

WET OXIDATION OF HUMAN WASTE

by

CORDELIA MAE PRICE

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ABSTRACT

The wet oxidation of human urine and feces was studied at pressures ranging from 2275 to 4050 psig and temperatures from 277 C to 443 C. The results can be used in the development of a closed environment life support system, a method being investigated as a way of recycling wastes to grow plants to support life on board long term manned space missions.

A continuous flow system for oxidation at high temperatures and pressures was designed and built. A dilute slurry of urine and feces with a carbon concentration between 650 and 1800 ppm was oxidized with pure oxygen in stoichiometric or slightly excess proportions.

Conversions ranging from 56% to 93% were obtained. Pressure and temperature were found to increase conversion. Even at the lower conversion the liquid product was clear and had only a slight odor. Concentrations of calcium, magnesium, manganese, and phosphorous in the solid phase increased after wet oxidation. Most of the nitrogen, carbon, hydrogen, and potassium did not remain in the solid phase after oxidation.

The conversions obtained were lower than those obtained by others at similar temperature, pressure and residence time. This difference is discussed and an explanation given as to why this is the case. Recommendations are also given as to how the conversions can be increased and how quantitative data on the inorganic components can be obtained.

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Summary

I. Introduction

In the future long term manned space missions will require methods that recycle supplies on board. Non-regenerative methods of life support which have been used in the past will become too costly. Research has been started on one such method, a closed environment life support system (CELSS) in which all gaseous, liquid, and solid waste streams from humans and animals must be recycled to plants grown aboard to support life. The heart of a CELSS is an oxidation system to convert organic carbon, hydrogen, and oxygen to CO_2 and H_2O . Lockheed Missiles and Space Company has developed and demonstrated a wet oxidation system but like other researchers failed to demonstrate how their waste processing system would convert the waste to nutrients in a form that could be used by growing plants. Direct comparison of the different systems is also difficult due to the use of different waste input models. The results and recommendations of Lockheed and other researchers were used to build a wet oxidation system and to define operating parameters for the initiation of a program to carry wet oxidation from representative waste inputs to plant nutrients.

II. Background

Wet oxidation is the term used to describe oxidation which takes place in an aqueous environment. Carbonaceous organic matter is converted to CO_2 and H_2O . Organic amine nitrogen is converted to ammonia, sulfur compounds to sulfates, and phosphorous compounds to insoluble phosphates.

Wet oxidation has been operated from 160°C to 320°C and 600 to 2500

psig (1, 11, 9, 13, 20). It has been used to oxidize a variety of materials commercially and on a research level in order to study the kinetics and mechanism of oxidation.

Most researchers agree that wet oxidation consists of thermal decomposition followed by oxidation. Wet oxidation breaks down organic compounds producing lower organic acids whose conversion to CO_2 and H_2O is slower and appears to be the rate controlling step.

Because wet oxidation is a gas-liquid reaction, most researchers have found that agitation enhances the rate of oxidation. Pruden and Le (11) who used a bubbling reactor found mass transfer effects to be small. Lockheed observed no effect of agitation on reduction in total organic carbon (TOC) in their continuous flow system.

Pressure in most cases has been found to increase conversion. As pressure increases its effect on conversion decreases. This verifies a model presented by Pruden and Le which predicts that pressure has its greatest effect near the vapor pressure of water.

The amount of oxidizing gas depends upon the TOC of the waste material, the quantity of material, and the desired degree of oxidation. An amount in excess of the theoretical has usually been found to be necessary.

Temperature was the major independent variable for most researchers. Higher temperatures increased rate. One researcher, Teletze(16), claims that the higher temperatures also increase final conversion, i.e. at lower temperatures conversion leveled off at a lower level.

Residence time was also found to increase conversion, having the greatest effect at higher temperatures. Residence times used vary from 20 to 90 minutes.

The Barber-Coleman company found that a pH between 1 and 5 should produce an additional 10% reduction in Chemical Oxygen Demand (COD). Lockheed used a RuCl_3 catalyst to suppress ammonia formation causing the pH in the reactor to be acidic. A reduction in TOC was also observed with the catalyst which could have been due to the acidity.

Wet oxidation has an effect on chemical composition of sludge also. Sommers et al (12) claim that total nitrogen levels in sludges are decreased by more than 50%. Other components (P, Co, Zn, Ni, Cd, and Pb) remain unchanged. Total soluble phosphorous decreases and phosphorous in the particulate phase increases. According to Modell et al (8) all mineral nutrients including nitrogen are expected to stay in the aqueous phase from which the heavy metal ions (Ca, Mg, Fe, Cu, Zn, Mn, etc.) will precipitate as insoluble phosphates and/or sulfates. Little carbonate precipitation should occur in the presence of these ions and loss of fixed nitrogen should be small. Lockheed found most of the effluent carbon and nitrogen in the gas phase and the sulfur and phosphorous in the liquid phase.

