Bench-Scale Studies on Fluid-Bed Pyrolysis of Wood

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August 1988

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SUMMARY

Results of bench-scale studies on fluid-bed pyrolysis of wood with carbon dioxide (CO_2), methane (CH_4), and hydrogen (H_2) contact gases are described in this report. The primary objective of these studies was to determine the effect of thermal treatment with these gases on product yields, primarily yield of condensible hydrocarbons. The results of these studies were analyzed to determine the effects of temperature, contact gas, wood feed rate, and gas contact time on the yields of gases, liquids, and char. The yield of condensible organics is compared to the yield from steam gasification.

Fluid-bed pyrolysis tests with each of the contact gases were conducted at temperatures from 650°C (1200°F) to 800°C (1470°F) and gas residence times of 1 and 2 s. The wood feed rate varied between 1 and 1.4 kg/h (2 and 3 lb/h). Results reported for the different contact gases (CH_4 , CO_2 , and H_2) are based on data from a single test at each set of experimental conditions. Consequently, yields at each set of conditions were not verified. Data from these single tests indicate general trends. These trends are not of sufficient significance to justify additional experiments at this time.

Variations of the wood feed rate had no effect on product yields within the range of rates tested. Decreasing the gas residence time showed slight trends toward reduced yields of gas and char and increased yield of condensible organics.

In tests with H_2 and CH_4 , samples of condensible hydrocarbons were collected by three methods: 1) scrubbing the entire product gas with water at room temperature, 2) scrubbing a gas slipstream with methylene chloride (MeCl) at 0°C (32°F), and 3) hydrocarbons from a slipstream scrubbed at -20°C (-4°F). Total weight yield of condensible hydrocarbons was determined from the weight collected at -20°C (-4°F) less the weight of water in the gas stream. In tests with CO_2 a secondary bed of zeolite catalyst was used, and condensibles were collected in the MeCl scrubbers only. The MeCl scrub solutions were subjected to gas chromatography analysis for determination of $\text{C}_6\text{-C}_{20}$ hydrocarbons. Analyses indicated that only from 13% to 20% of the

benzene/toluene/xylene fraction was collected by scrubbing the gas stream at room temperature compared to the quantity collected at -20°C (-4°F).

At 725°C (1340°F), the yield of condensible organics collected in the MeCl scrubbers showed a slight trend with $\text{CH}_4 > \text{H}_2\text{O} > \text{CO}_2 = \text{H}_2$. Results with CH_4 , CO_2 , and H_2 are from single tests, whereas results with H_2O are the average of 15 tests.

Results are reported showing the effects of operating conditions with different contact gases on yields of condensibles, gases, and char. The general trends shown by the data should aid analysis of different thermal treatment methods for influencing the yield of tars in biomass-derived gases and should be helpful in determining the effect of using recycle gas for wood gasification.

ACKNOWLEDGMENTS

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INTRODUCTION

Pacific Northwest Laboratory (PNL) is conducting studies to improve the conversion efficiency of biomass gasification. These studies are sponsored by the Biofuels and Municipal Waste Technology Division of the U.S. Department of Energy (DOE). Part of the research includes thermal conversion of biomass by fluid-bed contact with gases not commonly used for gasification to determine their effect on product yields.

Commercial gasification processes convert carbonaceous matter, including biomass, into fuel gases and some condensible liquids (Von Fredersdorff and Elliot 1963; Fritz, Gordon, and Nguyen 1979). Although there are exceptions with some refractory carbonaceous materials, the residues from gasification processes comprise principally the inert mineral constituents of the feedstock. These residues are essentially devoid of significant quantities of carbon. In contrast, residues from pyrolysis, which results from biomass contact at high temperatures with nonreactive gases such as those used in this study, contain a substantial quantity of carbon from the original feedstock. These residues are classified as char.

Both gasification and pyrolysis of carbonaceous materials produce a mixture of gaseous products as a result of the complex parallel, competitive, and sequential reactions. Alternative thermal treatment methods, such as recycle of combustion gases to the process, can influence the composition of gaseous products. Of particular interest is the effect of these alternative methods on the yield from biomass of condensible hydrocarbons in wastewater treatment systems. Condensible hydrocarbons can plug lines and deposit on downstream equipment and thus adversely affect wastewater treatment and environmental control.

The primary objective of this study was to determine the effects of different contact gases and experimental conditions on product yields from fluid-bed wood pyrolysis. The yield of condensible hydrocarbons was of particular interest. The contact gases employed included carbon dioxide (CO_2), methane (CH_4), and hydrogen (H_2). Reaction temperatures ranged from 650°C to 800°C , and gas contact time was between 1 and 2 s. Tests with CO_2

contact gas used a secondary vessel of catalyst for cracking of condensibles generated in the primary gasifier. Results of earlier studies at PNL (Mudge, Sealock, and Weber 1979; Mitchell et al. 1980; Mudge et al. 1981, 1983; Baker and Mudge 1986) showed the effectiveness of various catalysts for destruction of condensible hydrocarbons.

Analyses of results on the effects of contact gas, reaction temperature, gas contact time, and wood feed rate are presented in this report, along with a description of experimental equipment and methods. Data were obtained from single tests at each set of experimental conditions. Conditions were not repeated to determine the amount of experimental error. Material balance closures were generally quite good for the experimental tests, within 10%. A complete listing of all data collected in the tests is given in the appendix, along with definitions of table entries.

EXPERIMENTAL BENCH-SCALE EQUIPMENT

Bench-scale equipment, shown schematically in Figure 1, was used in these studies. A detailed description of the equipment and operating procedures is presented in an earlier report (Mudge et al. 1983).

The gasifier was fabricated from a 2-ft (61 cm) length of 3-in. (7.6 cm) Sch 40 304L stainless steel pipe and a 1-ft (30 cm) length of 5-in. (12.7 cm) Sch 40 pipe. A bed depth of 1 ft (30 cm) was maintained by vacuum withdrawal of bed material during operation of the gasifier as a fluidized bed. The upper enlarged section of the gasifier was provided for de-entrainment of solids.

FIGURE 1. Equipment Arrangement for Dual-Vessel Tests

Wood mixed with sand was auger fed continuously into a 1-in. (2.5 cm) tube where it was entrained by the fluidizing gases and carried into the gasifier. Sand was mixed with the wood to replace inert solids lost from the bed during fluid-bed operation.

Tests with different contact gases were completed at temperatures from 1200°F (650°C) to 1470°F (800°C). Gas contact time in the tests ranged from 1 to 2 s.

The primary emphasis of the tests was to determine the effect of contact gases and operating conditions on yields and compositions of condensible organics. Initial tests were completed with **CO₂** as the contact gas with the configuration shown in Figure 1. A measured gas sample, which represented about 1% of the total gas flow, was taken before and after the secondary vessel and passed through two scrubbers (shown as "cold scrub, 0°C" in Figure 1) in series filled with methylene chloride (**MeCl**) and maintained at 32°F (0°C). The MeCl solutions were then analyzed by gas chromatography (GC) to determine organic yields and compositions. A zeolite, LZ-Y82, was used in the secondary vessel maintained at a temperature of 1020°F (550°C).

Nitrobenzaldehyde was used as an internal standard to analyze for organics in the MeCl solution. This method did not identify all the **condens-**ible organics generated in the test. With the arrangement shown in Figure 1, condensible organic yields could be verified independently only from the secondary vessel by analysis of condensate collected at about 80°F (27°C). Most of the condensible organics produced in the gasifier were destroyed in the secondary catalyst bed. Tests with **H₂** and **CH₄** were therefore conducted with the configuration shown in Figure 2. A separate measured slipstream sample was passed through a small scrubber maintained at -4°F (-20°C). The scrubber was weighed before and after each test to determine the yield of all **condensibles**.

With the arrangement shown in Figure 2, yield could also be verified by analysis of condensate from the **condenser/scrubber** and by collection of condensate at -4°F (-20°C). Condensate from the condenser scrubber was drained and allowed to settle at least 24 h before the phases were separated by decantation. The total organic carbon was determined for the aqueous phase,

FIGURE 2. Equipment Schematic for Single-Vessel Tests

and the organic phase was analyzed for C, H, and N. In Figure 2, MeCl was used in the "cold scrub, 0°C." For material balance purposes, the water-soluble organics were assumed to have the same elemental composition as wood.

The feedstock used in these studies was densified pine flakes obtained from Thomas A. Miles Consulting Engineers, Portland, Oregon. Analysis of the feedstock is presented in Table 1. Screen size used in the tests was -14 U.S. Sieve No. Wood was dried at 100°C overnight and was considered to be completely dry for material balance calculations. Tests with this material gave results identical to previous tests with sawdust.

Silica sand obtained from Martin Marietta Industrial Sand Division was used to stabilize the fluid bed. The sand was 99.88% silica with a bulk density of 100 lb/ft³ (1.6 g/cm³) in the size range of -30 to +100 U.S. Sieve No. (0.42 to 0.21 mm).

TABLE 1. Analysis of Feedstock

<u>Element</u>	<u>Weight Percent</u>
C	50.3
H	6.4
O (by diff)	42.7
Ash	0.6

Higher Heating Value

8,770 Btu/lb

20,400 kJ/kg

EXPERIMENTAL RESULTS

Results of tests with CO_2 , CH_4 , and H_2 contact gases are presented in this section. Conditions used in these tests were temperatures from 650°C to 800°C (1200°F to 1470°F), gas contact times from 1 to 2 s, and wood flow rates from 2 to 3 lb/h (0.9 to 1.4 kg/h).

