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CONVERSION OF BIOMASS MATERIALS

INTO GASEOUS PRODUCTS

Phase II

Interim Technical Report

for the Bench Scale Pilot Plant Studies

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INTRODUCTION

In July of 1977 the Garrett Energy Research and Engineering Co., Inc. (GERE) published the final technical report for Phase I, or a brief exploratory study of the thermal conversion of biomass materials into gaseous products. A bench scale pilot plant that simulated individual hearths of a multiple hearth reactor was constructed and employed in the program. In this manner the needed processing steps of drying, pyrolysis, steam-char reaction, and combustion were all individually studied. An economic estimate was then made of a commercial processing plant using this data, which appeared to be quite promising.

Based upon these favorable results a continuation of the program was authorized, and a process development unit (PDU) constructed. While it was under construction and being installed work continued on the operation of the bench scale pilot plant. Some runs were made on all of the processing steps, but emphasis was given to the pyrolysis and drying operations, which are the most critical. This work has now been completed and the PDU is put into operation. Consequently, the results from these tests have been summarized and analyzed, and this data and its correlations presented in the following report. Only the new, Phase II work is considered, and for a more comprehensive review of the entire bench scale program, the Phase I final report must also be consulted. In the Phase II final report all of the bench scale pilot plant work will be combined.

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EXPERIMENTAL DATA

LABORATORY STUDIES

Isothermal Drying of Manure in a Laboratory Oven

A beaker was filled with moist manure and suspended in an oven
with a wire attached to an external balance. The oven temperature
was held constant throughout the experiment. The gross weight was
recorded with time until all the moisture had been removed from the
sample. Nine experiments were conducted in the first series, and two
in the second (Table 1):

Expt. No.	Avg. Temp.	Comment
1	195.7°C	Burned.
2	141.6°	Did not come to constant weight.
3	149.3°	Too much draft from open door.
4	150.8°	O.K.
5	156.5°	O.K.
6	198°	Did not come to constant weight.
7	180.3°	O.K.
8	122.9°	O.K.
9	100.8°	O.K.
10	100°	Apparent slow rate.
11	130°	Apparent slow rate.

Table 1

Laboratory Isothermal Drying of Manure

Run 9, Average Temperature 100.8^{0}C

Drying Time (min)	Weight (gram)	Temperature (^{0}C)	Drying Time (min)	Weight (gram)	Temperature (^{0}C)
0	211.5	100	270	181.9	100
15	210.8	102	285	180.8	101.5
30	209.2	100	300	179.7	102
45	207.0	98	315	179.0	103
60	204.7	100	330	177.9	104
75	202.4	99	345	177.1	102.5
90	200.3	99.5	360	176.4	102
105	198.4	100	375	175.7	101
120	196.2	100	390	175.2	101
135	194.4	100.5	405	174.5	101.5
150	192.5	99.5	420	173.9	100
165	191.1	99.5	435	173.6	103
180	189.4	100.5	450	173.2	101
195	188.0	101.5	465	172.7	103
210	186.6	100.5	480	172.5	100.5
225	185.3	100	495	172.3	101
240	184.1	100	510	172.3	100
255	182.9	101	525	172.3	103.5

Weight of beaker & copper wire	140.8g
Weight of beaker & copper wire & Manure	173.8g
Volume of Manure	80 ml
Depth (cm)	1.6 cm
Weight of beaker & copper wire & H_2O & Manure	213.6g
Volume of Manure	125 ml
Depth (cm)	2.6 - 3.4 cm

Table 1 (Cont.)

Run 8, Average Temperature 122.9°C

Drying Time (min)	Weight (gram)	Temperature (°C)
0	211.1	120
15	210.4	121.5
30	208.5	121
45	204.4	121
60	200.5	122
75	197.1	120.5
90	194	121
105	191.5	120.5
120	189	122.0
135	186.5	120.0
150	184.8	120.5
165	183	120.5
180	181	121.0
195	179.5	120.5
210	178.5	122
225	177.1	124
240	175.9	124.5
255	175.0	123.5
270	173.9	126.0
285	173.4	125.5
300	172.8	127.0
315	172.1	126.5
330	171.8	125.5
345	171.6	127.5
360	171.4	126.5
375	171.4	126.5
390	171.4	125.0

Weight of beaker & copper wire	140.8g
Weight of beaker & copper wire & Manure	173.9g
Volume of Manure	90 ml
Depth (cm)	1.9 cm
Weight of beaker & copper wire & H_2O & Manure	211.6g
Volume of manure	110 ml
Depth (cm)	2.5 cm

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Table 1 (Cont.)

Laboratory Isothermal Drying of Manure

Run 4, Average Temperature 150.8°C

Drying Time (min)	Weight (gram)	Temperature (°C)
0	213.1	142
14	211.4	143
28	206.7	150
40	203.0	149
50	200.6	147.5
70	196.3	151.0
81	194.1	156.0
90	192.6	149.5
105	190.3	149.5
120	188.4	152
135	186.6	149
154	184.4	151
174	182.9	152
200	181.3	150
210	180.9	153
240	179.6	150
258	179.0	155
270	178.8	153
300	178.8	153

	Weight (gram)
Beaker & copper wire	141.5
Beaker & copper wire & Manure (24.4% moisture content)	191.0
Water added	22.1
Weight when dry	178.8

·Table 1 (Cont.)

Run 5, Average Temperature 156.5^{o}C

Drying Time (min)	Weight (gram)	Temperature (^{o}C)
0	241.4	148
20	239.3	162
35	235.4	142
50	228.4	153
60	223.3	152
75	217.1	150
98	206.2	158
105	203.7	154
120	198.0	152
135	193.5	157
150	189.5	154
165	185.5	152.5
180	182.5	156
195	180	155
205	178.5	156
210	177.5	159
225	176.0	159
240	174.0	160
257	171.7	156
270	170.7	162
285	169.6	159
301	168.9	159
316	168.4	156
330	168.4	152

	Weight (gram)
Beaker & copper wire	141.7
Beaker & copper wire & Manure (24.4% moisture content)	174.4
Water added	67.0
Weight when dry	168.4

Table 1 (Cont.)

Run 7, Average Temperature 180.3^{o}C

Drying Time (min)	Weight (gram)	Temperature (^{o}C)
0	212.3	180
10	211.0	182.5
20	205.2	182.0
30	199.9	182.5
40	194.7	178.0
50	190.7	181.5
60	187.1	179.0
70	184.1	178.5
80	181.5	178.5
90	179.3	180.0
100	177.3	180
110	176.4	181
120	174.6	179.5
130	173.4	181.5
140	172.5	182.0
150	171.8	181.0
160	171.3	178.0

Manure started to burn.

Weight of beaker & copper wire (empty)	140.5g
Weight of beaker & copper wire & Manure (30g) (dry)	173.6g
Volume of Manure (dry)	80 ml
Depth (cm) in beaker	1.8 cm
Diameter (cm) in beaker	7.5 cm
Weight of beaker & copper wire & Manure + H_2O (30g)	212.3g
Volume of Manure after adding H_2O	100 ml
Depth (cm) in beaker	2.8 cm
Diamater (cm) in beaker	7.5 cm

Table 1 (Cont.)

Run 10

Temperature	100°C	(Second Series of Isothermal Drying Tests)
% Moisture	35.37%	
Inches of Vacuum	0	

Time in Run (min)	Weight (g)
0	318.1
30	317.8
60	317.7
90	317.4
120	317.2
150	317.0
180	316.8
210	316.5
240	316.4
270	316.3
300	316.0
330	315.8
360	315.6
4680	300.8

Empty Bottle	199.6g
Empty Bottle & Manure	248.5g
Entire System	318.1g
Manure	48.9g
Water Removed	17.3g

(Note:

Diameter of jar used	5.5 cm
Approx. height of manure	5.5 cm

for each run)

Run 11

Temperature	130°C
% Moisture	41.9%
Inches of Vacuum	0

Time in Run (min)	Weight (g)
0	317.5
30	315.3
60	312.7
90	309.5
120	308.5
150	306.5
180	305.3
210	304.3
240	303.3
270	302.6
320	301.6
390	299.8
1110	296.7

Empty Bottle	199.3g
Empty Bottle & Manure	248.9g
Entire System	317.5g
Manure	49.6g
Water Removed	20.8

Volatiles in Manure at Various Temperatures

A sample of the manure currently used in our pilot plant was subjected to pyrolysis at increasing temperatures.

T	Volatiles	Amount Removed, %*
$500^{\circ}C$	37.18 wt %	85. 3
600	41.03	94.1
700	41.03	94.1
800	42.31	97.1
1000	43.59	100.0

Based upon this data, $600^{\circ}C$ appears to be high enough for fairly complete volatiles removal in pyrolysis. Higher temperatures, however, will give slightly higher yields and promote the water gas reaction.

*based upon $1000^{\circ}C$

VACUUM DRYING

The purpose of the first experiments was to measure the heat transfer coefficients for the screw feeder. No vacuum was applied to the inner chamber, and the moisture content of the product was not measured (it was very small). Steam at one atmosphere pressure was condensed in the jacket. The holdup volume and the condensate flow rate were measured. The inlet and outlet solids temperatures were also measured, along with the solids flow rate and moisture content. The rotation rate of the screw was varied to provide the experimental data given in Table 2. Laboratory vacuum drying runs were next made, and are shown in Table 3.

Table 2

Screw Feeder as a Heat Exchanger

Experimental

Run No.	Feed Moisture, Wt %	Speed, ω RPM	Feed Rate, gm/hr	Product Temp., °C	Ambient Temp., °C	Holdup, gm	Steam Pressure, mm Hg abs.	Condensate Flow Rate, gm/hr	
12-09-A	37.34	1	2724	77.	7.	1168	774	608	
12-09-B	37.34	2	4848	81.5	11.5	1210	774	592	
12-09-C	37.34	3	7376	76.	12.	1152	765	592	
12-09-D	37.34	0			12.		793	336	To determine heat loss.
12-12-A	50.0	1	1610	69.	10.	1351	780	560	Prod. temp. (69°) in doub·
12-12-B	50.0	2	3742·	77.	12.	1713	777	592	
12-12-C	50.0	3	4504	75.	13.	1132	776	576	50 wt% manure is tacky.

Calculated

Run No.	Steam Temp., °C	Residence Time, τ_R min	Heat Transf. Rate, cal/min	$(\Delta T)_{lm}$, °C	UA, cal/min°C	U, cal/min cm^2°C	$\frac{U \cdot \sqrt{\pi \alpha \tau_R}}{k}$ Dimensionless	$\frac{\omega \tau_R}{N}$ Dimensionless
12-09-A	100.5	25.73	1744	50.69	34.41	$1.007(10^{-2})$	1.225	2.57
12-09-B	100.5	14.98	3104	45.33	68.47	2.003	1.859	3.00
12-09-C	100.2	9.37	4318	49.49	87.25	2.553	1.874	2.81
12-09-D	101.2							
12-12-A	100.7	50.35	1058	56.12	18.85	0.552	0.501	5.04
12-12-B	100.6	27.47	2708	49.14	55.11	1.612	1.080	5.49
12-12-C	100.6	15.08	3109	50.40	61.69	1.805	0.896	4.52

$A = 3418$ cm^2. N = 10 threads.

Manure Properties[1]:

37.34 wt % moisture

$\rho = 32.30$ lbs/ft^3 bulk

$C_p = 0.5488$ BTU/lb°F

$k = .0774$ BTU/hr ft°F $= 1.922(10^{-2})$cal/min cm°C

$\alpha = 6.761(10^{-2})$cm^2/min

50.0 wt % moisture

$\rho = 44.62$ lbs/ft^3 bulk

$C_p = 0.6681$ BTU/lb°F

$k = .1619$ BTU/hr ft°F $= 4.021(10^{-2})$ cal/min cm °C

$\alpha = 8.409(10^{-2})$ cm^2/min

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(1) Houkom, Butchbaker, Brusewitz, "Effect of Moisture Content on Thermal Diffusivity of Beef Manure," Trans. ASAE, -, - (1974), pp. 973-977.

Table 3

Isothermal Vacuum Drying of Manure in the Laboratory Oven

Temperature   130°C
% Moisture   37.0%
Inches of Vacuum   15

Time in Run (min)	Weight (g)	Time in Run (min)	Weight (g)
0	351.5	165	338.6
30	348.8	180	338.1
45	347.0	195	337.5
60	344.7	210	337.5
75	343.7	225	
90	343.2	240	337.0
105	342.2	300	336.0
120	341.1	360	335.0
135	340.0	1080	333.0
150	339.1		

Empty Bottle	199.5g
Empty Bottle & Manure	249.5g
Entire System	351.5g
Manure	50.0g
Water Removed	18.5g

Temperature   100°C
% Moisture   38.0%
Inches of Vacuum   15

Time in Run (min)	Weight (g)	Time in Run (min)	Weight (g)
0	350.5	210	345.4
30	350.5	270	344.6
60	349.6	330	344.4
90	349.0	420	342.5
120	347.4	480	341.5
150	346.3	1200	341.0
180	345.6		

Empty Bottle	199.5g
Empty Bottle & Manure	249.5g
Entire System	350.5g
Manure	50.0g
Water Removed	19.0g

DIRECT CONTACT DRYING

In the first set of pilot plant experiments (Table 4) runs 10-21-A through 10-28-B, the residence times were quite snort, so the rabble tooth angle was reduced. This increased the residence times, but it also resulted in wide bands of manure between the teeth (Runs 11-03-E, through 11-03-E$_3$). The holdup could not be measured except by increasing the rabble tooth angle, so new rabble teeth and arms were fabricated. The teeth were 3 in. wide and could be spaced 1 in. apart on the arms. For the first operation they were spaced 2 in. apart alternately, i.e. 1, 3, 5, 7 on one arm and 2, 4, 6, 8 on the other (Runs 12-13 through 12-14-B). For run 12-13, the manure residence time was nearly 30 min. When the teeth were spaced 1 in. apart, the holdup was the same for all rabble tooth angles. The clearances in this case were so small that the manure and rabble teeth clung together as a solid body.

On the derived data sheet, Table 5, Q is based on the solids inlet and outlet temperatures and moisture contents. This is "delivered" heat, unaffected by the heat losses. The log mean ΔT used was:

$$(\Delta T)_{lm} = \frac{\{(T_G)_i - (T_S)_o\} - \{(T_G)_o - (T_S)_i\}}{\ln \dfrac{(T_G)_i - (T_S)_o}{(T_G)_o - (T_S)_i}}$$

Note that, while expedient, the use of this $(\Delta T)_{lm}$ is incorrect because the solids and gas flow are not countercurrent. However, using this $(\Delta T)_{lm}$, UA was calculated for each run. If (UA) were based on a correct $(\Delta T)_{lm}$, then it ought to depend only on the gas velocity, i.e. it should be the same for all the runs. For these particular experiments where the gas holes in the base-

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Table 4

Direct Contact Drying - Experimental Data

Run No.	Product Flow Rate, gm/hr	Product Moisture, wt. fract.	Feed Moisture, wt. fract.	Holdup, gm	Holdup Moisture, wt. fract.	Gas Flow, SCFM	Inlet Flue Gas Dry Bulb Temp., °C	Inlet Flue Gas Humidity, gm H$_2$O/ gm dry gas	Jacket Temp., °C	Ambient Temp., °C	Outlet Flue Gas Dry Bulb, °C	Outlet Flue Gas Wet Bulb, °C
10-21-A	3500	.192	.385	255	.190	12.2	207	.039	103	20	93	52.5
10-21-B	3785	.252	.385	325	.236	12.2	149	.026	75.8	23	69	47
10-25-A	3505	.221	.385	182	.191	12.2	198	.049	94	25	86.9	51.5
10-25-B	4012	.253	.385	222	.253	12.2	151	.030	78.3	29	71.2	47.5
10-26-A	3969	.243	.385	106	.216	12.2	198.6	.058	88.6	19	83.8	51
10-26-B	4086	.279	.385	105	.264	12.2	149.8	.030	81.2	23	74	47
10-27-A	3796	.247	.373	68	.234	12.2	199.4	.054	89.2	15.5	83	51
10-27-B	4185	.269	.373	57	.281	12.2	151.3	.026	76.4	19	70.5	46
10-28-A	7376	.239	.334	973	.247	12.2	200.4	.041	80	21	73.4	51
10-28-B	10150	.282	.334	1120	.255	12.2	152	.025	71	24	60.6	45
11-01-A	10200	.3139	.3735	98	.3228	12.2	201	.044	93	21.5	79.4	51.0
11-01-B	10458	.3611	.3735	147	.3454	12.2	148	.024	76	24.5	67.4	45.0
11-02-B	10266	.3376	.3735	387	.3344	12.2	151	.030	66	19.0	59.3	44.5
11-03-E$_1$	9572	.3433	.3530	(1294)	.2948	12.2	200	.044	81	24.0	69.2	50.5
11-03-E$_2$	10135	.2728	.3530	(605)	.2665	12.2	199.5	.049	90	28.5	76.4	51.5
11-03-E$_3$	8959	.2380	.3540	(1842)	.289	12.2	201.8	.0535	84	18.0	68.4	52.0
12-13	3331	.2804	.384	1390	.1998	12.2	144	.025	55	14	75	48
12-14-A	6895	.3364	.384	2055	.2933	12.2	148	.0325	55	17	59	45.5
12-14-B	7382	.3526	.384	750	.2148	12.2	150	.025	55	19	67	46

In Runs 10-21-A through 11-02-B, the holdup measurements are at best estimates, because some manure between the rabble teeth could not be swept out, nor could some manure between the rabble reeth and the warped baseplate. In Runs 11-03-E through 11-03-E$_3$, the holdups were measured correctly, but after the series of experiments was completed. In Runs 12-13 through 12-14-B, holdup was measured correctly. The inlet flue gas was measured by weighing the moisture absorbed from a measured volume of gas. In Runs 10-21-A through 11-03-E$_3$, the two rabble arms were identical. In Runs 12-13 through 12-14-B, the rabble teeth were staggered--1, 3, 5, 7 on one arm and 2, 4, 6, 8 on the other.

Table 4

Buildup moisture, fract.	Gas Flow, SCFM	Inlet Flue Gas Dry Bulb Temp., °C	Inlet Flue Gas Humidity, gm H₂O/ gm dry gas	Jacket Temp., °C	Ambient Temp., °C	Outlet Flue Gas Dry Bulb, °C	Outlet Flue Gas Wet Bulb, °C	Product Temp., °C	Rabble Tooth Angle, degrees	Rabble Tooth Spacing, inches	Rabble Tooth Width, inches	Shaft Rotation Rate, RPM	Contacts Per Minute, CPM
190	12.2	207	.039	103	20	93	52.5	63	45	2.125	2.0	2	4
236	12.2	149	.026	75.8	23	69	47	51	45	2.125	2.0	2	4
191	12.2	198	.049	94	25	86.9	51.5	63	45	2.125	2.0	3	6
253	12.2	151	.030	78.3	29	71.2	47.5	56	45	2.125	2.0	3	6
216	12.2	198.6	.058	88.6	19	83.8	51	56	45	2.125	2.0	5	10
264	12.2	149.8	.030	81.2	23	74	47	51	45	2.125	2.0	5	10
234	12.2	199.4	.054	89.2	15.5	83	51	53	45	2.125	2.0	12	24
281	12.2	151.3	.026	76.4	19	70.5	46	50	45	2.125	2.0	12	24
247	12.2	200.4	.041	80	21	73.4	51	56	45	2.125	2.0	2	4
255	12.2	152	.025	71	24	60.6	45	48	45	2.125	2.0	2	4
3228	12.2	201	.044	93	21.5	79.4	51.0	57.7	45	2.125	2.0	12	24
3454	12.2	148	.024	76	24.5	67.4	45.0	50.7	45	2.125	2.0	12	24
3344	12.2	151	.030	66	19.0	59.3	44.5	47.3	45	2.125	2.0	5	10
2948	12.2	200	.044	81	24.0	69.2	50.5	55.0	11.25	2.125	2.0	12	24
2665	12.2	199.5	.049	90	28.5	76.4	51.5	56.5	22.5	2.125	2.0	12	24
289	12.2	201.8	.0535	84	18.0	68.4	52.0	58.0	5	2.125	2.0	12	24
1998	12.2	144	.025	55	14	75	48	47	5	1.000	3.0	1	1
2933	12.2	148	.0325	55	17	59	45.5	47	5	1.000	3.0	1	1
2148	12.2	150	.025	55	19	67	46	46	5	1.000	3.0	5	5

ts are at best estimates, because some manure between the rabble
tween the rabble reeth and the warped baseplate. In Runs 11-03-E
but after the series of experiments was completed. In Runs 12-13
nlet flue gas was measured by weighing the moisture absorbed from a
-E₃, the two rabble arms were identical. In Runs 12-13 through
n one arm and 2, 4, 6, 8 on the other.

Table 5

Direct Contact Drying – Derived Data

Run No.	Outlet Gas Humidity, gm H_2O/gm dry gas	Dry Solids Flow Rate, gm/min	Solids Residence Time, τ_R min	Solids Temp., In °C	Solids Temp., Out °C	Solids Moisture In, gm/gm	Solids Moisture Out, gm/gm	ΔT_S °C	ΔM_S gm/gm	λ_S cal/gm	q Heat Flow, cal/min
10-21-A	.077	58.33	3.541	20	63	.6260	.2376	43	.3884	561.1	15,661
10-21-B	.059	63.08	3.936	23	51	.6260	.3369	28	.2891	567.8	12,432
10-25-A	.076	58.42	2.520	25	63	.6260	.2837	38	.3423	561.1	12,087
10-25-B	.062	66.87	2.480	29	56	.6260	.3387	27	.2873	565.1	12,980
10-26-A	.073	66.15	1.256	19	56	.6260	.3210	37	.3050	565.1	14,280
10-26-B	.058	68.10	1.135	23	51	.6260	.3870	28	.2390	567.8	11,484
10-27-A	.075	63.27	0.823	15.5	53	.5949	.3280	37.5	.2669	566.8	12,288
10-27-B	.057	69.75	0.588	19	50	.5949	.3680	31	.2269	568.4	11,469
10-28-A	.079	122.93	5.960	21	56	.5015	.3141	35	.1874	565.1	17,543
10-28-B	.056	169.17	4.932	24	48	.5015	.3928	24	.1087	569.6	14,743
11-01-A	.077	170.0	0.390	21.5	57.7	.5962	.4575	36.2	.1387	564.1	20,354
11-01-B	.054	174.3	0.552	24.5	50.7	.5962	.5652	26.2	.0310	568.0	8,303
11-02-B	.054	171.1	1.505	19.0	47.3	.5962	.5097	28.3	.0865	570.1	13,987
11-03-E$_1$	.079	159.5	13.650	24.0	55.0	.5456	.5228	31.0	.0228	565.6	7,474
11-03-E$_2$	.080	168.9	6.436	28.5	56.5	.5456	.3751	28.0	.1705	564.8	21,447
11-03-E$_3$	.088	149.3	18.844	18.0	58.0	.5480	.3123	40.0	.2357	563.9	26,401
12-13	.063	39.95	27.842	14	47	.6234	.3897	33	.2337	570.2	6,870
12-14-A	.061	76.26	19.044	17	47	.6234	.5069	30	.1165	570.2	7,750
12-14-B	.060	79.65	7.394	19	46	.6234	.5446	27	.0788	570.8	6,106

$A = 2498 \text{ cm}^2$

$(C_P)_S = 0.55$ cal/gm °C

$\frac{\sqrt{\pi\alpha}}{k} = 23.98$

$\alpha = 6.761(10^{-2})$ cm^2/min

$k = 1.922(10^{-2})$ cal/min cm °C

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Table 5 (Cont.)

Gas Temp. In, ^{o}C	Gas Temp. Out, ^{o}C	(CPM) $(min)^{-1}$	(CPM)τ_R --	Tooth Angle, degrees	A Tooth Width, inches	S Tooth Spacing, inches	Holdup Volume, cm^3	$\bar{\delta}$ Mean Thickness, cm	ΔT_1 ^{o}C	ΔT_2 ^{o}C
207	93	4	17.48	45	2	2.125	638	0.255	144	73
149	69	4	20.61	45	2	2.125	813	0.325	98	46
198	86.9	6	18.70	45	2	2.125	455	0.182	135	61.9
151	71.2	6	19.92	45	2	2.125	. 555	0.222	95	42.2
198.6	83.8	10	16.02	45	2	2.125	265	0.106	142.6	64.8
149.8	74	10	15.42	45	2	2.125	263	0.105	98.8	51.0
199.4	83	24	25.80	45	2	2.125	170	0.068	146.4	67.5
151.3	70.5	24	19.61	45	2	2.125	143	0.057	101.3	51.5
200.4	73.4	4	31.66	45	2	2.125	2433	0.974	144.4	52.4
152	60.6	4	26.48	45	2	2.125	2800	1.121	104	36.6
201	79.4	24	13.82	45	2	2 125	228	0.091	143.3	57.9
148	67.4	24	20.23	45	2	2.125	342	0.137	97.3	42.9
151	59.3	10	22.62	45	2	2.125	900	0.360	103.7	40.3
200	69.2	24	327.6	11.25	2	2.125	3009	1.205	145.0	45.2
199.5	76.4	24	154.6	22.5	2	2.125	1407	0.563	143.0	47.9
201.8	68.4	24	452.2	5	2	2.125	4284	1.715	143.8	50.4
144	75	1	27.83	5	3	1.000	3475	1.391	97.0	61.0
148	59	1	19.04	5	3	1.000	5138	2.057	101.0	42.0
150	67	5	36.95	5	3	1.000	1875	0.751	104.0	48.0

(Cont.)

S Tooth Spacing, inches	Holdup Volume, cm^3	$\bar{\delta}$ Mean Thickness, cm	ΔT_1 °C	ΔT_2 °C	$(\Delta T)_{\ell m}$ °C	UA, cal/min °C	$\dfrac{U\bar{\delta}}{k}$ --	$\dfrac{\sqrt{\pi\alpha\tau}_R}{\bar{\delta}}$ --	$\dfrac{U\cdot\sqrt{\pi\alpha\tau}_R}{k}$ --
2.125	638	0.255	144	73	104.51	149.85	0.796	3.401	2.707
2.125	813	0.325	98	46	68.75	180.83	1.224	2.813	3.443
2.125	455	0.182	135	61.9	93.75	128.93	0.489	4.020	1.966
2.125	555	0.222	95	42.2	65.07	199.48	0.922	3.269	3.014
2.125	265	0.106	142.6	64.8	98.64	144.77	0.320	4.873	1.559
2.125	263	0.105	98.8	51.0	72.28	158.88	0.347	4.676	1.623
2.125	170	0.068	146.4	67.5	101.91	120.58	0.171	6.149	1.051
2.125	143	0.057	101.3	51.5	90.83	126.27	0.150	6.200	0.930
2.125	2433	0.974	144.4	52.4	90.76	193.29	3.921	1.155	4.529
2.125	2800	1.121	104	36.6	64.54	228.43	5.334	0.913	4.870
2 125	228	0.091	143.3	57.9	94.24	215.98	0.409	3.163	1.294
2.125	342	0.137	97.3	42.9	66.43	124.99	0.357	2.499	0.892
2.125	900	0.360	103.7	40.3	67.08	208.51	1.563	1.571	2.455
2.125	3009	1.205	145.0	45.2	85.62	87.29	2.191	1.413	3.096
2.125	1407	0.563	143.0	47.9	86.95	246.66	2.892	2.077	6.007
2.125	4284	1.715	143.8	50.4	89.09	296.34	10.585	1.167	12.353
1.000	3475	1.391	97.0	61.0	77.61	88.52	2.565	1.748	4.484
1.000	5138	2.057	101.0	42.0	67.24	115.26	4.938	0.978	4.829
1.000	1875	0.751	104.0	48.0	72.43	84.30	1.319	1.669	2.201

plate are spaced so far apart, increasing the solids flow rate should cause (UA) to increase.

A preliminary mass and heat balance for a few of the runs gives the following data:

Run	Evaporation Rate		Enthalpy Transfer Rate	
	From Solids	To Gas	To Solids	From Gas
	gm/min	gm/min	cal/min	cal/min
12-13	9.34	16.99	1144	-2631
12-14-A	8.88	12.74	2330	2198
12-14-B	6.28	15.65	2294	- 84

Drying of Manure in a Fixed Bed With Hot Gas

Two sets of experiments were next made on fixed-bed drying. The first are described in Table 6, and the second set in Table 7. The latter were similar except that the apparatus was thermally insulated and the outlet gas temperature, the inlet gas temperature, and the solids temperature were measured as functions of time.

Table 6

Direct Contact Drying of Manure in a Fixed Bed

Gas Temp. °C	Gas Flow SCFM	Sample Mass gm	Sample Moisture wt. fract.	Bed Temp. °C	Weight Loss gm/min	Rate $(min)^{-1}$	Rate Eqn. (2) $(min)^{-1}$
100	.5325	140.1	.385	30	4.2/10	.00811	
98	.5325	140.4	.385	30	4.1/10	.00789	
101	.5325	140.2	.385	30	8.3/20	.00812	
				Avg. 30		Avg. .00812	.00975
152	.5325	140.2	.385	34	5.7/10	.01116	
154	.5325	139.9	.385	35	6.3/10	.01244	
148	.5325	140.1	.385	34	12.4/20	.01306	
				Avg. 34.67		Avg. .01222	.01047
98	.7738	139.4	.380	29	5.0/10	.00991	
98	.7738	139.9	.380	29	5.3/10	.01050	
101	.7738	139.9	.380	30	11.6/20	.01231	
				Avg. 29.67		Avg. .01091	.01311

The bed was 13.6 cm diam. x 3 cm deep. Hot flue gas was blown through it at about the same mass flux as in the pilot plant. Oven drying is controlled by moisture diffusion, and the coefficient, $\exp\left(-\frac{B}{T}\right)$ is associated with the moisture diffusivity.[2] When drying is accomplished by blowing hot gas through the bed, however, the heat and moisture are transferred by the turbulent action of the gas. In this case the drying rate should depend on $D_v^{0.56}$[3] and on $V^{0.8}$. First note that 0.56(2474) = 1385 and that: $\frac{.01091}{.00812} = \left(\frac{.7738}{.5325}\right)^n$ n = .7903, which is close to the anticipated 0.8. Consequently a relationship can be established:

$$\frac{\partial \ln M}{\partial \tau} = -1.27 \left(\frac{V}{150.8}\right)^{0.8} \exp\left(-\frac{1385}{T_S}\right) \quad (min)^{-1} \tag{1}$$

where V is gas velocity, cm/min. It represents this data to within about 20%.

[2] Reid, Prausnitz, Sherwood, The Properties of Gases and Liquids, McGraw-Hill, New York (1977), p. 587.

[3] Brown, Unit Operations, John Wiley & Sons, New York (1950), p. 519

Table 7

Fixed Bed Direct Contact Drying of Manure

Sample Weight	Sample Moisture	Gas Flow	Bed Depth	Bed Diam.
139.4 gm	48.0 wt %	.7738 SCFM	3.0 cm	13.6 cm

τ	$(T_G)_i$	T_G	T_S
0	-	-	-
1 min	97°C	36°C	34°C
2	97	34	33
3	97	33	32
4	96	32	32
5	96	32	32
6	97	32	32
7	97	32	32
8	97	32	32
9	98	32	32
10	99	32	32

Evap. 5.4 gm H_2O/10 min

Sample Weight	Sample Moisture	Gas Flow	Bed Depth	Bed Diam.
139.7 gm	48.0 wt %	.7738 SCFM	3.0 cm	13.6 cm

τ	$(T_G)_i$	T_G	T_S
0	-	-	-
1 min	104°C	22°C	30°C
2	103	26	33
3	102	29	34
4	101	31	33
5	100	31.5	33
6	100	32	33
7	99	32	32.5
8	98.5	32	32
9	98	32	32
10	98	32	32

Evap. 8.3 gm H_2O/10 min

Table 7 (Cont.)