III. Objectives

The general objectives are to fill in the gaps in the literature and provide useful information to help build a CELSS. Specifically the objectives are to build a wet oxidation system to oxidize a slurry of urine and feces, determine the effects of operating conditions upon the efficiency of oxidation, close the material balance on carbon, and determine the effects of wet oxidation on other components of urine and feces.

The approach used to accomplish these objectives was to design a reactor without gas-liquid mass transfer effects. This meant a one phase

system in which the dissolved oxygen at reactor conditions and the feed were in at least stoichiometric proportions. The work of previous researchers was used to define operating parameters.

IV. Apparatus and Procedure

A continuous flow system was used. The feed, a slurry of urine and feces, deionized water, and oxygen were pumped up to pressure and the volume of the feed and water pumped were measured with respect to time. The water passed through a coiled length of tubing in a furnace to be preheated to reactor temperature or higher. The hot water, feed, and oxygen were then mixed together and passed through a Hastelloy reactor kept hot by another furnace. There the oxidation reaction occurred. The reactor effluent passed through a heat exchanger to be cooled and a solid product collector to have suspended particles removed. The stream then passed through a back-pressure regulator and upon expanding the phases were separated in a gas-liquid separator. The gas phase went to an on-line gas chromatograph which periodically analyzed a sample. The liquid passed to a collection bottle. Grab samples were periodically taken to be subsequently analyzed for total carbon, inorganic carbon, and total organic carbon with a TOC analyzer and inorganic components with ICPES. During a run flowrates, pressures, and temperatures were monitored. Data was collected once a system reached steady state. Figure 4-1 is a schematic of the apparatus.

V. Results

A. Residence Times

Residence times were calculated from liquid flowrates and the density of water at reactor conditions. They are reported in Table 5-4.