The results are based on data from single tests at each set of experimental conditions. In tests with CO_2 contact gas, a secondary bed of zeo-lite catalyst was used (see Figure 1). Condensible organics were destroyed by the bed of catalyst, which complicated analysis of yields from CO_2 pyrolysis for two reasons: 1) the gas volume from the primary bed was unknown since the measured volume from the secondary bed included gases generated by destruction of tars, and 2) condensible organics could not be collected in the condenser/scrubber since they were partially destroyed. For these reasons, subsequent tests with CH_4 and H_2 did not include a secondary bed of catalyst.

In the results below, three fractions of condensibles are reported: 1) the fraction collected in MeCl scrubbers, 2) the fraction collected in a cold trap at -4°F (-20°C), and 3) the fraction collected in the condenser/scrubber at about 80°F (27°C). Fraction 1 was identified in all tests with CO_2 , CH_4 , and H_2 and included the $\text{C}_6\text{-C}_{20}$ fraction. Fraction 2 was the condensate collected at -4°F (-20°C), which included water vapor in the gas stream. Water vapor per unit weight of wood was determined from the weight of aqueous phase collected in the condenser/scrubber and the weight of water vapor in the saturated gases leaving the condenser/scrubber. In tests with CH_4 and H_2 , the weight of condensible organics per unit weight of wood was calculated by subtracting the weight of water per unit weight of wood from the weight of condensate collected at -4°F (-20°C) per unit weight of wood. The fraction reported in the tables as "wt% cond org" (weight percent condensible organics) included all organics (such as acetic acid and methanol plus organics collected in the MeCl scrubbers) that condense above -4°F (-20°C). Fraction 3 included the condensate collected in the condenser/scrubber at about 80°F (27°C) and analyzed as described in the previous section.

TESTS WITH CARBON DIOXIDE

Tests with CO₂ as the contact gas were completed with a secondary bed of LZ-Y82 catalyst and the equipment flow configuration shown in Figure 1. Results from these tests are presented in Table 2, which shows the yields of gases, char, and condensibles from the gasifier. These same yields after

TABLE 2. Yields with Carbon Dioxide Contact Gas^(a)

Yields	Test Number (Gasifier Temp., °C)						
	LC-1 (650)	LC-2 (700)	LC-5 (700)	LC-7 (750)	LC-6 (750)	LC-4 (800)	LC-3 (800)
slv, ^(b) ft/s	0.96	1.01	1.40	0.92	1.46	1.16	1.53
gas cont time, s	2.1	2.0	1.4	2.2	1.4	1.7	1.3
wt CO ₂ /wt wood	3.2	3.0	4.2	1.5	4.0	3.5	4.2
lb wood/h-ft ³	40	42	42	71	44	39	42
wt% dry gas	52	62	63	71	84	74	74
% C in gas	45	55	59	65	75	71	71
% H in dry gas	40	47	48	58	60	63	61
% O in dry gas	61	71	70	79	98	78	78
wt% char	8	6	6	7	5	2	3
% C in char	14	11	10	12	8	4	5
% H in char	1.30	0.96	0.93	1.12	0.70	0.36	0.48
% O in char	2.70	1.99	1.93	2.33	1.44	0.74	0.99
wt% in C ₆ -C ₂₀	3.50	2.93	3.21	3.74	5.65	6.36	6.08
% C in C ₆ -C ₂₀	5.95	4.98	5.45	6.36	9.61	10.81	10.34
% H in C ₆ -C ₂₀	3.34	2.79	3.06	3.57	5.39	6.06	5.80
% water soluble C	1.31	0.86	0.89	0.76	0.85	0.87	0.92
wt% H ₂ O	14	12	15	9	13	10	13
% H in water	23	20	25	15	22	18	23
% O in water	27	24	30	18	26	21	27
C balance, %	67	71	75	85	93	87	88
H balance, %	67	71	77	78	88	87	90
O balance, %	91	96	101	100	126	100	106

(a) All yields are based on weight of wood feed.

(b) Superficial linear velocity.

catalytic treatment at 550°C in the secondary vessel are included in the appendix. The elemental yields are based on the C, H, and O in the input wood. It must be noted that the gas volume from the primary vessel is unknown since the volume measured by the dry test meter (see Figure 1) is after catalytic treatment, which destroys tars and increases gas volume. This volume was used as the gas volume from the primary vessel to estimate yields, which probably overestimates the gas yield from the primary vessel. The superficial linear velocity (slv) is based on the empty cross section of the reactor at reactor temperature and pressure. An slv of 1 ft/s (30 cm/s) corresponds to a gas residence time at reactor temperature of about 2 s. The gasifier was operated with a 1-ft (30 cm) bed depth and a wood feed rate of 2 lb/h (0.9 kg/h), which gives a rate based on reactor volume of 40 lb/h-ft³ (640 kg/h·m³).

For tests with CO₂ as the contact gas at 650°C and 700°C (1200°F and 1290°F), material balances for C, H, and O were less than usually obtained with the bench-scale equipment, as shown in Table 2. Part of the problem could be errors in determining the input gas flows. It appears, however, that all condensibles were not collected or identified. Weight yields of gases, char, and condensibles are listed in Table 3. The water yield includes water in the gas saturated at the temperature of the condenser. The char yield, which is low, is determined quite accurately by weighing and analyzing the chars collected in the knockout receiver and filter (see

TABLE 3. Weight Yields with Carbon Dioxide Contact Gas

Yields	Test Number (Gasifier Temp, °C)						
	LC-1 (650)	LC-2 (700)	LC-5 (700)	LC-7 (750)	LC-6 (750)	LC-4 (800)	LC-3 (800)
slv, ft/s	0.86	0.85	1.18	0.74	1.18	0.89	1.18
wt% dry gas	54	59	67	71	71	81	81
wt% char	8	6	6	7	5	2	3
wt% C ₆ -C ₂₀	2.75	4.12	6.85	4.14	4.51	6.26	6.01
wt% H ₂ O	14	12	15	9	13	10	13
wt% aq sol org	1	1	1	1	1	1	1
Total wt% rec	80	82	95	92	94	101	105

Figure 1) and in the fluid bed before and after each test. The net weight yield of gases is strongly influenced by the measured input rate of CO_2 , as discussed below and shown in Table 4. If the measured input is erroneously high, the weight yield of gas will be low. Since accountability improves with temperature as the gas yield increases, it appears that the main problem must have been the collection and analysis of condensibles. Carbon balances shown in Table 2 are much less than the weight accountabilities shown in Table 3.

An error in the measurement of the CO_2 flow rate significantly influences gas phase elemental yields calculated for carbon and oxygen. Table 4 shows the magnitude of a 5% error in determining the CO_2 flow on the yields of wood carbon and oxygen to the gas phase. For example, in Test LC-3, a

TABLE 4. Effect of Carbon Dioxide Flow on Gas Yield^(a)

Yields	Test Number (Gasifier Temp, °C)						
	LC-1 (650)	LC-2 (700)	LC-5 (700)	LC-7 (750)	LC-6 (750)	LC-4 (800)	LC-3 (800)
Meas. L/min CO_2	25.9	25.7	35.7	22.3	35.5	26.9	35.5
wt% dry gas	52	59	67	71	71	74	81
% C in gas	45	54	59	65	66	71	75
% H in dry gas	40	52	41	56	53	63	59
% O in dry gas	61	66	79	78	80	78	91
L/min CO_2 + 5%	27.20	26.99	37.49	23.42	37.28	28.25	37.28
wt% dry gas	38	44	46	63	52	64	60
% C in gas	38	46	47	60	55	66	64
% H in dry gas	41	52	41	56	53	55	59
% O in dry gas	37	41	45	66	47	62	56
L/min CO_2 - 5%	24.61	24.42	33.92	21.19	33.73	25.56	33.73
wt% dry gas	70	74	88	78	91	98	102
% C in gas	55	62	70	69	77	84	87
% H in dry gas	41	52	41	56	53	55	59
% O in dry gas	91	92	114	91	113	119	125

(a) All yields are based on weight of wood feed.

measured CO₂ flow rate that is 5% too high gave a % C in gas (based on C in wood) and a % O in gas (based on O in wood) of 64 and 56, respectively. These respective values changed to 87 and 125 for a measured CO₂ flow rate that is 5% too low. Pressure fluctuations and gas cooling caused by evaporation of CO₂ made controlling the CO₂ rate difficult. Calculations in Table 4 show that the measured CO₂ flow drastically affects elemental balances for C and O. However, flow measurement should be well within the 5% error level. The sensitivity of material balance calculations to gas flow led to abandonment of the two-vessel system to allow checking of yield of condensibles.

The yield of condensible organics from the primary gasifier identified by GC analysis of the MeCl scrub solutions is presented in Table 5. This was the only organic yield determined from the CO₂ tests since the catalyst destroyed organic condensibles before they could be collected in the scrubber.

Gas composition and yield with CO₂ as the contact gas are shown in Table 6. Error in the measurement of CO₂ flow rate would affect the net CO₂ yield only. Nitrogen was used as a purge gas in the wood feed hopper.