Sample Weight 137.9 gm	Sample Moisture 48.0 wt %	Gas Flow .7738 SCFM	Bed Depth 3.0 cm	Bed Diam. 13.6 cm
τ	$(T_G)_i$	T_G	T_S	
0	–	–	–	
1 min	–	–	–	
2	–	–	–	
3	103°C	29°C	33°C	
4	103	30	32	
5	103	31	32	
6	102.5	32	32	
7	102.5	32	32	
8	102.5	32	32	
9	102.5	32	32	
10	102.5	32	32	
Evap.	6.1 gm H_2O/10 min			

Sample Weight 140.4 gm	Sample Moisture 48.0 wt %	Gas Flow .7738 SCFM	Bed Depth 3.0 cm	Bed Diam. 13.6 cm
τ	$(T_G)_i$	T_G	T_S	
0	–	–	–	
1 min	100°C	23°C	28°C	
2	100	24	31	
3	100	26	32	
4	100	28	32	
5	100	29	32	
6	100	30	32	
7	100	30	32	
8	99	31	32	
9	99	31	32	
10	99	32	32	
11	99	32	32	
12	98.5	32	32	
13	98	32	32	
14	98	32	32	
15	98	32	33	
16	98	32	33	
17	98	32	33	
18	97.5	32.5	34	
19	97.5	32.5	34	
20	97.5	33	34	
Evap.	13.4 gm H_2O/20 min			

Table 7 (Cont.)

Sample Weight 208.9 gm · Sample Moisture 48.0 wt % · Gas Flow .8913 SCFM · Bed Depth 4.0 cm · Bed Diam. 13.6 cm

τ	$(T_G)_i$	T_G	T_S
0	-		
1 min	103°C	24°C	27°C
2			
3	104	24	32
4			
5	104	28	33
6	103	30.5	33
7	102	32	33
8			
9	102	32	33
10	102	32	33
11			
12	100	32	33
13	99	32	33
14	98.5	32	32
15	97.5	32	32
16			
17	97	32	32
18			
19	96	32	32
20			

Evap. 15.2 gm H_2O/20 min

Sample Weight 209.0 gm · Sample Moisture 48.0 wt % · Gas Flow .8913 SCFM · Bed Depth 3.8 cm · Bed Diam. 13.6 cm

τ	$(T_G)_i$	T_G	T_S
0	-	-	-
1 min	100°C	21°C	28°C
2	100	23	33
3	100	26	34
4	99	29	34
5	99	31	34
6			
7	98	32	33
8			
9	98	32	33
10	97	32	33
11	97	32	33
12			
13	97	32	33
14	97	32	33
15	97	32	33
16	97	32	33
17	97	32	33
18	97	32	33
19	97	32	33
20			

Evap. 16.3 gm H_2O/20 min

Table 7 (Cont.)

Sample Weight	Sample Moisture	Gas Flow	Bed Depth	Bed Diam.
146.9 gm	48.0 wt %	.8913 SCFM	2.6 cm	13.6 cm

τ	$(T_G)_i$	T_G	T_S
0	-	-	-
1 min	104^oC	30^oC	36^oC
2	104	32	36
3	104	32	37
4	104	32	38
5	103	32	36
6	103	32	34
7	103	32	34
8	103	32	34
9	104	32	34
10			
11	103	32	33
12			
13	103	32	33
14			
15			
16			
17	101	32	33
18	101	32	33
19	101	32	33
20			

Evap. 19.8 gm H_2O/20 min

Sample Weight	Sample Moisture	Gas Flow	Bed Depth	Bed Diam.
69.7 gm	48.0 wt %	.8910 SCFM	-	13.6 cm

τ	$(T_G)_i$	T_G	T_S
0	-	-	-
1 min	148^oC	30^oC	39^oC
2	148	36	41
3			
4	148.5	37	49
5	148	37	53
6	148	37	59
7			
8	148	37	64
9	148	37	67
10	148	37	73

Evap. 8.0 gm H_2O/10 min

Table 7 (Cont.)

Sample Weight 69.5 gm	Sample Moisture 48.0 wt %	Gas Flow .8910 SCFM	Bed Depth 1.5 cm	Bed Diam. 13.6 cm
τ	$(T_G)_i$	T_G	T_S	
0	-	-	-	
1 min	153^0C	34^0C	42^0C	
2	152	37	44	
3	152	37	49	
4				
5	151	38	59	
6	150	38	58	
7				
8				
9	150	38	75	
10	149	38	73	
11				
12	149	38	84	
13				
14	149	38	89	
15				
16	149	38	94	
17				
18	149	38	96	
19				
20	148	40	98	

Evap.   22.2 gm H_2O/20 min

Sample Weight 70.0 gm	Sample Moisture 48.0 wt %	Gas Flow .8910 SCFM	Bed Depth 1.3 cm	Bed Diam. 13.6 cm
τ	$(T_G)_i$	T_G	T_S	
0	-	-	-	
1 min	155^0C	32^0C	41^0C	
2	155	37	43	
3				
4	155	37	45	
5	154	37	45	
6	154	37	53	
7				
8				
9				
10				
11				
12				
13				
14	151	38	80	
15				
16	151	38	88	
17				
18	150	39	94	
19				
20	150	39	97	

Evap. 23.0 gm H_2O/20 min

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PYROLYSIS EXPERIMENTS

In the first experiments manure samples of different moisture
contents were pyrolyzed at about 650°C. A similar set of experiments
were later made over a wide temperature range. All of the data is shown
in Table 8 for manure and Table 9 for sawdust. "Product char" is
defined as the char caught in the receiver. "Dynamic holdup" is the
remaining char that can be swept out of the reactor by the rabble teeth.
"Static holdup" is the remainder of the remaining char. The static
holdup is quite large, mostly because of the reactor geometry. In the
PDU, the static holdup should be small compared to the dynamic holdup.
Since these pyrolysis experiments lasted only about one solids residence
time, the dynamic and static holdups are essential to the material balance.

The pyrolysis gas first passed through a condenser, and then through
an automobile air filter. This removed most of the tarry aerosol. Then
the gas flowed into a closed container filled with water. When the water
pressure rose to 1 cm H_2O, a solenoid valve was tripped and some of the
water in the bottle was allowed to escape. The gas pressure thus is limited
to 1 cm H_2O. At the end of the run, the volume of the displaced liquid was
measured.

The solids temperature was measured directly by a thermocouple
attached to a rabble tooth. The junction of the thermocouple was mounted
on the front side of the rabble tooth about 1/4 in. above the reactor
floor. There were three thermocouples in the reactor: (1) one was located
on the outermost rabble tooth where the char falls from the reactor,
(2) a second one was located on the innermost rabble tooth, just inside

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Table 8

Run 4-5-78 Pyrolysis of Manure T_S = 495°C, T_G = 459°C, τ_R = 15.10 min.

Feed 3025 g/47 min   Receiver Char 512 g

	Wt. Fract.		Wt. Fract.
Moisture	.3323	Moisture	.0824
Volatile (750°C)	.3107	Volatile (750°C)	.1569
Carbon (750°C)	.0643	Carbon (750°C)	.1421
Ash	.2927	Ash	.6186
	1.0000		1.0000

Dynamic Holdup 399 g   Static Holdup 275 g

	Wt. Fract.		Wt. Fract.
Moisture	--	Moisture	--
Volatile (750°C)	.0913	Volatile (750°C)	.0983
Carbon (750°C)	.1959	Carbon (750°C)	.1341
Ash	.7128	Ash	.7676
	1.0000		1.0000

Condensate 576 g

Gas 1263 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.3596		12.255	
CO_2	.2287	.3571	19.049	.789
CO	.0911	.1423	4.830	.200
H_2	.2565	.4005	.971	.040
CH_4	.0605	.0945	1.832	.076
C_2H_4	.0036	.0056	.191	.008
C_2H_6	--	--	--	--
	1.0000	1.0000	26.873 dry	1.113
	wet	dry	1263.0 g/47 min	

Overall ash balance closure   91.7%

Volatiles (750°C) removed   84.7%

H_2O/C (750°C)   3.382 mol/mol

Carbon (750°C) gasified   3.5%

Gas flow by difference.
Temperature falling rapidly.

Pyrolysis gas heating value (low)   246.0 BTU/SCF
(including CO_2 but not H_2O)

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Table 8 (Cont.)

Run 5-15-78 Pyrolysis of Manure $T_S = 522^{\circ}C$, $T_G = 411^{\circ}C$, $\tau_R = 18.35$ min.

<u>Feed</u> 6806 g/90 min   <u>Receiver Char</u> 1054 g

	Wt. Fract.			Wt. Fract.
Moisture	.3215	Moisture	--	
Volatile ($750^{\circ}C$)	.2946	Volatile ($750^{\circ}C$)	.1244	
Carbon ($750^{\circ}C$)	.0995	Carbon ($750^{\circ}C$)	.2033	
Ash	.2844	Ash	.6723	
	1.0000		1.0000	

<u>Dynamic Holdup</u> 552 g   <u>Static Holdup</u> 1182 g

	Wt. Fract.			Wt. Fract.
Moisture	--	Moisture	--	
Volatile ($750^{\circ}C$)	.0995	Volatile ($750^{\circ}C$)	.0664	
Carbon ($750^{\circ}C$)	.1854	Carbon ($750^{\circ}C$)	.1428	
Ash	.7151	Ash	.7908	
	1.0000		1.0000	

Condensate 1492 g

<u>Gas</u> 2526 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.3958		16.578	
CO_2	.1982	.3281	20.296	.681
CO	.0787	.1303	5.130	.172
H_2	.2929	.4848	1.363	.046
CH_4	.0343	.0568	1.278	.043
C_2H_4	--	--	--	--
C_2H_6	--	--	--	--
	.9999	1.0000	28.067 dry	.942
	wet	dry	2526 g/90 min	

Overall ash balance closure   105.3%

Volatile ($750^{\circ}C$) removed   86.8%

H_2O/C ($750^{\circ}C$)   2.556

Carbon ($750^{\circ}C$) gasified   28.3%

                                              Gas flow by difference

Pyrolysis gas heating value (low)   222.7 BTU/SCF
(including CO_2 but not H_2O)

26

Table 8 (Cont.)

Run 4-4-78 Pyrolysis of Manure $T_S = 580^{\circ}C$, $T_G = 469^{\circ}C$, $\tau_R = 18.90$ min.

<u>Feed</u> 4041 g/60 min

<u>Reciever Char</u> 708 g

	Wt. Fract.		Wt. Fract.
Moisture	.3149	Moisture	.0744
Volatile ($750^{\circ}C$)	.3143	Volatile ($750^{\circ}C$)	.1613
Carbon ($750^{\circ}C$)	.0954	Carbon ($750^{\circ}C$)	.1143
Ash	.2753	Ash	.6500
	.9999		1.0000

<u>Dynamic Holdup</u> 520 g

<u>Static Holdup</u> 272 g

	Wt. Fract.		Wt. Fract.
Moisture	--	Moisture	.0060
Volatile ($750^{\circ}C$)	.1265	Volatile ($750^{\circ}C$)	.1174
Carbon ($750^{\circ}C$)	.1995	Carbon ($750^{\circ}C$)	.1596
Ash	.6740	Ash	.7170
	1.0000		1.0000

Condensate 1289 g

<u>Gas</u> 746 g

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.6881		21.483	
CO_2	.1176	.3768	8.972	.325
CO	.0400	.1283	1.944	.070
H_2	.1179	.3782	.409	.015
CH_4	.0320	.1026	.888	.032
C_2H_4	.0044	.0141	.214	.008
C_2H_6	--	--	--	--
	1.0000	1.0000	12.427 dry	.450
	wet	dry	745.6 g/60 min	

Overall mass balance closure	87.5%
Overall ash balance closure	90.4%

Poor closure. Omit.

Volatiles ($750^{\circ}C$) removed	83.3%
H_2O/C ($750^{\circ}C$)	2.611
Carbon ($750^{\circ}C$) gasified	40.8%

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Table 8 (Cont.)

Pyrolysis of Manure: Pilot Plant Data

Run 4-4-78 $\qquad$ $T_S = 591^{\circ}C$, $T_G = 472^{\circ}C$, $\tau_R = 49.4$ min.

Temperatures falling.

Feed 4041 gm/60 min

Moisture	.3149	wt. fract.
Volatile ($750^{\circ}C$)	.3143	
Carbon ($750^{\circ}C$)	.0955	
Ash	.2753	
	1.0000	wt. fract.

	Receiver Char 708g		Dynamic Holdup 520g	Static Holdup 272g
Moisture	.0744 wt. fract.		-	.0060 wt. fract.
Volatile ($750^{\circ}C$)	.1493		.1265 wt. fract.	.1167
Carbon ($750^{\circ}C$)	.1747		.1995	.1646
Ash	.6016		.6740	.7127
	1.0000 wt. fract.		1.000? wt. fract.	1.0000 wt. fract.

Condensate 1289g

Gas   1252g (by difference)

CO_2	.3768 vol. fract.	15.065 g/min	.546 g/g DAF feed
CO	.1283	3.264	.118
H_2	.3782	.687	.025
CH_4	.1026	1.492	.054
C_2H_4	.0141	.359	.013
C_2H_6	-	-	-
	1.0000 vol. fract.	20.867 g/min	.756 g/g DAF feed
		1252 g/60 min	

Overall ash balance closure	87.2%
Volatiles ($750^{\circ}C$) removed	84.0%
H_2O/C ($750^{\circ}C$)	2.874 mol/mol
Carbon ($750^{\circ}C$) gasified	29.5%

Table 8 (Cont.)

Run 2-13-78 Pyrolysis of Manure. $T_S = 605^oC$, $T_G = 402^oC$, $\tau_R = 15.06$ min.

<u>Feed</u> 4070 g/75 min   <u>Receiver Char</u> 915 g

	Wt. Fract.		Wt. Fract.
Moisture	.2560	Moisture	.004
Volatile (750^oC)	.3494	Volatile (750^oC)	.1139
Carbon (750^oC)	.0952	Carbon (750^oC)	.2581
Ash	.2994	Ash	.624
	1.0000		1.0000

<u>Dynamic Holdup</u> 380 g   <u>Static Holdup</u> 465 g

	Wt. Fract.		Wt. Fract.
Moisture	.006	Moisture	.007
Volatile (750^oC)	.1185	Volatile (750^oC)	.0798
Carbon (750^oC)	.2315	Carbon (750^oC)	.1722
Ash	.644	Ash	.741
	1.0000		1.0000

Condensate 1360 g

<u>Gas</u> 683 g

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.7145		18.133	
CO_2	.1082	.379	6.714	.278
CO	.0311	.109	1.229	.051
H_2	.1142	.400	.322	.013
CH_4	.0254	.089	.573	.024
C_2H_4	.0036	.0125	.141	.006
C_2H_6	.0030	.0105	.127	.005
	1.0000	1.0000	9.106 dry	.377
	wet	dry	683.0 g/75 min	

Overall mass balance closure   93.4%   Seems to be an error in C(750^oC)
Overall ash balance closure   95.2%   analyses.

Volatiles (750^oC) removed   86.9%   Ignore these data.
                                              They seem to be in error.
H_2O/C (750^oC)   2.714
Carbon (750^oC) steam gasified   Negative (?)

Table 8 (Cont.)

Run 5-12-78 Pyrolysis of Manure T_S = 615°C, T_G = 503°C, τ_R = 27.62 min.

Feed 4440 g/75 min   Receiver Char 165 g

	Wt. Fract.		Wt. Fract.
Moisture	.2992	Moisture	--
Volatile (750°C)	.3121	Volatile (750°C)	.1415
Carbon (750°C)	.0918	Carbon (750°C)	.2567
Ash	.2969	Ash	.6018
	1.0000		1.0000

Dynamic Holdup 687 g   Static Holdup 1071 g

	Wt. Fract.		Wt. Fract.
Moisture	--	Moisture	--
Volatile (750°C)	.0917	Volatile (750°C)	.0810
Carbon (750°C)	.2016	Carbon (750°C)	.1404
Ash	.7067	Ash	.7786
	1.0000		1.0000

Condensate 656 g (?)

Gas 800 g

	Vol. Fract.	g/min
H_2O		8.747
CO_2	.2943	7.164
CO	.1548	2.398
H_2	.4876	.540
CH_4	.0633	.560
C_2H_4	--	-
C_2H_6	--	-
	1.0000	10.662 dry
		799.7 g/75 min

Overall mass balance closure   76.1%

Steam was escaping uncondensed.
Ignore these data.

Table 8(Cont.)

Run 5-19-78 Pyrolysis of Manure $T_S = 620^{\circ}C$, $T_G = 451^{\circ}C$, $\tau_R = 43.82$ min.

Feed 3936 g/120 min		Receiver Char 211 g	
	Wt. Fract.		Wt. Fract.
Moisture	.0671	Moisture	--
Volatile $(750^{\circ}C)$	.4127	Volatile $(750^{\circ}C)$	.1485
Carbon $(750^{\circ}C)$	.0827	Carbon $(750^{\circ}C)$	.2519
Ash	.4375	Ash	.5996
	1.0000		1.0000

Dynamic Holdup 857 g		Static Holdup 976 g	
	Wt. Fract.		Wt. Fract.
Moisture	--	Moisture	--
Volatile $(750^{\circ}C)$	.0675	Volatile $(750^{\circ}C)$	.0618
Carbon $(750^{\circ}C)$	.1988	Carbon $(750^{\circ}C)$	.1530
Ash	.7337	Ash	.7852
	1.0000		1.0000

Condensate 436 g

Gas 712 g

	Vol. Fract.	g/min
H_2O		3.633
CO_2	.2394	3.055
CO	.2753	2.235
H_2	.3960	.230
CH_4	.0893	.414
C_2H_2	--	-
C_2H_6	--	-
	1.0000	5.934 dry
	dry	712.1 g/120 min

Overall mass balance closure   81.1%
Overall ash balance closure   88.4%

Poor closure. Omit.

Volatiles $(750^{\circ}C)$ removed

H_2O/C $(750^{\circ}C)$

Carbon $(750^{\circ}C)$ gasified

Table 8 (Cont.)

Run 2-10-78 Pyrolysis of Manure T_S = 630°C, T_G = 376°C, τ_R = 16.02 min.

Feed 3184 g/60 min   Receiver Char 392 g

	Wt. Fract.			Wt. Fract.
Moisture	.478	Moisture		.037
Volatile (750°C)	.232	Volatile (750°C)		.1868
Carbon (750°C)	.069	Carbon (750°C)		.1752
Ash	.221	Ash		.601
	1.000			1.0000

Dynamic Holdup 295 g   Static Holdup 355 g

	Wt. Fract.			Wt. Fract.
Moisture	.0044	Moisture		.0087
Volatile (750°C)	.0856	Volatile (750°C)		.0788
Carbon (750°C)	.273	Carbon (750°C)		.1835
Ash	.637	Ash		.729
	1.0000			1.0000

Dondensate 1316 g

Gas 952 g

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.6207		21.933	
CO_2	.1322	.3619	11.422	.715
CO	.0486	.0954	2.671	.167
H_2	.1663	.4549	.653	.041
CH_4	.0274	.0749	.860	.054
C_2H_4	.0039	.0106	.213	.013
C_2H_6	.0008	.0023	.049	.003
	.9999	1.0000	15.868 dry	.993
	wet	dry	952.1 g/60 min	

Overall mass balance closure	104.0%
Overall ash balance closure	97.0%
Volatile (750°C) removed	82.9%
H_2O/C (750°C)	5.063
Carbon (750°C) steam gasified	2.4%
Pyrolysis gas heating value (low) (including CO_2 but not H_2O)	239.5 BTU/SCF

Table 8 (Cont.)

Run 2-8-78 Pyrolysis of Manure T_S = 635°C, T_G = 437°C, τ_R = 16.46 min.

Feed 3170 g/60 min   Receiver Char 390 g

	Wt. Fract.		Wt. Fract.
Moisture	.4316	Moisture	.018
Volatile (750°C)	.2353	Volatile (750°C)	.1561
Carbon (750°C)	.0954	Carbon (750°C)	.1974
Ash	.2377	Ash	.6285
	1.0000		1.0000

Dynamic Holdup 295 g   Static Holdup 343 g

	Wt. Fract.		Wt. Fract.
Moisture	.003	Moisture	.015
Volatile (750°C)	.1067	Volatile (750°C)	.0089
Carbon (750°C)	.1894	Carbon (750°C)	.2384
Ash	.7009	Ash	.7378
	1.0000		1.0000

Condensate 1304 g

Gas 772 g

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.6480		21.733	
CO_2	.1084	.308	8.885	.509
CO	.0395	.112	2.060	.118
H_2	.1658	.471	.618	.035
CH_4	.0313	.089	.935	.054
C_2H_4	.0053	.015	.275	.016
C_2H_6	.0018	.005	.098	.006
	1.0001	1.0000	12.871 dry	.738
	wet	dry	772 g/hr	

Overall mass balance closure   97.9%
Overall ash balance closure   93.6%

Volatiles (750°C) removed   87.2%

H_2O/C (750°C)   3.610 mol/mol

Carbon (750°C) steam gasified   29.0%

Pyrolysis gas heating value (low)   272.6 BTU/SCF
(including CO_2 but not H_2O)

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Table 8 (Cont.)

Run 5-22-78 Pyrolysis of Manure T_S = 636°C, T_G = 437°C, τ_R = 36.82 min.

Feed 3443 g/120 min   Receiver Char 19 g

	Wt. Fract.			Wt. Fract.
Moisture	.0725	Moisture	--
Volatile (750°C)	.4460	Volatile (750°C)	.1416
Carbon (750°C)	.1029	Carbon (750°C)	.2700
Ash	.3786	Ash	.5884
	1.0000		1.0000

Dyanmic Holdup 571 g   Static Holdup 1203 g

	Wt. Fract.			Wt. Fract.
Moisture	--	Moisture	--
Volatile (750°C)	.0746	Volatile (750°C)	.0514
Carbon (750°C)	.2249	Carbon (750°C)	.1407
Ash	.7005	Ash	.8079
	1.0000		1.0000

Condensate 335 g

Gas 1315 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.2188		2.792	
CO_2	.1790	.2289	5.584	.355
CO	.1918	.2454	3.808	.242
H_2	.3145	.4028	.446	.028
CH_4	.0923	.1181	1.047	.066
C_2H_4	.0037	.0047	.073	.005
C_2H_6	--	--	--	--
	1.0001	.9999	10.958 dry	.696
	wet	dry	1315 g/120 min	

Overall ash balance closure   106.1%

Volatiles (750°C) removed   93.0%

H_2O/C (750°C)   1.090

Carbon (750°C) gasified   14.5%

Gas flow by difference.

Pyrolysis gas heating value (low)   299.1 BTU/SCF
(including CO_2 but not H_2O)

Table 8 (Cont.)

Run 2-9-78 Pyrolysis of Manure T_S = 640°C, T_G = 428°C, τ_R = 14.05 min.

Feed 2775 g/60 min   Receiver Char 770 g

	Wt. Fract.		Wt. Fract.
Moisture	.0589	Moisture	.010
Volatile (750°C)	.4141	Volatile (750°C)	.1426
Carbon (750°C)	.2144	Carbon (750°C)	.2307
Ash	.3126	Ash	.6168
	1.0000		1.0000

Dynamic Holdup 330 g   Static Holdup 350 g

	Wt. Fract.		Wt. Fract.
Moisture	.007	Moisture	.008
Volatile (750°C)	.1192	Volatile (750°C)	.0754
Carbon (750°C)	.2582	Carbon (750°C)	.2222
Ash	.6157	Ash	.6944
	1.0000		1.0000

Condensate 595 g

Gas 1134 g

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.3993		9.917	
CO_2	.2012	.335	12.210	.420
CO	.0918	.153	3.548	.122
H_2	.2091	.348	.577	.020
CH_4	.0769	.128	1.697	.058
C_2H_4	.0114	.019	.440	.015
C_2H_6	.0102	.017	.422	.015
	.9999	1.000	18.894 dry	.650
	wet	dry	1134 g/hr	

Overall mass balance closure   114.6%
Overall ash balance closure   106.2%

Volatile (750°C) removed   84.7%
H_2O/C (750°C)   1.016 mol/mol
Carbon (750°C) steam gasified   42.7%

Pyrolysis gas heating value (low)   312.5 BTU/SCF
(including CO_2 but not H_2O)

Table 8 (Cont.)

Run 2-6-78   Pyrolysis of Manure T_S = 657°C, T_G = 460°C, τ_R = 9.70 min

<u>Feed</u> 2700 g/60 min   <u>Receiver Char</u> 600 g

	Wt. Fract.			Wt. Fract.
Moisture	.052	Moisture		.012
Volatile (750°C)	.4143	Volatile (750°C)		.1225
Carbon (750°C)	.1969	Carbon (750°C)		.3004
Ash	.3368	Ash		.5651
	1.0000			1.0000

<u>Dynamic Holdup</u> 230 g   <u>Static Holdup</u> 595 g

	Wt. Fract.			Wt. Fract.
Moisture	.009	Moisture		.006
Volatile (750°C)	.0842	Volatile (750°C)		.0696
Carbon (750°C)	.2676	Carbon (750°C)		.2336
Ash	.6392	Ash		.6908
	1.0000			1.0000

Condensate 466 g

<u>Gas</u> 875 g

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.3976		<u>7.767</u>	
CO_2	.1860	.309	8.885	.323
CO	.1065	.177	3.238	.118
H_2	.2119	.352	.460	.017
CH_4	.0760	.126	1.320	.048
C_2H_4	.0128	.021	.390	.014
C_2H_6	.0090	.015	.295	.011
	.9998	1.000	14.588 dry	.531
	wet	dry	875 g/hr	

Overall mass balance closure   102.4%
Overall ash balance closure   98.7%

Volatiles (750°C) removed   88.0%

H_2O/C (750°C)   1.409 mol/mol

Carbon (750°C) steam gasified   28.4%

Pyrolysis gas heating value (low)   319.3 BTU/SCF
(including CO_2 but not H_2O)

Run 4-10-78   Pyrolysis of Manure $T_S = 660^oC$, $T_G = 535^oC$, $\tau_R = 18.30$ min.

Feed 3832 g/60 min   Receiver Char 673 g

	Wt. Fract.			Wt. Fract.
Moisture	.3667	Moisture		.0420
Volatile (750^oC)	.2804	Volatile (750^oC)		.1013
Carbon (750^oC)	.0790	Carbon (750^oC)		.2144
Ash	.2739	Ash		.6423
	1.0000			1.0000

Dynamic Holdup 440 g   Static Holdup 350 g

	Wt. Fract.			Wt. Fract.
Moisture	.0292	Moisture		.0263
Volatile (750^oC)	.0717	Volatile (750^oC)		.0625
Carbon (750^oC)	.1713	Carbon (750^oC)		.1087
Ash	.7277	Ash		.8025
	.9999			1.0000

Condensate 995 g

Gas 1374 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.4327	·	16.583	
CO_2	.1511	.2663	14.152	.617
CO	.0811	.1430	4.836	.211
H_2	.2607	.4597	1.110	.048
CH_4	.0639	.1126	2.176	.095
C_2H_4	.0105	.0185	.626	.027
C_2H_6	--	--		
	1.0000	1.0001	22.900 dry	.998
	wet	dry	1374 g/60 min	

Overall ash balance closure   98.5%

Volatiles (750^oC) removed   88.7%   Gas flow by difference.

H_2O/C (750^oC)   3.511 mol/mol

Carbon (750^oC) gasified   14.9%

Pyrolysis gas heating value (low)   297.9 BTU/SCF
(including CO_2 but not H_2O)

Table 8 (Cont.)

Run 5-16-78 Pyrolysis of Manure $T_S = 661^\circ C$, $T_G = 499^\circ C$, $\tau_R = 28.85$ min.

Feed 4123 g/105 min   Receiver Char 56 g

	Wt. Fract.			Wt. Fract.
Moisture	.3018		Moisture	--
Volatile ($750^\circ C$)	.3071		Volatile ($750^\circ C$)	.1239
Carbon ($750^\circ C$)	.0998		Carbon ($750^\circ C$)	.2643
Ash	.2913		Ash	.6118
	1.0000			1.0000

Dynamic Holdup 465 g   Static Holdup 1008 g

	Wt. Fract.			Wt. Fract.
Moisture	--		Moisture	--
Volatile ($750^\circ C$)	.0866		Volatile ($750^\circ C$)	.0627
Carbon ($750^\circ C$)	.2037		Carbon ($750^\circ C$)	.1219
Ash	.7097		Ash	.8154
	1.0000			1.0000

Condensate 962 g

Gas 1632 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.3808		9.162	
CO_2	.1647	.2659	9.686	.606
CO	.0969	.1564	3.625	.227
H_2	.2895	.4678	.774	.048
CH_4	.0681	.1100	1.457	.091
C_2H_4	--	--	--	--
C_2H_6	--	--	--	--
	1.0000	1.0001	15.543 dry	.972
	wet	dry	1632 g/105 min	

Overall ash balance closure   98.8%   Gas flow by difference.

Volatiles ($750^\circ C$) removed   91.3%

H_2O/C ($750^\circ C$)   2.744

Carbon ($750^\circ C$) gasified   43.5%

Pyrolysis gas heating value (low)   274.0 BTU/SCF
(including CO_2 but not H_2O)

38

Table 9

Run 3-22-78 Pyrolysis of Sawdust. $T_S = 631^O C$, $T_G = 381^O C$, $\tau_R = 69.89$ min.

Feed 1866 g/60 min   Receiver Char 35 g

	Wt. Fract.		Wt. Fract.
Moisture	.0995	Moisture	--
Volatile $(750^O C)$	.7164	Volatile $(750^O C)$	.1773
Carbon $(750^O C)$	.1797	Carbon $(750^O C)$	.7427
Ash	.0044	Ash	.0800
	1.0000		1.0000

Dynamic Holdup Char 194 g   Static Holdup Char 94 g

	Wt. Fract.		Wt. Fract.
Moisture	--	Moisture	--
Volatile $(750^O C)$	.0741	Volatile $(750^O C)$	.0860
Carbon $(750^O C)$	.8766	Carbon $(750^O C)$	.8674
Ash	.0493	Ash	.0466
	1.0000		1.0000

Condensate 235.5 g

Gas 1307.5 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.1916		3.925	
CO_2	.1895	.2344	9.492	.341
CO	.2730	.3376	8.699	.312
H_2	.1915	.2370	.436	.016
CH_4	.1312	.1624	2.391	.086
C_2H_4	.0137	.0170	.438	.016
C_2H_6	.0095	.0117	.324	.012
	1.0000	1.0000	21.780 dry	.783
	wet	dry	1306.8 g/60 min	

Volatiles $(750^O C)$ removed   97.9%

H_2O/C $(750^O C)$ 0.936 mol/mol

Carbon $(750^O C)$ gasified   17.2%

Gas flow by difference.

