSES OF PRODUCT GAS

	Dry volume, percent						
	CO_2	CO	O_2	H_2	CH_4 + CnHm	N_2	H.H.V. Btu/cu. ft.
Ford hardwood (4)	37.9	23.4	2.4	2.2	18.0	16.1	290
Rubber	25.9	45.1	0.2	2.8	20.9	5.1	366
White pine sawdust	20.3	29.4	0.9	21.7	25.5	2.2	423
Balsam Spruce	35.0	23.9	0.0	9.4	28.2	3.5	394
Hardwood leaf mixture	33.3	19.9	0.9	22.2	21.7	2.0	356
Newspaper I	22.9	30.1	1.3	15.9	21.5	8.3	366
II	21.2	29.5	1.1	22.0	20.8	5.4	378
Corrug. box paper	28.9	29.3	1.6	15.2	17.7	7.3	323
Brown paper	28.0	27.8	1.6	17.5	17.7	7.4	326
Magazine paper I	30.0	27.0	0.9	17.8	16.9	7.4	316
II	33.9	28.9	2.0	4.8	18.7	11.7	298
Lawn grass	32.7	20.7	0.0	18.4	20.8	7.4	337
Citrus fruit waste	43.1	15.7	1.4	15.8	17.9	6.1	284
Vegetable food waste	36.7	20.9	1.0	14.0	21.0	6.4	326

TABLE 4. YIELDS OF PRODUCTS, LB. PER TON OF REFUSE

	CO_2	CO	O_2	H_2	CH_4+ CnHm	N_2	H_2O	CnHmOx	S	Carbon in char	Ash in char
Ford hardwood	203.0*	97.7*	0.0*	0.6	41.7	3.0*	638.6	416.0	1.2	588.6	9.6
Rubber	136.4	151.2	0.3	0.7	40.1	17.1	78.2	849.0	40.0	510.0	177.0
White pine sawdust	161.0	148.5	5.2	7.8	73.6	11.1	655.5	491.0	7.2	436.3	2.8
Balsam spruce	332.5	144.5	0.0	4.0	97.5	21.1	420.6	572.1	3.8	342.5	61.4
Hardwood leaf mixture	261.5	99.4	5.1	7.9	62.0	10.0	637.3	245.5	3.0	591.9	76.4
Newspaper I	208.8	174.0	8.6	6.6	70.5	47.9	678.5	203.0	2.8	570.7	28.6
II	240.5	212.0	9.0	11.4	84.8	28.2	627.2	216.0	2.8	539.5	28.6
Corrug. box paper	252.0	162.0	10.1	6.0	56.0	40.3	718.6	115.9	4.0	533.9	101.2
Brown paper	199.0	125.8	8.3	5.6	45.7	33.5	862.0	57.6	2.0	640.3	20.2
Magazine paper I	197.0	112.8	4.3	5.3	40.3	30.9	518.8	216.8	1.8	422.6	449.4
II	148.8	126.9	8.8	21.1	82.1	51.4	418.2	203.5	1.8	388.0	449.4
Lawn grass	290.0	116.8	0.0	7.4	67.1	41.7	494.6	229.1	8.0	621.5	123.8
Citrus fruit waste	412.6	95.6	9.7	6.8	62.3	37.2	599.7	350.1	2.2	360.2	63.6
Vegetable food waste	320.7	116.2	6.3	5.5	66.7	35.6	542.9	404.9	4.0	399.4	97.8

*Adj. for air leakage and oxidation by air.

The weights of gases, water, hydrocarbon liquids, char carbon and char ash were calculated on the basis of a ton of partially dried refuse of the analyses given in Tables 1 and 2. The results are tabulated in Table 4. Sulfur probably remains largely with the ash, although some will exist in the gases as H_2S and other forms. Because of the low sulfur content of the refuse, the sulfur distribution was not studied.

Calculation of the Ford [4] data indicate that the liquids other than water can be closely represented by a hypothetical compound of analysis C_6H_8O.