TABLE 5. Yield of Organics in Methylene Chloride Solution^(a)

Yields	Test Number (Gasifier Temp, °C)						
	LC-1 (650)	LC-2 (700)	LC-5 (700)	LC-7 (750)	LC-6 (750)	LC-4 (800)	LC-3 (800)
slv, ft/s	0.96	1.01	1.40	0.92	1.46	1.16	1.53
lb wood/h-ft ³	40	42	42	71	44	39	42
wt BTX, ^(b) g	8.7	18.9	19.49	48.3	63.31	51.1	52.9
wt% BTX	0.80	1.03	1.11	2.37	3.68	3.19	3.12
% C in BTX	1.46	1.87	2.03	4.31	6.70	5.81	5.68
wt C ₈ -C ₂₀ oil, g	29.3	34.8	46.1	28	33.4	51.1	48.8
wt% C ₈ -C ₂₀ oil	2.70	1.90	2.06	1.37	1.94	3.19	2.88
% C in C ₈ -C ₂₀ oil	4.59	3.22	3.51	2.33	3.30	5.43	4.89

(a) All yields are based on weight of wood feed.

(b) Benzene/toluene/xylene.

TABLE 6. Gas Composition and Yield with Carbon Dioxide Contact Gas

Yields	Test Number (Gasifier Temp, °C)						
	LC-1 (650)	LC-2 (700)	LC-5 (700)	LC-7 (750)	LC-6 (750)	LC-4 (800)	LC-3 (800)
slv, ft/s	0.96	1.01	1.4	0.92	1.46	1.16	1.53
lb/h-ft ³	40	42	42	71	44	39	42
<u>Gas Comp, vol%</u>							
H ₂	3.62	4.3	2.8	47.24	4.04	4.94	4.05
CO ₂	67.33	63.68	70.28	49.14	68.25	59.89	65.71
C ₂	0.62	0.98	0.95	1.81	1.14	1.23	1.18
CH ₄	2.42	2.82	2.44	5.3	2.99	3.14	2.66
CO	8.16	11.16	10.22	19.82	12.26	14.79	13.3
C ₃	0.3	0.3	0.28	0.498	0.253	0.3	0.3
C ₄	0.1	0.1	0.1	0.1	0.1	0.1	0.1
N ₂	17.59	16.25	12.12	13.85	10.16	14	11.72
H ₂ O	2.39	2.39	2.47	2.47	2.65	2.39	2.39
g H ₂ /100 g wood	0.83	0.97	0.79	1.13	1.13	1.31	1.18
g CH ₄ /100 g wood	4.44	5.08	5.43	6.61	6.68	6.66	6.22
g CO/100 g wood	26.18	35.15	39.82	43.24	47.92	54.87	54.46
g CO ₂ /100 g wood	16.00	15.11	10.80	14.08	21.83	4.29	4.57

TESTS WITH METHANE

Tests with CH₄ contact gas were completed with the flow configuration shown in Figure 2 to improve material accountability. Results of tests with CH₄ as the contact gas are summarized in Table 7. The weight yield of condensibles shown in Table 7 was determined as described in the introduction to this section from the weight of condensibles collected at -4°F (-20°C) in the measured slip stream. The "% wt yield" shown in Table 7 was determined from the sum of the weight of all products (gases, condensibles at -4°F, and char) divided by the weight of the wood feed.

Gas composition and yield with CH₄ as the contact gas are given in Table 8. A small error in the measured flow of CH₄ will influence the net yield of CH₄ only. Negative CH₄ yields in Tests M-2 and M-3 are believed to result from an erroneously high measured CH₄ flow. Otherwise, the hydrogen

TABLE 7. Yields with Methane Contact Gas^(a)

Yields	Test Number (Gasifier Temp, °C)					
	M-3 (650)	M-6 (650)	M-1 (725)	M-4 (725)	M-2 (800)	M-5 (800)
slv, ft/s	1.08	2.19	1.04	2.45	1.21	2.33
gas contact time, s	1.9	0.9	1.9	0.8	1.7	0.9
wt methane/wt wood	1.35	1.93	0.83	2.34	0.94	1.8
lb wood/h-ft ³	39	55	57	47	54	54
wt% dry gas	59	53	69	64	78	78
% C in gas	57	51	66	57	72	71
% H in dry gas	45	59	67	53	63	67
% O in dry gas	64	56	75	74	88	89
wt% char	6	7	7	5	5	4
% C in char	10	12	12	9	8	7
% H in char	1	1	1	1	1	1
% O in char	2	2	2	2	1	1
wt% oil frac	21	23	10	21	17	14
% C in oil	29	31	16	33	29	23
% H in oil	23	26	9	22	16	14
% O in oil	11	13	2	8	3	3
wt% aq sol org	6	1	3	3	1	1
% C in aq sol org	6.41	1.24	2.55	3.03	0.99	0.91
% H ₂ O	19	17	15	9	5	8
% H in H ₂ O	33	30	26	15	9	14
% O in H ₂ O	40	36	31	18	11	16
% wt yield	111	102	104	102	105	104
C balance, %	102	96	97	102	109	102
H balance, %	102	116	104	91	89	95
O balance, %	117	107	110	102	104	109

(a) All yields are based on weight of wood feed.

TABLE 8. Gas Composition and Yield with Methane Contact Gas

Yields	Test Number (Gasifier Temp. °C)					
	M-3 (650)	M-6 (650)	M-1 (725)	M-4 (725)	M-2 (800)	M-5 (800)
slv, ft/s	1.08	2.19	1.04	2.45	1.21	2.33
lb/h-ft ³	39	55	57	47	54	54
<u>Gas Comp, vol%</u>						
H ₂	4.571	2.249	7.863	3.471	9.608	5.566
CO ₂	2.732	1.682	3.549	1.437	2.607	1.555
C ₂	3.462	0.997	3.689	0.81	4.298	1.476
CH ₄	61.476	75.135	52.225	73.593	50.127	67.595
CO	7.29	5.569	12.655	6.992	15.719	10.803
C ₃	0.5	0.157	0.601	0.25	0.509	0.257
C ₄	0.382	0.015	0.242	0.018	0.118	0.018
N ₂	16.821	9.209	15.589	8.444	14.126	8.704
H ₂ O	3.457	5.357	3.029	4.292	3.457	4.292
g H ₂ /100 g wood	1.22	0.75	1.59	1.40	2.16	1.89
g CH ₄ /100 g wood	-4.46	8.14	1.72	3.25	-3.80	3.41
g CO/100 g wood	27.13	26.05	35.73	39.40	49.39	51.42
g CO ₂ /100 g wood	10.17	7.87	10.02	8.10	8.19	7.40

yield would increase more than the values shown. A 5% decrease in the input flow rate of CH₄ in Tests M-2 and M-3 would give positive CH₄ yields of 0.9 and 2.3 g CH₄/100 g wood, respectively. With the 5% decrease, the net weight yields of total products for Tests M-2 and M-3 would increase to 105% and 104%, respectively.

Since the measured input flow rate of CH₄ influences the gas weight yield and the C and H balances, the magnitude of potential error was evaluated. The effect of a 5% error in the measured CH₄ flow rate is shown in Table 9. Measurements of CH₄ flow should be within 5%.

The amounts and compositions of oils collected in the condenser/scrubber are given in Table 10 for tests with CH₄ as the contact gas. These oils for

TABLE 9. Effect of Methane Flow on Gas Yield^(a)

Yields	Test Number (Gasifier Temp. °C)					
	M-3 (650)	M-6 (650)	M-1 (725)	M-4 (725)	M-2 (800)	M-5 (800)
meas L/min CH ₄	29	59	26	61	28	54
wt% dry gas	59	53	69	64	78	78
% C in gas	57	51	66	57	72	71
% H in dry gas	45	59	67	53	63	67
% O in dry gas	64	56	75	74	88	89
L/min CH ₄ + 5%	30.45	61.95	27.30	64.05	29.40	56.70
wt% dry gas	52	44	65	52	73	69
% C in gas	47	37	60	40	65	57
% H in dry gas	18	22	51	7	44	32
% O in dry gas	64	56	75	74	88	89
L/min CH ₄ - 5%	27.55	56.05	24.70	57.95	26.60	51.30
wt% dry gas	65	63	74	75	82	87
% C in gas	67	66	73	75	79	85
% H in dry gas	71	97	83	98	81	102
% O in dry gas	64	56	75	74	88	89

(a) All yields are based on weight of wood feed.

Tests M-1 and M-2 were not analyzed. Condenser/scrubber and the water soluble organics accounted for only a fraction of the condensible organics collected at -4°F (-20°C), as noted in Table 10, "wt condenser oils/wt -4°F org." Apparently, scrubbing at -4°F (-20°C) was much more efficient than scrubbing at 80°F (27°C).

Table 11 presents yield of organics collected in the MeCl scrubbers (shown as "cold scrub, 0°C" in Figure 2) and identified by GC analysis (as C₆-C₂₀ organics) for tests with CH₄ contact gas. The yield of these hydrocarbons relative to the total yield of condensible organics at -4°F (-20°C) is also shown.

TABLE 10. Condenser Oil Yield with Methane Contact Gas^(a)

Yields	Test Number (Gasifier Temp, °C)					
	M-3 (650)	M-6 (650)	M-1 (725)	M-4 (725)	M-2 (800)	M-5 (800)
slv, ft/s	1.08	2.19	1.04	2.45	1.21	2.33
lb wood/h-ft ³	39	55	57	47	54	54
wt condenser oil, g	147	214	31	189	126	117
wt% condenser oil	10	9	5	11	6	5
% C in cond oil	13	13	10	18	11	8
% H in cond oil	11	10	5	12	6	5
% O in cond oil	5.38	5.38	0.60	4.09	1.32	0.93
wt condenser oils/ wt -4°F oils	0.76	0.43	0.8	0.67	0.41	0.43
cond oil comp, wt%						
C	69.25	68.3		77.69		85.18
H	7.1	7.05		6.74		6.45
N	0.11	0.33		0.26		0.26
O	23.54	24.32		15.31		8.11

(a) All yields are based on weight of wood feed.