Pyrolysis gas heating value (low)   360.6 BTU/SCF
(including CO_2 but not H_2O)

Table 9 (Cont.)

Run 3-28-78 Pyrolysis of Sawdust. $T_S = 640^{\circ}C$, $T_G = 404^{\circ}C$, $\tau_R = 26.22$ min

Feed 1811 g/60 min   Receiver Char 53 g

	Wt. Fract.
Moisture	.1245
Volatile ($750^{\circ}C$)	.6744
Carbon ($750^{\circ}C$)	.1945
Ash	.0066
	1.0000

	Wt. Fract.
Moisture	.0082
Volatile ($750^{\circ}C$)	.1458
Carbon ($750^{\circ}C$)	.7983
Ash	.0477
	1.0000

Dynamic Holdup Char 182 g   Static Holdup Char 42 g

	Wt. Fract.
Moisture	.0097
Volatile ($750^{\circ}C$)	.0840
Carbon ($750^{\circ}C$)	.8776
Ash	.0287
	1.0000

	Wt. Fract.
Moisture	.0020
Volatile ($750^{\circ}C$)	.0808
Carbon ($750^{\circ}C$)	.8778
Ash	.0394
	1.0000

Condensate 299 g

Gas 1235 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.2425		4.983	
CO_2	.1863	.2460	9.360	.357
CO	.2438	.3219	7.796	.297
H_2	.1817	.2397	.415	.016
CH_4	.1228	.1621	2.243	.086
C_2H_4	.0134	.0177	.429	.016
C_2H_6	.0095	.0126	.326	.012
	1.0000	1.0000	20.569 dry	.784
	wet	dry	1234.1 g/60 min	

Volatiles ($750^{\circ}C$) removed   97.8%

H_2O/C ($750^{\circ}C$)   0.990 mol/mol

Carbon ($750^{\circ}C$) gasified   32.2%

Gas flow by difference.

Pyrolysis gas heating value (low)   358.6 BTU/SCF
(including CO_2 but not H_2O)

40

Table 9 (Cont.)

Run 5-25-78 Pyrolysis of Sawdust. $T_S = 640^0C$, $T_G = 403^0C$, τ_R =?

Feed 1778 g/150 min   Receiver Char 0 g

	Wt. Fract.				Wt. Fract.
Moisture	.2459		Moisture		--
Volatile (750^0C)	.5991	(est.)	Volatile (750^0C)		--
Carbon (750^0C)	.1522	(est.)	Carbon (750^0C)		--
Ash	.0029	(est.)	Ash		--
	1.0001				--

Dynamic Holdup 14 g   Static Holdup 217 g

	Wt. Fract.				Wt. Fract.
Moisture	--		Moisture		--
Volatile (750^0C)	.05	(est.)	Volatile (750^0C)		.0442
Carbon (750^0C)	.87	(est.)	Carbon (750^0C)		.8527
Ash	.08	(est.)	Ash		.1031
	1.00				1.0000

Condensate 354 g

Gas 1193 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.2682		2.360	
CO_2	.1714	.2344	3.687	.414
CO	.2060	.2819	2.820	.317
H_2	.2087	.2844	.204	.023
CH_4	.1282	.1755	1.003	.113
C_2H_4	.0175	.0239	.239	.027
C_2H_6	--	--	--	--
	1.0090	1.0001	7.953 dry	.894
	wet	dry	1193 g/150 min	

Volatiles (750^0C) removed	99.0%
H_2O/C (750^0C)	1.551 mol/mol
Carbon (750^0C) gasified	27.1%
Pyrolysis gas heating value (low) (including CO_2 but not H_2O)	359.4 BTU/SCF

Gas flow by difference.
The run duration was too
short.

41

Table 9 (Cont.)

Run 3-29-78 Pyrolysis of Sawdust. $T_S = 653^{\circ}C$, $T_G = 417^{\circ}C$, $\tau_R = 72.61$ min.

Feed 2320 g/60 min		Receiver Char 42 g	
	Wt. Fract.		Wt. Fract.
Moisture	.2995	Moisture	.0696
Volatile (750°C)	.5558	Volatile (750°C)	.1216
Carbon (750°C)	.1429	Carbon (750°C)	.7596
Ash	.0018	Ash	.0492
	1.0000		1.0000

Dynamic Holdup 190 g		Static Holdup 50 g	
	Wt. Fract.		Wt. Fract.
Moisture	.0645	Moisture	.0536
Volatile (750°C)	.0779	Volatile (750°C)	.0724
Carbon (750°C)	.8310	Carbon (750°C)	.8246
Ash	.0266	Ash	.0494
	1.0000		1.0000

Condensate 703 g

Gas 1335 g (by difference)

	Vol. Fract.		g/min	g/g DAF feed
H_2O	.4091		11.717	
CO_2	.1462	.2473	10.236	.379
CO	.1863	.3152	8.302	.307
H_2	.1458	.2470	.464	.017
CH_4	.0941	.1592	2.396	.089
C_2H_4	.0123	.0208	.548	.020
C_4H_6	.0062	.0106	.298	.011
	1.0000	1.0000	22.244 dry	.823
	wet	dry	1334.6 g/60 min	

Volatiles (750°C) removed	98.2%
H_2O/C (750°C)	1.918 mol/mol
Carbon (750°C) gasified	30.3%

Gas flow by difference.

Pyrolysis gas heating value (low)   357.3 BTU/SCF
(including CO_2 but not H_2O)

the feed drop point, and (3) the third one was located just outside the feed drop point. In the experiments it became clear that the incoming manure heated to the pyrolysis temperature very rapidly. For example, as the two inside thermocouples passed under the feed drop hole, the temperature dropped suddenly. When the feed was very wet, the temperature drop sometimes was as large as $400^{0}C$. After this sudden drop, the solids temperature as measured by these thermocouples increased rapidly. By the time the thermocouples had gotten back to the feed drop location, the solids had heated up to the pyrolysis temperature.

Additional pyrolysis runs were next made at a higher temperature (Table 8), and sawdust was also used as a feed stock (Table 9). Unfortunately, it appeared that there was a serious gas leak in the apparatus as these experiments were done. Accordingly, the weight of the gas produced was determined by difference. During run 4/4/78 (on manure) the temperature level was falling, so the reactor was not at equilibrium. The feed moisture content was high (33 wt %) and so was the H_2O/C ($750^{0}C$) ratio. About 30% of the carbon ($750^{0}C$) was steam-gasified in spite of the low solids temperatures.

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WATER GAS REACTION

The feed for the water gas experiments was incompletely pyrolyzed char. Of the volatiles ($750^{o}C$) contained in raw manure, about 14% remained in this char. These water gas experiments, as well as the previous pyrolysis experiments, were done at comparatively low temperatures. To get reasonable water gas reaction rates, it is necessary to get good steam-char contact. In the present pilot plant apparatus, steam was passed through the hollow shaft and then into the moving bed of char through the hollow rabble teeth. The resultant steam-char contact was probably only moderately effective. Also, during some runs the solids and gas temperatures did not reach steady-state. In Run 3-8-78, for example, the solids temperature fell from about $660^{o}C$ to about $570^{o}C$ in 90 minutes. In the later runs the contact time was long enough to obtain steady state. The data is presented in Table 10.

Table 10

Water Gas Reaction: Pilot Plant Data

Run 3-6-78 $\qquad$ $T_S = 564^\circ C$, $T_G = 343^\circ C$, $\tau_R = 23.18$ min.

Feed 5371 g/75 min manure char $\qquad$ Receiver Char 2064 g

	Wt. Fract. $\frac{g}{min}$			Wt. Fract.
Moisture	--		Moisture	--
Volatile (750°C)	.1536		Volatile (750°C)	.1125
Carbon (750°C)	.2007		Carbon (750°C)	.2253
Ash	.6457	46.24	Ash	.6622
	1.0000	71.61		1.0000

Dynamic Holdup Char 1490 g $\quad$ DAF 25.36 $\quad$ Static Holdup Char 1007 g

	Wt. Fract.		Wt. Fract.
Moisture	--	Moisture	--
Volatile (750°C)	.0944	Volatile (750°C)	.0951
Carbon (750°C)	.1864	Carbon (750°C)	.1446
Ash	.7192	Ash	.7603
	1.0000		1.0000

Condensate 850 g

Steam Input 875 g, .460 g DAF

Gas 370.4 g/75 min

	Vol. Fract.		g/min	g/g DAF
H_2O	.6971	--	11.333	
CO_2	.0960	.3165	3.814	.1503
CO	.0235	.0775	.594	
H_2	.1677	.5538	.303	
CH_4	.0158	.0521	.228	
C_2H_4	--	--	--	
C_2H_6	--	--	--	
	1.0001	1.0000	4.939 dry	.1947
	wet	dry		.0444 (w/o CO_2)

Overall material balance closure $\qquad$ 91.4%
Overall ash balance closure $\qquad$ 92.4%
Volatiles (750°C) removed $\qquad$ 43.2%

Reactor H_2O/C(750°C) $\qquad$ 1.219 mol/mol
Carbon (750°C) steam gasified $\qquad$ 17.6%

Table 10 (Cont.)

Water Gas Reaction: Pilot Plant Data

Run 3-1-78   No steam applied. $T_S = 597^oC$, $T_G = 280^oC$, $\tau_R = 29.87$ min.

Feed 4891 g/90 min manure char   Receiver Char 2321 g

	Wt. Fract. $\frac{g}{min}$			Wt. Fract.
Moisture	--		Moisture	--
Volatile (750°C)	.1626		Volatile (750°C)	.1308
Carbon (750°C)	.1795		Carbon (750°C)	.2010
Ash	.6579	35.75	Ash	.6682
	1.0000	54.34		1.0000
		DAF 18.59		

Dynamic Holdup Char 1423 g   Static Holdup Char 728 g

	Wt. Fract.			Wt. Fract.
Moisture	--		Moisture	--
Volatile (750°C)	.0851		Volatile (750°C)	.0843
Carbon (750°C)	.1643		Carbon (750°C)	.1586
Ash	.7506		Ash	.7571
	1.0000			1.0000

Condensate 98 g

Steam Input 0 g

Gas 357.0 g/90 min

	Vol. Fract.		g/min	g/g DAF
H_2O	.2183	--	1.089	
CO_2	.1961	.2509	2.391	.1286
CO	.1286	.1646	.998	
H_2	.3735	.4778	.207	
CH_4	.0835	.1067	.370	
C_2H_4	--	--	--	
C_2H_6	--	--	--	
	1.0000	1.0000	3.966 dry	.2133
	wet	dry		.0847 (w/o CO_2)

Overall material balance closure	100.7%
Overall ash balance closure	98.5%
Volatiles (750°C) removed	38.9%
Reactor $H_2O/C(750^oC)$	0.140 mol/mol
Carbon (750°C) steam gasified	7.1%

Table 10 (Cont.)

Water Gas Reaction: Pilot Plant Data

Run 3-8-78 $\qquad$ $T_S = 606^oC$, $T_G = 342^oC$, $\tau_R = 32.37$ min.

Feed 3993 g/90 min manure char $\qquad$ Receiver Char 1214 g

	Wt. Fract.	$\frac{g}{min}$		Wt. Fract.
Moisture	--		Moisture	--
Volatile (750°C)	.1441		Volatile (750°C)	.1106
Carbon (750°C)	.2006		Carbon (750°C)	.2426
Ash	.6553	29.07	Ash	.6468
	1.0000	44.37		1.0000
	DAF	15.29		

Dynamic Holdup Char 1282 g $\qquad$ Static Holdup Char 918 g

	Wt. Fract.			Wt. Fract.
Moisture	--		Moisture	--
Volatile (750°C)	.0890		Volatile (750°C)	.0774
Carbon (750°C)	.1770		Carbon (750°C)	.1504
Ash	.7340		Ash	.7722
	1.0000			1.0000

Condensate 639 g

Steam Input 641 g, .466 g/g DAF

Gas 294.8 g/90 min

	Vol. Fract.		g/min	g/g DAF
H_2O	.6918	--	7.100	
CO_2	.1026	.3328	2.574	.1683
CO	.0258	.0837	.412	
H_2	.1693	.5492	.193	
CH_4	.0105	.0343	.096	
C_2H_4	--	--	--	
C_2H_6	--	--	--	
	1.0000	1.0000	3.275 dry	.2141
	wet	dry		.0458 (w/o CO_2)

Overall material balance closure	92.9%
Overall ash balance closure	93.1%
Volatiles (750°C) removed	44.5%
Reactor H_2O/C(750°C)	1.451 mol/mol
Carbon (750°C) steam gasified	17.7%

Table 10 (Cont.)

Water Gas Reaction: Pilot Plant Data

Run 4-12-78 T_S = 650°C, T_G = 464°C, τ_R = 19.937 min.

Feed 6454 g/60 min manure char   Receiver Char 2470 g

	Wt. Fract. $\frac{g}{min}$			Wt. Fract.
Moisture	.0792		Moisture	--
Volatile (750°C)	.1683		Volatile (750°C)	.1263
Carbon (750°C)	.1878		Carbon (750°C)	.2254
Ash	.5646	60.73	Ash	.6483
	.9999	107.57		1.0000
	DAF	38.30		

Dynamic Holdup Char 1685 g   Static Holdup Char 820 g

	Wt. Fract.		Wt. Fract.
Moisture	--	Moisture	--
Volatile (750°C)	.0867	Volatile (750°C)	.0747
Carbon (750°C	.1947	Carbon (750°C)	.1498
Ash	.7186	Ash	.7755
	1.0000		1.0000

Condensate 534 g

Steam Input 577 g, .251 g/g DAF

Gas 1522 g/60 min (by difference)

	Vol. Fract.		g/min	g/g DAF
H_2O	.2617	--	8.900	
CO_2	.2002	.2712	16.646	.4346
CO	.1229	.1665	6.503	
H_2	.3906	.5290	1.476	
CH_4	.0245	.0332	.741	
C_2H_4	--	--	--	
C_2H_6	--	--	--	
	.9999	.9999	25.366 dry	.6622
	wet	dry		.2277 (w/o CO_2)

Ash balance closure   94.6%
Volatiles (750°C) removed   52.2%

Carbon (750°C) steam gasified 16.9%
H_2O/C (750°C) 0.732 mol/mol

Entrainment of Manure Particles in the Reactor

In the cross-flow drying of biomass materials the drying
gas is passed through the bed of solids which is flowing in a direction
perpendicular to the flow of gas. At certain gas rates solid particles
are lifted against gravity and kept in suspension by the gas stream. This,
for a bed of uniform-sized particles, marks the point of bed expansion.
As the gas rate increases further, the solid bed continues to expand
and eventually is carried away by the gas. For a bed of uneven particle
sizes, smaller-sized particles at certain locations are suspended and
sometimes even carried away without any evidence of bed expansion. This
is particularly true for the case of cattle manure. It not only has an
uneven distribution of particle sizes but also has a stickiness of
nature so that it is virtually impossible to offer any theoretical
treatment on its fluidization behavior. The amount of entrainment
(carried-away) of cattle manure is studied here because it determines
the amount of loss of solids, and more importantly the degree of
possible clogging in flue gas transport lines. In the case of more than
one drying stage being used, the base plate holes may easily clog for
the next drying stage.

Experimental Procedure and Method of Calculation. Entrainment fraction
is defined as the ratio of the solids entrained to the feed rate. This
quantity is expected to be a function of the physical properties and
particle geometry of the solid, and the properties and velocity of the
gas. It is not a function of solid rate. Therefore experiments to
determine it can be carried out with fixed solid flow rates. Two solid
feed rates were used with an experimental procedure as follows:

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1. Starting the gas flow through the base plate at a given rate,

2. Starting the screw feeder to feed the manure into the reactor,

3. Allowing 15 minutes from the time the first quantity of solid appears at the outlet to ensure steady conditions, 4. Connecting collection bags at the solid outlet and air outlet. The collection bag at the air outlet has small openings to allow for air discharge and to avoid pressure buildup in the reactor, 5. Allowing 30 minutes for the collection and then weighing the materials collected.

The feed rate (F) is equal to the sum of discharge rate (W_D), the entrainment rate (E) and moisture lost into the air stream ($\Delta m_A W_A$), i.e.:

$$F = W_D + E + \Delta m_A W_A \tag{1}$$

where Δm_A is the change of the absolute humidity (lb of H_2O/lb dry air) and W_A is the mass flow rate of dry air. Thus the entrainment fraction is defined by:

$$X_E = \frac{E}{W_D + E + \Delta m_A W_A} \tag{2}$$

Equation 2 is true, however, only if the entrained solid retains its original moisture content, namely the moisture content of the feed. In the experimental procedure described above, the entrainment moisture content is expected to be less than or equal to the solid moisture content at the discharge point because of additional drying of the suspended solid. In the case where the moisture content of the entrained solid and discharge solid are equal, the correct equation to be used to calculate entrainment fraction should be:

$$X_E = \frac{E}{W_D + E} \tag{3}$$

When additional drying of the entrained solid occurs, the value of X_E calculated by equation 3 using measured quantities as indicated in the experimental procedure would yield values lower than the corrected values. The difference in the worst case where there was no drying for the throughput solids, but complete drying for the entrained solids is equal to the moisture content of the feed. This maximum difference is 24% for high and 12% for low moisture feed material tested.

Results and Discussion. The results of the experiment are tabulated in Table 9 and plotted in Figure 1. The calculation of the entrained fraction X_E is based on equation 3. The difference between the moisture content of the entrained and discharged solids is assumed to be negligible at this stage. It is seen in Table 11 that the air temperature was kept low (ambient) to minimize the evaporation effects. The air flow rate in the reactor is assumed to be equal to the flow rate at standard conditions. This assumption encompasses a maximum error of $\pm$ 3%. In examining the curves of Figure 3, two conclusions can be drawn:

1. The entrainment fraction increases with increasing air velocity. The relationship is not a direct proportionality but indicates characteristics somewhat similar to the cumulative weight fraction versus particle size distribution. The slope of the curve tends to zero as the air velocity approaches zero. An attempt to determine the particle size distribution will be presented later.

2. The entrainment fraction follows an inverse relationship with solid moisture content. The higher the moisture content, the lower the entrainment fraction is for a given air velocity. This indicates that

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Table 11

Solids Entrainment in the Reactor
(Reactor Cross-sectional Area = 12.57 ft^2)

Run	Q_G	T_G	m_o	Δt	W_D	E	V_{SG}	X_E	D_P
1	7	15	23.4	30	2277.	1.	1.132	0.044	0.018
2	8.6	--	23.4	30	2104.	5.	1.391	0.237	0.027
3	10.0	--	23.4	30	2050.	8.	1.617	0.389	0.037
4	1:.2	--	23.4	30	2100.	14.	1.811	0.662	0.046
5	12.2	--	23.4	30	2122.	23.5	1.973	1.095	0.055
6	13.0	17	23.4	30	1977.5	35.5	2.102	1.764	0.062
7	14.0	--	23.4	30	2019.	46.5	2.264	2.251	0.072
8	15.8	--	23.4	30	1957.	50.0	2.555	2.491	0.092
9	17.2	18	23.4	30	1939.	82.5	2.781	4.081	0.109
10	18.7	--	23.4	30	1854.	118.5	3.024	6.008	0.129
11	20.0	--	23.4	30	1895.5	137.0	3.234	6.740	0.147
12	7	9.5	12.0	30	1575.	7.0	1.132	0.442	0.017
13	10	11.0	12.0	30	1743.	37.0	1.617	2.079	0.035
14	13	12.0	12.0	30	1725.	114.0	2.102	6.199	0.060
15	17.2	15.0	12.0	30	1655.	203.0	2.781	10.926	0.105
16	20.0	17.0	12.0	30	1605.	251.0	3.234	13.524	0.142

Q_G Gas Flow (scft/min)
T_G Mean Gas Temperature (^{o}C)
m_o Feed Moisture Content (%)
Δt Duration of Measurement (min)
W_D Mass of Solid Discharge (wet basis) (g)
E Entrainment Collected (g)
V_{SG} Superficial Gas Velocity (cm/s)
X_E Entrainment Fraction (%)
D_P Maximum Particle Diameter of Entrained Solid (10^{-3} mm)

Figure 1

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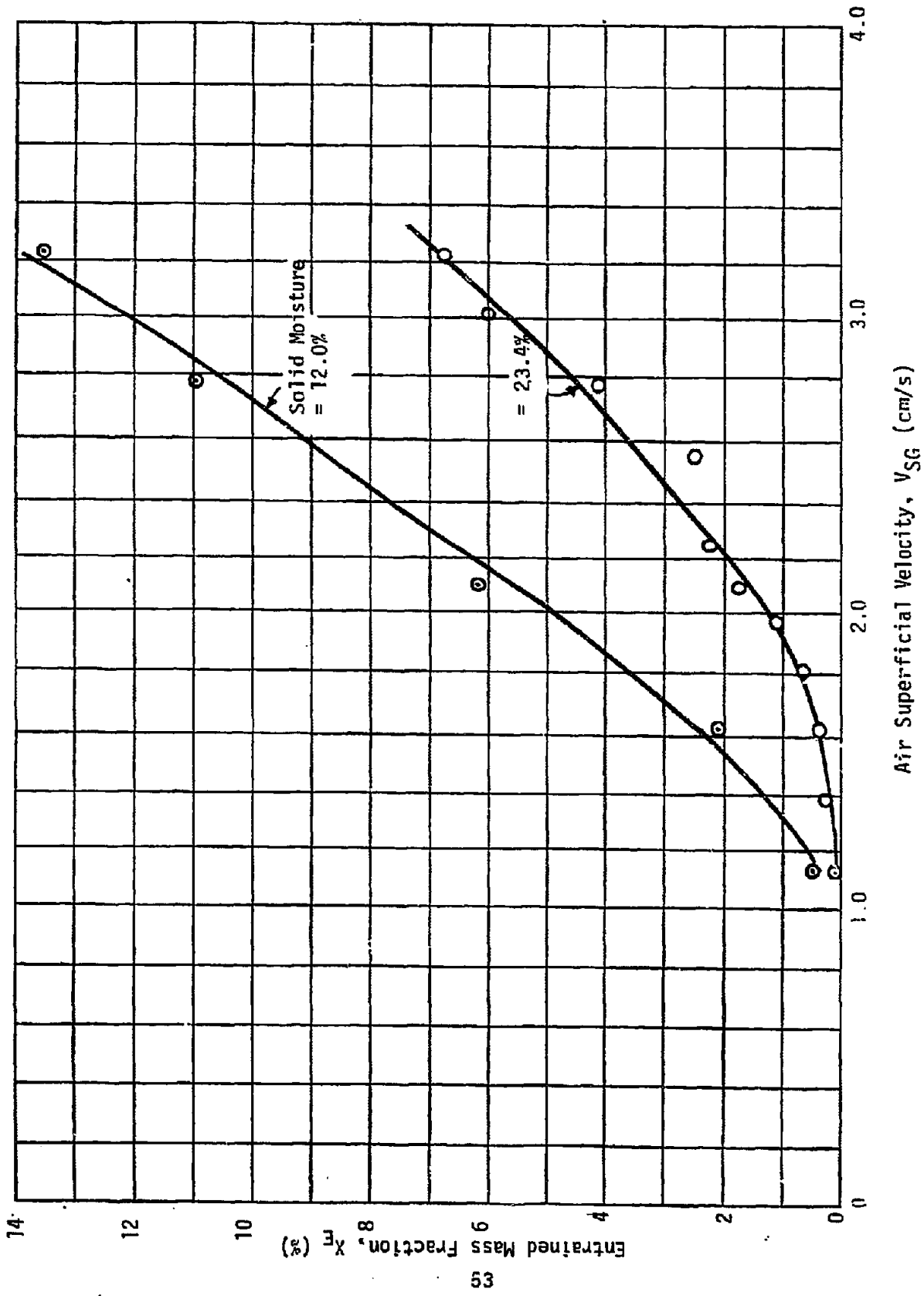
an increase in the solid moisture content would either a) increase

the particle density without changing its size distribution at one

extreme, or b) increase the size of particles and hence alter the size

distribution without changing particle density at the other extreme.

Cellulose materials have a specific gravity ranging from 1.32 for wool

to 1.50 for cotton, flax or hemp[4] and are major constituents of cattle

manure. Hence it is reasonable to assume that the presence of water in

the solid has an effect closer to the extreme b) than the extreme a).

Particle Density. The particle density according to the above argument

can be determined as a function of moisture content. Let the particle density

be ρ_P g/cm^3 and the moisture content m gH$_2$O/g wet solid. In 1 cm^3 of solid

which weighs ρ_P g there are $m\rho_P$ g of water of density ρ_W g/cm^3. Thus the

total volume is:

$$\frac{m\rho_P}{\rho_W} + \frac{(1-m)\rho_P}{\rho_S} = 1 \tag{4}$$

where ρ_S is the dry solid density. The particle density has been calculated

for the experimental conditions assuming ρ_W = 0.998 g/cm^3 and ρ_S = (1.32 +

1.50)/2 = 1.41 g/cm^3. They were 1.34 g/cm^3 and 1.29 g/cm^3 for the 23.4%

and 12.0% moisture contents, respectively.

Particle Size Distribution in the Entrained Solids. Assume that the distance

between the entrained particles is large enough that the velocity gradients

surrounding each particle are not affected by the presence of neighboring

particles. The minimum entraining gas velocity will be equal to the terminal

velocity of the suspending particles. The terminal velocity v_T of a particle

can be determined according to Newton's law as follows:

$$v_T = \frac{4(\rho_P - \rho_G)gD_P}{3C_D\rho_G}$$

---

[4] Perry, Chemical Engineers' Handbook, 5th ed., McGraw-Hill, N. Y., 1969.

where ρ_p and ρ_G are the densities of solid and gas particles, respectively,

D_p is the diameter of a sphere having the particle volume, g the

gravitational acceleration, and C_D the drag coefficient which is correlated

with the particle sphericity Ψ as follows[5]:

$$C_D = 5.31 - 4.88\Psi \tag{6}$$

Equation 6 applies to the range $10^3 < Re < 2(10^5)$, and is probably

not applicable here. Instead, Figure 70, page 76, of Brown's Unit

Operations[6] has been used. This is a plot of friction factor (i.e. drag

coefficient), f_D, versus Re with Ψ, sphericity, as the parameter.

$$D = \frac{3\rho_G v^2}{4g(\rho_S - \rho_G)} \cdot f_D = 7.695(10^{-7}) \cdot f_D \text{ in cgs units, } 20^oC,$$

1 atm, dry air. $\rho_S \sim 1.2$ gm/cm^3 . $\left[\frac{\mu}{\rho}\right]_G = 0.157$ cm^2/sec

$$Re = \frac{Dv}{(\mu/\rho)_G} = \frac{3\rho_G v^3}{4g(\rho_S - \rho_G)\left[\frac{\mu}{\rho}\right]_G} \cdot f_D$$

Given v, a straight line of slope 1 with intercept dependent on

$$\frac{3_G v^3}{4g(\rho_S - \rho_G)\left[\frac{\mu}{\rho}\right]_G} \quad \text{can be plotted. The intersection with the curve for}$$

$\Psi = 0.874$ gives f_D. Now Re and D can be calculated. (A = 3283 cm^2 was the

total drying area.

[5]Gaudin, Am M., Principles of Mineral Dressing, McGraw-Hill, N. Y., 1939

[6]John Wiley and Sons, New York (1950).

Gas Velocity (v),	Manure Particle Size (D),	Reynolds Number, Re	Drag Coefficient, f_D
cm/sec	microns		
1.007	17.95	$1.151(10^{-2})$	2300
1.236	21.16	1.666	1800
1.438	23.87	2.186	1500
1.610	24.93	2.557	1250
1.754	23.67	2.645	1000
1.869	22.85	2.654	850
2.013	24.32	3.118	780
2.156	26.11	3.586	730
2.271	26.19	3.789	660
2.473	27.30	4.299	580
2.688	29.47	5.045	530
2.875	31.80	5.824	500

The small inconsistencies in D are due to graph-reading errors. It appears that this manure contains quite a lot of fine material smaller than 30μ. This would indicate of designing for a superficial gas velocity of 1 cm/sec to avoid entrainment.

Sphericity of Entrained Particles Sphericity of a particle is defined as the ratio of the surface area of a sphere having the particle volume to the surface area of the particle. For example, a fiber having equal length and diameter would have a sphericity of:

$$\psi = \frac{\pi(6v_p/\pi)^{2/3}}{A_p} = \frac{\pi(6D^3/4)^{2/3}}{\pi D^2 + \pi D^2/2} = \frac{2}{3}(\frac{3}{2})^{2/3} = 0.874$$

The cylindrical fiber having an equal length and diameter has a minimum surface area per unit volume. From an energy point of view such a configuration is most stable for a cylinder and is therefore often considered as the final product in the grinding process of fibers.

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Moisture often has a glueing effects on small particles. Because
of the nature of the surface tension wet lumps of particles usually
have near-spherical shape. Thus the sphericity of such lumps should be
close to unity. From this consideration and the consideration of the
cylindrical fibers above, it is possible that the sphericity of entrained
manure particles is about 0.87. The other variables were assumed to be:

$$C_D = 1.064$$

$$\rho_G = 0.00129 \text{ g/cm}^3$$

$$\rho_p = 1.34, 1.29 \text{ g/cm}^3$$

$$g = 9.81 \text{ cm/s}^2$$

$$v_T = \text{in cm/s}$$

COMBUSTION

Several trial combustion runs were initially made using commercial charcoal as feed. It was noticed that the bed burned red hot directly above each air hole, but not elsewhere. This suggested poor contact between the air and the burning char. It was also noticed that when the ash layer was too thin or when the rabble arm rotation rate was too fast, whole sections of the bed might go out and become difficult to reignite. The number of 1/8 in. holes through the baseplate was consequently doubled, the ash thickness maintained at at least 1 in., and the rabble arm speeds were kept slow.

In the pilot plant tests with manure char, the reactor was first filled with a layer of char which was burned down to ash as new char fed into the reactor at a constant rate. After about two hours the initial char had been reduced to ash, and a steady state run was started. The flue gas was passed through a settling chamber where the larger fly ash particles were removed and weighed. The flue gas was analyzed for H_2, N_2, O_2, CO_2, CO, and H_2O. The feed char was analyzed for moisture and ash, and the ash and fly ash were analyzed for their ash content. (Volatiles [750^oC] were small in these samples and ignored). The flue gas temperature and two char temperatures were measured directly. This data is shown in Table 12.