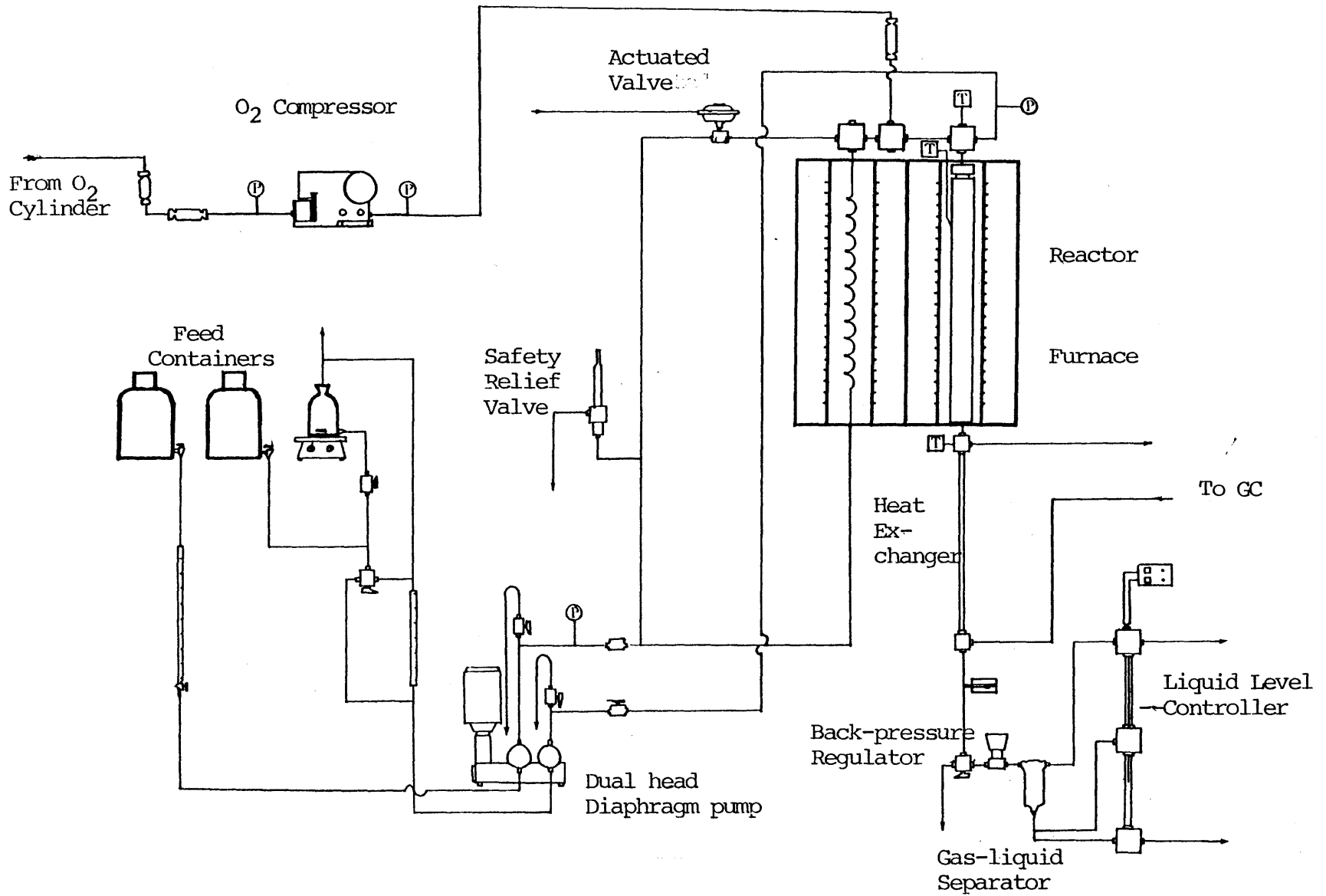


Figure 4-1. System Schematic

B. Gaseous Results

Gas composition with time was recorded for all runs. The average concentration for each component normalized to account for the water vapor is reported in Table 5-1 for each run. The average gas flowrates are also reported.

C. Liquid Results

Liquid results are tabulated in Table 5-2. Total carbon in the feed, organic carbon in the liquid effluent, and inorganic carbon in the liquid effluent are reported in units of moles C/min and ppm.

Most of the liquid products were clear with a slight odor although a few contained a small amount of either a brown or a white particulate. Results of ICPES analysis of some of the liquid products are found in Table 5-3.

D. Carbon Conversion and Carbon Balance

Carbon conversion was calculated from the change in organic carbon concentration. The carbon in the feed, carbon in the product, and conversion are reported in Table 5-4.

A carbon material balance was done by checking the amount of carbon in the gas phase and liquid phase products against the amount of carbon in the feed. These results are reported in Table 5-5.

E. Solid Results

Solid products were analyzed for inorganics using ICPES and organics using an elemental analyzer. The results are presented in Table 5-6.

TABLE 5-1

Gas Results

Date	Flow rate (cc/min)	%C	Gas Composition (% by Volume)						
			H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ S
7/8	180.3 \pm 99.2	46.553	.037	35.559	50.773	.341	.000	10.982	.0123
8/8	47.9 \pm 16.2	8.029	.105	8.011	88.851	.552	.000	.018	.008
8/11	56.6 \pm 28.2	9.912	.075	9.680	87.072	.641	.008	.232	.008
8/14	97.9 \pm 11.9	7.084	.014	6.961	89.654	.373	.008	.133	.008
8/24	87.1 \pm 22.1	3.041	.055	2.868	94.517	.088	.008	.173	.008
9/1	141.1 \pm 6.8	27.708	.260	17.314	69.221	.577	.045	10.219	.065
9/6	123.3 \pm 5.7	31.161	.291	21.608	65.762	.800	.019	9.458	.038
9/22	135.7 \pm 11.3	17.234	.339	11.149	79.874	.287	.025	6.018	.021
9/24	127.1 \pm 4.8	3.575	.112	.309	93.313	.717	.014	3.222	.015
10/19 ^a	171.0 \pm 13.2	22.364	.557	12.381	74.434	.414	.405	9.426	.076

a 10/19 run also had C₃s with a concentration of .015.