TESTS WITH HYDROGEN

Results and conditions of tests with H₂ as the contact gas are listed in Table 12. In these tests, the measured flow of input gas had no effect on the calculated yields of C and O to the gas phase. Weight of the condensible organics (cond org) was determined from the total condensibles at -4°F (-20°C), as described above. Carbon accountability and total weight yield was a little lower than desirable in tests at 650°C (1200°F).

Gas composition and yield for tests with hydrogen as the contact gas are shown in Table 13. Error in the measurement of the hydrogen flow rate will influence the yield of H₂ only. The negative H₂ yield in Test H-2 probably results from an erroneously high value measured for the input hydrogen

TABLE 11. Yield of Organics in Methylene Chloride with Methane Contact Gas^(a)

Yields	Test Number (Gasifier Temp, °C)					
	M-3 (650)	M-6 (650)	M-1 (725)	M-4 (725)	M-2 (800)	M-5 (800)
slv, ft/s	1.08	2.19	1.04	2.45	1.21	2.33
lb wood/h-ft ³	39	55	57	47	54	54
wt BTX, g	36	57	38	53	48	66
wt% BTX	2.39	2.52	2.76	3.20	2.44	2.76
% C in BTX	4.37	4.60	5.05	5.84	4.46	5.04
wt C ₈ -C ₂₀ oils, g	26	50	28	27	36	54
wt % C ₈ -C ₂₀ oils	1.73	3.21	2.03	1.63	1.83	2.26
% C in C ₈ -C ₂₀	2.93	3.01	3.46	2.77	3.11	3.83
wt C ₆ -C ₂₀ oils/ wt cond org	0.2	0.2	0.5	0.2	0.3	0.4

(a) All yields are based on weight of wood feed.

flow. A 5% decrease in the input hydrogen flow would increase the calculated H₂ net yield to a positive 0.69 g/100 g wood and give a 100% H balance and a 104% weight yield of products.

The yield of organics collected in the condenser and analyses for C, H, and O are presented in Table 14, along with the ratio to the condensable organics (cond org) collected at -4°F (-20°C). The amount of organics collected at room temperature ranged from about 30% to over 50% of the condensable organics collected at -4°F (-20°C).

The yield of C₆ to C₂₀ in the MeCl scrub solutions identified by GC analysis are shown in Table 15. The GC analysis identified organics from C₆ to C₂₀.

TABLE 12. Yields with Hydrogen Contact Gas^(a)

Yields	Test Number (Gasifier Temp, °C)					
	H-1 (650)	H-3 (650)	H-2 (725)	H-4 (725)	H-5 (800)	H-6 (800)
slv, ft/s	1.05	2.26	1.12	1.73	1.13	2.20
1b wood/h-ft ³	34	69	49	43	40	47
wt H ₂ /wt wood	0.19	0.2	0.13	0.22	0.14	0.24
wt% dry gas	51	38	67	62	78	73
% C to gas	47	33	65	60	76	73
% H in dry gas	47	53	40	57	60	57
% O in dry gas	57	44	74	66	84	77
wt% char	6	8	8	7	4	3
% C to char	10	14	14	11	6	5
% H in char	1	1	1	1	1	1
% O in char	2	3	3	2	1	1
wt% cond org	17	21	14	17	11	10
% C to oils	26	28	22	26	19	18
% H in oils	19	25	15	18	12	11
% O in oils	7	13	6	6	2	2
wt% aq sol org	5.12	9.63	2.53	3.16	0.78	0.86
% C in aq sol org	5	10	3	3	1	1
wt% H ₂ O	15	21	13	11	5	7
% H in H ₂ O	25	37	23	19	8	11
% O in H ₂ O	30	45	28	22	10	14
% wt yield	94	99	105	99	98	94
C balance, %	88	84	103	99	102	96
H balance, %	92	116	80	95	81	79
O balance, %	96	104	111	97	97	94

(a) All yields are based on weight of wood feed.

TABLE 13. Gas Composition and Yield with Hydrogen Contact Gas

Yields	Test Number (Gasifier Temp., °C)					
	H-1 (650)	H-3 (650)	H-2 (725)	H-4 (725)	H-5 (800)	H-6 (800)
slv, ft/s	1.05	2.26	1.12	1.73	1.13	2.20
1b/h-ft ³	34	69	49	43	40	47
Gas Comp, vol%						
H ₂	69.60	78.02	58.88	74.16	59.92	70.96
CO ₂	1.71	1.66	2.52	1.37	1.60	0.98
C ₂	0.71	0.41	1.72	1.17	2.08	1.45
CH ₄	2.50	1.55	4.66	2.90	4.54	3.13
CO	7.28	5.04	14.01	8.61	15.04	10.04
C ₃	0.25	0.16	0.41	0.20	0.10	0.09
C ₄	0.04	0.02	0.04	0.02	0.01	0.09
N ₂	14.63	7.95	15.88	10.88	13.78	9.99
H ₂ O	3.24	4.47	3.34	3.57	3.03	3.45
g H ₂ /100 g wood	0.85	2.06	-0.59	0.72	0.23	0.06
g CH ₄ /100 g wood	5.65	3.48	7.75	7.23	8.93	8.57
g CO/100 g wood	28.78	19.85	40.76	37.58	51.78	48.16
g CO ₂ /100 g wood	6.74	6.53	7.33	5.97	5.49	4.71

TABLE 14. Yield of Condenser Oils with Hydrogen Contact Gas^(a)

Yields	Test Number (Gasifier Temp, °C)					
	H-1 (650)	H-3 (650)	H-2 (725)	H-4 (725)	H-5 (800)	H-6 (800)
slv, ft/s	1.05	2.26	1.12	1.73	1.13	2.20
1b wood/h-ft ³	34	69	49	43	40	47
wt condenser oil	77	269	100	57	60	95
wt% condenser oil	7	12	7	5	3	4
% C in cond oil	11	16	10	8	6	7
% H in cond oil	8	14	7	6	3	4
% O in cond oil	3	7	3	2	1	1
wt condenser oils/ wt -4°F oils	0.71	1.0	0.68	0.48	34	0.48
cond oil comp, wt%						
C	74.09	66.94	79.01	77.13	85.3	85.33
H	6.9	7.53	7.01	6.98	6.63	6.48
N	0.24	0.48	0.45	0.23	0.26	0.38
O	17.94	25.01	18.48	15.59	7.81	7.81

(a) All yields are based on weight of wood feed.

TABLE 15. Yield of Organics in Methylene Chloride
with Hydrogen Contact Gas^(a)

Yields	Test Number (Gasifier Temp, °C)					
	H-1 (650)	H-3 (650)	H-2 (725)	H-4 (725)	H-5 (800)	H-6 (800)
slv, ft/s	1.05	2.26	1.12	1.73	1.13	2.20
1b wood/h-ft ³	69	49	43	40	47	--
wt BTX, g	23	42	29	25	50	58
wt% BTX	2.18	1.87	1.92	2.37	2.78	2.51
% C in BTX	3.99	3.42	3.51	4.32	5.07	4.58
wt C ₈ -C ₂₀ oil, g	14	39	19	18	25	41
wt% C ₈ -C ₂₀ oils	1.33	1.74	1.26	1.70	1.39	1.77
% C to C ₈ -C ₂₀ oil	2.26	2.96	2.14	2.89	2.36	3.01
wt C ₆ -C ₂₀ oils/ wt -4°F oils	0.21	0.17	0.23	0.24	0.38	0.43

(a) All yields are based on weight of wood feed.

DISCUSSION OF RESULTS

The results of the study were analyzed to determine the effects of temperature, contact gas, and gas contact time on the yields of gases, liquids, and chars. These results are based on data from single tests at each set of experimental conditions and show general trends. The significance of these general trends does not justify additional tests at this time.

EFFECT OF TEMPERATURE ON YIELD OF CONDENSIBLES

The effects of temperature on total yield of condensible organics collected at -4°F (-20°C) are shown in Figure 3 for CH_4 and H_2 contact gases. This fraction of condensibles should include all condensible organics generated, as described earlier. The yield of these condensible organics decreased with increasing temperature except with CH_4 contact gas at 1 ft/s (30 cm/s) slv, which gives a minimum yield at 1340°F (725°C). The same phenomenon was noted for the yield of water-insoluble oils collected at ambient temperature in the condenser (Figure 4). This appears to be experimental error, but material balances were excellent for these tests, as was shown in Table 7.

The yield of condenser oils with a CH_4 contact gas (Figure 4) showed a minimum at 1340°F (725°C) with an slv of about 1 ft/s (30 cm/s) (about a 2-s gas residence time) and a maximum at this temperature with an slv of 2 ft/s (60 cm/s). A steady decrease in the amounts of condenser oil occurred with H_2 as the contact gas. Material balances were good for the tests with CH_4 contact gas (see Table 7).

The yield of water-soluble organics is shown to decrease with temperature in Figure 5, except for the unusually low yield at 1200°F (650°C) for CH_4 contact gas at an slv of about 2 ft/s. Experimental error could easily account for this measured low yield.