Table 12

Pilot Plant Combustion Tests

Run Duration	40 min.
Solids Flow Rate	82.25 g/m

Carbon	.3097
Ash	.6903
	1.0000

Combustion Air	8.6 SCFM
Excess Air @ Total Carbon Input	7.48%

$$\{\frac{12(8.6)(28.316)(.210)}{82.25(.3097)(22.414)} - 1\}$$

Baseplate Area	2.745 ft^2

$$\frac{2550}{(30.48)^2}$$

Flue Gas Composition (Dry)

		vol
	H_2	.0037
	N_2	.7966
	O_2	.0468
	CO_2	.1436
	CO	.0093
		1.0000

Fly Ash Collected	177.8 g/40 min

Carbon	.1885	.0183 g fly ash/1
Ash	.8115	
	1.0000	

Combustion Efficiency, % C Burned	78.3%

$$\frac{8.6(28.316)(40)(.1529)(12)}{22.414(92.25)(.3097)(40)}$$

Char Heat of Combustion (net)	12,972 cal/gm carbon
Heat Flux	12,468 BTU/hr ft^2

$$\frac{60(82.25)(.3097)(1783)(12972)}{453.59(2.745)}$$

Flue Gas Temperature	644°C
Char Temperature	820°C

PILOT PLANT OPERATING CHARACTERISTICS

Action of The Rabble Teeth

The average radial velocity of the solids is A Sinα.(CPM). Assuming that there are no gaps between the teeth, the volumetric solids flow rate, a constant at steady state, is:

$$Q_S = 2\pi r \delta.A \ Sin\alpha.(CPM)$$

The holdup volume is $\int_{a_1}^{a_2} 2\pi r \delta dr = \dfrac{(a_2 - a_1).Q_S}{A \ Sin\alpha.(CPM)}$

Therefore, the residence time is:

$$\tau_R = \frac{(a_2 - a_1)}{A \ Sin\alpha.(CPM)}$$

Note that:

$$\delta r = \frac{Q_S}{2\pi A \ Sin\alpha(CPM)}$$

In any given experiment, $\delta(r)$ is hyperbolic. δ could be constant if $r \cdot Sin\alpha$ were made constant, i.e. if the angle of the teeth is made to decrease as r increases. When there are gaps between the teeth the above relationships need to be modified. The product $\tau_R(CPM) Sin\alpha$ should be constant. Using 2" teeth spaced 2-1/8" apart in the present pilot plant, $\tau_R(CPM) sin\alpha$ is about 16 ± 6. Typical reactor holdup calculations are shown in Table 13.

A	width of rabble teeth, cm
(CPM)	contacts per minute
Q_S	volumetric solids flow rate, cm^3/min
r	radius, cm
a_1	inner radius of reactor, cm
a_2	outer radius of reactor, cm
α	angle
δ	manure layer thickness, cm
τ_R	holdup volume/volumetric flow rate, min.

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Table 13

Typical Reactor Holdup Calculations

Expt. No.	Feed Rate gm/min	Vol. Feed Rate cm^3/min	Holdup gm	τ_R min	(RPM) (min)$^{-1}$	(CPM) Contacts/min	α Degrees	$\{\tau_R(CPM) Sin\alpha\}$ Dimensionless
10-21A	58.33	133.8	255	4.371	2	4	45	12.363
10-21B	63.08	144.7	325	5.152	2	4	45	14.572
12-25A	58.42	134.0	182	3.116	3	6	45	13.220
10-25B	66.87	153.4	222	3.320	3	6	45	14.086
10-26A	66.15	151.7	106	1.602	5	10	45	11.328
10-26B	68.10	156.2	105	1.542	5	10	45	10.904
10-27A	63.27	145.1	68	1.075	12	24	45	18.243
10-27B	69.75	160.0	57	.817	12	24	45	13.865
10-28A	122.93	282.0	973	7.915	2	4	45	22.387
10-28B	169.17	388.0	1120	6.621	2	4	45	18.727
11-01A	170.0	389.9	98	.576	12	24	45	9.775
11-01B	174.3	399.8	147	.843	12	24	45	14.306
11-02B	171.1	392.4	387	2.262	5	10	45	15.995
--	188.0	431.2	605	3.218	12	24	22.5	29.555
--	190.9	437.9	1479	7.748	12	24	11.25	36.277
--	188.2	431.7	1109	5.893	12	24	11.25	27.592
--	184.0	422.1	1797	9.766	12	24	5.00	20.428
--	207.0	474.7	1887	9.116	12	24	5.00	19.068

DATA ANALYSIS

LABORATORY STUDIES

Isothermal Drying

The drying of manure in a laboratory oven provides data of the falling-rate type, and for any given oven temperature the slope of the rate of evaporation per gm of dry solids versus the moisture content (gm H_2O/gm dry solids) curve is constant. Since "gm dry solids" cancels out, one can simply use "gm H_2O evaporated/min" versus "gm H_2O remaining" in the data correlation. In each run the data obtained while the sample was warming up was not considered. Since the evaporation rate is necessarily zero when the moisture content is zero ($T > 100^0C$), the slope of the best (least squares) straight line that passes through the origin can be used for each set of data. This is:

$$\text{Best slope} = \frac{\Sigma}{\Sigma \ (W_i)^2}$$

$R_i \quad$ gm H_2O evaporated/min

$W_i \quad$ gm H_2O remaining, mean over interval

A plot of ln(slope) versus $\frac{1}{T}$ $(^0K)^{-1}$ gives a straight line of slope -2474 (r^2 = .982) (Figure 2). These data are represented by:

$$\frac{\delta \ln W}{\delta \tau} = 4.2698 \ \exp \ \left(- \frac{2474}{T}\right) \qquad (min)^{-1}$$

Figure 2

$$\frac{\delta \ln W}{\delta \tau} = 4.2698 \, \exp\left(\frac{-2474}{T}\right)$$

BATCH DRYING OF MANURE

ln(Slope)

$\frac{1}{T}$ $(°K)^{-1} \times 10^3$
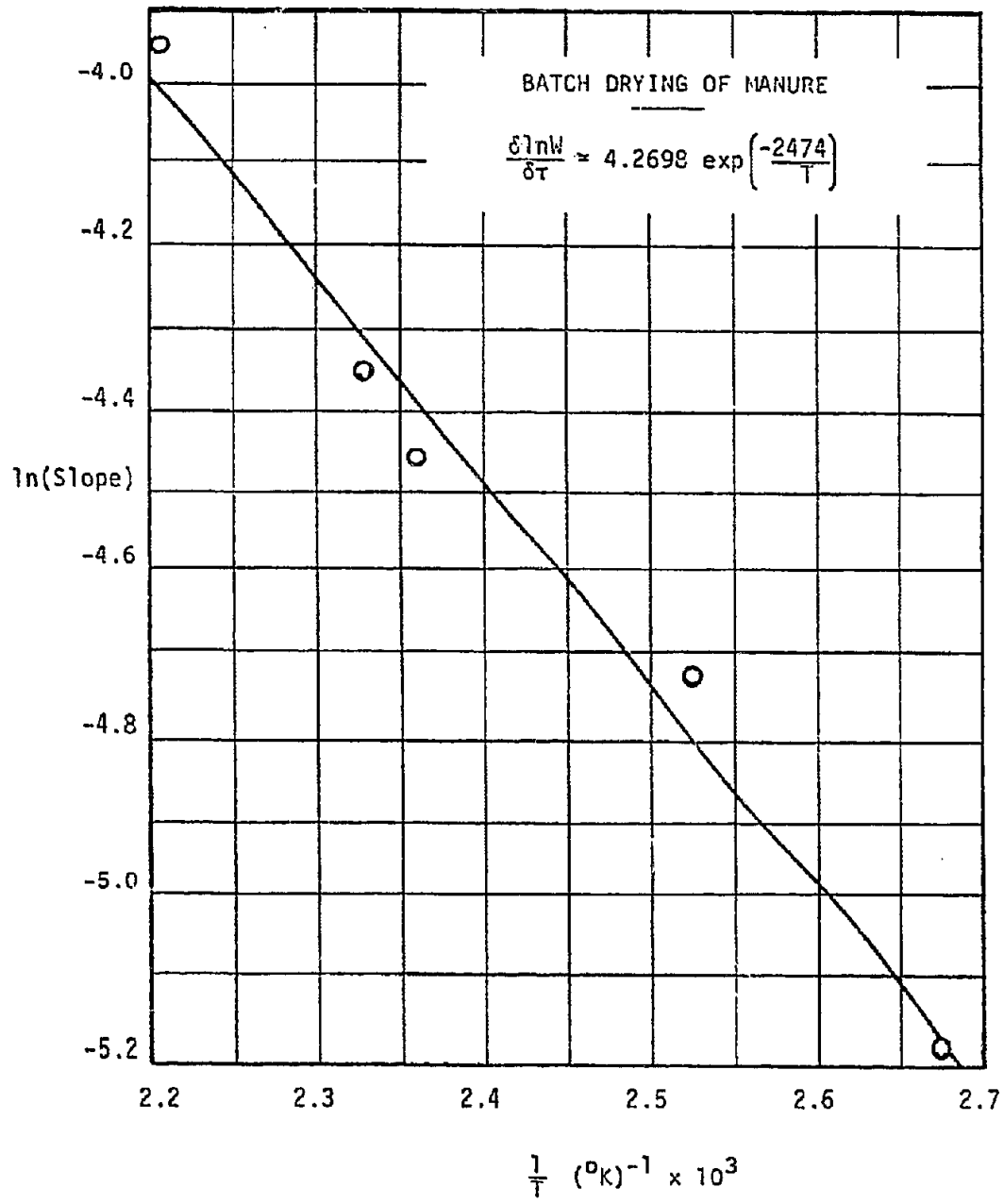
Parker[7] obtained:

$$\frac{\delta \ln W}{\delta \tau} = 2.8(10^4) \exp\left[-\frac{5250}{T}\right] \quad (\text{min})^{-1}$$

His experiments, however, were not isothermal. At $100^\circ C$, the lower end of these tests and his upper end, this data predicts $.0056 \; (\text{min})^{-1}$, while Parker predicts $.0216 \; (\text{min})^{-1}$ for the drying rate.

Conclusion

To dry manure in the oven at $180^\circ C$ from 35 to 10 wt % moisture would require:

$$\tau_D = \frac{\ln\frac{.35}{.10} \cdot \frac{.90}{.65}}{.0181} = 87.2 \; \text{minutes}$$

In the earlier contact drying experiments, the solids residence times were not longer than about 12 minutes. The solids flow rates appear to have been too high, so lower feed rates with small rabble tooth angles and high rabble arm rotation rates were next attempted. Smaller rabble tooth angles produce thicker layers, while higher rotation rates produce more stirrings per solids residence time and thinner layers. This provided thicker and better stirred manure layers in the drying section.

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[7]Parker, "Reaction Kinetics and Thermophysical Properties of Feedlot Waste During Drying and Pyrolysis," AIChE Symposium Series, No. 162, Vol. 73 (1977), pp. 216-223.
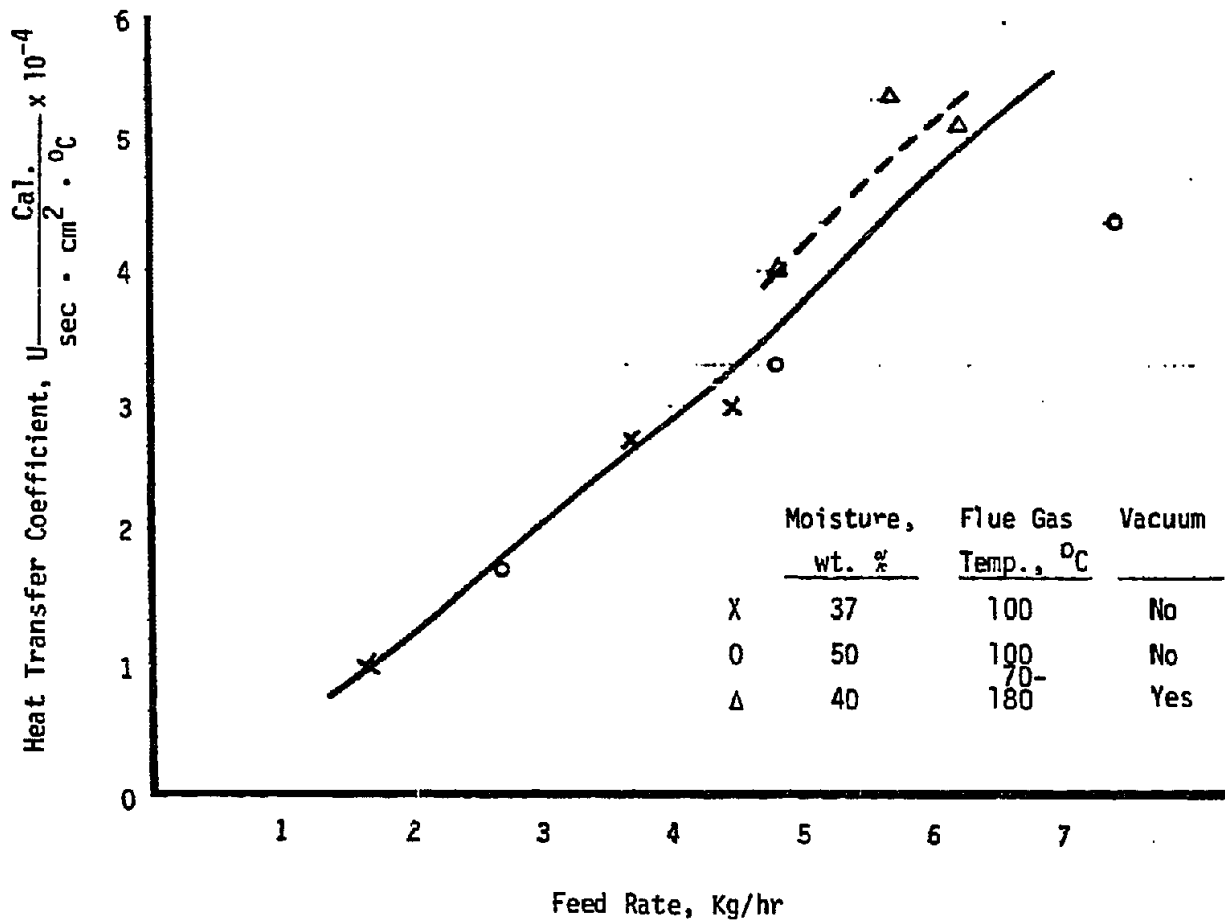
VACUUM DRYING

All of the run data of Table 2 appears to be of good quality except for run 12-12-A which probably should be omitted since the product temperature may be in error. The dimensionless number $\frac{\omega\tau_R}{N}$ in the table is: (solids residence time/thread)/(screw rotation time/thread). If the solids did not stick to the solid surfaces, $\omega\tau_R/N$ would relate to the thoroughness of the solids mixing--the larger $\omega\tau_R/N$, the better the mixing.

The dimensionless number $\frac{U\sqrt{\pi\alpha\tau_R}}{k}$ is the (actual heat transfer rate)/(conductive heat transfer rate to a continuous solid cylinder of manure). The penetration depth is relatively small compared to the diameter of the screw chamber, so the flat plate theory should apply. For non-sticking solids, $U\sqrt{\pi\alpha\tau_R}/k$ ought to increase as $\omega\tau_R/N$ increases. The experimental data of 12-9 show that it does.

The experimental data of 12-12 relate to tacky manure that probably stuck to the solid surfaces in the screw feeder. There was probably very little mixing, and $U\sqrt{\pi\alpha\tau_R}/k$ appears to be about unity. These data together with the isothermal drying data allow a calculation of drying rates.

A direct plot of the feed rate with the overall heat transfer coefficient has been made in Figure 3. This relationship should be able to be scaled-up to larger screw conveyors on an equal feed rate to circumference basis. Over the range tested, manure moisture content, flue gas temperature, and the degree of vacuum did not significantly influence the results.

Figure 3

Screw Conveyor
(Vacuum) Drying

	Moisture, wt. %	Flue Gas Temp., °C	Vacuum
X	37	100	No
0	50	100	No
Δ	40	70–180	Yes

Heat Transfer Coefficient, U $\frac{Cal.}{sec \cdot cm^2 \cdot \,^oC} \times 10^{-4}$

Feed Rate, Kg/hr

DIRECT CONTACT DRYING

Pilot Plant Data Correlation

The pilot plant direct contact drying data were correlated according
to the improved enthalpy transfer model. The calculations are shown below:

$(UA)_A$ = 70 B/h °F

	$(UA)_S$	$(C_p)_S W_F$	$(C_p)_G W_G$	$(UA)^*_S$	ψ_1	ψ_2	T_S (Calc)	T_S (Meas)	K
	B/h °F	B/h °F	B/h °F	B/h °F	--	°C	°C	°C	(min)$^{-1}$
10/21A	2.1571	3.939	15.704	13.689	21.246	1367.1	64.3	63	--
10/21B	0.6069	4.253	15.297	14.701	19.914	1093.4	54.9	51	--
10/25A	3.6625	3.942	15.822	12.553	20.942	1407.7	67.2	63	--
10/25B	0.8552	4.508	15.389	14.557	18.755	1150.8	61.4	56	--
10/26A	5.4488	4.461	15.901	11.238	18.221	1114.5	61.2	56	--
10/26B	1.2174	4.589	15.336	14.166	18.342	1018.8	55.5	51	--
10/27A	4.1792	4.168	15.875	12.201	19.721	1183.6	60.0	53	--
10/27B	1.0459	4.596	15.270	14.259	18.333	938.9	51.2	50	--
10/28A	3.1284	7.521	15.757	12.919	11.024	691.5	62.7	56	--
10/28B	2.1035	10.398	15.244	13.279	8.009	427.0	53.3	48	--
11/01A	3.4706	11.214	15.770	12.655	7.371	467.9	63.5	57.7	--
11/01B	1.3069	11.500	15.205	13.952	7.300	393.8	53.9	50.7	--
11/02B	3.5258	11.288	15.283	12.135	7.276	352.2	48.4	47.3	--
11/03E1	3.8846	10.175	15.796	12.352	8.094	522.7	64.6	55.0	--
11/03E2	3.9054	10.730	15.875	12.413	7.681	537.6	70.0	56.5	--
11/03E3	3.9346	9.484	16.039	12.550	8.704	549.9	63.2	58.0	--
12/13	--	--	--	--	--	--	--	47	1.61
12/14A	2.2710	7.718	15.408	13.297	10.792	533.3	49.4	47	1.02
12/14B	0.4321	8.260	15.297	14.870	10.274	531.6	51.7	46	1.70

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$$(UA)_S = 59.080\{.24 + .445 \frac{H_1 + H_2}{2}\} \ln \frac{(T_G)_1 - \bar{T}_S + \dfrac{\lambda_S H_1}{\{.24 + .445 \dfrac{H_1 + H_2}{2}\}(1.8)}}{(T_G)_2 - \bar{T}_S + \dfrac{\lambda_S H_2}{\{.24 + .445 \dfrac{H_1 + H_2}{2}\}(1.8)}} \qquad \frac{BTU}{hr^oF}$$

$$(C_p)_S W_F = \frac{W_F(1 - f_m)}{453.59} \{.2 + \bar{M}\} \qquad \frac{BTU}{hr^oF}$$

$$(C_p)_G W_G = 59.080\{.24 + .445 \frac{H_1 + H_2}{2}\} \qquad \frac{BTU}{hr^oF}$$

$$(UA)_S^* = (C_p)_G W_G [1 - \exp\{- \frac{(UA)_S}{(C_p)_G W_G}\}] \qquad \frac{BTU}{hr^oF}$$

$$\Psi_1 = \frac{(UA)_S^* + (UA)_A}{(C_p)_S W_F} \qquad --$$

$$\Psi_2 = \frac{1}{(C_p)_S W_F} \cdot [(UA)_S^* \{(T_G)_1 + \frac{\lambda_S H_1}{\{.24 + .445 \frac{H_1 + H_2}{2}\}(1.8)}\} + (UA)_A \cdot T_A] \qquad ^oC$$

$$T_S = \frac{\Psi_2}{\Psi_1} [1 - (1 - \frac{\Psi_1 T_A}{\Psi_2}) \exp\{-\Psi_1\}] \qquad ^oC$$

$$\kappa = \frac{1}{\tau_R} \cdot \ln \frac{M_1}{M_2} \cdot \exp \left(\frac{1385}{\bar{T}_S}\right) \qquad (min)^{-1}$$

Mathematical Models

Initial Calculation. When hot gas is passed through a fixed bed of moist manure, as time passes the moisture is removed. At steady state, the radial solids velocity across the base plate of the pilot plant reactor should be constant. Therefore, τ, time in the fixed bed, corresponds to $\frac{r}{U_R}$ in the pilot plant. The solids residence time in the pilot plant, $\tau_R = \frac{a}{U_R}$, corresponds to the same τ_R in the fixed bed. Manure drying is in the falling-rate period when $M_0 < 1.0$ approximately. In the pilot plant

$$- \frac{\delta \ln M}{\delta \tau} = 1.27 \cdot \left(\frac{V}{150.8}\right)^{0.8} \cdot \exp\left(- \frac{1385}{T_S}\right)$$

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Figure 4

Calculated Versus Measured Solids Temperature: Direct Contact Drying
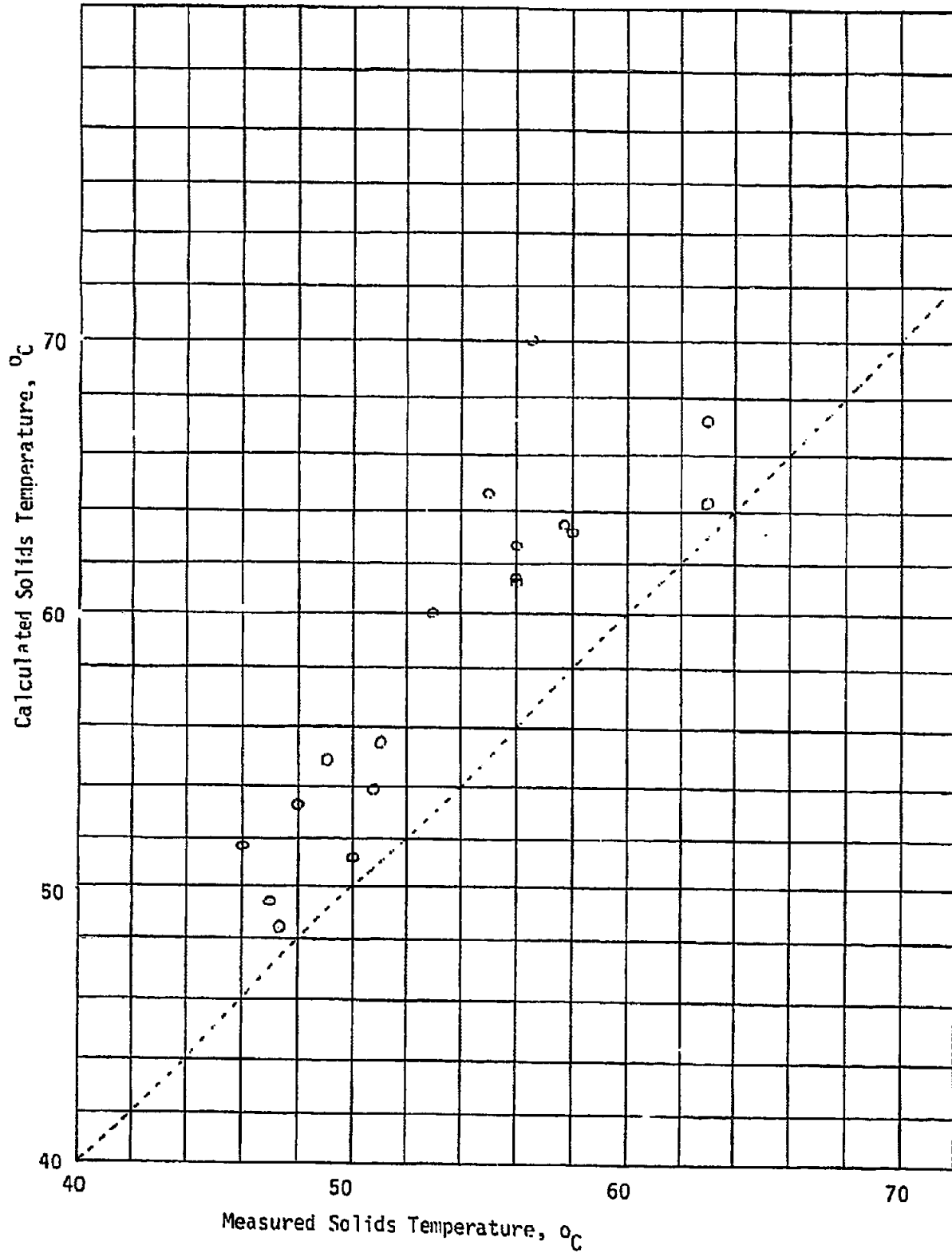
V is the velocity (cm/min) of the hot gas; T_S is in $^\circ K$; M is in gm H_2O/ gm dry solids.

Heat from the hot gas is used to increase the temperature level of the moist bed and to supply the latent heat of evaporation. Both the solid and gas phases offer resistance to the heat transfer, and the overall heat transfer coefficient, UA, cal/min $^\circ C$, is assumed to depend only on $V^{0.8}$. Assuming that the bed is sufficiently thin that variations in temperature with depth are negligible, T_S should be a function of τ alone. The heat transfer coefficient UA is based upon a log-mean temperature difference:

$$(\Delta T)_{lm} \frac{(T_G)_i - (T_G)_o}{\ln \dfrac{(T_G)_i - T_S}{(T_G)_o - T_S}} \tag{1}$$

The heat balance reads:

$$T_S = \frac{1}{(1 + M) C_p} \cdot \left| \frac{(UA)}{W_S} \cdot (\Delta T)_{lm} + \lambda \cdot \Delta M \right|, \tag{2}$$

where C_p is the heat capacity, cal/(gm moist solid) $(^\circ C)$, and depends upon M. $(1 + M) C_p$ is in cal/(gm dry solid) $(^\circ C)$. $W_S (1 + M) C_p \Delta T_S$ is the rate of sensible heat accumulation, cal/min. W_S is gm dry solids/min. λ is the latent heat, so $W_S \lambda \Delta M$ is the rate of latent heat transfer, cal/min. $(UA)(\Delta T)_{lm}$ is the total rate of heat transfer, cal/min.

$$C_p = .1128 + 1.335 \left[\frac{M}{1 + M}\right] - .4486 \left[\frac{M}{1 + M}\right]^2 \tag{3}$$

A heat balance on the gas reads:

$$(T_G)_o = (T_G)_i - \frac{W_S (C_p \Delta T_S - \lambda \Delta M)}{124 W_G} \tag{4}$$

W_G is gm dry gas/min, and 0.24 is its specific heat, cal/(gm dry gas) $(^\circ C)$.

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Rewriting the drying equation:

$$\Delta M = - A \, M \, \exp\left[-\frac{B}{T_S}\right] \, \Delta t \tag{5}$$
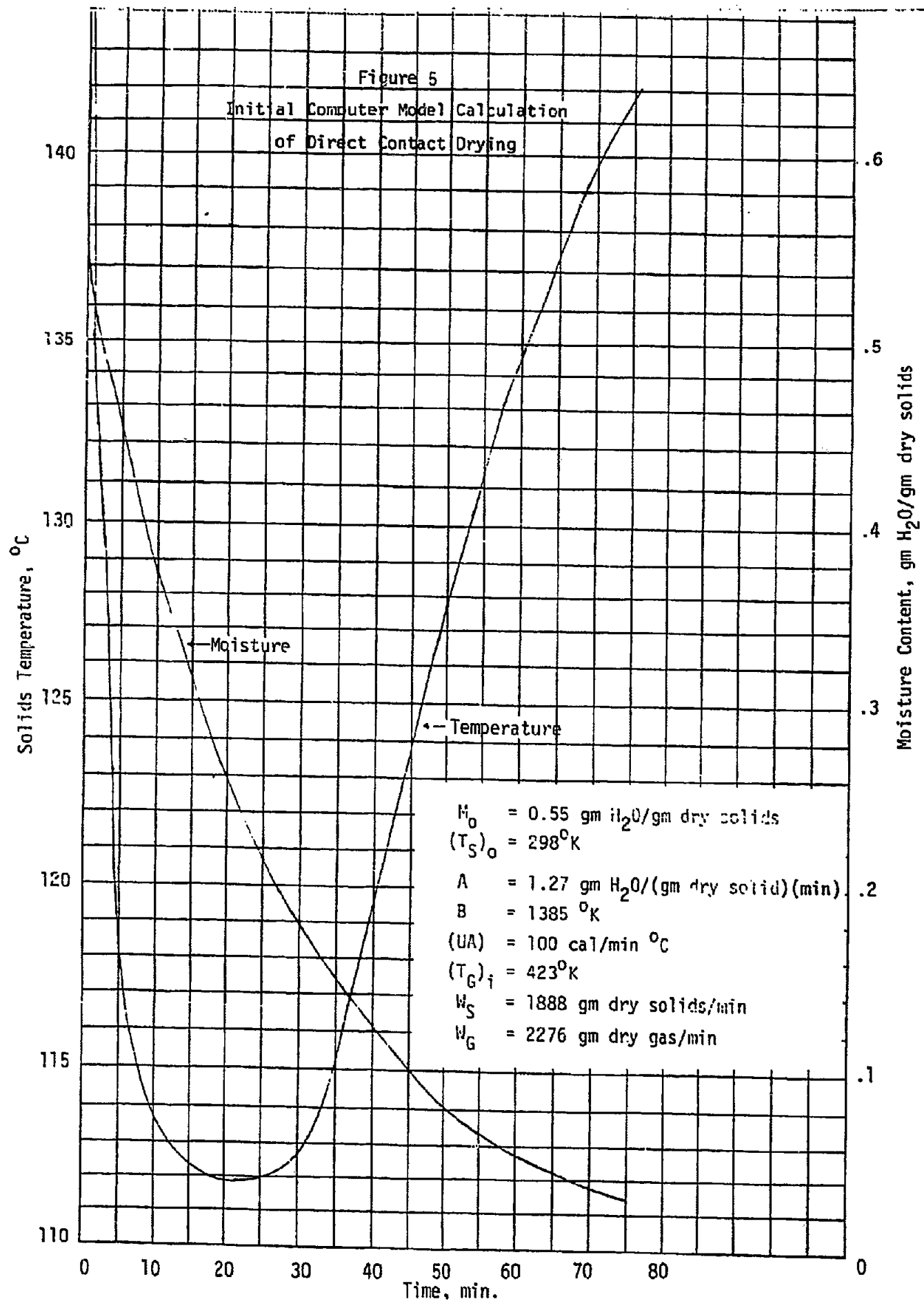
If V were a variable, $\left(\frac{V}{V_o}\right)^{0.8}$ would modify A in (5) and (UA) in (1).

Initial Numerical Integration. A HP-67 was used to calculate numerical solutions to this set of five equations, using a naive time step approach. There is a HP Runge-Kutta program available, but this program requires too many steps and so it couldn't be used. Starting with a cold bed, the HP-67 has to run about 3 hours to get to a nearly (M = 0.05) dry bed. Substantial errors are incurred in the integration because of the size of the Δt's that must be used. A sample problem was worked out, and the results are shown on Figure 5. The constants used were

Initial Values	τ_o	0 min
	M_o	0.55 gm H_2O/gm dry solids
	$(T_S)_o$	298 ^{o}K (25 ^{o}C)
	$(\Delta \tau)_o$	.0001 min
Constants	A	1.27 gm H_2O/(gm dry solids) (min)
	B	1385 ^{o}K
	(UA)	100 cal/min ^{o}C
	$(T_G)_i$	423 ^{o}K (150 ^{o}C)
	W_S	1888 gm dry solids/min
	W_G	2276 gm dry gas/min

W_S and W_G are based on 3 T dry solids/day in a 4 ft. diam. reactor. The values for A and B are based on the laboratory data. The value (UA) = 100 cal/min ^{o}C is a guess.