TABLE 5-2

Liquid Results

Date	Feed Flow rate Total $\frac{\text{cc}}{\text{min}}$	Feed Flow rate moles $\frac{\text{C}}{\text{min}}$	Total Carbon in Feed (ppm)	Organic Carbon in Liq. Effluent (ppm)	Organic Carbon $\frac{\text{moles}}{\text{min}}$	Inorganic Carbon in Liq. Effluent (ppm)	Inorganic Carbon $\frac{\text{moles}}{\text{min}}$
7/8	16.79 $\pm .97$	0.00604 $\pm .00050$	4316 ± 450	1876 ± 493	0.00262 $\pm .00075$	36 ± 38	0.00005 $\pm .000056$
8/8	16.18 $\pm .74$	0.00100 $\pm .00010$	742 ± 108	27 ± 129	0.000037 $\pm .00018$	102 ± 28	0.00014 $\pm .000041$
8/11	16.31 $\pm .66$	0.00092 $\pm .00014$	678 ± 110	318 ± 261	0.00043 $\pm .00037$	144 ± 9	0.00020 $\pm .000021$
8/14	16.38 $\pm .89$	0.00112 $\pm .00015$	819 ± 115	150 ± 5	0.00020 $\pm .000007$	130 ± 4	0.00018 $\pm .000014$
8/24	16.19 $\pm .79$	0.00117 $\pm .00021$	870 ± 149	170 ± 6	0.00023 $\pm .000018$	133 ± 4	0.00018 $\pm .000014$
9/1	25.32 $\pm .49$	0.00352 $\pm .00013$	1670 ± 76	207 ± 14	0.00044 $\pm .000038$	415 ± 22	0.00088 $\pm .00006$
9/6	25.96 $\pm .55$	0.00380 $\pm .00026$	1755 ± 121	201 ± 8	0.00044 $\pm .000027$	423 ± 21	0.00092 $\pm .000065$
9/22	19.28 $\pm .27$	0.00284 $\pm .00016$	1766 ± 118	139 ± 20	0.00022 $\pm .00003$	353 ± 100	0.00057 $\pm .00017$
9/24	26.11 $\pm .47$	0.00146 $\pm .00009$	713 ± 51	51 ± 11	0.00011 $\pm .000026$	386 ± 64	0.00084 $\pm .000015$
10/19	25.82 ± 1.25	0.00356 $\pm .00028$	1653 ± 168	202 ± 21	0.00043 $\pm .000066$	229 ± 137	0.00049 $\pm .00032$

TABLE 5-3

Inorganic Components in Liquid Products^d

Sample Number	Ca	P	K
9-24 #1 Blank ^a	<.001	N.D. ^e	<.009
9-24 #4	≤.001	0.8	.041
9-24 #5	<.001	7.0	.054
9-24 #6	<.001	12.0	1.058
9-24 #7	<.001	15.0	.075
10-19 #3 ^b	<.001		.081
10-19 #4	<.001		.091
10-19 #2 ^c	<.001		.047
10-19 #3	<.001		.055

^a white solids filtered with 5 micron filter

^b brown solids filtered

^c brown solids digested with concentrated HNO₃ and 3% H₂O

^d units are mg/gm; multiply by 1000 to get ppm

^e N.D. - not detected

TABLE 5-4

Carbon Conversion

Date	P (psig)	T (°C)	θ (min)	Feed (moles C/min)	Feed (ppm)	Total Organic Carbon (TOC) Liquid Effluent (ppm)	Liquid Effluent (moles C/min)	% Conversion
7/8	2275	277	23.2 ± 1.4	0.00604 ± 0.0005	4316 ± 450	1876 ± 428	0.00262 ± 0.00075	56.5 ± 18.8
8/8	2375	303	23.7 ± 0.9	0.00100 ± 0.0001	742 ± 108	27.2 ± 129	0.000037 ± 0.00018	96.3 ± 474.4
8/11	2275	292	23.3 ± 1.3	0.00092 ± 0.00014	678 ± 110	318 ± 261	0.00043 ± 0.00037	53.1 ± 52.2
8/14	3200	289	23.8 ± 1.3	0.00112 ± 0.00015	819 ± 115	150 ± 5	0.00020 ± 0.000007	81.7 ± 14.1
8/24	2550	295	23.9 ± 1.1	0.00117 ± 0.00021	870 ± 149	170 ± 5.6	0.00023 ± 0.000018	80.5 ± 16.4
9/1	4050	409	4.1 ± 0.1	0.00352 ± 0.00013	1670 ± 76	207 ± 14	0.00044 ± 0.000038	87.6 ± 9.9
9/6	3825	400	3.8 ± 0.1	0.00380 ± 0.00026	1755 ± 121	201 ± 8	0.00044 ± 0.000027	88.5 ± 9.6
9/22	3825	404	5.1 ± 0.1	0.00284 ± 0.00016	1766 ± 118	139 ± 20	0.00022 ± 0.00003	92.1 ± 19.4
9/24	3825	402	3.7 ± 0.1	0.00155 ± 0.00009	713 ± 51	51 ± 11	0.00011 ± 0.000026	92.8 ± 26.6
10/19	3850	443	2.4 ± 0.1	0.00356 ± 0.00028	1653 ± 168	202 ± 21	0.00043 ± 0.00007	87.7 ± 18.0