TABLE 5. YIELDS, PERCENT OF REFUSE, WEIGHT BASIS

	Gas	Water	CnHmOx	Char C+S	Ash
Ford hardwood	17.30	31.93	20.80	29.54	0.43
Rubber	17.29	3.91	42.45	27.50	8.85
White pine sawdust	20.41	32.78	24.50	22.17	0.14
Balsam spruce	29.98	21.03	28.61	17.31	3.07
Hardwood leaf mixture	22.29	31.87	12.27	29.75	3.82
Newspaper I	25.82	33.92	10.15	28.68	1.43
II	29.30	31.36	10.80	27.11	1.43
Corrug. box paper	26.32	35.93	5.79	26.90	5.06
Brown paper	20.89	43.10	2.88	32.12	1.01
Magazine paper I	19.53	25.94	10.84	21.22	22.47
II	21.96	25.91	10.17	19.49	22.47
Lawn grass	26.15	24.73	11.46	31.47	6.19
Citrus fruit waste	31.21	29.99	17.50	18.12	3.18
Vegetable food waste	27.55	27.15	20.24	20.17	4.89

The liquids are a mixture of methyl alcohol, allyl alcohol, methyl acetone, ketones, methyl acetate, oils and tars known as pyroligneous acid. No doubt the proportions will vary with the refuse composition.

Considering the simplicity of the apparatus, a reasonably close check on the material balances was obtained.

The yields of gases, water, organic liquids, char and char ash are presented on a weight percentage basis in Table 5.

The above yields ranged as follows, weight percent:

Gas	17.29 - 31.21%	mean 24.25%
Water	3.91 - 43.10	mean 23.50
CnHmOx liq.	2.88 - 42.45	mean 22.67
Char C+S	17.31 - 32.12	mean 24.72
Ash	0.14 - 22.47	mean 11.30

The mean values indicate that the yields were almost equally divided among gas, water, organic liquids and char C+S, with ash as an independent variable.

EFFECT OF RATE OF HEATING

In an attempt to increase the gas and liquid yields and to decrease the char residue, the effect of higher rates of heating was investigated in a series of runs. The same apparatus was used. For the highest rates the furnace was preheated and then rolled into place around the retort. All tests were conducted with shredded newspaper, the sample weights varying randomly between 4.37 and 5.20 gm.

The gas analyses, with initial air deducted, are given in Table 6.

TABLE.6. EFFECT OF RATE OF HEATING ON GAS ANALYSIS FROM NEWSPAPER

Minutes to 1500 F:	Volume percent of gas, dry basis								
	1	6	10	21	30	40	60	60	71
CO_2	15.01	19.16	23.11	25.1	24.7	25.7	22.9	21.2	24.01
CO	42.60	39.59	35.20	36.3	31.3	30.4	30.1	29.5	26.87
O_2	0.92	1.61	1.80	2.5	2.3	2.1	1.3	1.1	1.91
H_2	17.93	9.85	12.15	10.0	15.0	13.7	15.9	22.0	14.48
CH_4	17.54	21.70	19.95	20.1	20.1	19.9	21.5	20.8	22.18
N_2	6.00	8.09	7.79	6.0	6.6	8.2	8.3	5.4	10.55
Btu/cu. ft.	372	380	355	354	354	344	367	378	358
Gas vol. cu. ft./ton	11,000	7,500	6,800	6,170	6,750	6,560	7,260	9,170	8,760