The first phase is rapid warm up. Within 0.5 min. from the start, T_S shoots up almost to the gas temperature. During this time very little

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Figure 5
Initial Computer Model Calculation
of Direct Contact Drying

M_0 = 0.55 gm H_2O/gm dry solids
$(T_S)_0$ = 298° K

A = 1.27 gm H_2O/(gm dry solid)(min)
B = 1385 °K
(UA) = 100 cal/min °C
$(T_G)_i$ = 423° K
W_S = 1888 gm dry solids/min
W_G = 2276 gm dry gas/min

moisture evaporates. The calculation is very tedious because T_S changes so rapidly. In the second phase evaporation is very rapid, so rapid that the heat transfer rate from the gas is insufficient to meet the demand. T_S falls off, the $(\Delta T)_{lm}$ and the overall heat transfer rate increase. Eventually a balance is struck and T_S passes through a minimum. In the third period the moisture content and evaporation rate decrease slowly, while T_S rises just rapidly enough to maintain the balance. After a very long time, M goes to zero and T_S goes to $(T_G)_i$.
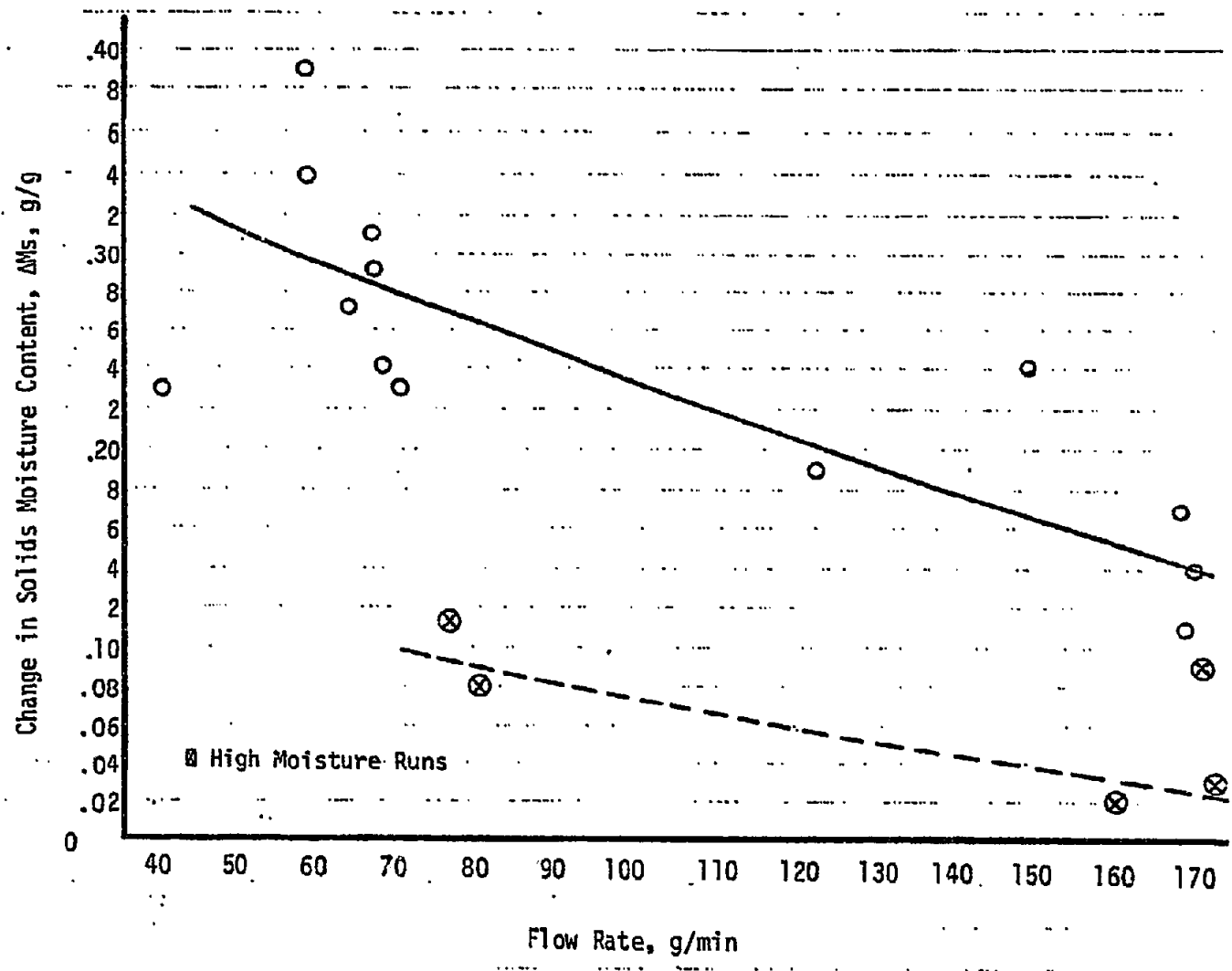
For this particular calculation, M goes to 0.1 in about 45 min. and to 0.05 in about 60 min. (UA) = 100 cal/min ^{O}C appears to be too large, so in the pilot plant the corresponding solids residence times are probably somewhat longer than these. In the pilot plant the longest residence time to date has been about 30 minutes. The (UA) calculated from the pilot plant data is not the same (UA) used in this calculation.

A second calculation was also made using (UA) = 10 instead of 100 cal/min ^{O}C. The solids temperature shot up to only 73 ^{O}C in Phase I. In Phase II, T_S plummeted to 260 ^{O}C (-13 ^{O}C, frozen!) at which point the work was stopped. Thus, a realistic (UA) must be in the 10-100 cal/min ^{O}C range.

In order to more simply review the major functions in direct contact drying, it appears in Figure 5b that the rate of water evaporation is directly proportional to the residence time (or inversely to flow rate). Very high moisture contents (greater than 50%) also appear to greatly reduce the evaporation rate. Flue gas temperature and moisture content (below 50%) do not appear to influence the rate of drying.

Figure 5a

Direct Contact Drying

moisture evaporates. The calculation is very tedious because T_S changes so rapidly. In the second phase evaporation is very rapid, so rapid that the heat transfer rate from the gas is insufficient to meet the demand. T_S falls off, the $(\Delta T)_{lm}$ and the overall heat transfer rate increase. Eventually a balance is struck and T_S passes through a minimum. In the third period the moisture content and evaporation rate decrease slowly, while T_S rises just rapidly enough to maintain the balance. After a very long time, M goes to zero and T_S goes to $(T_G)_i$.

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Analysis. The connection between the model and contact drying in the pilot plant is that time, τ, in the model corresponds to $\int \frac{dr}{u_r}$ in the pilot plant. The superficial gas velocity, W_G/A, is the same in the model and in the pilot plant, but the outlet gas temperature in the pilot plant corresponds to

$$\frac{1}{\tau_R} \cdot \int_0^{\tau_R} T_G \cdot d\tau$$

in the model. Here τ_R is the residence time of the solids in the pilot plant.

It turns out that the plant problem is somewhat simpler than this, since (UA) is essentially infinite for the bed thicknesses of interest. When (UA) is essentially infinite, $T_G = T_S$, i.e. thermal equilibrium is attained between the gas and solid. In a well-insulated fixed bed the bed temperature, outlet gas temperature, and inlet gas temperature were measured as functions of time. The outlet gas temperature, and inlet gas temperature were measured as functions of time. The outlet gas temperature and solids temperature were the same in these experiments. Thus, simplified reduced calculations could read as follows:

$$W_G(C_p)_G\{(T_G)_i - T_G\} = M_S\{(C_p)_S \frac{\delta T_S}{\delta \tau} - \lambda_v \frac{\delta M}{\delta \tau}\} \quad \text{Heat Balance} \quad (5)$$

$$T_S = T_G \qquad\qquad\qquad \text{Gas/Solid Thermal Equilibrium} \quad (6)$$

$$-\frac{\delta M}{\delta \tau} = A^* \cdot M \cdot \left(\frac{W_G}{A}\right)^{0.8} \cdot \exp\left(-\left(\frac{B}{T_S}\right)\right) \quad \text{Rate of Moisture Transfer} \quad (7)$$

$$-M_S \cdot \frac{\delta M}{\delta \tau} = W_G \cdot (H - H_i) \qquad\qquad \text{Moisture Balance} \quad (8)$$

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The moisture balance is not very important, since it has only a minor influence on $(C_p)_G$.

For the solids and gas heat capacities:

$$(C_p)_S = (1 + M) \cdot \{.1128 + 1.335 \left(\frac{M}{1+M}\right) - .4486 \left(\frac{M}{1+M}\right)^2 \} \qquad (9)$$

$$(C_p)_G = 0.24 + 0.445 \, H \qquad (10)$$

Equations (5) through (10) were programmed on the HP-67. Using the proper initial condition (discussed below), the calculation proceeds smoothly with Δt's of reasonable size. When (UA) is essentially infinite, the solids temperature, T_S, and the outlet gas temperature, T_G, converge very rapidly-- so rapidly that very little drying occurs in this time. During this initial warm-up period, Equations (5) and (7) become approximately

$$W_G (C_p)_G \{(T_G)_i - T_G\} = M_S \{(C_p)_S \frac{\delta T_S}{\delta \tau} + A*M^0 \left(\frac{W_G}{A}\right)^{0.8} \exp \left(- \frac{B}{T_S}\right)\} \text{ for small } \tau \quad (11)$$

where M^0 is the initial moisture content of the solids, gm H_2O/gm dry solids. Starting from a low value, T_S first passes through a maxima, and then through a minima. (See Figure 2). For the present purpose, it is assumed that $T_{i,}$ becomes T_S just as T_S passes through its minima, and that this temperature is the above-mentioned proper initial condition for the numerical integration of the reduced problem. This initial temperature, T_S^0, is the root of the following equation:

$$W_G (C_p)_G \{(T_G)_i - T_S^0\} = M_S \cdot A* \cdot M^0 \cdot \left(\frac{W_G}{A}\right)^{0.8} \cdot \exp \left(-\frac{B}{T_S^0}\right) \qquad (12)$$

Comparison of Pilot Plant Data and Model. In the pilot plant experiments 10-21-A through 11-03-E_3 (Table 4) the holdup volumes were not measured properly. The holdup volumes were measured properly in the final three experiments, 12-13 through 12-14-B, and so these data will be used for comparison with the model:

Experiment 12-13 $A** = \dfrac{A*}{(150.8)^{0.8}} = 1.185$; B = 1385 throughout.

M_S = 1112 gm dry solids

$V_G = W_G/A$ = 138.3 cm/min

W_G/M_S = .4021 gm dry gas/(min)(gm dry solids)

$(T_G)_i$ = 417°K

H_i = .025 gm H_2O/gm dry gas

M^O = .6234 gm H_2O/gm dry solids

τ_R = 27.842 min

Calculated T_S^O = 347°K

At τ = 27.842 min:

	Calculated	Measured
T_S	386.2°K	320.2°K
M	.3103 gm/gm	.3897 gm/gm
$\dfrac{1}{\tau_R} \cdot \displaystyle\int_0^{\tau_R} T_G \cdot d\tau$	358.4°K	348.2°K

Experiment 12-14-A

M_S = 1452 gm dry solids

$V_G = W_G/A$ = 138.3 cm/min

W_G/M_S = .3079 gm dry gas/(min)(gm dry solids)

$(T_G)_i$ = 421°K

H_i = .033 gm H_2O/gm dry gas

M^O = .6234 gm H_2O/gm dry solids

τ_R = 19.044 min

Calculated T_S^O = 337°K

At τ = 19.033 min:

	Calculated	Measured
T_S	352.5°K	320.2°K
M	.4160 gm/gm	.5069 gm/gm
$\dfrac{1}{\tau_R} \cdot \displaystyle\int_0^{\tau_R} T_G \cdot d\tau$	343.9°K	332.2°K

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Experiment 12-14-B

M_S = 588.9 gm dry solids

V_G = W_G/A = 138.3 cm/min

W_G/M_S = .7592 gm dry gas/(min)(gm dry solids)

$(T_G)_i$ = 423°K

H_i = .025 gm H_2O/gm dry gas

M^O = .6234 gm H_2O/gm dry solids

τ_R = 7.394 min

Calculated $T_S{}^O$ = 373°K.

At τ = 7.394 min:

	Calculated	Measured
T_S	379.7°K	319.2°K
M	.4995 gm/gm	.5446 gm/gm
$\frac{1}{\tau_R} \cdot \int_0^{\tau_P} T_G \cdot d\tau$	375.9°K	340.2°K

Discussion. This mathematical model does not consider heat losses, so the calculated T_S and $\frac{1}{\tau_R} \cdot \int_0^{\tau_R} T_G \cdot d\tau$ should be higher than the measured solids and outlet gas temperatures. Similarly, the calculated M should be lower than the measured final moisture content of the solids.

The measured solids temperature, however, seems too low to be explained by heat losses alone. Intially this temperature was measured outside the reactor, and the solids had probably cooled somewhat. Later equipment was installed to measure the solids temperature inside the reactor (using a thermocouple attached to a rotating rabble tooth).

Improved Mathematical Model. Enthalpy transfer rates, rather than heat transfer rates, appear to have some advantages in forming the model. In addition to being more correct, they appear to greatly simplify the analysis. When the drying gas in direct contact drying contains insufficient heat to dry the manure, its temperature falls below 100^0C and its humidity approaches saturation. Since manure behaves in a somewhat hygroscopic manner, the corresponding equilibrium moisture contents, M_e, become large. The drying rates, which vary as $(M-M_e)$, fall to low levels.

Enthalpy Balance:

$$W_G(C_P)_G \left[(T_G)_i - T_G + \frac{\lambda_v}{(C_P)_G} \cdot \{H_i - H\} \right] =$$

$$M_S(C_P)_S \frac{\partial T_S}{\partial \tau} + (UA)_A \{T_S - T_A\} \tag{1}$$

Enthalpy Transfer Rate:

$$W_G(C_P)_G \left[(T_G)_i - T_G + \frac{\lambda_v}{(C_P)_G} \cdot \{H_i - H\} \right] =$$

$$(UA)_s \cdot \frac{(T_G)_i - T_G + \frac{\lambda_v}{(C_P)_G} \cdot \{H_i - H\}}{\ln \frac{(T_G)_i - T_S + \frac{\lambda_v}{(C_P)_G} \cdot H_i}{T_G - T_S + \frac{\lambda_v}{(C_P)_G} \cdot H}} \tag{2}$$

Which can also be written:

$$\frac{T_G - T_S + \frac{\lambda_v}{(C_p)_G} \cdot H}{(T_G)_i - T_S + \frac{\lambda_v}{(C_p)_G} \cdot H_i} = \exp\left[- \frac{(UA)_S}{(C_p)_G \, W_G}\right] \tag{3}$$

Moisture Balance:

$$W_G\{H - H_i\} = -M_S \frac{\partial M}{\partial \tau} \tag{4}$$

Drying Rate:
(Falling Rate Period)

$$-\frac{\partial M}{\partial \tau} = A \left[\frac{V}{V_o}\right]^{0.8} \cdot (M - M_e) \cdot \exp\left[- \frac{B^*}{T_S}\right] \tag{5}$$

where M_e is a function of $\frac{H}{H_{sat}}$ and T_G.

Equations (1) and (3) can be combined to read

$$-\frac{1}{\psi_1} \cdot \frac{\partial n}{\partial \epsilon} + n - 1 = 0 \tag{6}$$

The solution is

$$\frac{1-n}{1-n_0} = \exp(-\psi_1 \theta) \tag{7}$$

where

$$\theta = \frac{\tau}{\tau_R} \quad ; \quad n = \frac{\psi_1 T_S}{\psi_2} \tag{8), (9}$$

$$\psi_1 = \frac{(C_p)_G \, W_G}{(C_p)_S \, W_F} \cdot \left[1 - \exp\left(- \frac{(UA)_S}{(C_p)_G \, W_G}\right)\right] + \frac{(UA)_A}{(C_p)_S \, W_F} \tag{10}$$

$$\psi_2 = \frac{(C_p)_G\, W_G}{(C_p)_S\, W_F}\left[1 - \exp\left(-\frac{(UA)_S}{(C_p)_G\, W_G}\right)\right]\left\{(T_G)_i + \frac{\lambda_v}{(C_p)_G}\cdot H_i\right\} + \frac{(UA)_A}{(C_p)_S\, W_F}\cdot T_A \tag{11}$$

Nomenclature

A	Empirical constant, $(min)^{-1}$
B^*	Empirical constant, ^oK
$(C_p)_G$	Heat capacity of gas, cal/(gm dry gas)(^oK)
$(C_p)_S$	Heat capacity of solids, cal/(gm dry solids)(^oK)
H	Humidity of gas, gm H_2O/gm dry gas
H_i	Humidity of gas at inlet, gm H_2O/gm dry gas
H_{sat}	Saturated humidity of gas at temperature T_G, gm H_2O/gm dry gas
M	Moisture content, gm H_2O/gm dry solids
M_S	Solids holdup, gm
T_A	Temperature of ambient air, ^oK
T_G	Temperature of gas leaving bed, ^oK
$(T_G)_i$	Temperature of gas entering bed, ^oK
T_S	Temperature of solids, ^oK
$(UA)_A$	Rate of heat loss to ambient air/($T_S - T_A$), cal/min ^oK
$(UA)_S$	Rate of enthalpy transfer in the bed/(Difference in enthalpy between gas and solids), cal/min ^oK
V	Superficial gas velocity, cm/min
W_F	Solids flow rate, gm dry solids/min
W_G	Gas flow rate, gm dry gas/min
λ_v	Latent heat of evaporation at T_G, cal/gm
τ	Time, min
$\tau_R = M_S/W_F$	Solids residence time, min

PYROLYSIS

The material balances on the total manure and on the ash close satisfactorily. A summary of the manure pyrolysis runs is given in Table 14. Runs at 580 and 591°C are essentially duplicates of each other. Between 83-91% of the volatiles (750°C) were released as gas and tar at solids temperatures of from 495 to 660°C. In the proximate analysis, pyrolysis is continued at 750°C under inert gas until no more gas is evolved. (The temperature 750°C has been selected as an arbitrary reference). In all cases the static holdup which was at the solids temperature for the longest times had the lowest volatiles (750°C) content of the three types of char.

In these experiments between 2 and 44% of the residual carbon (left behind after pyrolysis) was gasified by the steam present in the feed, or generated during pyrolysis. This appears to be consistent with Phase I steam/char reaction results. In Phase I the char residence times for Runs 5 and 6 were 33 and 30 min. respectively. Solids temperatures were not measured, but judging from the measured baseplate and outlet gas temperatures, the solids temperatures were probably in the 700°C range. In Run 5, 36.0% of the carbon was gasified, and in Run 6, 34.6% of the carbon was gasified.

When the solids temperature is above 635°C, and the gas phase contains a high concentration of steam, CH_4 and the higher hydrocarbons might be hydrocracked down to H_2 and CO. When the feed manure contained about 45 wt % moisture, the pyrolysis gas (at 635°C) contained about .054 gm CH_4/gm DAF

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Table 14

Summary of Manure Pyrolysis Experiments

Temp., °C	Feed Moisture, wt %	Volatiles Removed, %	Carbon Gasified, %	Heating Value, BTU	Gas Yield, g/g	Gas Yield, w/o CO_2	Gas Analysis, Vol. % CO_2	CO	H_2	CH_4	C_2^+	Comments
495	33.2	84.7	3.5	246	1.11	.324	35.7	14.2	40.1	9.5	.6	
522	32.2	86.8	28.3	223	.94	.261	32.8	13.0	48.5	5.7	--	
580	31.5	83.3	40.8	--	.45	.125	37.7	12.8	37.8	10.3	1.4	Poor Run
591	31.5	84.0	29.5	--	.76	.210	37.7	12.8	37.8	10.3	1.4	Poor Run
605	25.6	86.9	--	--	.38	.099	37.9	10.9	40.0	8.9	2.3	Poor Run
615	29.9	--	--	--	--	--	29.4	15.5	48.8	6.3	--	Poor Run
620	6.7	--	--	--	--	--	23.9	27.5	39.6	8.9	--	Poor Run
630	47.8	82.9	2.4	240	.99	.278	36.2	9.5	45.5	7.5	1.29	
635	43.2	87.2	29.0	273	.74	.229	30.8	11.2	47.1	8.9	2.0	
636	7.3	93.0	14.5	299	.70	.341	22.9	24.5	40.3	11.8	.5	
640	5.9	84.7	42.7	313	.65	.230	33.5	15.3	34.8	12.8	3.6	
657	5.2	88.0	28.4	319	.53	.208	30.9	17.7	35.2	12.6	3.6	
660	36.7	88.7	14.9	298	1.00	.381	26.6	14.3	46.0	11.3	1.9	
661	30.2	91.3	43.5	274	.97	.366	26.6	15.6	46.8	11.0	-- 1.86	
Average 611	26.2	86.8	25.2	276	.85	.291	29.1	15.3	42.0	9.7	1.33	

feed and about .022 gm $(C_2H_4 + C_2H_6)$/gm DAF feed. When the feed moisture was about 5 wt %, the pyrolysis gas (at 740 and 651°C) contained .048 to .058 gm CH_4/gm DAF feed and .025 to .030 gm $(C_2H_4 + C_2H_6)$/gm DAF feed. Even if the feed were perfectly dry, the pyrolysis gas would contain a great deal of steam. Thus, the data seem to suggest that either the hydro-cracking reactions are frozen at the existing temperature, or the steam derived from the feed moisture simply adds to an already gross excess of pyrolytic steam. The variation of gas yields and volatiles removed with temperature are shown in Figure 6. As would be expected, the higher the temperature the greater the gas yield. Equilibrium for the reaction $CO + H_2O \rightleftarrows CO_2 + H_2$ shifts to the left as the temperature increases.

The runs performed on sawdust (summarized in Table 15) were at tempera-tures of from 631 to 653°C. Wood has a very large volatiles (750°C) content-- about 79 wt % dry basis--and about .82 g gas/g DAF feed were produced. The wood pyrolysis gas contained about 16.5 vol % CH_4 and about 2.9 vol % C_2^+ giving it a relatively high volumetric heating value (360 BTU/SCF). Here also about 30% of the carbon was steam-gasified in spite of the low solids temperatures. The ash content of wood char is low (5.9%), but the steam-gasification rates did not change for lack of a catalysis in the ash. (An average of 25.2% carbon gasification occurred with manure at 611°C and 26.2% moisture in the feed, compared to 26.7% of the carbon gasified from sawdust at 641°C and a 19.3% feed moisture content). It is interesting to note, however, that apparently the ash in manure did catalyze the $CO \rightarrow CO_2$ shift conversion. The gas averaged 15.3% CO and 42.0% H_2 from the pyrolysis of manure, and 31.4% CO and 25.2% H_2 from sawdust. However, the CO_2 was 29.1% from manure, and 24.0% from sawdust, so perhaps the high ash content in manure accelerated the $H_2O + CO \rightleftarrows CO_2 + H_2$ reaction.
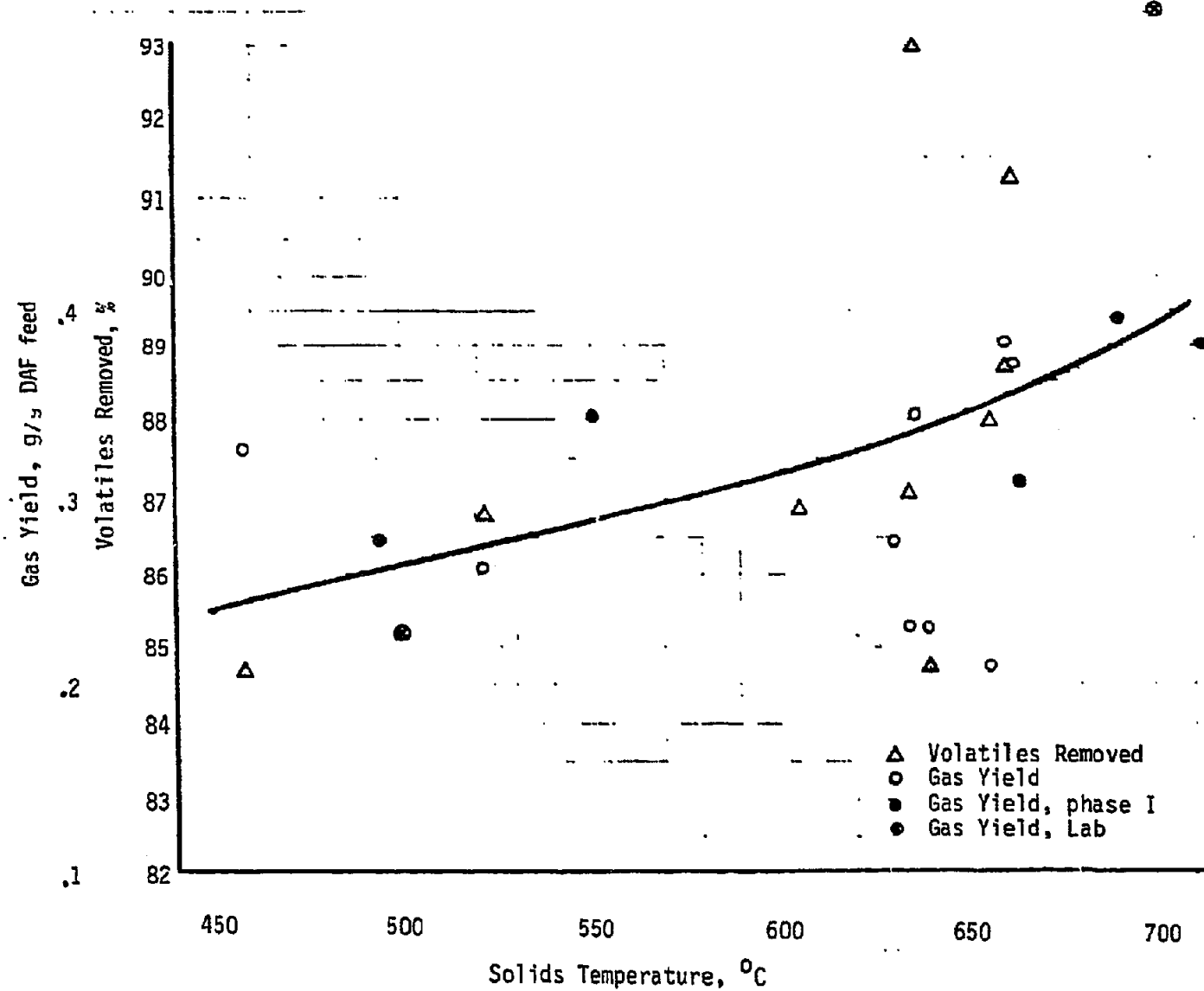
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Figure 6

Manure Pyrolysis Yields

Figure 7
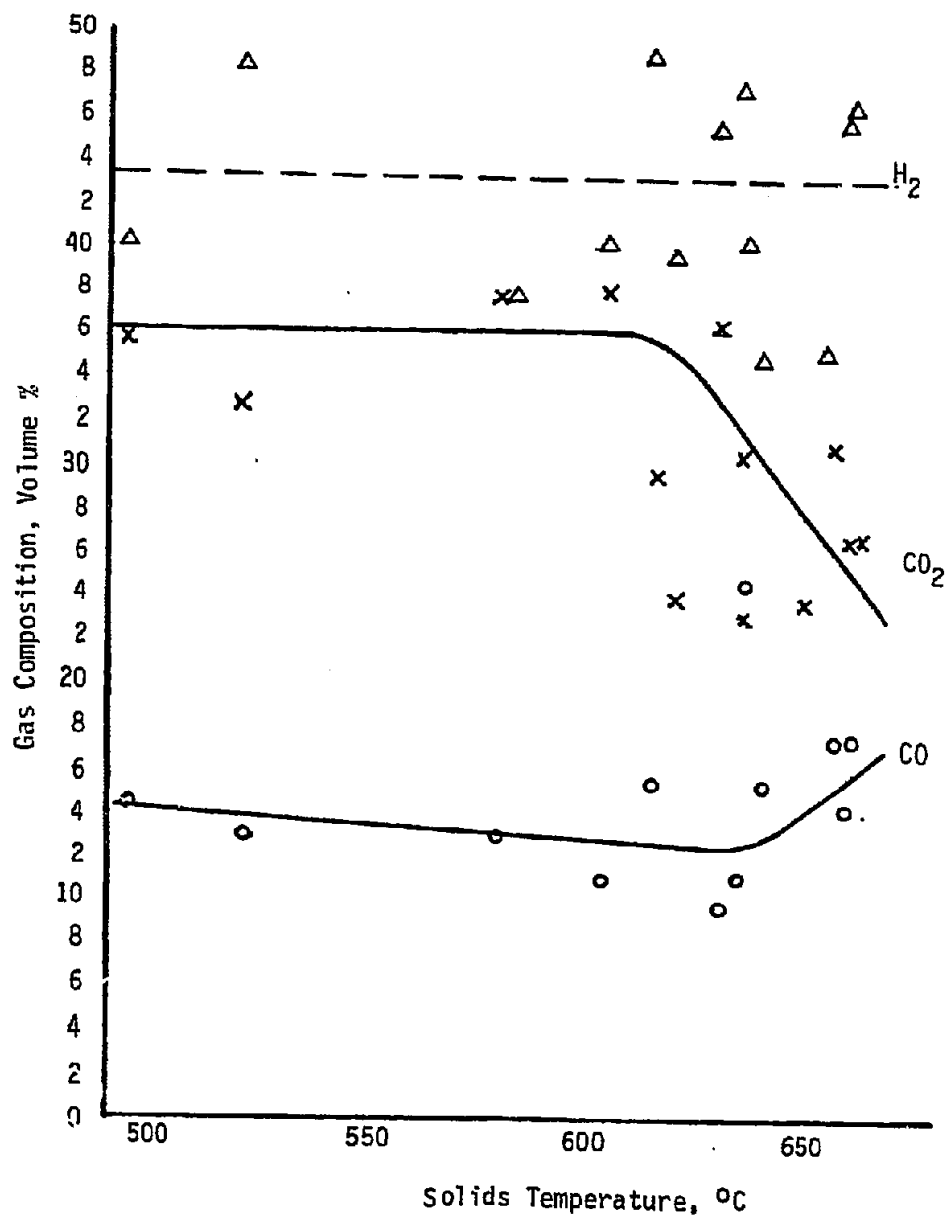
Manure Pyrolysis Gas Composition

Table 15

Summary of Sawdust Pyrolysis Experiments

Temp. °C	Feed Moisture, wt. %	Volatiles Removed, %	Carbon Gasified, %	Heating Value, BTU	Gas Yield, g/g	w/o CO_2	Gas Analysis, Vol. %					Char, Volatiles	wt. % Ash
							CO_2	CO	H_2	CH_4	C_2^+		
631	10.0	97.9	17.2	361	.783	.441	23.4	33.8	23.7	16.2	2.9	17.7	8.0
640	12.5	97.8	32.2	359	.784	.427	24.6	32.2	24.0	16.2	3.0	14.6	4.8
640	24.6	99.0	27.1	359	.894	.480	23.4	28.2	28.4	17.6	2.4+	--	--
653	30.0	98.2	30.3	357	.823	.444	24.7	31.5	24.7	15.9	3.1	12.2	4.9
Average 641	19.3	98.2	26.7	359	.821	.448	24.0	31.4	25.2	16.5	2.9	14.8	5.9

WATER GAS REACTION

Run 3-1-78 served as a "blank", where the completely dry feed char contained 16 wt % volatile (750^{0}C) matter, and about 39% of it was removed. Pyrolytic water was formed, and this gasified about 7% of the carbon (750^{0}C).

Runs 3-6-78 and 3-8-78 were similar, but steam was present in excess in both cases. About 18% of the carbon (750^{0}C) was gasified. The solids temperatures were low, 564^{0} and 606^{0}C respectively, and this is why the gasification rates are low. About 44% of the volatiles (750^{0}C) were removed in these runs.