TABLE 5-5

Carbon Balance

Date	Gas Flow rate (moles $\frac{C}{min}$)	% of Feed C	Feed (moles $\frac{C}{min}$)	Liquid Effluent		Carbon Accounted For (%)
				(moles $\frac{IC}{min}$)	(moles $\frac{TOC}{min}$)	
7/8	.0038 \pm .0021	62.1 \pm 34.9	.00604 \pm .0005	.00005 \pm .000056	.00262 \pm .00075	106.3 \pm 56.9
8/8	.00017 \pm .00006	17.0 \pm 8.7	.00100 \pm .0001	.00014 \pm .000041	.000037 \pm .00018	34.7 \pm 22.3
8/11	.00025 \pm .00012	27.2 \pm 21	.00092 \pm .00014	.00020 \pm .000021	.00043 \pm .00037	95.6 \pm 33.9
8/14	.00031 \pm .00004	27.7 \pm 6.7	.00112 \pm .00015	.00018 \pm .000014	.00020 \pm .000007	61.6 \pm 13.5
8/24	.00012 \pm .00003	10.3 \pm 3.9	.00117 \pm .00021	.00018 \pm .000014	.00023 \pm .000018	45.3 \pm 13.4
9/1	.00175 \pm .00008	49.7 \pm 4.6	.00352 \pm .00013	.00088 \pm .00006	.00044 \pm .000038	87.2 \pm 8.4
9/6	.00172 \pm .00008	45.3 \pm 3.1	.00380 \pm .00026	.00092 \pm .000065	.00044 \pm .000027	81.8 \pm 10.1
9/22	.00104 \pm .00009	36.6 \pm 5.4	.00284 \pm .00016	.00057 \pm .00017	.00022 \pm .00003	64.4 \pm 13.7
9/24	.00020 \pm .00001	12.9 \pm 1.0	.00146 \pm .00009	.00084 \pm .000015	.00011 \pm .000026	78.8 \pm 8.1
10/19	.00171 \pm .00013	48.0 \pm 7.3	.00356 \pm .00028	.00049 \pm .00032	.00043 \pm .00066	73.9 \pm 18.2

TABLE 5-6

Organic and Inorganic Composition of Feed and Solid Products^a

Sample	Ca	K	Mg	Mn	P	C	H	N	S	Total
Urine	.21	2.42	.083	.0002	1.2	19.76	4.7	20.50	1.77	50.64
Feces	.40	.91	.19	.0038	.71	46.61	6.82	4.44	.5	60.08
9-6-1 ^b	5.8	<.0009	3.6	.087	16.0	1.46	.26	.06		27.27
9-6-2 ^c	2.2	<.0009	1.2		7.0	1.52	.35	.14		12.41
9-6-3 ^d	5.5	<.0009	3.0	.12	15.0	.38	.1	.03		24.13
9-22-1 ^e	13.4	<.0009	5.0			1.43	.21	.02		20.06
9-22-2 ^f						2.34	.44	.16		2.94
10-19 ^g	4.2		2.9							7.10

^aunits- weight %

^bsolids deposited in fittings before reactor

^csolids collected in solid separator

^dsolids deposited on reactor walls

^fsolids washed out of the system after run was completed and collected at solid separator; supernatant liquid was yellow and allowed to evaporate off without washing solids

^{e,g}solids washed out of the system at end of run

VI. Discussion of Results

A. Wet Oxidation System

The goal of building a wet oxidation system to oxidize urine and feces was accomplished but the system had operational problems which led to errors in the results.

Temperature control was not very good and there was no way to measure the temperature inside the reactor.

Pressure control was better with average fluctuations of about 4%. Clogs in the lines caused uncontrolled pressure rises which eventually led to shutdown.

The double diaphragm pump had difficulty pumping anything greater than 170 mesh particle size so the feces had to be ground. There were large errors in flowrate measurement because of the small pipet that was used to measure flowrate.

Gas phase flowrates fluctuated a lot especially at subcritical conditions.

Leaks in the reactor prevented start-up or caused shutdown. The reactor was the limiting factor in determining the number of runs which could be completed. Attempts at making the reactor leak-free had a temporary effect. This was one of the reasons the original set of experiments was not completed.

Another was the oxygen flowrates which were too low for proper operation of the compressor. The subcritical runs were not smooth and conversions were low, therefore runs were made at supercritical conditions to increase conversion and to achieve smooth operation.

B. Efficiency of Oxidation

Lockheed obtained higher conversions at similar pressure, temperature, and residence time; 88% at 288°C and 2200psig compared to 56% at 292°C and 2275 psig.

Other differences in the experiments may explain the differences in conversion. Lockheed used agitation and their reactor was designed with baffles. They used a much higher oxygen flowrate. They used a RuCl_3 catalyst to suppress ammonia formation and found that it enhanced oxidation also. Their feed had about fifteen times as much urine as feces with 28% carbon, whereas in this thesis equal amounts of urine and feces were used resulting in a 41% carbon content.

The solid product obtained has less C, H, and N than Lockheed's. This can probably be attributed to a longer solid residence time.