Figures 6 and 7 illustrate the effect of temperature on the yield of organics collected in the MeCl scrubbers and identified by GC analysis. The data in these figures are for tests with an slv of about 1 ft/s. Figure 6 shows the change in the yield of the BTX fraction, while Figure 7 shows the

FIGURE 3. Effect of Temperature, Contact Gas, and Gas Velocity on Yield of Condensable Organics

change for all organics collected in the MeCl scrubbers. These figures show a maximum in the yield of these organics at 1340°F (725°C) for CH₄ contact gas. Table 11 showed the same maximum for an slv of about 2 ft/s, which indicates a similar trend as in Figure 4 for a shorter gas residence time. Determination of organic yield by independent means showed the same maximum in the yield at 1340°F (725°C) for CH₄ contact gas at a gas residence time of 1 s for all fractions collected.

The organic condensibles that could be identified by analysis of the MeCl scrub solution comprised less than 50% of the oils collected in the

FIGURE 4. Effect of Operating Conditions on Yield of Condenser Oils

condenser. Condenser oils from three different tests were dissolved in MeCl to determine the fraction that could be identified by GC analysis. The weight percents of the condenser oils identified are shown in Table 16. This table indicates that GC analysis of the MeCl scrub solution did not identify all condensable organics and shows the need for alternative collection systems.

Data from Tables 11, 15, and 16 show that the BTX fraction was not retained in the condenser since this is the major fraction (over 50%) in the MeCl solutions but a minor fraction (4% to 8%) in the condenser oils. In

FIGURE 5. Effect of Operating Conditions on Yield of Aqueous Soluble Organics

Tests M-6, H-1, and H-6 the fractions of BTX retained in the condenser oils compared to the MeCl scrub solutions were 0.15, 0.2, and 0.13, respectively.

EFFECT OF TEMPERATURE ON GAS YIELD

The effect of temperature on the total yields of dry gases is shown in Figure 8. As expected, the gas yield increases continuously with temperature. Some of this increase is at the expense of the oil yield and part at the expense of the char yield. Because hydrogen is a light gas, data on gas

FIGURE 6. Effect of Temperature and Contact Gases on Benzene/Toluene/Xylene Yield in Methylene Chloride Scrub Solutions

weight yields with hydrogen are expected to be more accurate than data for other gases. Error in the measurement of the input hydrogen flow will not influence the weight yield as much as an error in the flow measurement of other gases, especially CO₂.

Figures 9 through 12 show the effect of temperature on the yield of individual gas components, CO, CO₂, CH₄, and H₂, respectively. A steady increase in the CO yield with increasing temperatures is evident for all contact gases. Possible errors in flow measurement made determination of the yield of the contact gas component uncertain, as shown by the erratic results for the contact gases in Figures 10 through 12. It is therefore difficult to determine directly from these data if the contact gas reacts. The yield of H₂ shown in Figure 12 indicates that CH₄ may react to produce some H₂. On

FIGURE 7. Effect of Temperature and Contact Gas on Yield of C₆-C₂₀ Organics

TABLE 16. Percentage of C₆-C₂₀ Components in Condenser Oil

Test No.	Temp., °C	Contact Gas	Superficial Linear Velocity	% Components		
				C ₆ -C ₂₀	BTX	C ₈ -C ₂₀
M-6	650	CH ₄	2.2	18	4	14
H-1	650	H ₂	1.1	30	6	24
H-6	800	H ₂	2.2	49	8	41

the other hand, CO₂ may consume some H₂ to yield CO (as confirmed by Figure 9), which makes the H₂ yield with CH₄ appear higher than with CO₂ (Figure 12).

FIGURE 8. Effect of Temperature on Gas Yield

The effect of temperature on the weight yield of char is shown in Figure 13 for tests with different contact gases at 1 and 2 ft/s slv. Char yield generally decreased with temperature. A maximum in char yield at 1 ft/s slv occurred with CH₄ and H₂ contact gases. It appears that this maximum may result from the predominance of reactions that form char in preference to liquids at these conditions.

FIGURE 9. Effect of Temperature and Contact Gas on Yield of Carbon Monoxide

EFFECT OF CONTACT GAS

As noted in the previous discussion, yields of gases, liquids, and char depended on the contact gas as well as the temperature. Tests with CO₂ were completed with the dual-vessel system shown in Figure 1. As a consequence, condenser oils were destroyed by the LZ-Y82 catalyst. Also, no condensate was collected at -4°F (-20°C) with CO₂.

In general, the yield of condensable organics was higher with CH₄ contact gas than with H₂ contact gas. As illustrated in Figure 3, the yield of

FIGURE 10. Effect of Temperature and Contact Gas on Yield of Carbon Dioxide

total condensible organics collected at -4°F (-20°C) was greater for CH₄ with a 1-s contact time (2 ft/s slv) than for H₂ with a 1-s contact time. With a 2-s contact time a minimum yield was evident for CH₄ gas. In all other cases at similar conditions the yield of total condensible organics with CH₄ exceeded the yield with H₂.

The yield of oils collected at room temperature in the condenser was also higher with CH₄ contact gas than with H₂ contact gas except for several tests shown in Figure 4. Again, a low yield with CH₄ at 1340°F (725°C) and a 2-s contact time (1 ft/s slv) was apparent. Also, at 650°C the yield with H₂ and a 1-s contact time (2 ft/s slv) exceeded the yield with CH₄. It should be noted that separation of condenser oils from the aqueous phase is difficult, and these results are from a single test. The trends indicated do not justify additional tests at this time.

FIGURE 11. Effect of Temperature and Contact Gas on Yield of Methane

The yield of water-soluble organics appears to be unaffected by contact gas at 1340°F and 1470°F (725°C and 800°C) (Figure 5). The unusually low yield for CH₄ at a 1-s contact time and 1200°F (650°C) probably results from experimental error.

Figures 6 and 7 showed that the yields of BTX and C₆-C₂₀ organics were similar, within the accuracy of determination, for CO₂, CH₄, and H₂ contact gases. Specific components in the organics from the MeCl scrub solutions were not identified, but chromatograms of samples with all contact gases had the same predominant peaks. Essentially no variation in composition was noted with change of contact gas.

In the course of catalyst development studies at PNL, many tests with steam as the contact gas have been completed in the equipment arrangement

FIGURE 12. Effect of Temperature and Contact Gas on Yield of Hydrogen

shown in Figure 1. These tests were conducted at 1340°F (725°C) with a 2-s gas residence time. The yield of condensible organics was determined by scrubbing a slipstream with MeCl at 32°F (0°C), as described previously. Yields of condensible organics (C₆-C₂₀ organics) with steam are compared to H₂, CH₄, and CO₂ contact gases in Figure 14. At the conditions of these tests, the general trend indicates that yield of these condensible organics was greatest for CH₄ contact gas and smallest for H₂ and CO₂ contact gases. The differences were not very significant. The yield shown for steam in Figure 14 is the average of 15 tests in which the range in yield was from 3.5 to 5 wt%.

Analysis of the effect of contact gases on the yield of gas components is complicated by the sensitivity of the calculation of the yield of a

FIGURE 13. Effect of Temperature, Contact Gas, and Gas Velocity on Yield of Char

component to input gas flow rate if that component is the contact gas. Figures 9 and 12 indicated that the reverse water-gas shift reaction occurs when CO₂ and H₂ are contact gases, which results in high yield of CO with CO₂ contact gas in Figure 9 and a low yield of H₂ with CO₂ contact gas in Figure 12.

Figure 11 showed that the CH₄ yield is greater for H₂ contact gas than for CO₂ contact gas. It appears that additional CH₄ to the amount from

FIGURE 14. Effect of Contact Gas on Yield of Condensable Organics

pyrolysis was formed with H₂ as the contact gas. Additional CH₄ can be formed by reaction of H₂ with char but probably results from H₂ preventing CH₄ destruction that apparently occurs when CO₂ is the contact gas.

No indication of CH₄ reaction was directly evident in Figures 9 through 12. Negative CH₄ yield with CH₄ as the contact gas (Figure 11) probably results from an error in the measurement of the input gas flow rate.

No clear trend for the effect of contact gas on char yield was evident in Figure 13. At 1470°F (800°C) the char yield with CH₄ contact gas appeared to be higher than for H₂ and CO₂. At 1340°F (725°C) yield of char with H₂ contact gas was highest. Variation of char-contact gas reaction kinetics with temperature could influence char yield. Differences probably result from experimental error.

EFFECT OF GAS CONTACT TIME

Gas residence time at reactor temperature, or contact time, was varied from 1 s to 2 s with H₂ and CH₄ gases. High flow rates for a 1-s contact time could not be maintained with CO₂, as discussed previously.

The effect of residence time on the yield of condensible organics collected at -4°F (-20°C) was not clear from the data plotted in Figure 3. The yield was higher for a 1-s residence time than for 2 s at all temperatures except 1470°F (800°C). Oils could be expected to be destroyed at high temperature and increased residence time, but this does not appear to be the case. The same general trend, which could result from experimental error, was also shown in Figure 4 for the yield of condenser oils collected at room temperature. Decreased residence time appeared to increase the yield of water-soluble organics except for CH_4 contact gas at 1200°F (650°C), as was shown in Figure 5.