The equation involved in the steam-char or water gas reaction is:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \tag{1}$$

Both thermogravimetric analysis and the pilot plant data show that the reaction between biomass char and steam is comparatively fast even when the reaction temperature is as low as 650^{0}C. The reaction rates of biomass char and steam are much higher than the corresponding reaction rates of the various coal chars and steam[8, 9, 10].

In the thermogravimetric work, the biomass char samples were very small (3-5 mg) and sieved into fractions containing different particle

[8] Linares, A., Mahajan, O. P., Walker, P. L., "Reactivities of Heat-Treated Coals in Steam," ACS Div. Fuel Chemistry Symp., Vol. 22, No. 1 (March 1977), p. 1.

[9] Tomita, A., Mahajan, O. P., Walker, P. L., "Catalysis of Char Gasification by Minerals," ACS Div. Fuel Chemistry, Symp., Vol. 22, No. 1 (March 1977), p. 4.

[10] Walker, P. L., Mahajan, O. P., Yarzab, R., "Unification of Coal Char Gasification Reactions," ACS Div. Fuel Chemistry Symp., Vol. 22, No. 1 (March 1977), p. 7.

sizes (100/200, 200/250, and -250 mesh) in order to reduce the diffusional component of the overall reaction rate. In spite of this, the steam-carbon reaction appeared to be primarily controlled by the diffusion rate of steam to the reaction sites when the reaction temperature was higher than about $600^{\circ}C$.

In the pilot plant pyrolysis experiments, the data showed that only a small part of the pyrolytic carbon had been steam-gasified when the solids temperature was as low as $600^{\circ}C$, but considerably more started to react when the temperature was raised to $650^{\circ}C$. (See the Gas Yield in the summary, Table 16). Pyrolytic carbon is defined as the carbon remaining in a laboratory batch pyrolysis experiment done at $750^{\circ}C$ in which there is essentially zero contact time between the solids and the evolved gases. It is also apparent from Table 16 that the shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) must have taken place to a considerable extent because of the comparatively low CO_2 and high CO content in relation to the hydrogen.

A simplified analysis of the diffusion-controlled steam-carbon reaction is presented here. A pile of char is reacting with steam at its surface. As time proceeds, the ash-char interface recedes further into the mass. The volume of the ash layer is less than the volume of the char it replaces. The temperature is so high that the carbon-steam reaction is very fast. The humidity of the gas phase at the ash-char interface is essentially zero. There is a net outflow of gas through the ash layer, and the steam must diffuse into the ash layer against this outflow. Also, the water gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2}$$

occurs throughout the ash layer and in the micropores of the carbon at the ash-char interface. Equilibrium for this reaction shifts to the right at

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Table 16

Water Gas Reaction of Manure Char

Temp. °C	Volatiles in feed, %	Steam Added g/g Feed	H$_2$O/C (mole/mole)	Volatiles Removed, %	Carbon Gasified, %	Gas Yield, g/g DAF	Gas Yield w/o CO$_2$	Gas Analysis			
								CO$_2$	CO	H$_2$	CH$_4$
564	15.4	.46	1.22	43.2	17.6	.195	.044	31.7	7.8	55.4	5.2
597	16.3	0	.14	38.9	7.1	.213	.085	25.1	16.5	47.8	10.7
606	14.4	.47	1.45	44.5	17.7	.214	.046	33.3	8.4	54.9	3.4
650	16.8	.25	.73	52.2	16.9	.662	.228	27.1	16.7	52.9	3.3
Average 604	15.7	.30	.89	44.7	14.8	.321	.101	29.3	12.4	52.8	5.7

lower temperatures. For this simplified analysis and data correlation, it is assumed that at about $600^{\circ}C$ the pseudo reaction:

$$C + \frac{7}{4} H_2O \rightarrow \frac{1}{4} CO + \frac{3}{4} CO_2 + \frac{7}{4} H_2 \tag{3}$$
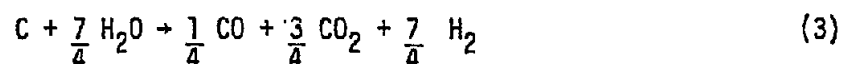
occurs at the ash-char interface and that the reactant and product gases diffuse through the ash layer without reaction. The diffusion equation for this stoichiometry is:

$$N_{H_2O} = \frac{-c\mathfrak{D}_{im}}{(1 + \frac{4}{7} \cdot X_{H_2O})} \cdot \frac{\partial X_{H_2O}}{\partial Z} \tag{4}$$

N_{H_2O} is constant with Z. $X_{H_2O} = 0$ at $Z = \delta$. $X_{H_2O} = X_{H_2O}^{o}$ at $Z = 0$. The integral is:

$$\ln\{1 + \frac{7}{4} \cdot X_{H_2O}\} = (1 - \frac{Z}{\delta}) \cdot \ln\{1 + \frac{7}{4} \cdot X_{H_2O}^{o}\} \tag{5}$$

And so:

$$N_{H_2O} = + \frac{c\mathfrak{D}_{im}}{\delta} \cdot \ln\{1 + \frac{7}{4} \cdot X_{H_2O}^{o}\} \tag{6}$$

The char is assumed to contain only carbon and ash. As carbon is gasified, the ash layer thickens.

$$\frac{\partial \delta}{\partial \tau} = \frac{4}{7} \cdot \frac{12}{\rho_A} \cdot \frac{f_A}{f_c} \cdot N_{H_2O} = \frac{4}{7} \cdot \frac{12}{\rho_A} \cdot \frac{f_A}{f_c} \cdot \frac{c\mathfrak{D}_{im}}{\delta} \cdot \ln\{1 + \frac{7}{4} \cdot X_{H_2O}^{o}\} \tag{7}$$

$$\frac{\partial \delta}{\partial \tau} = \frac{4}{7} \cdot \frac{12}{\rho_A} \cdot \frac{f_A}{f_c} \cdot \frac{1}{22414} \cdot (22414 \ N_{H_2O}) \tag{7a}$$

$(22414 \ N_{H_2O})$ is the velocity, cm/sec, of the steam molecules in the ash layer. $\frac{\partial \delta}{\partial \tau}$ is the rate of increase, cm/sec, of the ash layer thickness. Since $\frac{4}{7} \cdot \frac{12}{\rho_A} \cdot \frac{f_A}{f_c} \cdot \frac{1}{22414} \ll 1$, the use of a quasi-steady state diffusion equation, Equation (4), is justified. The integral of Equation (7) is:

$$\delta = 2\sqrt{\frac{4}{7} \cdot \frac{12}{\rho_A} \cdot \frac{f_A}{f_c} \cdot c_{im} \cdot \ln\{1 + \frac{7}{4} \cdot X^0_{H_2O}\} \cdot \tau} \tag{8}$$

And

$$N_{H_2O} = \frac{1}{2}\sqrt{\frac{7}{4} \cdot \frac{\rho_A}{12} \cdot \frac{f_c}{f_A} \cdot \frac{c_{im} \cdot \ln\{1 + \frac{7}{4} X^0_{H_2O}\}}{\tau}} \tag{9}$$

The amount of carbon gasified in time τ is:

$$\int_0^\tau N_{H_2O} \, d\tau = \sqrt{\frac{7}{4} \cdot \frac{\rho_A}{12} \cdot \frac{f_c}{f_A} \cdot c_{in} \, \ln\{1 + \frac{7}{4} \cdot X^0_{H_2O}\} \cdot \tau} \tag{10}$$

The fraction of all the carbon in the pile that has reacted in time τ is:

$$(1 - Y) = \frac{12A_c}{f_c M_c}\sqrt{\frac{7}{4} \cdot \frac{\rho_A}{12} \cdot \frac{f_c}{f_A} \cdot c_{im} \cdot \ln\{1 + \frac{7}{4} \cdot X^0_{H_2O}\} \cdot \tau} \tag{11}$$

In the pilot plant reactor the char is contacted four times by the rabble teeth as it moves across the baseplate. Steam in the gas space above the char layer reacts with the char. Suppose, then, that the pilot plant situation can be simulated by four reaction stages, each $\tau_R/4$ seconds in duration at which time the char is thoroughly mixed to start the next reaction stage. The starting values for f_c, f_A, and M_c must be recomputed at the beginning of each new reaction stage.

$$\frac{(M_c)_{i+1}}{(M_c)_i} = 1 - (f_c)_i(1 - Y_i) \tag{12}$$

$$\frac{(f_A)_{i+1}}{(f_A)_i} = \frac{1}{1 - (f_c)_i(1 - Y_i)} \tag{13}$$

$$\frac{(f_c)_{i+1}}{(f_c)_i} = \frac{Y_i}{1 - (f_c)_i(1 - Y_i)} \tag{14}$$

Pilot Plant Data Correlation. In Table 17 pilot plant data for the steam-gasification of manure char are compared with the simplified theory.

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Table 17

PILOT PLANT STEAM-MANURE CHAR REACTION DATA COMPARED WITH THEORY

		3/1/78		3/6/78		3/8/78	
N	stages	4		4		4	
$X^0_{H_2O}$	mol fraction	.2183		.6971		.6918	
T	^0K	870^0		837^0		879^0	
τ_R	seconds	1792		1390		1942	
$(f_c)_0$	wt. fract. carbon (750^0C)	.2144		.2371		.2344	
$(f_A/f_c)_0$	wt. ash/wt. carbon (750^0C)	3.665		3.217		3.267	
$(M_c)_0$	gms dry weight	1360		1405		1229	
		Theory	Meas.	Theory	Meas.	Theory	Meas.
$(1 - Y)$	fract. carbon (750^0) gasified	.0948	.071	.1179	.176	.1649	.177

The solids residence time is:

$$\tau_R = \frac{\text{Holdup Ash (gm)}}{\text{Ash Input Rate (gm/sec)}}$$

The presence of volatiles ($750^{\circ}C$) in the char complicates the data. $(M_c)_o$ is the equivalent devolatilized char mass, $W_F(f_c + f_A)_F \, \tau_R$.

$$(f_c)_o = \left\{ \frac{f_c}{f_c + f_A} \right\}_F$$

$$\vartheta_{im} = BT^{1.75} \quad (11)$$

The constant

$$12A_c \sqrt{\frac{7}{4} \cdot \frac{\rho_A}{12} \cdot c\beta}$$

was taken to be .003 to best correlate the pilot plant data.

[11] Perry and Chilton (Ed.), Chemical Engineers' Handbook, Mc-Graw-Hill, New York (1973), pp. 3-233.

CONSIDERATION OF AN ENTRAINED BED REACTOR

FOR THE STEAM-CHAR REACTION

GENERAL

The general configuration of an entrained bed tubular pyrolysis reactor is illustrated in Figure 8. To design such a system it is necessary to first consider two problems: 1) Biomass particles are not uniform, with some ranging from 0.01 to about 3 mm. The amount of biomass lifted is a function of the gas rate at the entrance, and 2) Considerable heat must be delivered to the reactor.

Particle Size vs. Gas Rate

In analyzing the entrance region where steam and/or air and recycle gas are mixed with the biomass, only those particles which have a terminal velocity in the gas equal to or less than the gas velocity are kept in suspension or lifted through the reactor. The larger particles will fall and deposit in the collector (see Figure 9). If the particle size distribution is known, it is possible to calculate the fraction which is lifted through the reactor at given flow rates.

A particle of diameter D_p falling in stagnant fluid will accelerate until it reaches a point where the drag exerted on it by the fluid equals its weight. The particle velocity at this point is called the terminal velocity and, according to Newton's laws, is:

$$V_T^2 = \frac{4 \ \Delta \rho g D_p}{3 \ C_D \rho} \tag{1}$$

where

ρ = steam density at the mixing zone where the pressure and temperature are assumed to be 1.3 atm. and 130°C, respectively. ρ = 0.000713 g/cc
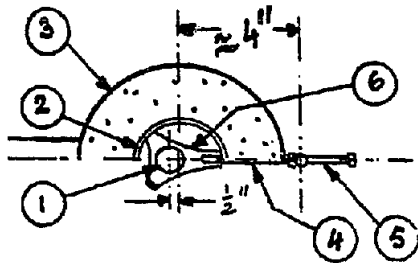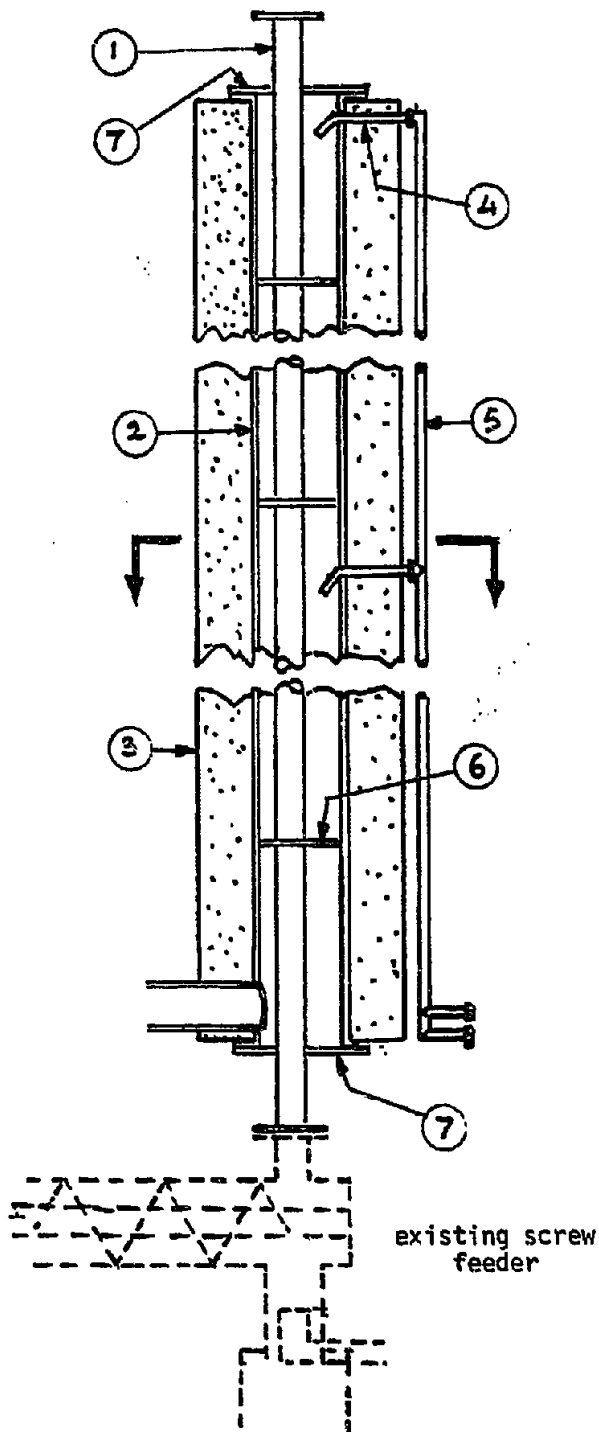
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Figure 8

Preliminary Design of
Entrained Bed Reactor

ITEM	DESCRIPTION	QTY.	MATL.
1	Reactor. 20' long x 1" dia. Flanges at two ends for connection with screw feeder and condenser.	1	Inconel
2	Heating chamber. 19' long x 3" dia. Flanges at both ends for enclosing. Flue gas outlet is 2" Dia.	1	Inconel
3	2" thick insulation	1	Refractory
4	Burners. ½" diameter long flame burner at 5' spacing from the top.	4	Stainless steel
5	Burner feed. ½" dia. tube with connections for burners.	1	Stainless steel
6	Positioning braces. Any shape provided flow of flue gas is not blocked. 2' spacing.	10	Inconel
7	Lids. The top sliding fit on reactor, the bottom welded on reactor.	2	Inconel

existing screw
feeder

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$\Delta\rho$ = density difference between particle and steam;

particle density, ρ_p = 1.3 g/cc

g = 981 cm/s^2

D_p = particle diameter

C_D = drag coefficient

The drag coefficient is correlated against particle Reynolds number defined by:

$$Re = \frac{\rho V_T D_p}{\mu} \qquad (2)$$

where μ = steam viscosity = 130 x 10^{-6} poise at 1.3 atm. and 130°C. The correlation is reported in many text books including Perry's handbook (5th ed. pages 5-62) and Foust et al. (1960).

Rearrangement of equations 1 and 2 to eliminate V_T gives:

$$C_D = \frac{4\rho \, \Delta\rho \, g \, D_p^3}{3\mu^2} \, Re^{-2} = K \, Re^{-2} \qquad (3)$$

with K equal to:

$$K = \frac{4 \times 0.000713 \times 1.3 \times 981}{3 \, (130 \times 10^{-6})^2} \, D_p^3$$

$$= 71714.46 \, D_p^3 \qquad D_p \text{ in mm} \qquad (4)$$

Equation 3 can be represented by a straight line in log-log plot of C_D vs Re, having slope equal to -2. This straight line will intersect the correlation curve C_D as a function of Re at the point of solution. The method requires the knowledge of K which is a function of D_p (equation 4). The method of calculation is shown in Figure 9 and the results for different values of K are tabulated in Table 18. The value of Re at the intercept is substituted into equation 2 to determine V_T using:

$$Re = \frac{0.000713}{0.000130} \, \frac{V_T \, D_p}{10} \qquad \left(\begin{matrix} D_p \text{ in mm} \\ V_T \text{ in cm/s} \end{matrix} \right)$$

$$= 0.548 \, V_T \, D_p \qquad (5)$$

Table 18

Steam Consumption Versus Particle Size and Reactor Diameter

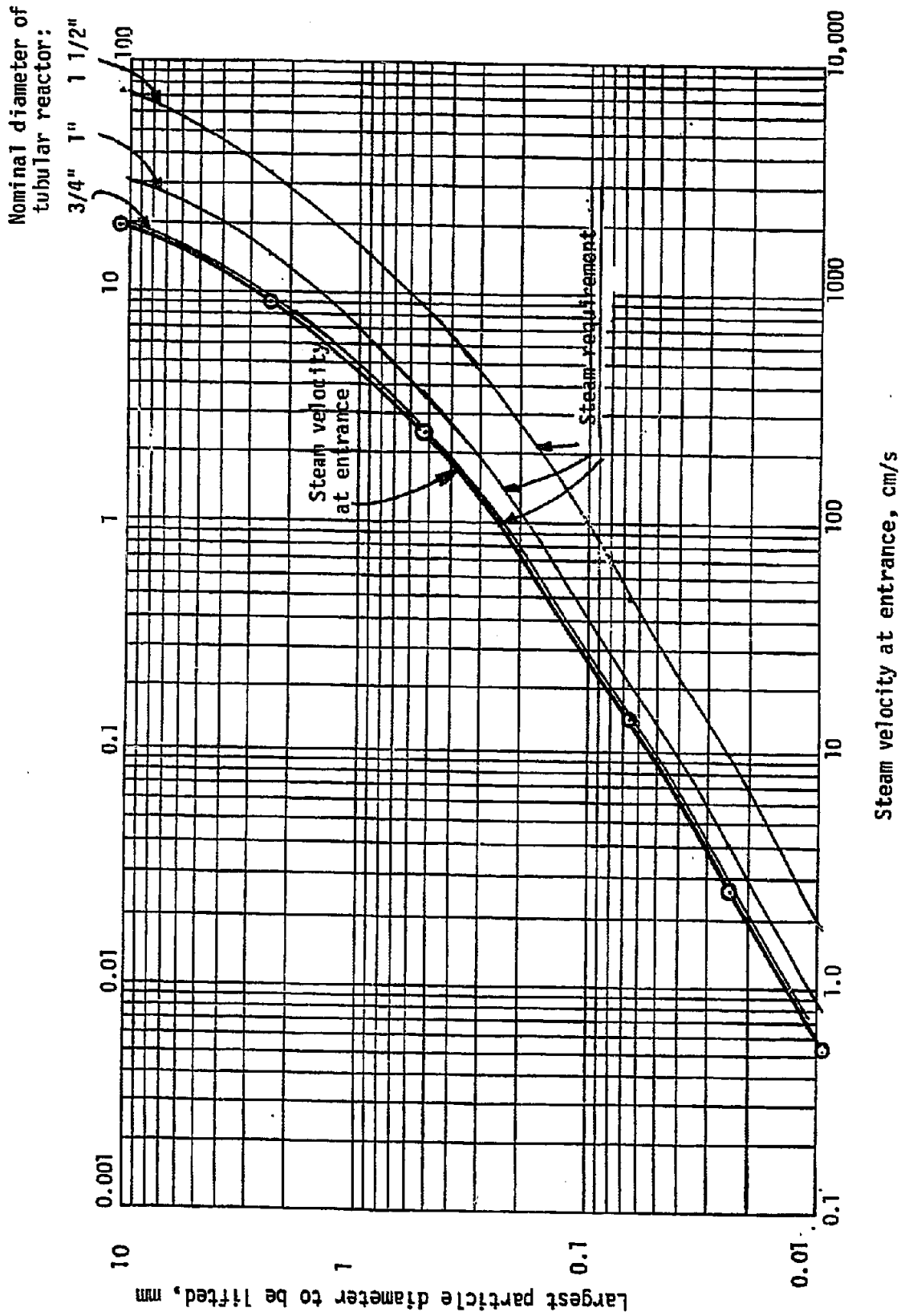| Re	K	D_p (mm)	V_T (cm/s)	Steam Requirement (Kg/hr)			
				3/4" 1.050" 0.884"	1" 1.315" 1.097"	1-1/2" 1.900" = OD 1.682" = ID	SCH10S
12,000	10^8	11.17	1959.12	19.9053	30.6532	72.0635	
1,200	10^6	2.41	909.33	9.2391	14.2278	33.4484	
70	10^4	0.519	246.21	2.5015	3.8522	9.0563	
0.5	20	.0653	13.96	.1418	.2184	.5134	
0.035	1	.0241	2.65	.0269	.0415	.0976	
0.0027	0.06	.0094	.523	.0053	.0082	.0192	

Table 19

Sieve Analysis of Beef Manure According to Houkom et al.

Sieve #	Aperture (mm)	25% Moisture (w.b.) Fraction of Smaller (%)	% on Sieve	(Wet Screening) 85% Moisture (w.b.) Fraction of Smaller (%)	% on Sieve
4	4.75	96.20	3.8	96.80	3.2
8	2.38	60.80	35.4	89.70	7.1
16	1.190	33.00	27.8	77.80	11.9
30	.595	14.70	18.3	68.10	9.7
50	.297	5.20	9.5	60.20	7.9
100	.140	1.80	3.4	56.60	3.6
140	.104	0.80	1.0	55.30	1.3
pan	< .104		0.8		55.3

Houkom, R. L., Butchbaker, A. F., Brusewitz, G. H., Trans. ASAE, pp. 973-977, 1974.

Figure 9.

Steam required, (Kg/hr)

Steam velocity at entrance, cm/s

Largest particle diameter to be lifted, mm

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The gas rate required can then be determined from the knowledge of the gas velocity, density, and pipe inside diameter (see Table 18). The results of Table 18 are plotted in Figure 9. To use these curves first assume that 70% by weight of biomass particles have a diameter of about 1 mm or less and that the reactor is 1 inch schedule 10S pipe. To pass 70% of the feed through the reactor, the gas rate (as steam) must be at least 7 Kg/hr. At 7 Kg/hr, the steam velocity is 4.50m/s (see Figure 9), the residence time of a 1 mm particle is theoretically infinity, and of a 0.7 mm diameter particle, which has $V_T = 3.25m/s$, or about:

$$t = \frac{\text{length of reactor}}{4.50 - 3.25} \tag{6}$$

Heating of the Reactor

The reactor is designed to be heated to, and maintained at, at least 860^0C. To heat the reactor evenly, an electric heater will be expensive, and a better solution may be to use gas. However, regardless of whether electricity or gas is used, the crucial problem is the insulation of the reactor and the possible overheating in local areas of the reactor wall.

The heat required can be calculated approximately by assuming that the heat of pyrolysis is zero, and the heat capacity of the biomass is about 0.6 Btu/(lb.^{0}F), and an 80% heat loss. The heat to be removed in the double-pipe condenser can also be estimated in a similar manner. The heat required in the steam generator, and therefore the capacity of the heating element in the boiler, can be estimated when the maximum requirement of steam is decided.

Design of the Unit

Houkom et al. (1974) reported a sieve analysis for beef manure which is reproduced in Table 19. From these results it can be seen that the wet

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screening test resulted in more fines than dry screening. Table 19
also shows that a substantial amount of manure has a size between
1.19 - 2.38 mm, and therefore 2.0 mm might be taken as the particle
size limit in the design.

To decide on the reactor diameter, the heat transfer requirement
needs to be considered. The heat required to heat steam at 1.3 atm.
from $120^\circ C$ to $1000^\circ C$ is $1107.2 - 648.2 = 459.0$ kcal/kg or $= 459.0 \times 1.80 = $
826.20 Btu/lb. The total amount of heat transferred, Q, is calculated
assuming that the reactor is used to heat steam only, and shown in Table 3.
The steam Reynolds number calculated for the purpose of heat transfer co-
efficient determination is also shown in Table 20 for three pipe
sizes using 2.0 mm as the limiting particle diameter. The heat transfer
factor j_H, according to correlations reported in Kern (1950), is defined by:

$$j_H = \frac{h_i D_i}{k} \left(\frac{C_p}{k}\right)^{-\frac{1}{3}} \left(\frac{\mu}{\mu_w}\right)^{-0.14} \tag{7}$$

where the viscosity ratio between the bulk material and the wall, μ/μ_w,
can be taken as unity. The thermal conductivity k, heat capacity C_p, and
the voscosity μ are listed for the inlet and outlet conditions as follows:

	Inlet, $120^\circ C$	Outlet, $1000^\circ C$	
Heat capacity, C_p	0.165	0.500	Btu/(lb $^\circ F$) or Cal/(g $^\circ C$)
Viscosity, μ	125	485	10^{-6} micropoise
Thermal conductivity, k	26.5	142.0	mW/(m $^\circ K$)
	15.32	82.10	x 10^{-3} Btu/(ft hr $^\circ F$)
$(C_p\mu/k)^{-\frac{1}{3}}$	1.453	1.118	
$(C_p\mu/k)^{-\frac{1}{3}}$ /k	9.48	13.62	Btu/(ft ln $^\circ F$) $^{-1}$

The values for the heat transfer coefficient, h_i, of steam calculated for the
inlet and outlet are listed in Table 20. As an approximation, the heat

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Table 20

Heat Transfer Calculations For Three Reactor Diameters

I. D. (in.)	Steam (Kg/hr)	Q (Btu/hr)	Re	J_H	h_i (Btu/hr ft² °F)			Q/A Btu/(hr ft²)	Δt_m (°F)		Δt_m (°C)	
					(inlet)	(outlet)	(mean)		L=15'	L=20'	L=15'	L=20'
0.884	8.0	14,559	9,726	35	50.1	34.9	42.50	62,909/L	98.7	74.0	54.8	41.1
1.097	12.6	22,930	12,069	42	48.4	33.7	41.05	79,842/L	129.7	97.3	72.1	54.1
1.682	27.8	50,591	50,591	64	48.1	33.5	40.80	114,889/L	187.7	140.8	104.3	78.2

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transfer resistance of the pipe wall is neglected. Then, the log mean temperature difference can be calculated by:

$$\Delta t_m = \frac{Q/A}{h_i} \qquad (8)$$

where A is the heating surface based upon the inside diameter of the reactor. The values of Δt_m are listed for two reactor lengths and in ^oF and ^oC in Table 20.

The resultant Δt_m shows that the smaller the reactor diameter the less the Δt_m has to be. However, the magnitudes of Δt_m appear to be reasonable for all three diameters and should be achievable without much difficulty. Selection should thus be based upon other factors such as the diameter ratio between the particles and the reactor, material availability and costs, etc. Because of the lack of information on these factors the choice of reactor diameter is arbitrary, and a 1" sch. 10S pipe has been chosen.

General

It appears likely that the water gas reaction:

$$C_{(S)} + H_2O \quad H_2 + CO \qquad (1)$$

is much faster when the source of the carbon is biomass than when it is lignite. For instance, it has been suggested that the rate of reaction (1) might be 23 times faster for biomass char than it is for lignite char. On this basis it can be calculated that a 3-second residence time in an entrained bed reactor at 1000^oC ought to be sufficient time to almost completely steam-gasify biomass carbon.

While the use of excess steam increases the rate of reaction, it would probably be better to use as little excess as possible, since if this steam comes from an external source any excess represents wasted heat. The water gas reaction requires 1.5 gm steam/gm carbon, or roughly

0.75 gm steam/gm char. At $1000^{\circ}C$, the density of steam is $1.72(10^{-4})$ gm/cm^3 while the density of the char is about 2 gm/cm^3, so a .75 gm steam/gm char stoichiometric ratio is equivalent to a mixture containing only 115 ppm char.

The steam flow classifies the feed solids into particles larger than, and particles smaller than, the particle whose terminal velocity just equals the steam velocity. There is no need to screen the feed. Thus an inlet steam velocity of 1000 cm/min should be high enough to entrain all but the largest particles in dried manure. If the wall of a 1" vertical pipe is at $1000^{\circ}C$, and steam injected at the stoichiometric ratio into the bottom at $100^{\circ}C$, and the unit is designed for a three-second residence time: 1000(3)/60 is 50 cm for the heated length of the pipe, and the gas will leave the tube close to $1000^{\circ}C$,

$$\text{Steam, } 100^{\circ}C: \quad (Re)_{in} = \frac{\overset{D}{(2.664)}\overset{v}{(16.67)}}{\underset{U/P}{.217}} = 204. \quad \begin{array}{l} 1" \text{ pipe:} \quad 2.664 \text{ cm} = \\ 1.049 \text{ in inside} \\ \text{diameter} \end{array}$$

$$(H_2 + CO), 1000^{\circ}C: \quad (Re)_{out} = \frac{(2.664)(16.67)(2)\ (1273)}{7.38\ (373)} = 41.1$$

There is no excess steam. There are 2 mols $(H_2 + CO)/mol\ H_2O$ reacted. The kinematic viscosity of H_2 at $1000^{\circ}C$ is quite high. The flow is laminar throughout.

For fully-developed laminar flow in a tube with a constant wall temperature, $Nu = 3.656$.

$$(h)_{in} = \frac{\overset{Nu}{3.656}(12)\overset{k}{(.0145)}}{\underset{D}{1.049}} = .6064\ \frac{BTU}{hr\ ft^2\ ^{\circ}F} = .2961\ \frac{cal}{hr\ cm^2\ ^{\circ}C}$$

$$(h)_{out} = \frac{3.656(12)(.169)}{1.049} = 7.08\ \frac{BTU}{hr\ ft^2\ ^{\circ}F} = 3.46\ \frac{cal}{hr\ cm^2\ ^{\circ}C}$$

$(h)_{out}$ is so large because the thermal conductivity of H_2 at $1000^{\circ}C$ is very high. The gas is nearly invisible to radiation from the wall. The particles,

however, receive radiant heat from the wall. Some of this heat is lost to
the surrounding gas.