Other researchers obtained better results with sewage sludge. Some of the difference is probably due to reactor design and residence time. Most used agitation and longer residence times.

C. Effect of Operating Conditions on Oxidation

The results show that conversion increases with pressure. Since the conversions were so low, the oxygen concentration must not have reached saturation. The rate of oxidation would have been higher otherwise. There were probably two phases present in the reactor which did not have time to equilibrate within a 20 minute residence time.

The supercritical runs had higher conversions although residence times were shorter. The increased conversions are probably due to the increased temperatures. The reaction also was not limited by oxygen solubility since according to Pray (10) at supercritical conditions oxygen

must be infinitely soluble. These results are lower than those obtained with other feeds at supercritical conditions such as glucose. This is partially due to the shorter residence times used here.

D. Effects of Wet Oxidation on Inorganic Components of Urine and Feces

Calcium, phosphorous, magnesium, and manganese have higher concentrations in the solid product than in the feed. The concentration of potassium decreased in the solid phase. This is the expected result. This result differs with Lockheed whose material balance test showed most of the phosphorous in the liquid phase.

Calcium precipitates out as expected from the liquid phase because very little was detected in it and a lot in the solid phase. Not much more can be said about the effect of oxidation on inorganics in the liquid phase since the concentrations in the feed are not known.

E. Carbon Balance Results

The results in Table 5-5 indicate that a lot of carbon is unaccounted for. Only one run gave a material balance closure greater than 90%. Absorbed CO_2 in the liquid product probably desorbed before TOC analysis was done.

VII. Conclusions

1. Conversion obtained at a similar pressure, temperature, and residence time was less than that obtained by Lockheed. The differences may be due to differences in pH, reactor configuration, oxygen flow-rate, feed, the presence of a catalyst, or errors in both investigators' results.
2. The wet oxidation system is capable of oxidizing waste but contains

several design deficiencies which cause errors in the results.

3. At subcritical conditions pressure increases lead to increases in conversions and liquid phase resistance to oxygen diffusion exists.

4. An increase in temperature causes an increase in conversion.

5. Wet oxidation of urine and feces at the conditions tested produces a solid product with a higher content of calcium, magnesium, manganese, and phosphorous than in the feed.

6. Wet oxidation of urine and feces produces a clear liquid product with a slight odor even at conversions as low as 56%.

7. Most of the nitrogen, carbon, hydrogen, and potassium do not remain in the solid phase after oxidation.

VIII. Recommendations

1. Reduce error in the results through changes in the experimental system.

2. After the design deficiencies in the system have been corrected check the results in this thesis.

3. If better and acceptable conversions are obtained then pursue the answers to other questions about wet oxidation of urine and feces.

4. If the conversions do not improve try one of the following:

a. Increase residence times, pressure, and/or oxygen flowrates.

b. Lower the pH to the acidic range in the reactor.

c. Devise a way to insure the pure water and oxygen are in equilibrium before either enters the reactor.

I. Introduction

In the future long term manned space missions will require methods that replenish or recycle supplies on board. Non-regenerative methods of life support which have been used on space missions in the past will become too costly. The quantity of supplies will increase with the duration of the flight and since the cost of supplies required for the journey is proportional to the weight at launch (8), the cost will also increase. At some breakeven point launching and transporting the equipment to recycle the supplies from waste will probably be less costly than using the supplies up on a once-through basis. Thus a need for study of the technology requirements for recycling supplies on board exists.

Present research is aimed at closed environment life support systems (CELSS). In a CELSS all gaseous, liquid, and solid waste streams from humans and animals must be recycled to plants grown aboard to support life. The liquid and solid waste streams which will include feces, urine, and the uneaten portions of animals and plants must be converted to forms acceptable as nutrients by growing plants. The waste processing system must do this as well as convert the organic carbon, hydrogen, and oxygen into CO_2 and H_2O which are necessary for photosynthesis. After the oxidation step, separation of certain components present and conversion of others to the proper ionic states suitable for plant uptake will be required. The method of separation will depend upon the method of oxidation.

The National Space and Aeronautics Administration (NASA) has sponsored previous research and development on such waste treatment systems.

Wet and dry oxidation systems have been built and tested on a demonstration scale. The input waste models were so different that no direct comparison of the alternative methods of waste treatment could be made without significant extrapolation of experimental results. The previous research also failed to address how the waste processing scheme would deal with the conversion of the waste to nutrients in a form that can be used to grow vegetation. Thus a need for a standardized waste input model and a program to carry through waste processing from representative inputs to plant nutrients exists. Any research which further defines wet or dry oxidation within the above context will help define the technology requirements for CELSS that would be appropriate for long term space missions.