The yield of condensible organics collected in the MeCl scrubbers, particularly the BTX fraction, was slightly greater at 1-s contact time (2 ft/s slv) than at 2 s (1 ft/s slv) at all temperatures with CH_4 contact gas, as noted by data in Table 11. The same consistent trend was not shown by the data in Table 15 for H_2 contact gas. Results for CO_2 contact gas in Table 5 showed a trend to an increased BTX yield with increased slv (shorter residence time) similar to the data for CH_4 .

Figure 8 showed that gas yields increase with increased gas residence time, as expected. At temperatures of 1340°F and 1472°F (725°C and 800°C) the char yield is higher at 2-s residence time than at 1-s for both CH_4 and H_2 contact gases (see Figure 13), which is somewhat surprising. If both gas and char yields are less at 1-s residence time than at 2-s residence time, then it follows that the liquid yield must be higher at the shorter residence time.

EFFECT OF WOOD FEED RATE

No effort was made to determine the effect of wood feed rate by its systematic variation. Nevertheless, the feed rate, which was determined by weighing the wood before and after each test, did vary substantially. The rate of wood addition to the gasifier was controlled by the rpm of the feed auger.

Usually, but not always, a high input gas rate resulted in a high feed rate. Figure 15 shows the yield of gases as a function of the wood feed rate

FIGURE 15. Effect of Wood Feed Rate on Gas Yield

(based on fluidized-bed volume) at different temperatures. At each temperature, the gas yield is more a function of gas contact time than wood feed rate. Without exception an increase in the gas contact time results in an increase in gas yield with H₂ and CH₄ contact gases. For CH₄ and H₂ the gas yield both increased and decreased with increased wood feed rate, depending on gas contact time. No clear trend for the effect of wood feed rate was evident.

These results do not conclusively show that wood feed rate does not influence yields. Char residence time (char inventory in the gasifier divided by 0.3 times the wood feed rate) in the tests was in the range of 10 to 30 min, so wood feed rate is probably unimportant.

CONCLUSIONS AND RECOMMENDATIONS

Tests with different contact gases for fluid-bed pyrolysis of wood were conducted to determine the effect of these thermal treatment methods on product yields, primarily yield of condensible hydrocarbons. Results of these tests showed slight trends for the effects of temperature, contact gas, and gas contact time on the yields of gases, liquids, and chars. These trends were not significant enough to justify verification by additional tests at this time.

The yield from wood pyrolysis of organics collected in MeCl scrubbers at 32°F (0°C) was slightly higher for CH₄ contact gas than for H₂ and CO₂ contact gases. The yield of this C₆-C₂₀ organic fraction was similar, within the accuracy of determination, for H₂ and CO₂ contact gases. The yield with water as the contact gas was slightly less than the yield with CH₄ but greater than the yield with CO₂ and H₂.

Retention, quantification, and identification of condensible hydrocarbons from fluid-bed pyrolysis of wood was extremely difficult. Retention of the BTX fraction in a condenser/scrubber operating at about 77°F (25°C) was found to range from 13% to 20% of the amount that was retained in a MeCl scrubber operating at 32°F (0°C).

For all contact gases, increasing the pyrolysis temperature from 1200°F to 1470°F (650°C to 800°C) increased gas yield while reducing yields of condensibles and char. The yield of the BTX fraction was fairly constant at about 2.5 g/100 g wood over this temperature range for all contact gases.

Reduction of the gas residence time from 2 s to 1 s showed trends for reduced gas and char yields and increased yield of condensibles.

Some reaction of H₂ and CO₂ contact gases was evident at temperatures over 1340°F (725°C). The reverse water-gas shift was the main reaction noted.

Yields from wood gasification/pyrolysis were more a function of temperature than contact gas. Some slight trends in yields with different contact gases were noted but were not highly significant. This implies that recycle

gases (recycled product gases or flue gases) could be used for wood gasification without significantly reducing gas yield at a given operating temperature. Substituting recycle gases for steam could benefit the gasification process by reducing the amount of wastewater.

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APPENDIX

EXPERIMENTAL DATA

APPENDIX

EXPERIMENTAL DATA

Experimental data and calculated results of bench-scale tests with different contact gases are tabulated in this appendix. Entries used in the tables are self explanatory in most cases and correspond to terms used in the text. Entries that are not self explanatory are defined below.

Table A.1 presents results of tests with CO_2 contact gas. In these tests a secondary fixed bed of LZ-Y82 catalyst was used to crack tars in the gases from the primary gasifier. Two data columns are used for each test: the first, labeled LC-1 through 7, refers to compositions and yields from the primary gasifier; the second, labeled LC-1P through 7P, refers to compositions and yields from the catalyst bed. Composition and yield of items like char and condensate (cond) have a single value. The weight of condensate includes about 550 g of water added to the condenser scrubber at the start of each test. Char composition did not vary much in the tests and was about 85 wt% C, 1 wt% H, and 14 wt% O for the combustible fraction. The weight of char shown in the tables is for the combustible fraction only. Gas flow is measured after the secondary catalytic reactor so the intermediate gas flow from the gasifier is unknown. In Table A.1 the intermediate gas flow is assumed to be the same as the product flow in L/g of wood.

The LZ-Y82 catalyst effectively destroyed organics in the gas stream such that no water-insoluble phase was collected in the condenser scrubber. Only the condensate from LC-7 was analyzed for total organic carbon, and the two values obtained (8900 and 10078 mg/L) are shown in Table A.1.

The C_6 - C_{20} oils were collected in MeCl scrubbers and analyzed on the GC. The BTX is part of these oils.

Tables A.2 and A.3 list data from tests with CH_4 and H_2 contact gases, respectively. The "% condensibles" shown in these tables refers to the weight collected at -20°C (-4°F). The "Wtoil fraction, g" is the weight of these condensibles minus the condensate water and water in the gas saturated

at the condenser temperature. For calculation of yields, this oil fraction was assumed to have the same composition as oils collected in the condenser/scrubber, which are listed as "wt cond oil." The "wt oils, g" includes the non-BTX fraction collected in the MeCl scrubbers. The "Wt H₂O, g" includes condenser water and water in the gas saturated at condenser temperature.

Table entries are defined below:

CO ₂ /Wood, g/g :	The weight ratio of contact gas rate (CO ₂ in this listing) to wood rate.
CO ₂ C/Wood C:	Weight ratio of elemental carbon in the CO ₂ contact gas to elemental carbon in the wood feed.
CO ₂ O/Wood O:	Weight ratio of elemental oxygen in the CO ₂ contact gas to elemental oxygen in the wood feed.
slv/ ft/sec:	Superficial linear velocity of the contact gas calculated from its volumetric flow rate divided by the cross-sectional area of the gasifier.
lb/hr-ft ³ :	Wood feed rate in pounds per hour per cubic foot of fluid-bed volume.
Wt wood, g:	Weight of wood in grams fed to the gasifier during the test.
Gas flow, l/g:	Total volume of product gas in liters measured by the wet test meter divided by the grams of wood fed to the gasifier.
Wt % dry gas:	Weight of product gas (excluding water) times 100 divided by the weight of wood fed to the gasifier.
% C to gas:	The percent of wood carbon found in the product gas.
% H in dry gas:	The percent of wood hydrogen that goes to the product gas, excluding water.
% O in dry gas:	The percent of wood oxygen that goes to the product gas, excluding water.
g H ₂ /100 g wood:	Weight of hydrogen in the product gas in grams for every 100 grams of wood fed to the gasifier.
g CH ₄ /100 g wood:	Same as the preceding entry but for methane.

g CO/100 g wood:	Same as preceding entry but for carbon monoxide.
g CO ₂ /100 g wood:	Same as preceding entry but for carbon dioxide.
Btu H ₂ /lb wood:	Energy content of hydrogen (in Btu) in product gas per pound of wood fed to the gasifier.
Btu CH ₄ /lb wood:	Same as preceding entry but for methane in product gas.
Btu CO/lb wood:	Same as preceding entry but for carbon monoxide in product gas.
% Btu in gas:	Energy content of gas relative to the combustible energy content of the wood, also known as cold gas efficiency.
Char yield, g:	Weight of char (in grams) accumulated during the test.
Char in bed, g:	The average char inventory in the fluid bed, or one half the sum of the starting and final char inventory in the fluid bed.
% C to char:	The percent of elemental carbon in the wood that is contained in the char yield.
% H to char:	Same as preceding entry but for elemental hydrogen in the wood.
% O to char:	Same as preceding entry but for the elemental oxygen in the wood.
Min char res t:	Minutes of char residence time in the fluid bed calculated by dividing the weight of char in the fluid bed by 30% of the wood feed rate.
Total cond, g:	Total weight of condensibles (including water) collected at -4°F (-20°C).
% condensibles:	The preceding entry times 100 divided by the weight of wood fed to the gasifier.
% char:	The percent of wood converted to char.
% wt yield:	The weight percent of the wood fed to the gasifier collected as dry gases, condensibles, and char.
Wt oil fraction:	Weight (in grams) of condensibles collected at -4°F (-20°C) minus the condenser water and water vapor.
% C to oil:	Weight percent of the wood carbon in the preceding condensibles.