At the inlet ($100°C$): $\frac{\pi}{4} \overset{D^2}{(2.664)^2} \overset{V}{(1000)} \frac{273}{373} \underset{\text{molar vol.}}{\overset{MW}{\frac{18}{22414}}} (60) = 196.6$ gm steam/hr

Using a mean C_p of about 0.4 cal/gm$°C$ for the gas phase, and ignoring
the indirect heat transfer from the wall, to the particles, to the gas:

$$\underset{W}{196.6}\underset{C_p}{(.4)}\overset{\substack{\text{Temp.}\\\text{rise}}}{(T-100)} = \overset{\text{Area}}{\pi(2.664)(50)} \frac{\overset{(h\cdot\Delta T)_{lm}}{3.46\ T - 3194}}{\ln\frac{.2961(1000 - 100)}{3.46\ (1000 - T)}} \quad \begin{array}{l} T = \text{Gas outlet} \\ \quad \text{temperature} \end{array}$$

The root, T, is 973.6$°C$. This is close enough to 1000$°C$ to justify the
above calculations. 196.6 gm H_2O/hr will oxidize 131.1 gm carbon/hr.

Design Assuming a Plug Flow

The previous discussion dealt with a model of a well-mixed steam gasification reactor. Sample calculations were presented which were based on some lignite char gasification data from the literature. A plug flow entrained steam gasification reactor is modeled next, and some calculations of carbon yield presented using an estimated rate constant, A*, for biomass char.

Assumptions:

Tube has constant cross section.

The tube and the material flowing through it are isothermal.

There are no radial gradients.

Plug flow with no axial dispersion.

Steady state.

No resistance to heat or mass transfer.

The gasification rate is proportional to the product of the steam concentration and the exposed carbon concentration. "Exposed" means carbon atoms exposed on the internal BET surfaces.

$$\overline{U} \cdot \frac{\delta[C]}{\delta Z} = -A*[C]\{1 + \frac{B}{A} - \frac{[C]}{[C]_i}\}[H_2O] \ \exp \ \{- \frac{E}{RT}\} \tag{1}$$

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \tag{2}$$

At Z = 0 there is just steam and char. The gas velocity increases as gasification proceeds.

$$\overline{U} = \{2 - \frac{[C]}{[C]_i}\} \cdot \frac{(Q_s)_i}{A} \tag{3}$$

A simple material balance gives:

$$[H_2O] = [H_2O]_i - [C]_i + [C] \qquad (4)$$

Equation (1) now reads:

$$\int_Y^1 \frac{(2 - \phi)d\phi}{\phi\left(1 + \frac{B}{A} - \phi\right)\left(\frac{[H_2O]_i}{[C]_i} - 1 + \phi\right)} = \frac{A^* \ AZ \ [C]_i}{(Q_S)_i} \cdot \exp\{- \frac{E}{RT}\} \qquad (5)$$

$\{\frac{[H_2O]_i}{[C]_i} - 1\}$ is "excess steam". B/A depends on the nature of the material.

For example, a good raw material for activated carbon would have a small B/A, say, less than 0.1. Lignite char has a B/A of 0.4.

<u>Sample Calculations</u>   Take $A^* = 1(10^6)$. This is some 23 times larger than the constant obtained for lignite char.

Take B/A = 0.4 as it is for lignite.

Take $E = 31000$ cal/gm mol ^{0}K as it is for lignite.

$\frac{AZ}{(Q_S)_i}$ is the residence time.

The inlet steam concentration, $[H_2O]_i$, is 1 atm. Thus, the inlet carbon concentration, $[C]_i$, and the "excess steam" are mutually dependent.

Fraction carbon gasified (1 - Y) was calculated as a function of residence time, excess steam, and temperature.

$\frac{AZ}{(Q_S)_i} = 1$ sec; $\frac{B}{A} = 0.4$ Table gives (1 - Y), fraction carbon gasified.

Excess Steam	Temperature	1100°K	1150°K	1200°K	1250°K	1300°K
0		.243	.391	.549	.686	.788
0.5		.254	.419	.604	.767	.884
1.0		.259	.434	.632	.805	.920
3.0		.268	.457	.675	.857	.959

$$\frac{AZ}{(Q_S)_i} = 3 \text{ sec}; \quad \frac{B}{A} = 0.4$$

Excess Steam	Temperature	1100^0K	1150^0K	1200^0K	1250^0K	1300^0K
0		.525	.689	.805	.879	.924
0.5		.576	.771	.903	.972	.1.000
1.0		.602	.809	.937	1.000	1.000
3.0		.642	.860	.972	1.000	1.000

It is likely that the ash would melt if the temperature were 1250^0K or higher.

Notation

A	Cross sectional area of tube, cm^2
A*	Empirical constant, $(atm\ sec)^{-1}$
B/A	Empirical constant, dimensionless
E	Activation energy, cal/(gm mol) (^0K)
[C]	Concentration of carbon at Z
$[C]_i$	Concentration of carbon at Z = 0
$[H_2O]$	Concentration of steam at Z
$[H_2O]_i$	Concentration of steam at Z = 0
$(Q_S)_i$	Volumetric flow rate of steam at Z = 0, cm^3/sec
R	Gas constant
T	Temperature, ^0K
$\overline{U}$	Mean gas velocity, cm/sec
$Y = [C]/[C]_i$	Yield
Z	Distance along tube, cm
$\phi = [C]/[C]_i$	Dimensionless variable

Figure 10

Carbon Gasified vs. Distance in a Plug – Glow Entrained
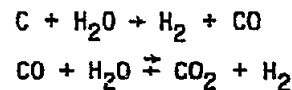
Bed Steam – Gasification Reactor
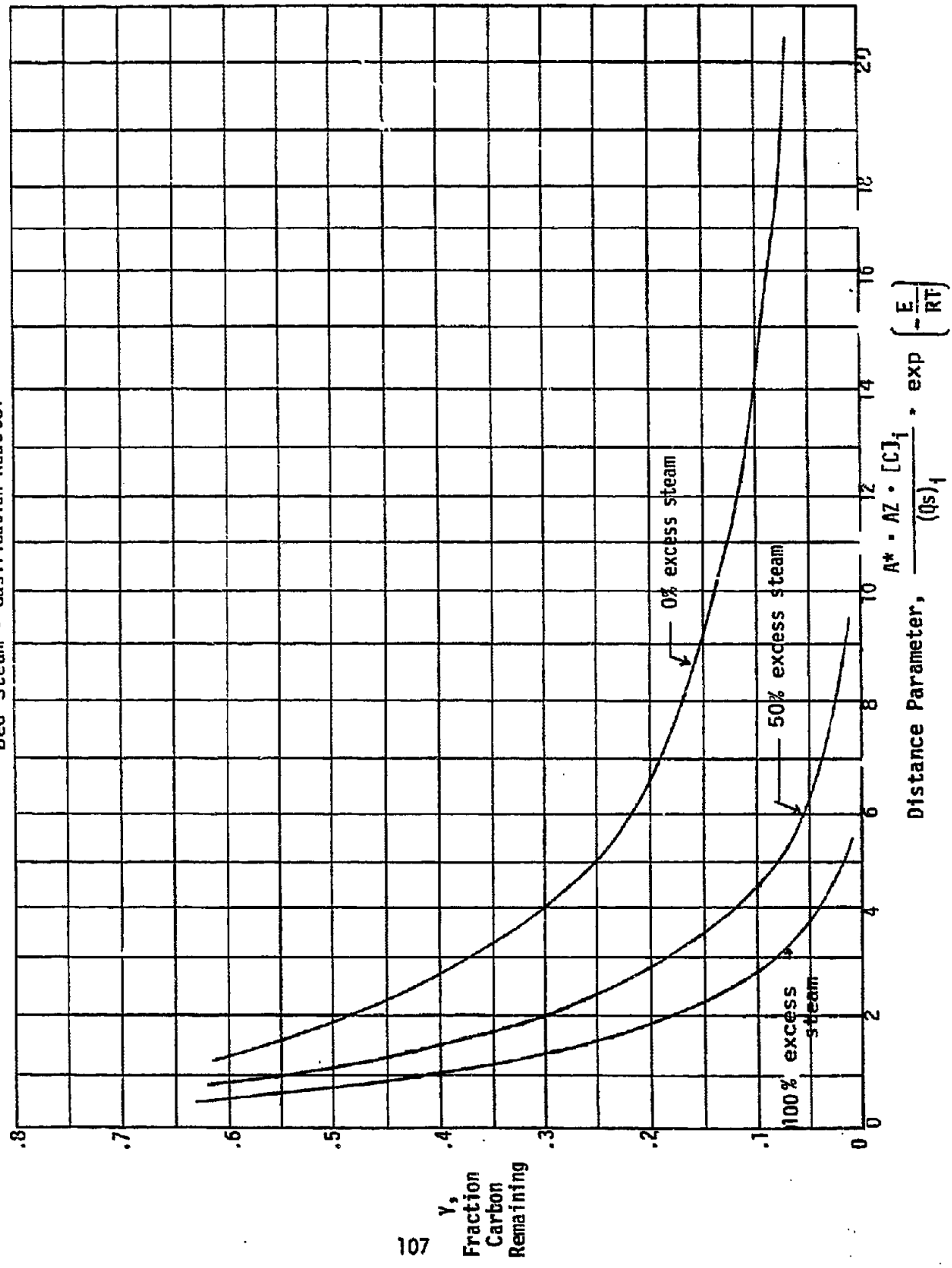
WATER GAS KINETICS

Theory

In a steady state entrained reactor of volume V and temperature T in which the reactions:

$$C + H_2O \rightarrow H_2 + CO$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

occur, and in which the char particles are infinitesimally small (no diffusion resistance),

$$\frac{1}{V} \cdot \{W_i \cdot [C]_i - W_o [C]\} = A^* [C] \cdot \{1 - \frac{[C]}{[C]_i} + \frac{B}{A}\}[H_2O] \exp\{-\frac{E}{RT}\} \quad (1)$$

where $W_i = 22.4 \cdot b \cdot P$

and $W_o = 22.4 \cdot b \cdot P\{1 + (1 - Y)\frac{a}{b}\}$

A^*	constant, $(atm \cdot sec)^{-1}$
b	mols steam fed/sec
a/b	mols carbon/mol steam in the feed
P	total pressure, atm
W_i	volumetric gas flow, inlet, l/sec
W_o	volumetric gas flow, outlet, l/sec
A, B	rate constants, $(atm \cdot sec)^{-1}$
$[C]_i$	concentration of carbon in the feed, gm/l
$[C]$	concentration of carbon in the reactor, gm/l
$[H_2O]$	concentration of steam in the reactor, atm
V	reactor volume, l
E	activation energy, cal/mol
R	gas constant, cal/mol ^oK
T	reactor temperature, ^oK
Y	carbon yield, $[C]/[C]_i$, dimensionless

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The factor:

$$\{1 - \frac{[C]}{[C]_i} + \frac{B}{A}\} \cdot A \cdot [C]$$

is the concentration of "reactive" carbon in the reactor. The rate of gasification, then, is second order, being proportional to the steam concentration and to the concentration of "reactive" carbon in the reactor.

Equation (1) can be rewritten:

$$\frac{W_i}{V} = \frac{A^*}{\frac{1}{Y} - \{1 - (1 - Y)\frac{a}{b}\}} \cdot \{1 - Y + \frac{B}{A}\} \cdot [H_2O] \cdot \exp\{-\frac{E}{RT}\} \qquad (2)$$

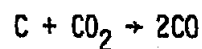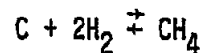|	Input			Output	
				Solid	Gas
C	a mols/ sec		C	Y·a	
H_2O	b mols/sec		H_2O	---	b - (1 - Y)a mols/sec
			H_2	---	(1 - Y)a
			CO + CO_2	---	(1 - Y)a
			Total gas		b + (1 - Y)a mols/sec

Therefore:

$$[H_2O] = \frac{1 - (1 - Y)\frac{a}{b}}{1 + (1 - Y)\frac{a}{b}} \cdot P$$

$$\frac{22.4\, a}{V} = \frac{A^* \cdot \frac{a}{b}}{\frac{1}{Y} - \{1 - (1 - Y)\frac{a}{b}\}} \cdot \{1 - Y + \frac{B}{A}\} \cdot \frac{1 - (1 - Y)\frac{a}{b}}{1 + (1 - Y)\frac{a}{b}} \cdot \exp\{-\frac{E}{RT}\} \qquad (3)$$

Discussion

Two other reactions occur:

$$C + 2H_2 \rightleftharpoons CH_4$$

$$C + CO_2 \rightarrow 2CO$$

When T is about 1173 °K (900 °C), these reactions are slow compared to

$$C + H_2O \rightarrow H_2 + CO$$

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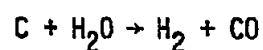
At higher temperatures these reactions may become significant.

Char particles cannot be infinitesimal, so as T is increased, there will be some point at which the gasification rate becomes controlled by the diffusion processes. "Reactive" carbon means exposed or BET (adsorptive) surface contained in the micropores. This surface varies linearly with the burnoff.

Calculations

According to Coates[11], E is about 31,000 cal/mol ^{o}K.

Using data from Walker, et al.[12] for lignite:

$$A = 1.7906(10^{-3}) \quad (atm \cdot sec)^{-1}; \frac{A}{B} = 2.5$$

$$B = 0.7162(10^{-3}) \quad (atm \cdot sec)^{-1}$$

$$A^* = 43659 \quad (atm \cdot sec)^{-1}$$

A^* and $\frac{A}{B}$ may be quite different for manure char. For a sewage solids char[13], A/B was about 12. Walker et al. worked with coal chars from various ranks of coal, from anthracite to lignite. Lignite chars are more reactive than bituminous chars which are more reactive than anthracite chars. Manure char should be more reactive than lignite char.

Using Equation (3), $\frac{V}{22.4\ a}$ was calculated as a function of Y, a/b, and T. For a 3 dry T/D plant, a = .3156 mols C/sec assuming 20 wt% ash and 15 wt% fixed carbon in the dry manure. The reactor volume, V, has been calculated in Table 21.

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[11] Coates, "Kinetic Data from a High Temperature Entrained Flow Reactor," _ACS Div. Fuel Chemistry_, _22_, 1 (1977), pp. 84-87.

[12] Walker, Mahajan, Yarzab, "Unification of Coal Char Gasification Reactions," _ACS Div. Fuel Chemistry_, _22_, 1 (1977), pp. 7-11.

[13] Bosch, Kleerebezem, Mars, "Activated Carbon from Activated Sludge," _Journ. WPCF_, _48_, 3 (1976), pp. 551-561.

Table 21

Residence Time Requirements for Entrained Bed Steam Gasification

T →			1000 °C			1500 °C			2000 °C			2500 °C		
Y →			0.2	0.1	0.05	0.2	0.1	0.05	0.2	0.1	0.05	0.2	0.1	0.05
a/b = 1.	$\frac{V}{22.4a}$		174.1	699.6	2786 sec	5.485	22.04	87.80 sec	.7911	3.179	12.66 sec	.2294	.9219	3.672 sec
0% excess steam	V		1230	4946	19699 T	38.77	155.8	620.7 T	5.592	22.48	89.53 T	1.621	6.517	25.96 T
a/b = 0.8	$\frac{V}{22.4a}$		106.5	277.6	648.7 sec	3.355	8.747	20.44 sec	.4838	1.262	2.948 sec	.1403	.3658	.8548 sec
25% excess steam	V		752.6	1962	4586 T	23.71	61.83	144.5 T	3.420	8.918	20.84 T	.9917	2.586	6.043 T
a/b = 0.5	$\frac{V}{22.4a}$		82.73	185.3	391.9 sec	2.607	5.840	12.35 sec	.3760	.8422	1.781 sec	.1090	.2442	.5164 sec
100% excess steam	V		584.9	1310	2771 T	18.43	41.28	87.30 T	2.658	5.954	12.59 T	.7070	1.726	3.651 T

p

MATERIAL BALANCES FOR TOTAL GASIFICATION IN AN ENTRAINED BED REACTOR

For pyrolysis at $900^{\circ}C$, Schlesinger, Sanner, and Wolfson[14] give the yields of gas, char, water, tar, and NH_3 as well as the ultimate analyses of the manure and char and the gas composition.

Basis: 1 gm dry manure.

Feed

C   .412 g

H   .057

O   .333

N   .023

S   .003

Ash .172

    1.000 g dry manure

     .037 g moisture

    1.037 g total

Pyrolysis Products

Char .363 gm		Gas .431 g			Tar .0665 g	
C	.504	CO_2	.4857 wt fract	.245 vol fract	C	.647 wt fract
H	.004	CO	.2271	.180	H	.045
O	.004	H_2	.0248	.275	O	.012
N	.011	CH_4	.1637	.227	N	.268
S	.003	C_2^+	.0987	.073	S	.028
Ash	.474		1.000 wt fract	1.000 vol fract		1.000 wt fract
	1.000 wt fract					Analysis by difference.

Water .175 g

NH_3 .0015 g

[14]Schlesinger, Sanner, Wolfson, "Energy from the Pyrolysis of Agricultural Wastes," Chapter 9 of Symposium: Processing Agricultural and Municipal Wastes, Avi Publishing Co., Westport, Conn. (1973), pp. 93-100.

Reference (14) gives .385 g gas/gm dry feed and 13940 SCF gas/ton dry feed. These figures do not quite agree, so 13940 SCF/ton dry feed was used, which comes out to .431 gm gas/gm dry feed. In the char analysis, 49.4 wt % C was given, and 50.4 wt % C was used. Similarly 48.4 wt % ash was given, but 47.4 wt % ash used. This makes the ash balance. The tar ultimate analysis was worked out by difference. These tar numbers are small differences between large numbers, and are therefore not to be taken as seriously as the rest.

Water-Gas Gasification

It is assumed that the total dry feed plus varying amounts of moisture are pyrolyzed and steam-gasified in one step. Further, all of the carbon and tar are assumed to be gasified, since the calculations below are not valid for partial gasification. The gas temperature is assumed to be high enough that the water gas shift reaction equilibriates in the reaction tube, but methane and the higher hydrocarbons formed in pyrolysis are assumed to be frozen against their decomposition by steam. The calculations below are based on the data of Reference (14).

D_0 = gm H_2O used/gm DAF feed

$$E_0 \frac{.1637(.431)}{.828} = .085211 \text{ g } CH_4/\text{g DAF feed}$$

Gas CO_2 a gm/gm DAF feed

   CO b

   H_2 c

   H_2O d

   CH_4 E_0

   C_2H_6 F_0

   C_2H_4 G_0

   $NH_3 \frac{17}{14} N$

   $H_2S \frac{34}{32} S$

   _____

   $(1 + D_0)$ gm/gm DAF feed

$$F_0 \frac{.0987(.431)}{.828} = .051376 \text{ g } C_2H_6/\text{g DAF feed}$$

$$G_0 = 0$$

Feed   C .4976 g/g DAF feed

   H .0688

   O .4022

   N .0278

   S .0036

   _____

   1.0000 g/g DAF feed

Carbon Balance $\dfrac{a}{44} + \dfrac{b}{28}$ $= \dfrac{C}{12} - \dfrac{E_0}{16} - 2\dfrac{F_0}{30} - 2\dfrac{G_0}{28}$ $= P_1$

Hydrogen Balance $2 \cdot \dfrac{c}{2} + 2\dfrac{d}{18} = \dfrac{H}{1} + 2\dfrac{D_0}{18} - 4\dfrac{E_0}{16} - 6\dfrac{F_0}{30} - 4\dfrac{G_0}{28} - 3\dfrac{N}{14} - 2\dfrac{S}{32} = P_2$

Oxygen Balance $2\dfrac{a}{44} + \dfrac{b}{28}$ $+ \dfrac{d}{18} = \dfrac{O}{16} + \dfrac{D_0}{18}$ $= P_3$

Water Gas Shift Equilibrium $\dfrac{ac}{bd} = \dfrac{(44)(2)}{(28)(18)} \cdot K_1$

The solution is Let $\xi = \dfrac{d}{18}$.

$2(1 - K_1)\xi^2 - [2(P_3 - P_1) + P_2 + 2K_1(2P_1 - P_3)]\xi + P_2(P_3 - P_1) = 0$

$a = 44(P_3 - P_1 - \xi)$

$b = 28(2P_1 - P_3 + \xi)$

$c = (P_2 - 2\xi)$

Sample Calculations

$T = 900°C \qquad K_1 = .7377$

D_o = gm H_2O/gm DAF feed

	.136411 g/g		.25 g/g		.60 g/g		.70 g/g		1.00 g/g	
	g/g DAF feed	vol	g/g DAF feed	vol	g/g DAF feed	vol	g/g DAF feed	vol	g/g DAF feed	vol
CO_2	-	-	.127286	.0406	.398634	.0999	.455195	.1075	.591382	.1190
CO	.916045	.5037	.835045	.4185	.662369	.2608	.626376	.2324	.539711	.1707
H_2	.046197	.3556	.051982	.3647	.064317	.3545	.066888	.3474	.073078	.3235
H_2O	-	-	.0615174	.0430	.300511	.1841	.377373	.2178	.621661	.3058
CH_4	.085211	.0820	.085211	.0747	.085211	.0587	.085211	.0553	.085211	.0471
C_2H_6	.051376	.0264	.051376	.0240	.051376	.0189	.051376	.0178	.051376	.0152
NH_3	.033757	.0306	.033757	.0279	.033757	.0219	.033757	.0206	.033757	.0176
H_2S	.003825	.0017	.003825	.0016	.003825	.0012	.003825	.0012	.003825	.0011
	1.136411	1.0000	1.249999	1.0000	1.600000	1.0000	1.700001	1.0000	2.000001	1.0000

Heating Value
BTU (low)/lb DAF feed

.136411	.25	.60	.70	1.00
9298.6	9245.6	9132.8	9109.2	9052.6

Product Gas

Gas	vol	vol	vol	vol	vol
CO	.5205	.4745	.3764	.3559	.3067
H_2	.3675	.4135	.5116	.5321	.5813
CH_4	.0847	.0847	.0847	.0847	.0847
C_2H_6	.0272	.0272	.0272	.0272	.0272
	.9999	.9999	.9999	.9999	.9999

Volumetric Heating Value
BTU (low)/SCF

.136411	.25	.60	.70	1.00
382.8	380.6	375.9	374.9	372.6

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D_o = .136411 gm H_2O/gm DAF feed is the minimum. Less water than this will not completely gasify the feed. The thermal recovery, i.e. the heating value of the product gas/gm DAF feed, decreases slightly as D_o is increased. Reference (1) gives 7110 BTU/lb feed. This would be 8904 BTU/lb DAF feed. In this process the water gas reactions are endothermic, and so it is theoretically possible to produce a gas that has a higher heating value than the feed material itself. This seems to be the case here. The volumetric heating value of the product gas decreases slightly as D_o is increased.

It is especially interesting to work with manure at a moisture content of 1.0 gm H_2O/gm dry feed. If D_o' is the moisture content at the reactor inlet, then $(1 - D_o')$ gm water/gm dry feed was removed in the pre-dryer. To do this predrying, $(1 \cdot D_o')$ gm water/gm dry feed is needed in the reactor outlet gas to condense. The calculations show that the feed should be predried to about 0.65 gm H_2O/gm dry feed (about 40 wt %) to accomplish this balance.

Methane, and especially the higher hydrocarbons, do react to some extent with steam at 900°C. These reactions are far from equilibrium; the equilibrium concentrations of CH_4 at 900°C in these mixtures would be very low.

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Hanford Manure

This is a repeat of BIO II - General II, except that the raw material is now Hanford manure and the pyrolysis temperature is 750°C.

Hanford manure was analyzed by Truesdail Labs. The results are shown below.

Feed

C	.3306	Moisture	.0006
H	.0389	Volatile (750°C)	.4158
O	.1470	Carbon (750°C)	.1295
N	.0236	Ash	.4541
S	.0058		1.0000
Ash	.4541		
	1.0000 g		
H_2O	.0006		
	1.0006		

Pyrolysis Products (750°C)

Char   .6396 g

C	.2651	Moisture	.0109
H	.0067	Volatile (750°C)	.0408
O	.0037	Carbon (750°C)	.2383
N	.0082	Ash	.7100
S	.0063		1.0000
Ash	.7100		
	1.0000		

From our pilot plant data, take

E_0 = .053 g CH_4/g DAF feed

F_0 = .015 g C_2H_4/g DAF feed

G_0 = .011 g C_2H_6/g DAF feed

C	.6056 gm/gm DAF feed
H	.0713
O	.2693
N	.0432
S	.0106
	1.0000 gm/gm DAF feed

$$P_1 = \frac{C}{12} - \frac{E_0}{16} - 2\frac{F_0}{28} - 2\frac{G_0}{30}$$

$$P_2 = \frac{H}{1} + 2\frac{D_0}{18} - 4\frac{E_0}{16} - 4\frac{F_0}{28} - 6\frac{G_0}{30} - 3\frac{N}{14} - 2\frac{S}{32}$$

$$P_3 = \frac{O}{16} + \frac{D_0}{18}$$

$$K_1 \ (750^{0}C) = \exp. \ (.558) = 1.747$$

$K_1 = 1.747$ at 750^0C

D_o, gm H_2O/gm DAF feed	0.513326		0.6		0.8	
D_o^*, gm H_2O/gm dry feed	0.280225		.327540		.436720	
	g/g DAF feed	vol. fract.	g/g DAF feed	vol. fract.	g/g DAF feed	vol. fract.
CO_2	-	-	.123464	.0259	.367113	.0699
CO	1.269783	.4380	1.191215	.3932	1.036166	.3101
H_2	.100824	.4876	.106436	.4918	.117511	.4924
H_2O	-	-	.036165	.0186	.136491	.0636
CH_4	.053	.0320	.053	.0306	.053	.0278
C_2H_4	.015	.0052	.015	.0050	.015	.0045
C_2H_6	.011	.0035	.011	.0034	.011	.0031
NH_3	.052457	.0298	.052457	.0285	.052457	.0259
H_2S	.011263	.0032	.011263	.0031	.011263	.0028
	1.513327	.9999	1.600000	1.0001	1.800000	1.0001

Product Gas	vol. fract.	vol. fract.	vol. fract.
CO	.4536	.4255	.3701
H_2	.5042	.5323	.5877
CH_4	.0331	.0331	.0331
C_2H_4	.0054	.0054	.0054
C_2H_6	.0037	.0037	.0037
	1.0000	1.0000	1.0000

Volumetric Heating Valve BTU (low)/SCF	323.2	321.9	319.2

p

0.6		0.8		1.0		1.831837	
.327540		.436720		.5459		1.000000	
q/q DAF feed	vol. fract.	q/q DAF feed	vol. fract.	q/q DAF feed	vol. fract.	q/q DAF feed	vol. fract.
.123464	.0250	.367113	.0699	.563336	.0982	1.066134	.1372
1.191215	.3932	1.036166	.3101	.911297	.2495	.591334	.1196
.106436	.4918	.117511	.4924	.126430	.4847	.149284	.4226
.036165	.0186	.136491	.0636	.256219	.1091	.882365	.2775
.053	.0306	.053	.0278	.053	.0254	.053	.0188
.015	.0050	.015	.0045	.015	.0041	.015	.0030
.011	.0034	.011	.0031	.011	.0028	.011	.0021
.052457	.0285	.052457	.0259	.052457	.0237	.052457	.0175
.011263	.0031	.011263	.0028	.011263	.0025	.011263	.0019
1.600000	1.0001	1.800000	1.0001	2.000000	1.0000	2.831837	1.0002

vol. fract.	vol. fract.	vol. fract.	vol. fract.
.4255	.3701	.3255	.2112
.5323	.5877	.6323	.7466
.0331	.0331	.0331	.0331
.0054	.0054	.0054	.0054
.0037	.0037	.0037	.0037
1.0000	1.0000	1.0000	1.0000
321.9	319.2	317.1	311.6

Discussion

For Hanford manure, the stoichiometric D_o is .513326 gm H_2O/gm DAF feed (.280225 gm H_2O/gm dry feed, or 21.9 wt.% moisture).

For Schlesinger, et al manure, stoichiometric D_o is .136411 gm H_2O/gm DAF feed (.112948 gm H_2O/gm dry feed, or 10.1 wt.% moisture).

If less than stoichiometric moisture is used, gasification can not go to completion. If gross excess of moisture is present, the Volumetric heating value of the product gas goes down and useless CO_2 is produced.

Hanford manure yields slightly less gas per gm DAF feed then does Schlesinger, et al, manure, and its gas has a substantially lower heating value. This appears to be due to the lower yields of CH_4, C_2H_4, and C_2H_6 on a gm/gm DAF feed basis that we have obtained in the pilot plant.

HEAT BALANCES FOR TOTAL GASIFICATION IN AN ENTRAINED BED REACTOR

These calculations are based on the experimental work of Schlesinger, Sanner, and Wolfson[15] and the previous mass balances.

Manure at $25^{O}C$ and containing 1.207729 gm H_2O/gm DAF feed (1.0 gm H_2O/ gm dry manure) is dried to D_0 gm H_2O/gm DAF feed at 200 mm Hg (T_{sat} = $66.5^{O}C$). The dried material is fed to an entrained bed reactor where it is completely gasified at $900^{O}C$ and 1 atm pressure. The product gas is passed through a spray tower from which no heat is recovered. Part of the purified and compressed product gas is burned in the jacket of the entrained bed reactor. The combustion air is heated by heat exchange with the flue gas. Flue gas at $200^{O}C$ is used in the dryer.

Basis: $H_2O_{(g)}$ @ $25^{O}C$ Assume C_p = 0.4 cal/gm ^{O}C for solids.
The heat requirement of the dryer is given by:

$$\{1.207729(.4)(66.5 - 25) - 1.207729(25.05 - 607.35) + D_0(66.48 - 607.35) +$$
$$(1.207729 - D_0)(625.53 - 607.35)\} \text{ cal/gm DAF feed}$$

The enthalpy of the entrained bed reactor feed is given by:

$$\{1.207729(.4)(66.5 - 25) + D_0 (66.48 - 607.35)\} \text{ cal/gm DAF feed.}$$

In Table 22, the reported heat of combustion ($25^{O}C$) of the manure is used to calculate the heat of combustion at $900^{O}C$. Then, the heat of formation ($900^{O}C$) of this manure is calculated to be -1569.6 cal/gm DAF feed. The heat of formation ($900^{O}C$) of ethane (not in the JANAF tables) was also calculated.

In Table 23, the heat of reaction ($900^{O}C$) for the complete gasification of this manure is calculated for several values of D_0.

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[15]Schlesinger, Sanner, and Wolfson, "Energy from the Pyrolysis of Agricultural Wastes," Chapter 9 of Symposium: Processing Agricultural and Municipal Wastes, Avi Publishing Co., Westport, Conn. (1973), pp. 93-100.

Tab. 22

Heat of Formation from Schlesinger, et al. Manure (900°C)

Heat of combustion = 4770.5 cal/gm DAF feed. Assume that this is a "gross @ 25°C" heat of combustion.