The NASA sponsored research on wet oxidation was performed by Lockheed Missiles and Space Company, Inc. A continuous flow system was developed and demonstrated (18). The results and recommendations of this research and other studies were used to build a wet oxidation system and to define operating parameters for the initiation of a program to carry wet oxidation from representative waste inputs to plant nutrients.

II. Background

Wet oxidation is the term used to describe oxidation which takes place in an aqueous environment. Insoluble carbonaceous organic matter is converted to CO_2 and H_2O . Organic amine nitrogen is ultimately converted to ammonia, sulfur compounds to sulfates, and phosphorous compounds to insoluble phosphates (1).

Wet oxidation systems have been operated anywhere from 160°C to 320°C and 600 to 2500 psig (1, 11, 9, 13, 20). A wet oxidation process has been commercialized by Zimpro, Inc. called the Zimmerman Wet Air Oxidation process. It has been put in operation in more than 160 locations around the world (19). Some of the applications of this process are destruction of hazardous materials such as acrylonitrile and coke oven gas scrubbing waste waters as well as conditioning of sewage sludge. Researchers have also used wet oxidation to oxidize glucose, the low molecular weight organic acids, proprionic and butyric (20), phenol and nitrilotriacetic acid (11), ethyl alcohol, iso-octane, pyrogalllic acid and charcoal (11). They have tried to study the kinetics and the mechanism of wet oxidation.

Lockheed Missiles and Space Company is the only researcher to study the wet oxidation of urine and feces solely. Their research was also different from other researchers for another reason. Concentrated industrial wastes are treated by wet oxidation to reduce Chemical Oxygen Demand (COD) before discharge to receiving water or a municipal sewage system. Sewage sludge is treated to eliminate potential health hazards arising from ultimate disposal of solids and to economically reduce the volume of solids. A 30% reduction in COD is usually sufficient to destroy the slimy nature of sludge and 30-40% reduction destroys its cellular and fibrous structure (16). Wet oxidation is used on urine and feces to completely recycle them to useful products; therefore, complete conversion is desirable.

Many researchers agree that wet oxidation consists of thermal decomposition followed by oxidation (1, 13, 14, 17). Bridges and Fassell (1) add that the overall wet oxidation reaction is a combination of

several chemical reactions which occur simultaneously and have rates governed by a number of physical processes. The reactions are hydrolysis of solids, heterogeneous (solid-surface) oxidation, and homogeneous (liquid-phase) oxidation. The reactions seem to proceed in two apparently interconnected rate-limiting steps both pseudo-first order with respect to COD content of the liquid phase and rate-determining over a range of percentage reduction in COD. Waste materials are hydrolyzed and/or oxidized rapidly from their initial complex structures to simpler, lower molecular weight compounds such as lower fatty acids. The conversion of these intermediates to CO_2 and H_2O is slower. This explains why oxidation is rapid until about two-thirds of the original COD organics have been oxidized and then continues at one-tenth the rate for the remainder. Williams et al. (20) also agree that wet air oxidation breaks down organic compounds producing lower organic acids. The oxidation of the acids is slow and may be the rate-controlling step. In their studies of two low molecular acids, butyric and propionic, they detected the presence of aliphatic hydrocarbons in the product gases and also conclude the existence of a free radical mechanism.

For two of the reactions to occur, the heterogeneous and homogeneous, an oxidizing medium in intimate contact with the oxidizable waste material is essential. Most workers claim the best way to accomplish this is through the geometry of the reactor and through agitation. The Barber-Coleman Company (1) employed vigorous agitation to disperse the solid carbonaceous waste materials so that they are more accessible to the liquid and gaseous phases. They say mixing disperses the oxidizing gas through the aqueous medium as fine bubbles thus increasing the effective interfacial area for mass transfer. It also increases

rate of convection which accelerates the rate of dissolved gas diffusion through the bulk of the liquid and therefore significantly affects the rate of wet oxidation. As a result of some tests the company made, they concluded that intensive agitation at moderate temperatures is more effective at equal time than non-agitated reactors at higher temperatures.

Most wet oxidation data obtained has been from reactor systems which employ vigorous agitation. Such systems are also used to show the absence of mass transfer effects. Williams et al (20) found that with mixing wet oxidation was kinetically controlled below 288°C. Higher temperatures were not tested. Since no effect of degree of mixing could be detected, they concluded that if the rate of reaction was independent of stirrer speed, the reaction could not be controlled by O₂ transfer from the gas phase to the liquid.