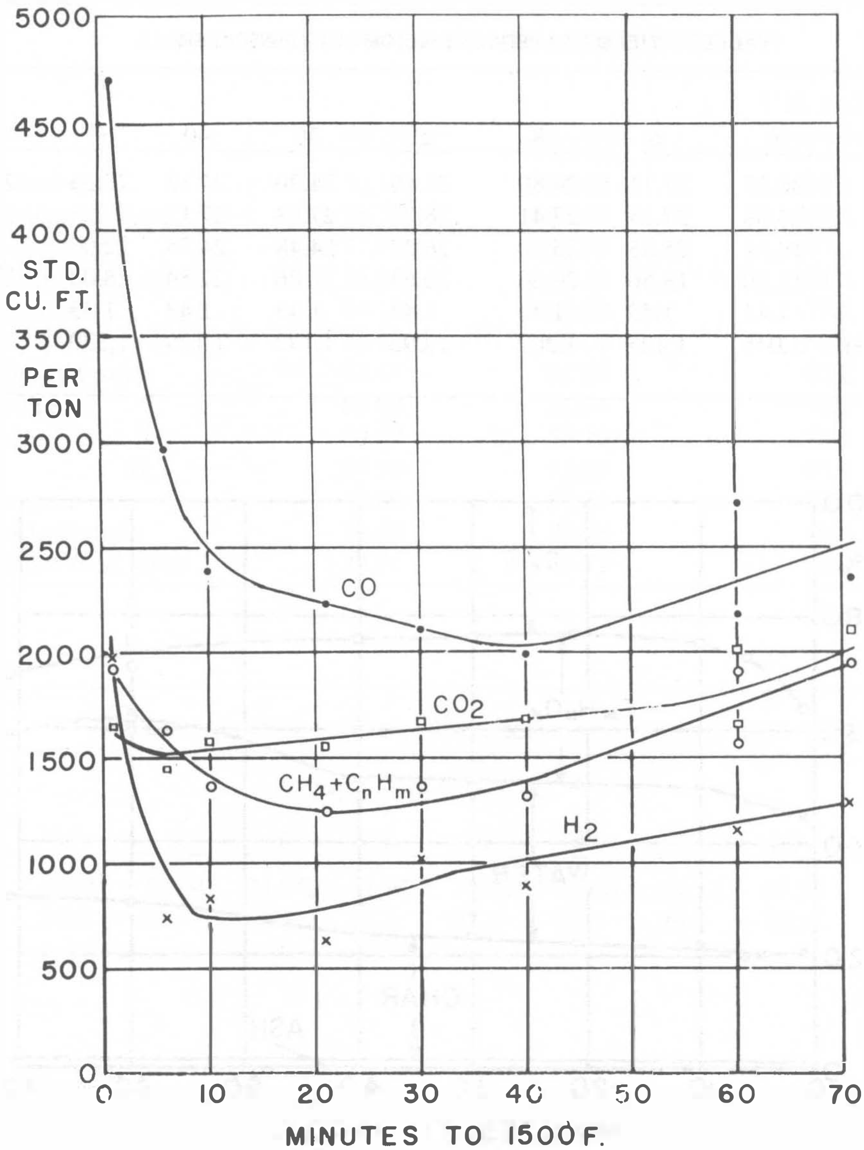

FIG. 3. GAS YIELDS FROM NEWSPAPER AS RELATED TO RATE OF HEATING

The volumes of CO_2, CO, H_2, and CH_4 per ton of newspaper are shown graphically in Figure 3. The gas yield is highest at the high and low rates of heating, with lowest yields at intermediate rates. CO, H_2, and CH_4 increased most, while CO_2 generally declined as the heating rate increased. The data suggest even higher yields are possible from flash heating.

The percentage yield of gas, water, organic liquids and char are given in Table 7 and are shown graphically in Figure 4.

It will be noted the weight of char combustible decreases and the gas increases when the rate of heating is increased. The water also decreases with increase in rate of heating. The heat of combustion of the gases is highest at the fastest rate of heating, and lowest in the 20 - 40 minute heating range.

DISCUSSION OF RESULTS

When the objective of refuse pyrolysis is the production of the maximum yield of gases and liquids, and minimum char, a rate of heating should be

TABLE 7. YIELDS, IN PERCENT WEIGHT OF NEWSPAPER

Minutes to 1500 F	1	6	10	21	30	40	60	60	71
Gas	36.25	27.11	24.80	23.48	24.30	24.15	25.26	29.85	31.10
Water	24.08	27.35	27.41	28.23	27.93	27.13	33.23	30.73	28.28
CnHmOx liq.	19.14	25.55	25.70	26.23	24.48	24.75	12.00	9.93	10.67
Char C+S	19.10	18.56	20.66	20.63	21.86	22.54	28.08	28.06	28.52
Ash	1.43	1.43	1.43	1.43	1.43	1.43	1.43	1.43	1.43
Btu in cold gas per lb. Newspaper	2,045	1,425	1,207	1,092	1,192	1,129	1,330	1,730	1,568