Assume C_p = 0.4 cal/gm °C for solids.

$$\frac{x}{x + .0435649} = \frac{23.69}{760}$$

x = .001402 mols H_2O/gm DAF feed in gas
.032998 mols H_2O/gm DAF feed condensate

	Heat of Combustion			Heat of Formation $\Delta H_f(900°C)$	
			$(H_{1173} - H_{298})$		
Products					
CO_2	10271 cal/mol	.0414667 mols/gm DAF feed	425.9 cal/gm DAF feed	-94406 cal/mol	-3914.7 cal/gm DAF feed
H_2O(g)	7962 cal/mol	.0344 mols/gm DAF feed	273.9 cal/gm DAF feed	-59484 cal/mol	-2046.2 cal/gm DAF feed
H_2O (l→g)		.032998 mols/gm DAF feed	345.9 cal/gm DAF feed		
NO_2	9920 cal/mol	.0019857 mols/gm DAF feed	19.7 cal/gm DAF feed	+7694 cal/mol	+ 15.3 cal/gm DAF feed
SO_2	10508 cal/mol	.0001125 mols/gm DAF feed	1.2 cal/gm DAF feed	-86499 cal/mol	- 9.7 cal/gm DAF feed
Ash	-	.2077 gm/gm DAF feed	72.7 cal/gm DAF feed	0 cal/mol	0
			1139.3 cal/gm DAF feed		-5955.3 cal/gm DAF feed
Reactants					
O_2	6885 cal/mol	.0481962 mols/gm DAF feed	331.8 cal/gm DAF feed	0 cal/mol	0 cal/gm DAF feed
Manure	-	1.2077 gm/gm DAF feed	422.7 cal/gm DAF feed		-1569.6
			754.5 cal/gm DAF feed		-1569.6 cal/gm DAF feed
			4770.5 cal/gm DAF feed		
			4385.7 cal/gm DAF feed		-4385.7 cal/gm DAF feed

Heat of Formation for Ethane (900°C)

Product

C_2H_6 20820 cal/mol

Reactants

2C 2(3738)	7476 cal/mol
$3H_2$ 3(6206)	18618 cal/mol
	26094 cal/mol
	-20236 cal/mol
ΔH_f^- (25°C)	-20236 cal/mol
ΔH_f (900°C)	-25510 cal/mol

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Table 23

Complete Gasification: Heat of Reaction (900°C)

D_o gm H_2O/gm DAF feed		.136411	.25	.60	1.00	1.207729 gm H_2O/gm DAF feed
Products	ΔH_f(900°C)					
CO_2	-94406 cal/mol	-	-273.1	-855.3	-1268.9	-1425.9 cal/gm DAF feed
CO	-27022	-884.0	-805.9	-639.2	-520.9	-475.9
H_2	0	-	-	-	-	-
H_2O	-59484	-	-203.3	-993.1	-2054.4	-2641.9
CH_4	-21811	-116.2	-116.2	-116.2	-116.2	-116.2
C_2H_6	-25510	- 43.7	- 43.7	- 43.7	- 43.7	- 43.7
NH_3	-13324	- 26.5	- 26.5	- 26.5	- 26.5	- 26.5
H_2S	-21627	- 2.4	- 2.4	- 2.4	- 2.4	- 2.4
Ash	0	-	-	-	-	-
		-1072.8	-1471.1	-2676.4	-4033.0	-4732.5
Reactants						
H_2O	-59484 cal/mol	- 450.8	- 826.2	-1982.8	-3304.7	-3991.1
Manure	-1569.7 cal/gm DAF feed	-1569.7	-1569.7	-1569.7	-1569.7	-1569.7
		-2020.5	-2395.9	-3552.5	-4874.4	-5560.8
ΔH_R(900°C) cal/gm DAF feed		+ 947.7	+ 924.8	+ 876.1	+ 841.4	+ 828.3 cal/gm DAF feed

+ = endothermic

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p

In Table 24, the heats of combustion ($900^{\circ}C$) for the product gases are calculated. Flue gas compositions are also calculated, and the heat available for drying is determined. The flue gas is assumed to enter the dryer at $200^{\circ}C$ and to leave at $80^{\circ}C$.

Table 25 shows the complete heat balances. The energy recovery for the ideal case--no heat losses--is calculated. The energy recovery for a non-ideal case--50% heat loss in the reactor and 20% heat loss in the dryer--is also calculated. These values of energy recovery are based on the heat of combustion of the incoming manure.

Table 26 shows a calculation of the fraction of the product gas that must be burned in the reactor and the corresponding excess air that must be used in the combustion. The flame temperature was taken to be $900^{\circ}C$, the same as the reactor temperature. The values of $(1-\Psi)$ correspond to the energy recovery values in Table 23. The values of $(1-\Psi)$ are somewhat smaller than the energy recovery values because they reflect the fact that the flue gas is cooled only to $80^{\circ}C$ rather than to $25^{\circ}C$ and that quite a lot of extra air was used in the combustion compared to stoichiometric air for the heat of combustion of the manure. The excess air requirement would be reduced if the flue gas could be used hotter than $200^{\circ}C$ in the dryer.

Discussion

As D_0 increases, the energy recovery worsens. This is because the heat contained in the steam in the reactor product gas is lost in the spray tower. At D_0 = .136411, there is no steam in the reactor product gas, and so the energy recovery is maximum. The calculations show that heat losses from the system have a very strong influence on the energy recovery. The residence time in the reactor has to be long enough, and the reaction tempera-ture high enough, that all the carbon and tar are gasified. Temperatures lower

Table 24

Heat of Combustion (900°C) for CO, H₂, CH₄, and C₂H₆

CO

		$\Delta H_f(900°C)$
Product	CO_2	-94406
Reactant	CO	-27702
	$\tfrac{1}{2}O_2$	0
		-27702
$\Delta H_C(900°C)$		-67384 cal/mol

H₂

		$\Delta H_f(900°C)$
	H_2O	-59484
Reactant	H_2	0
	$\tfrac{1}{2}O_2$	0
		0
		-59484 cal/mol

CH₄

		$\Delta H_f(900°C)$
	CO_2	-94406
	$2H_2O$	-118968
		-213374
	CH_4	-21811
	$2O_2$	0
		-21811
		-191563 cal/mol

C₂H₆

		$\Delta H_f(900°C)$
	$2CO_2$	-188812
	$3H_2O$	-178452
		-367264
	C_2H_6	-25510
	$\tfrac{7}{2}O_2$	0
		-25510
		-341754 cal/mol

Heat of Combustion (900°C) for Purified Product Gases of BIO II-General II

D_o	.136411		.25		.60		1.00		1.207729 gm H_2O/gm DAF feed	
CO	2204.5	35073	2009.6	31974	1594.0	25363	1298.9	20667	1186.7	18881
H_2	1374.0	21860	1546.0	24597	1912.9	30432	2173.5	34578	2272.4	36154
CH_4	1020.2	16225	1020.2	16225	1020.2	16225	1020.2	16225	1020.2	16225
C_2H_6	585.3	9296	585.3	9296	585.3	9296	585.3	9296	585.3	9296
	5184.0	82454	5161.1	82092	5112.4	81316	5077.9	80766	5064.6	80556
	cal/gm DAF feed	cal/mol	cal/gm DAF feed	cal/mol	cal/gm DAF feed	cal/mol	cal/gm DAF feed	cal/mol	cal/gm DAF feed	cal/mol

Flue Gas Heat (200°→80°C) .0628526 mols product gas/gm DAF feed.   e = excess air.

	$H_{200}-H_{80}$	.136411	.25	.60	1.00	1.207729
CO_2	1147 cal/mol	47.55	44.24	37.16	32.14	30.23 cal/gm DAF feed
H_2O	986	38.33	41.18	47.26	51.58	53.22 cal/gm DAF feed
N_2	841	131.44(1 + e)	131.44(1 + e)	131.44(1 + e)	131.44(1 + e)	131.44(1 + e) cal/gm DAF feed
O_2	868	36.06e	36.06e	36.06e	36.06e	36.06e cal/gm DAF feed
Flue Gas Heat		217.32 + 167.5e	216.86 +167.5e	215.86 + 167.5e	215.16 + 167.5e	214.89 + 167.5e cal/gm DAF feed
Remainder		4966.68 - 167.5e	4944.24 - 167.5e	4896.54 - 167.5e	4862.74 - 167.5e	4849.71 - 167.5e cal/gm DAF feed

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p

Table 25

D_o	.136411		.25		.60		1.00		1.207729 gm H_2O/gm DAF feed
Dryer Heat Demand	669.0	669.0	605.5	605.5	409.8	409.8	186.2	186.2	0 cal/gm DAF feed
Feed Enthalpy	-53.7		-115.2		-304.5		-520.8		-703.3 cal/gm DAF feed
Ash	72.7		72.7		72.7		72.7		72.7 "
CO_2	-		29.7		93.1		138.0		155.1 "
CO	215.1		196.1		155.5		126.7		115.8 "
H_2	143.3		161.3		199.6		226.8		237.1 "
H_2O	-		27.2		132.9		275.0		353.6 "
CH_4	65.2		65.2		65.2		65.2		65.2 "
C_2H_6	35.7		35.7		35.7		35.7		35.7 "
NH_3	20.3		20.3		20.3		20.3		20.3 "
H_2S	1.0		1.0		1.0		1.0		1.0 "
Product Enthalpy	553.3		609.2		776.0		961.4		1056.5 "
Heat of Reaction	947.7		924.8		876.1		841.4		828.3 "
Reactor Heat Demand	1554.7		1649.2		1956.6		2323.6		2588.1 cal/gm DAF feed
Heating Value of Feed	4770.5		4770.5		4770.5		4770.5		4770.5 "
Heating Value of Product Gas	5184.0		5161.1		5112.4		5077.9		5064.6 "
Energy Recovery: No Losses	62.1%		60.9%		57.6%		53.8%		51.9%
Energy Recovery: 50% Heat	26.0%		23.2%		14.4%		4.1%		-

Loss in Reactor, 20% Heat Loss in Dryer.

Table 26

.136411	.25	.60	1.00	1.2077

No Heat Losses

$\Psi(4966.68 - 167.50e) = 1554.7$ $\Psi(4944.24 - 167.50e) = 1649.2$ $\Psi(4896.54 - 167.50e) = 1956.6$ $\Psi(4862.74 - 167.50e) = 2323.6$ $\Psi(4849.7$

$\Psi(217.32 + 167.50e) = 669.0$ $\Psi(216.86 + 167.50e) = 605.5$ $\Psi(215.86 + 167.50e) = 409.8$ $\Psi(215.16 + 167.50e) = 186.2$ $\Psi(214.89$

$\Psi = .4290$ $\Psi = .4369$ $\Psi = .4629$ $\Psi = .4943$

$e = 8.0136$ $e = 6.9800$ $e = 3.9969$ $e = .9646$

50% Heat Loss in Reactor; 20% Heat Loss in Dryer

$\Psi(4966.68 - 167.50e) = 2(1554.7)$ $\Psi(4944.24 - 167.50e) = 2(1649.2)$ $\Psi(4896.54 - 167.50e) = 2(1956.6)$ $\Psi(4862.74 - 167.50e) = 2(2323.$

$\Psi(217.32 + 167.50e) = 1.25(669.0)$ $\Psi(216.86 + 167.50e) = 1.25(605.5)$ $\Psi(215.86 + 167.50e) = 1.25(409.8)$ $\Psi(215.16 + 167.50e) = 1.25(186$

$\Psi = .7611$ $\Psi = .7857$ $\Psi = .8656$ $\Psi = .9610$

$e = 5.2620$ $e = 4.4562$ $e = 2.2442$ $e = .1614$

Ψ = fraction of product gas burned

e = excess air

Table 26

| | .60 | 1.00 | 1.207729 gm H_2O/gm DAF feed |

Losses

9.2 $\psi(4896.54 - 167.50e) = 1956.6$ $\psi(4862.74 - 167.50e) = 2323.6$ $\psi(4849.71 - 167.50e) = 2588.1$

5.5 $\psi(215.86 + 167.50e) = 409.8$ $\psi(215.16 + 167.50e) = 186.2$ $\psi(214.89 + 167.50e) = 0$

$\psi = .4629$ $\psi = .4943$ —

$e = 3.9969$ $e = .9646$ —

: 20% Heat Loss in Dryer

$2(1649.2)$ $\psi(4896.54 - 167.50e) = 2(1956.6)$ $\psi(4862.74 - 167.50e) = 2(2323.6)$ $\psi(4849.71 - 167.50e) = 2(2588.1)$

$1.25(605.5)$ $\psi(215.86 + 167.50e) = 1.25(409.8)$$\psi(215.16 + 167.50e) = 1.25(186.2)$ $\psi(214.89 + 167.50e) = 1.25(0)$

$\psi = .8656$ $\psi = .9610$ —

$e = 2.2442$ $e = .1614$ —
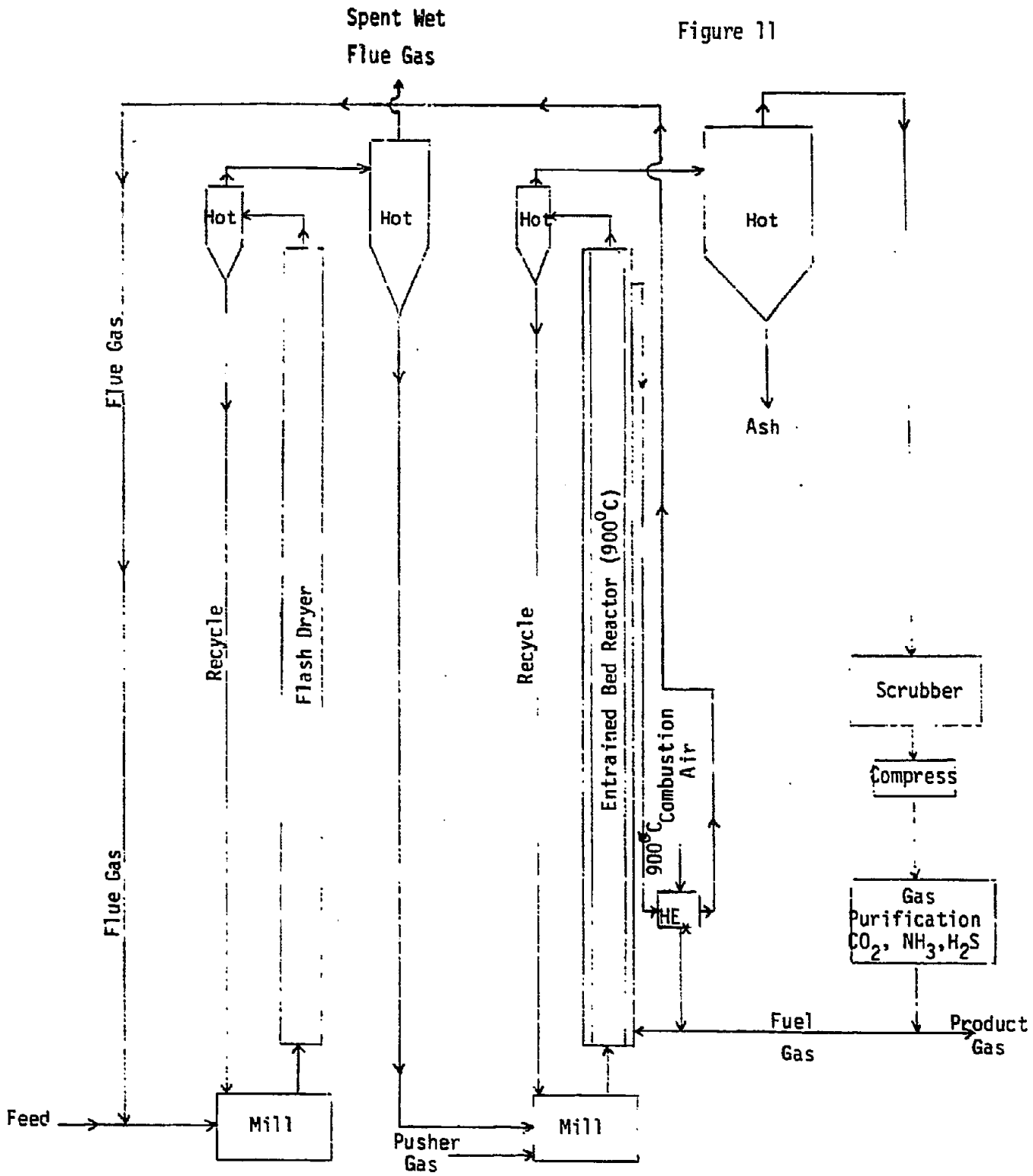
ψ = fraction of product gas burned

e = excess air

than 900°C may be possible in the entrained bed reactor. Lower temperatures would mean lower heat losses, fewer materials problems, and higher CH_4 and C_2^+ yields.

The diagram in Figure 11 shows a schematic diagram of the process. This scheme avoids the problem of recovering heat from a (probably) very dirty reactor product gas. The carrier gas (which could be some of the product gas or steam) flow rate needs to only be large enough to get the solids into the reactor. Once in the reactor, the heated solids generate enough gas and steam to carry them up through the reactor. In the flash dryer, large wet particles are recycled. In the entrained bed reactor, the recycle stream is used to control the solids residence time. In the pilot plant work a Torus Disc-type dryer would probably be used instead of the flash d-yer. In order to avoid corrosion problems, purified gas is burned in the jacket of the entrained bed reactor.

In the entrained bed reactor, each particle must "see" the radiation from the tube wall. This means that the tube diameter is limited. For scale-up, one would use externally fired multiple vertical tubes of fairly small diameter. The flash dryer can probably be scaled up by simply going to a larger diameter tube.
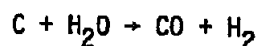
Biomass Gasification Process
Flash Dryer/Entrained Bed Reactor Combination

COMBUSTION

In the combustion experiments the O_2/C ratio was 1.0748 mol/mol,
and yet only 78.3% of the carbon burned. This is probably the result
of poor air-char mixing. In the PDU, there are many more perforations
in the baseplate than in the bench scale reactor, so the air-char mixing
should be better. The flue gas contained CO and H_2 in small amounts,
which may be due to pyrolysis or the reaction

$$C + H_2O \rightarrow CO + H_2$$

The moisture content of the flue gas was 0.64 g/ft^3. The concentrations
of CO and H_2 were probably equal. Using the gas chromatography equipment
concentrations lower than about 1 vol % are not too accurate.

The heat of combustion of manure char is based upon a laboratory
analysis, and indicates a heat flux through the plate above the burning
char of 12,972 BTU/hr ft^2. Based upon design calculations, a heat flux
of 15,506 BTU/hr ft^2 would be required for a "high moisture" manure in
commercial equipment. Assuming that the combustion efficiency of the PDU
is higher than that of the bench scale reactor, the required heat flux for
the worst case should be attainable.

In Run 6, Table 10.1 of the GERE Final Report, Phase I, the O_2/C ratio
was $\frac{11(.210)(28.316)(12)}{.414(67.7)(.2096)}$ = 2.47 mol/mol, while the combustion efficiency was
$\{1 - \frac{.1655(.6284)}{.2096(.8203)}\}$ = 39.5%. The flue gas temperature was indicated to be
only 335°C, and the rabble arm speed was 6 RPM. The very low combustion
efficiency was probably due to only patchy burning in the char layer. In
these runs a much higher combustion efficiency resulted from the more complete
air-char contact.

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GENERAL

Thermodynamics of Some Reactions Accompanying Pyrolysis

One of the important factors to be determined in this experimental program is the optimum water content of the biomass material before pyrolysis. One consideration is that the methane might be preferentially oxidized (before the char) by the steam to CO and H_2. Also, when dry biomass is pyrolyzed, H_2O is one of the products, so it is never possible to exclude H_2O. Since CO and H_2 have lower volumetric heating values than CH_4, the overall volumetric heating value of the pyrolysis gas would thereby be reduced. The free energy calculations below indicate that methane is not oxidized by steam when the temperature is $600^\circ C$ or less. The oxidation of methane by CO_2, and the oxidation of carbon by H_2O and/or CO_2 do not proceed when the temperature is $600^\circ C$ or less.

Calculations

	CO	CO_2	CH_4	H_2O
$700^\circ K$	-41.468	-94.510	-3.046	-49.915
800	-43.612	-94.556	-0.533	-48.646
900	-45.744	-94.596	+2.029	-47.352
1000	-47.859	-94.628	+4.625	-46.040
1100	-49.962	-94-658	+7.247	-44.712
1200	-52.049	-94.681	+9.887	-43.371
1300	-54.126	-94.701	+12.535	-42.022

Free Energy of Formation[16], kcal/mol

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[16] JANAF Thermochemical Tables - Second Edition, Natinal Bureau of Standards, U. S. Government Printing Office, Washington, D. C. (1971). SCI/QC 100/U573 No. 37.

$CH_4 + H_2O \rightleftarrows CO + 3H_2$ $\qquad$ $CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$

$700^{\circ}K$	+11.349 kcal/mol		+14.620
800	+5.567	$\leftarrow 620^{\circ}C$	+7.865
900	-0.421		+1.079
1000	-6.444		-5.715
1100	-12.497		-12.513
1200	-18.565		-19.304
1300	-24.639		-26.086

$C + H_2O \rightleftarrows CO + H_2$ $\qquad$ $C + CO_2 \rightleftarrows 2CO$ $\qquad$ $CO + H_2O \rightleftarrows CO_2 + H_2$

$700^{\circ}K$	+8.447		+11.574	$700^{\circ}K$	-3.127
800	+5.034		+7.332	800	-2.298
900	+1.608		+3.108	900	-1.500
1000	-1.819		-1.090	1000	-0.729
1100	-5.250		-5.266	1100	+0.016
1200	-8.678		-9.417	1200	+0.739
1300	-12.104		-13.551	1300	+1.447

The water gas shift reaction does occur at pyrolysis temperatures. Given a gross excess of steam, most of the CO will be driven to CO_2. Since CO is objectionable, this is good since the volumetric heating value of the pyrolysis gas decreases only slightly as the water gas shift reaction is driven to the right. Thermodynamics, of course, says nothing about reaction rates. CO and H_2 do not react at low temperatures and pressures to form C or CH_4 even though this is thermodynamically possible. Even though the oxidation of carbon by H_2O and/or CO_2 at $1200^{\circ}K$ has a large negative free energy change, the reaction is nevertheless rather slow. The water gas shift reaction, on the other hand, is fairly fast, "freezing" only at low temperatures.

Heat Balances for Gasification and Combustion in a Multiple Hearth Furnace

Data for the pyrolysis of bovine manure given by Schlesinger, Sanner, and Wolfson[17] were used for these calculations. Those data refer specifically to the pyrolysis of bovine manure containing 0.0447 gm H_2O/gm DAF manure, at 900^0C, and so then do these calculations. The reported pyrolysis was done in such a way that the contact time between the pyrolytic steam and the residual carbon was very short. In our pilot plant, on the other hand, this contact time is not so short and a significant portion of the residual carbon is steam-gasified. Nevertheless, in these calculations steam-gasification of carbon is ignored.

Bovine manure containing 1 gm H_2O/gm dry feed (1.207729 gm H_2O gm DAF feed) is dried at 200 mm Hg abs. (66.5^0C) to 0.0447 gm H_2O/gm DAF feed. Then it is pyrolyzed (without steam-gasification) at 900^0C. The off-gas is passed through a condenser which removes the steam and tar. No heat is recovered in the condenser. The tar, a small quantity of material, is not recycled. The pyrolytic char is burned to provide the heat necessary for pyrolysis, and the flue gas resulting from this combustion is used in the dryer. If there is more than enough pyrolytic char to satisfy the process heat demand, then the excess is steam-gasified, and the resulting water gas is mixed with the pyrolysis gas.

In Table 27 the heats of combustion of the pyrolytic char at 900^0C and 1100^0C are calculated. Then the heat of formation from the elements of the pyrolytic char at 900^0C is calculated by difference. Since pyrolytic char is essentially impure carbon ($\Delta H_f = 0$), its heat of formation is small. No

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[17] Schlesinger, Sanner, and Wolfson, "Energy from the Pyrolysis of Agricultural Wastes," Chapter 9 of <u>Symposium: Processing Agricultural and Municipal Wastes</u>, Avi Publishing Co., Westport, Conn. (1973), pp. 93-100.

Table 27

Heats of Combustion and Formation

Heat of Formation for Schlesinger, et al Char (900°C)

Heat of combustion (25°C)=7699.6 cal/gm DAF residue. Assume that this is "gross, 25°C" heat of combustion. Assume Cp=0.4 cal/gm°C for solids.

Products

	$H_{1173}-H_{298}$ cal/mol	$H_{1373}-H_{298}$ cal/mol	mols/gm DAF char	Heat of Combustion $H_{1173}-H_{298}$ cal/gm DAF char	$H_{1373}-H_{298}$ cal/gm DAF char	Heat of Formation (900°C) ΔH_f cal/mol	ΔH_f cal/gm DAF char
CO$_2$	10271	12991	.07985	820.1	1037.3	-94406	-7538.3
H$_2$O(g)	7962	10091	.0076	60.5	76.7	-59484	- 452.1
H$_2$O(1→g)	(582.3)	(582.3)	.004855	2.8	2.8		
NO$_2$	9920	12874	.001493	14.8	19.2	+ 7694	+ 11.5
SO$_2$	10508	13192	.000178	1.9	2.3	-86499	- 15.4
Ash			.901 gm/gm DAF char	315.4	387.4	0	0
				1215.5	1525.7		-7994.3

Reactants

	$H_{1173}-H_{298}$	$H_{1373}-H_{298}$		Heat Comb. H_{1173}	H_{1373}	ΔH_f	ΔH_f
O$_2$	6885	8602	.084846	584.2	729.8	0	0
Char			1.901 gm/gm DAF char	665.4	817.4		- 260.6 ←
				1249.6	1547.2		- 260.6
ΔH_c(25°C)				7699.6	7699.6		7699.6
ΔH_c				7733.7(900°C)	7721.1(1100°C)		-7733.7

No heat of combustion on ultimate analysis is given for the tar. Assume ΔH_f(900°C) = -1000 cal/gm tar.

$$\frac{X}{X+.085321} = \frac{23.69}{760}$$

X=.002745 mols H$_2$O/gm DAF residue in gas
.004855 mols H$_2$O/gm DAF residue condenses

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data are given fo. the heat of combustion or the ultimate analysis of the tar, so $\Delta H_F = 1,000$ cal/gm tar has been assumed. Since only a little tar is produced in pyrolysis, the resulting error should not be too important.

In Table 28 the heat of the pyrolysis reaction is calculated. Here manure at 66.5°C and containing .0447 gm H_2O/gm DAF feed is pyrolyzed at 900°C. ΔH_R is nearly zero.

In Table 29 the heat requirements of the dryer and the pyrolysis reactor are calculated. The feed to the dryer is manure at 25°C and containing 1.207729 gm H_2O/gm DAF feed. The dryer output is saturated steam at 66.5°C and dried manure at 66.5°C that contains .0447 gm H_2O/gm DAF feed. Pyrolysis occurs at 900°C. Gas, char, and tar all leave the reactor at 900°C.

In Table 30 the total heat available for drying and for pyrolysis are calculated as a function of e, excess combustion air, assuming that all the pyrolytic char is burned for heat. If there is a 20% heat loss in the dryer and a 38.3% heat loss in the pyrolysis reactor, then the assumption that all the pyrolytic char is burned for heat is just satisfied. When the initial feed manure is substantially drier than 50 wt % moisture (1.207729 gm H_2O/ gm DAF feed), there will be excess char to steam-gasify.

Discussion. Even when the pyrolysis feed is completely dry, the pyrolysis off-gas will contain pyrolytic steam. If the raw feed is relatively dry and there is a need to steam-gasify carbon, then it may be desirable to dry the incoming manure less completely so that the excess steam will promote the water gas reaction inside the pyrolysis reactor. If the raw feed is relatively wet and there is no excess carbon, then it may be desirable to completely dry the pyrolysis feed. In either case the heat contained in the steam in the pyrolysis reactor off-gas is not recovered.

It thus appears that when there is a need to steam-gasify carbon, it is

Table 28

Heat of Pyrolysis Reaction

Pyrolysis: Heat of Reaction (900°C)

D_o = 0.0447 gm H_2O/gm DAF feed

Products

Gas	ΔH_f, cal/mol	ΔH_f, cal/gm DAF feed
CO_2	-94406	-542.5
CO	-27022	-114.1
H_2	0	0
H_2O	-59484	-698.4
CH_4	-21811	-116.2
C_2H_6	-25510	- 43.7
NH_3	-13324	- 1.4
Char		-114.2
Tar		- 80.3
		-1710.8

Reactants

H_2O	-59484	-147.7
Manure		-1569.7
		-1717.4
ΔH_R(900°C)		+ 6.6

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Table 29

Dryer and Pyrolysis Reactor Heat Demands

Drying   Assume Solids C_p = 0.4 and Tar C_p = 0.8. Basis: $25^\circ C$, $H_2O(g)$

Input 1.207729 gm H_2O/gm DAF feed, 1.207729 gm dry solids/gm DAF feed ($25^\circ C$)

Output .0447 gm H_2O/gm DAF feed, 1.207729 gm dry solids/gm DAF feed +

   1.163029 gm steam/gm DAF feed ($66.5^\circ C$)

Heat Requirement:

   $1.207729(.4)(66.5 - 25) + .0447(1.0)(66.5 - 25) + 1.163029(625.53 - 25.05)$

   = 720.3 cal/gm DAF feed

Pyrolysis		$H_{1173}-H_{298}$	$H_{1173}-H_{298}$
Products ($900^\circ C$)	mols/gm DAF feed	cal/mol	cal/gm DAF feed
CO_2	$0.574595(10^{-2})$	10271	59.02
CO	$.422188(10^{-2})$	6575	27.76
H_2	$.645459(10^{-2})$	6206	40.06
H_2O	$1.174181(10^{-2})$	7962	93.49
CH_4	$.532568(10^{-2})$	12234	65.15
C_2H_6	$.171255(10^{-2})$	20820	35.66
NH_3	$.010656(10^{-2})$	10206	1.09
Char	.438406 gm/gm DAF feed	.4(900 - 25) cal/gm	153.44
Tar	.080314 gm/gm DAF feed	.8(900 - 25) cal/gm	56.22
			531.89

Reactants ($66.5^\circ C$)

H_2O	.0447 gm/gm DAF feed	-540.87 cal/gm	-24.18
Manure	1.207729 gm/gm DAF feed	.4(66.5 - 25) cal/gm	20.05
			- 4.13
Heat of Reaction			+ 6.6
Total			542.6 cal/gm DAF feed

Table 30

Overall Heat Balances

	mols/gm DAF char	mols/gm DAF feed	$H_{1373} - H_{353}$ cal/mol	Flue Gas Enthalpy Drop $H_{1373} - H_{353}$ cal/gm DAF feed
CO_2	.07985	.0184135	12476	229.7
H_2O	.0076	.0017526	9647	16.9
NO_2	.001493	.0003443	12369	4.2
SO_2	.000178	.0000410	12645	0.5
O_2	.084846e	.0195656e	8212	160.7e
N_2	$\frac{.79}{.21}$ (.084846)(1 + e)	.0736038(1 + 3)	7746	570.1(1 + e)

Heat Available for Drying	821.5 + 730.8e
Heat Available for Pyrolysis	958.9 - 730.8e
Total ΔH_C (900°C)	1780.5

Assume: No heat losses.

$(821.5 + 730.8e)\Psi = 720.3$

$(958.9 - 730.8e)\Psi = 542.6$

Ψ = 70.9% of char must be burned

e negative

Assume: 38.3% heat loss in pyrolysis reactor

20% heat loss in dryer

$(821.5 + 730.8e)\Psi = (1.25)(720.3)$

$(958.9 - 730.8e)\Psi = (1.621)(542.6)$

Ψ = 100% of the char must be burned

e = 0.108

preferable to do it in the pyrolysis reactor. One of the objectives of the pilot plant work is to determine whether or not this can be done. If the water gas reaction must be done separately, either in whole or in part, then external water would have to be vaporized and superheated for the purpose. This represents an additional heat requirement on the process.