% H to oil:	Same as preceding entry but for hydrogen.
% O to oil:	Same as preceding entry but for oxygen.
Wt cond oil, g:	Weight in grams of condensibles collected in the condenser/scrubber operating at ambient temperature.
% C in cond oil:	Weight percent of wood carbon in the preceding condensibles.
% H in cond oil:	Same as preceding entry but for hydrogen.
% O in cond oil:	Same as preceding entry but for oxygen.
Wt C ₆ -C ₂₀ oils:	The weight of organics (including BTX) collected and identified in the MeCl scrubbers.
% C to C ₆ -C ₂₀ oils:	The percent of wood C in the preceding condensibles.
% H to C ₆ -C ₂₀ oils:	Same as preceding entry but for hydrogen.
% O to C ₆ -C ₂₀ oils:	Same as preceding entry but for oxygen.
Wt oils, g:	The weight of organics (excluding BTX) collected and identified in the MeCl scrubbers.
% C to oils:	The percent of wood carbon in the preceding fraction.
Wt condensate, g:	These two table entries refer to the weight in grams of aqueous condensate collected in the condenser/scrubber.
Wt cond, g:	
TOC, mg/l:	The total organic carbon in the condensate.

TABLE A1. Results of Tests with Carbon Dioxide Contact Gas

Date	7/1/86	7/1/86	7/1/86	7/13/86	4/2/86	4/2/86	4/4/86
Test number-->	LC-1	LC-1a	LC-2	LC-2F	LC-3	LC-3F	LC-4
Temp, C	650	550	700	550	800	550	800
Catalyst		LZ-Y82		LZ-Y82		LZ-Y82	
Inert Material	Sand	LZ-Y82	Sand	LZ-Y82	Sand	LZ-Y82	Sand
Wood Mesh Size	-14		-14		-14		-14
Test time, min	77	74	115	115	109	109	112
Bed height, ft	1	1	1	1	1	1	1
Wt catalyst, g	956	956	956	956	956	956	956
g/min wood	14.68	14.68	15.96	15.96	15.56	15.56	14.29
l/min CO2	28.2	25.9	25.7	25.7	35.5	35.5	26.9
CO2/Wood, g/g	3.23	3.23	2.95	2.95	4.18	4.18	3.45
CO2 C/Wood C	1.76	1.76	1.61	1.61	2.28	2.28	1.88
CO2 O/Wood O	5.45	5.45	4.97	4.97	7.04	7.04	5.81
slv, ft/sec	.96	.86	1.01	.85	1.53	1.18	1.16
lb/hr-ft ²	.40	.40	.43	.43	.42	.42	.39
Wt wood, g	1086	1086	1835	1835	1696	1696	1600
Wood/catalyst	1.14	1.14	1.92	1.92	1.77	1.77	1.67
Gas comp, vol%							
HZ	2.744	3.937	4.214	5.662	3.966	3.907	4.544
CO2	67.581	64.771	62.374	60.658	64.868	65.458	59.775
CZ	.445	.68	.951	.839	1.231	1.106	1.381
CH4	1.884	2.646	2.762	3.211	2.574	2.521	2.925
CO	7.156	8.222	10.937	11.054	13.562	12.785	14.723
C3	.3	.3	.3	.3	.3	.3	.3
C4	.1	.1	.1	.1	.1	.1	.1
N2	17.74	16.807	15.92	15.693	11.011	12.115	14.222
H2O	2.39	2.39	2.39	2.39	2.39	2.39	2.39
Gas flow, l/g	2.75	2.75	2.7	2.7	3.51	3.51	3.18
Wt % dry gas	48	40	59	52	70	70	73
% C to gas	40	39	53	49	69	68	71
% H in dry gas	32	43	47	54	61	59	62
% O in dry gas	60	40	69	55	72	75	78
g H2/100 g wood	.63	.90	.95	1.27	1.16	1.14	1.20
g CH4/100 g wood	3.45	4.85	4.97	5.78	6.02	5.90	6.20
g CO/100 g wood	22.96	26.38	34.45	34.82	55.54	52.35	54.64
g CO2/100 g wood	17.26	3.10	13.53	5.04	-.85	2.95	3.38
Btu H2/1b wood	383	550	578	777	707	697	734
Btu CH4/1b wood	824	1157	1186	1379	1437	1408	1480
Btu CO/1b wood	997	1146	1496	1512	2412	2274	2373
% Btu in gas	26	34	38	43	54	52	54
Char yield, g	92	92	115	115	53	53	37
Avg char in bed, g	136	136	75.3	75.3	59	59	57
% C to char	14	14	11	11	5	5	4
% H to char	1.32	1.32	.98	.98	.49	.49	.36
% O to char	2.76	2.76	2.04	2.04	1.02	1.02	.75
Min char res t	31	31	16	16	13	13	13
Wt C6-C20 oils	37.99	29.91	53.74	75.63	103.16	101.97	101.72
% C to C6-C20 oils	5.95	4.68	4.98	7.01	10.34	10.22	10.81
% H to C6-C20 oils	3.39	2.67	2.84	3.99	5.89	5.82	6.16
% O to C6-C20 oils	.72	.56	.60	.84	1.24	1.23	1.30
Wt condensate, g	713	713	792	792	779	779	695
TDC, mg/l	10000	10000	10000	10000	10000	10000	10000
% C to cond	1.31	1.31	.86	.86	.92	.92	.87
Wt ETX, g	8.7	27.2	18.9	59.2	52.9	77.6	51.1
% C to BTX	1.46	4.56	1.87	5.87	5.68	8.33	5.81
Total H2O, g	223	223	321	321	306	306	219
% H to water	36		30	30	31	31	24
% O to water	42	42	36	36	37	37	28
C Balance, %	62	59	70	68	86	84	87
H Balance, %	72	83	81	89	99	97	93
O Balance, %	106	86	108	94	112	114	109

TABLE A1. Results of Tests with Carbon Dioxide Contact Gas (continued)

Date	4/4/86	4/13/86	4/13/86	4/22/86	4/22/86	4/28/86	4/29/86
Test number->	LC-4F	LC-5	LC-5P	LC-6	LC-6P	LC-7	LC-7P
Temp, C	550	700	550	750	550	750	550
Catalyst	LZ-Y82		LZ-Y82		LZ-Y82		LZ-Y82
Inert Material	LZ-Y82	Sand	LZ-Y82	Sand	LZ-Y82	Sand	LZ-Y82
Wood Mesh Size		-14	-14	-14		-14	
Test time, min	112	112	112	105	105	77	77
Bed height, in	1	1	1	1	1	1	1
Wt catalyst, g	956	956	956	956	956	956	956
g/min wood	14.29	15.6	15.6	16.38	16.38	26.48	26.48
l/min CO2	26.9	35.7	35.7	35.5	35.5	22.3	22.3
CO2/Wood, g/g	3.45	4.19	4.19	3.47	3.47	1.54	1.54
CO2 C/Wood C	1.88	2.29	2.29	2.17	2.17	1.84	1.84
CO2 O/Wood O	5.81	7.06	7.06	6.69	6.69	2.60	2.60
slv, ft/sec	.89	1.40	1.18	1.46	1.18	.92	.74
lb/hr-ft3	.39	.42	.42	.44	.44	.71	.71
Wt wood, g	1600	1750	1750	1720	1720	2039	2039
Wood/catalyst	1.67	1.83	1.83	1.80	1.80	2.13	2.13
Gas comp, vol%							
H2	5.187	2.456	2.922	3.471	3.784	6.736	7.212
CO2	59.288	70.38	70.655	67.331	67.750	47.05	49.183
C2	1.123	.83	.949	1.151	1.044	2.058	1.838
CH4	3.354	2.059	2.506	2.48	2.766	4.877	5.251
CO	15.388	9.912	10.21	11.54	11.513	19.64	19.733
C3	.3	.28	.28	.253	.25	.498	.5
C4	.1	.1	.1	.1	.1	.1	.1
N2	13.686	12.285	12.076	11.351	10.358	14.695	13.773
H2O	2.39	2.47	2.47	2.65	2.65	2.47	2.47
Gas flow, l/g	3.18	3.34	3.34	3.35	3.35	1.87	1.87
Wt % dry gas	73	61	66	75	76	70	71
% C to gas	71	56	60	67	69	65	65
% H in dry gas	66	43	50	54	57	57	59
% O in dry gas	77	71	75	87	82	80	81
g H2/100 g wood	1.37	.68	.81	.97	1.06	1.05	1.12
g CH4/100 g wood	7.11	4.58	5.58	5.54	6.18	6.08	6.55
g CO/100 g wood	57.09	38.62	39.78	45.10	45.00	42.85	43.05
c CO2/100 g wood	.54	11.41	13.09	16.13	18.80	13.77	14.22
Btu H2/lb wood	838	417	496	571	644	640	685
Btu CH4/lb wood	1697	1094	1331	1322	1474	1451	1562
Btu CO/lb wood	2480	1678	1728	1959	1954	1861	1870
% Btu in gas	59	38	42	46	48	46	48
Char yield, g	37	106	106	78	78	149	149
Avg char in bed, g	57	60	60	53	53	72	72
% C to char	4	10	10	8	8	12	12
% H to char	.36	.95	.95	.71	.71	1.14	1.14
% O to char	.75	1.97	1.97	1.48	1.48	2.38	2.38
Min char res t	13	13	13	11	11	9	9
Wt C6-C20 oils	100.19	56.1	119.94	97.25	77.55	76.3	84.3
% C to C6-C20 oils	10.65	5.45	11.65	9.61	7.66	6.36	7.03
% H to C6-C20 oils	6.07	3.11	6.64	5.48	4.37	3.63	4.01
% O to C6-C20 oils	1.28	.66	1.40	1.16	.92	.77	.85
Wt condensate, g	695	780	780	732	732	752	752
TDC, mg/l	10000	10000	10000	10000	10000	8900	10078
% C to cond	.87	.89	.89	.85	.85	.66	.74
Wt BTX, g	69.5	19.49	95.12	63.31	63.35	48.3	66.6
% C to BTX	7.91	2.03	9.89	6.70	6.70	4.31	5.94
Total H2O, g	219	388	388	307	307	278	278
% H to water	24	38	38	31	31	24	24
% G to water	28	46	46	37	37	28	28
C Balance, %	87	73	83	86	85	84	85
H Balance, %	96	85	96	91	93	85	88
O Balance, %	107	119	124	127	131	112	113