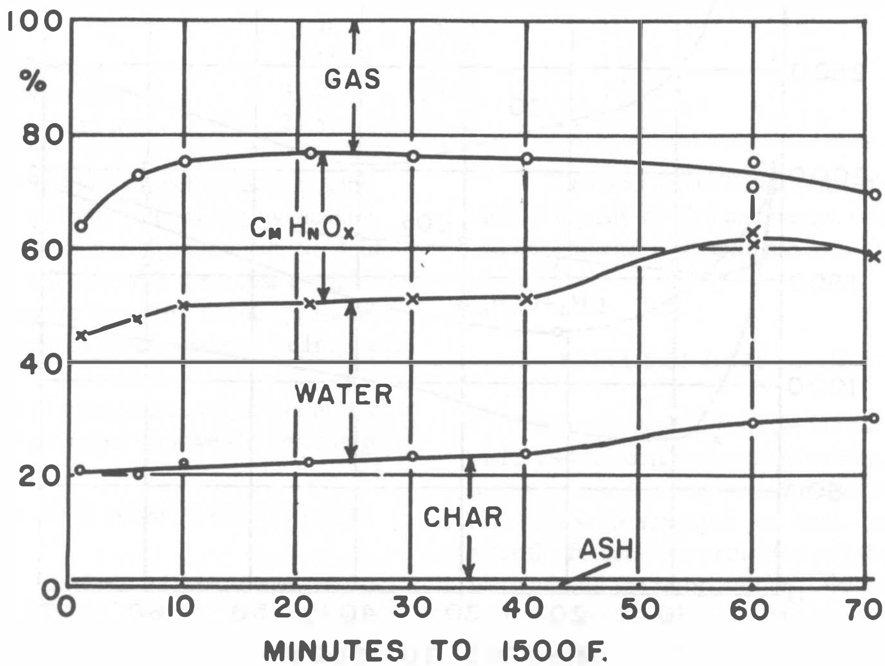

FIG. 4. YIELDS FROM NEWSPAPER AS RELATED TO RATE OF HEATING, IN WEIGHT PERCENT

chosen which is best for that purpose. The ASTM test for volatile matter is an index of such yields at rapid heating.

The potential for greater yields of volatile products is indicated by a closer approach to the high heating rate of the ASTM crucible.

The yields from newspaper given in Table 8 were similarly compared with the ASTM volatile-matter yield. Table 9 shows the effect of more rapid heating in approaching the ASTM value. For example, the weight of volatile matter by ASTM crucible was 81.12 percent of the weight of sample, which is considered as 100 percent of potential yield. The yield at 1 minute to 1500 F was 73.50 which is 90.5 percent of the ASTM yield, etc.

Table 9 shows a potential increase of 8.6 to 9.5 percent in yields of gas and liquid CnHmOx, and correspondingly less char, by more rapid heating of refuse newspaper. The same effects would probably apply to other refuse.

COMPLETE GASIFICATION

The gasification of the hot char carbon would be accomplished by supplying air or oxygen, pre-

TABLE 8. VOLATILE MATTER YIELDS, ASTM VS. PYROLYSIS

	ASTM	Pyrolysis	V.M. yield by pyrolysis %
Ford hardwood	76.10	70.03	92.0
White pine sawdust	78.76	70.69	89.8
Balsam spruce	77.75	75.95	97.6
Hardwood leaf mixture	66.92	56.46	84.4
Newspaper I	81.12	63.92	78.7
II	81.12	65.49	80.6
Corrug. box paper	77.47	62.84	81.2
Brown paper	83.92	61.04	72.7
Magazine paper I	66.39	52.20	78.1
II	66.39	53.93	81.1
Lawn grass	71.16	56.87	79.9
Citrus fruit waste	71.46	70.68	99.1
Vegetable food waste	73.31	69.51	94.9

TABLE 9. VOLATILE MATTER YIELDS COMPARED TO ASTM TEST

	Minutes to 1500 F								
ASTM	1	6	10	21	30	40	60	60	71
81.12	73.50	74.04	71.94	71.97	70.74	70.06	64.52	64.54	64.08
100.0	90.5	91.4	88.5	88.6	87.2	86.3	79.6	79.5	79.1

ferably with steam. The char gas would be a mixture of CO_2, H_2, CO and unreacted steam. The heat of the reactions would be ample to pyrolyze the oncoming raw refuse and thus produce the char to continue the process. The process could be carried out in two separate vessels, or in one reactor, such as the conventional updraft gas producer. Higher pressures would favor the increased production of methane. With highly preheated air-steam blast, or with an oxygen-steam blast, the ash could be slag tapped. The prior work on coal gasification would provide guidance for the process.

Future studies of refuse pyrolysis might well include laboratory studies of heats of reaction. With dry preheated refuse as feed stock, it is likely that exothermic reactions during gasification would supply the heat necessary to complete the destructive distillation. At least, that was the Ford experience.

As an extension of the laboratory tests, the gaseous and liquid products should be analyzed by gas chromatography. Exploratory runs have shown compounds that could be indentified [5], but others would need more study. Mixtures of refuse components should also be pyrolyzed. The yield at successive stages of heating will vary progressively.

SUMMARY

1) By heating to 1500 F out of contact with air, the organic matter in municipal refuse can be converted to gas, organic liquids, water and char in roughly equal proportions by weight.

2) The relative yields will be affected by the rate of heating. Higher yields of gas result from rapid heating.

3) The fixed gases have a calorific value of 350 - 400 Btu per standard cu. ft. The organic liquids range from alcohol to pitch.

4) An extension of the investigation to include complete gasification, and analyses by chromatography is suggested.

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