TABLE A2. Results of Tests with Methane Contact Gas

Date ==>	5/22/86	5/28/86	6/2/86	7/1/86	7/3/86	7/29/86
Test number->	M-1	M-2	M-3	M-4	M-5	M-6
Temp, C	725	800	8LC	725	800	650
Inert Material	Sand	Sand	Sand	Sand	Sand	Sand
Wood Mesh Size	-14	-14	-14	-14	-14	-14
Test time, min	05	09	105	09	120	111
Bed height, in	1	1	1	1	1	1
g/min wood	21	19.9	14.3	17.4	19.95	20.41
l/min CH4	25	23	29	61	54	59
CH4/Wood, g/g	.63	.94	1.35	2.34	1.80	1.93
slv, ft/sec	1.04	1.21	1.08	2.45	2.33	2.19
lb/hr-ft3	37	34	39	47	54	55
Wt wood, g	1376	1958	1506	1653	2394	2256
Gas comp, vol%						
H2	7.863	9.608	4.571	3.471	5.566	2.249
CO2	3.549	2.607	2.732	1.437	1.535	1.682
C2	3.689	4.293	3.462	.81	1.476	.997
CH4	52.225	50.127	61.476	73.593	67.595	75.135
CO	12.655	15.719	7.29	6.992	10.803	5.569
CO3	.601	.509	.5	.25	.257	.157
C4	.242	.118	.382	.018	.018	.013
N2	15.589	14.126	16.821	8.444	6.704	9.202
H2O	3.029	3.457	3.457	4.292	4.292	5.251
Gas flow, l/g	2.42	2.69	3.13	4.81	4.08	4.01
Wt % dry gas	69	73	59	64	78	53
% C to gas	65	72	57	57	71	51
% H in dry gas	67	63	45	53	67	59
% O in dry gas	75	88	64	74	89	56
g H2/100 g wood	1.59	2.16	1.22	1.40	1.89	.75
g CH4/100 g wood	1.72	-3.80	-4.46	3.25	3.41	8.14
g CO/100 g wood	35.73	49.39	27.13	39.40	51.42	26.05
g CO2/100 g wood	10.02	8.19	10.17	8.10	7.40	7.87
Btu H2/lb wood	967	1314	741	852	1154	458
Btu CH4/lb wood	410	-908	-1064	776	813	1943
Btu CO/lb wood	1552	2145	1173	1711	2234	1132
% Etu in gas	34	30	10	39	49	42
Char yield, g	95.5	89	87	88	103	162
Char in bed, g	122	84	106	88	77	58
% C to char	12	8	10	9	7	12
% H to char	1	1	1	1	1	1
% O to char	2	1	2	2	1	2
Min char res t	19	14	25	17	13	9
Total cond, g	339	435	600	499	512	917
% condensibles	25	22	40	30	21	40
% char	7	5	6	5	4	7
Wt % dry gas	70	76	59	64	78	54
% wt yield	101	105	104	99	104	101
Wt oil fraction	132	99	313	354	325	525
% C to oil	16	29	29	33	23	31
% H in oil	9	15	23	22	14	25
% O in oil	2	3	0	0	0	0
lit cond oil, g	31	123	147	189	117	214
% C in cond oil	4	11	13	18	8	13
% H in cond oil	2	6	11	12	5	10
% G in cond oil	.46	1.32	.03	.07	.03	.07
lit oils, g	28	36	26	27	54	50
% C to oils	3.46	3.11	2.93	2.77	3.83	3.01
Wt BTX, g	38	48	36	53	66	57
% C to Etx	5.05	4.46	4.37	5.84	5.04	4.60
Wt cond, g	608	505	674	453	435	649
TOC, mg/l	29000	19500	72000	55800	25200	21700
% C to cond	2.55	.99	6.41	3.03	.91	1.24
Wt H2O, g	207	102	287	145	187	392
% H2O	15	5	19	9	8	17
% H in H2O	26	9	33	15	14	30
% O in H2O	31	11	40	18	16	36
C Balance, %	97	109	102	102	102	96
H Balance, %	104	89	102	91	95	116
O Balance, %	110	104	105	94	106	94
Cond oil comp						
Wt % C	85	85	69.25	77.69	85.18	68.3
Wt % H	6.2	6.2	7.1	6.74	6.45	7.05
Wt % N			.11	.26	.26	.33
Wt % O	8.8	8.8	23.54	15.31	8.11	24.32

TABLE A3. Results of Tests with Hydrogen Contact Gas

Date ==>	7/31/86	8/26/86	8/28/86	9/3/86	9/10/86	9/12/86
Test number->	H-1	H-2	H-3	H-4	H-5	H-6
Temp, C	650	725	650	725	800	800
Inert Material	Sand	Sand	Sand	Sand	Sand	Sand
Wood Mesh Size	-14	-14	-14	-14	-14	-14
Test time, min	84	83	88	66	120	132
Bed height, ft	1	1	1	1	1	1
/mi wood	12.55	18.2	25.48	16	15	17.53
g/mi H ₂	28.3	28	60.9	43	26.1	51
H ₂ /Wood, g/g	.19	.13	.20	.22	.14	.24
slw. ft/sec	1.05	1.12	2.26	1.73	1.13	2.20
lb/hr-ft ²	34	49	69	43	40	47
Wt wood, g	1054	1509	2242	1057	1801	2314
Gas comp, vol%	AVG	AVG-N	AVG	AVG	AVG-N	AVG-N
H ₂	69.597	58.982	78.024	74.16	59.925	70.957
CO ₂	1.705	2.521	1.659	1.368	1.596	.983
CO	.714	1.72	.41	1.173	2.084	1.452
CH ₄	2.502	4.661	1.547	2.901	4.54	3.126
CO	7.285	14.013	5.041	8.613	15.045	10.043
CO ₂	.25	.414	.16	.2	.1	.09
CH ₄	.36	.042	.024	.024	.014	.09
N ₂	14.628	15.876	7.953	10.883	13.781	9.989
H ₂ O	3.239	3.34	4.47	3.57	3.029	3.449
Gas flow, l/g	3.39	2.493	3.375	3.74	2.95	4.11
Wt % dry gas	53	67	38	62	78	73
% C to gas	51	65	33	60	76	73
% H in dry gas	51	40	53	57	60	57
% O in dry gas	57	74	44	66	84	77
g H ₂ /100 g wood	.65	-.59	2.06	.72	.23	.06
CH ₄ /100 g wood	5.65	7.75	3.48	7.23	8.93	8.57
CO/100 g wood	28.78	40.76	19.85	37.58	51.78	48.16
CO ₂ /100 g wood	6.74	7.33	6.53	5.97	5.49	4.71
Btu H ₂ /lb wood	518	-358	1255	437	141	36
Btu CH ₄ /lb wood	1348	1948	831	1726	2130	2044
Btu CO/lb wood	1250	1770	862	1632	2249	2092
% Btu in gas	37	38	35	45	53	49
Char yield, g	62	126	181	70	65	66
Char in bed, g	116	118	107	114	111	82
% C to char	10	14	14	11	6	5
% H in char	1	1	1	1	1	0
% O in char	2	3	3	2	1	1
H in char res t	31	22	14	24	25	16
Total cond, g	338	412	960	289	290	394
% condensibles	32	27	43	27	16	17
% char	6	8	8	7	4	3
Wt % dry gas	54	67	39	62	73	74
% wt yield	91	103	90	96	98	93
Wt oil fraction	184	209	480	176	203	241
% C to oils	26	22	28	26	19	18
% H in oils	19	15	15	18	12	11
% O in oils	7	6	13	0	0	0
Wt cond oil	77	100	269	57	60	95
% C in cond oil	11	10	16	8	6	7
% H in cond oil	8	7	14	6	3	4
% O in cond oil	3	3	7	0	0	0
Wt oils, g	14	19	39	18	25	41
% C to oils	2.26	2.14	2.8t	2.89	2.36	3.01
Wt BTX, a	3.33	3.39	4.2	3.35	5.0	5.8
% C to BTX	3.99	3.81	3.11	4.32	5.07	4.58
Wt cond, g	587	680	E1?	579	510	505
TCC, mg/l	46300	28200	132600	29000	13900	19800
% C to cond	5.12	2.53	9.63	3.16	.78	.86
Wt H ₂ O, g	164	203	480	113	87	153
% H ₂ O	15	13	21	11	5	7
% H in H ₂ O	25	23	27	19	8	11
% O in H ₂ O	30	29	45	22	10	14
C Balance, %	92	103	84	99	102	96
H Balance, %	97	80	116	95	81	79
O Balance, %	96	111	104	91	95	92
Cond oil comp						
Wt % C	74.09	79.01	66.94	77.13	85.3	85.33
Wt % H	6.9	7.01	7.53	6.98	6.63	6.48
Wt % N	.24	.45	.48	.23	.26	.38
Wt % G	17.94	16.48	25.01	15.59	7.81	7.81

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