Pruden and Lee (11) used a bubbling reactor to determine mass transfer effects directly. They developed equations from which the conditions at which mass transfer would control or kinetics would control could be predicted. They concluded that as the concentration of the feed goes to zero the rate depends on that feed concentration no matter what the mass transfer effects are. For the bubbling reactor, the mass transfer effects were small. No mechanical agitation was necessary to achieve conversions as high as 99%.

Lockheed (18) used mechanical agitation for a batch reactor and a continuous flow reactor system for wet oxidation of urine and feces. For the batch system, stirring was found to enhance oxidation whereas stirring rate had no effect upon total organic carbon reduction of the feed in the continuous flow system.

Hudgins and Siveston (5) used a rocking autoclave and because their

rates had a small temperature dependence and decreasing the concentration in the feed increased the rate they concluded mass transfer was controlling. They suggested agitation to get rid of mass transfer control.

Many workers have described the effect of pressure on conversion. The pressure is determined by two factors: the vapor pressure of water at the highest temperature prevailing in the reactor plus the partial pressure of any other gas present. Fassell and Bridges (1) recommend maintaining a total pressure of between 50 and 200 psig above the vapor pressure of oxygen and to provide sufficient O_2 solubility in the liquid phase. If the oxidizing gas is not pure O_2 , the total system to afford a particular solubility will be even higher.

Pruden and Le (11) present an equation which explains and backs up the above statements. They say that for reaction to occur, oxygen from the gas bubbles has to diffuse through a gas, then a liquid interface to the bulk liquid where it reacts with the substance being oxidized. The gas phase resistance can usually be neglected for this type of situation (4) and the problem is formulated in terms of the liquid phase resistance and chemical reaction:

$$\frac{\Delta C}{C_0} = \frac{\theta(P - P_{H_2O}^{\circ})}{HC_0} / \left(\frac{1}{k_R C} + \frac{1}{k_L a S} \right) \quad (\text{Eqn. 2-1})$$

where ΔC is the change in feed concentration, C is the feed concentration, k_L is the mass transfer coefficient, a is the bubble surface per unit reactor volume, θ is the residence time in the reactor, k_R is the reaction rate constant, S is the stoichiometric ratio of feed to oxygen, C_0 is the initial feed concentration, P is the total pressure, and $P_{H_2O}^{\circ}$ is the vapor pressure of water, and H is Henry's law constant.

Assuming that $k_L a_S$ is constant, the effect of pressure increase will be large when P is close to $P^\circ_{H_2O}$. Therefore pressures near the vapor pressure of water should not be used for wet oxidation.

Pressure increases have been found to cause increases in conversion for a given residence time and temperature. Ploos van Amstel's data (9) was plotted on a graph of reduction in COD versus residence time at 240°C. Pressure was varied from 630 to 2205 psig. The effect of a pressure increase decreased as pressure increased. This is what Equation 2-1 predicted. The effect of pressure on rate at higher pressures is greater but going from 630 to 810 psig has a greater effect than going from 1470 to 2205 psig. This proves that the effect of pressure near the vapor pressure of H_2O is greater. At 240°C the vapor pressure of H_2O is 470 psig. Lockheed (18) also looked at the effect of pressure. An increase in pressure from 1795 to 2200 psig at 288°C increased the reduction in total organic carbon (TOC).

The amount of oxidizing gas required depends upon the COD or TOC of the waste material, the quantity of the material, and the desired degree of oxidation. Researchers at Barber-Coleman Co. (1) have found that even with efficient agitation, the oxygen input had to be 1.1 to 2 times the theoretical quantity to reduce the COD sufficiently. Lockheed (18) looked at the effect of O_2 flowrate on TOC reduction of urine and feces. They achieved the best conversions at eight times stoichiometric and if lowered to stoichiometric, conversion dropped from 91% to 78%.

Most workers say temperature is the major independent variable. Fassell and Bridges (1) observed a more rapid reaction at higher temperatures. They recommend an optimum temperature between 420 and 460°F (216-238°C) which they say is high enough for sufficient oxidation but

not so high that pressure has to be very high and equipment costs become too high. Teletzke (16) concluded that at temperatures of 250°C conversion levels off in a very short time. At lower temperatures, longer periods of time are required before a leveling off of conversion is observed and the level of oxidation is also lower. Ploos van Amstel (9) determined that temperature has a considerable affect on conversion rate. Unlike Teletzke's findings, at low temperatures the levels of oxidation were not much lower than at higher temperatures. It took much longer to reach these levels at lower temperatures as Teletzke stated. At 180°C and 1100 psig it took more than seven hours to reach a conversion of 90%. At 290°C conversion of 90% was reached in 40 minutes.

Residence time also has an effect upon conversion. Fassell and Bridges (1) state that a 30 minute to 1 hour residence time is enough to achieve 70% reduction in chemical oxygen demand of sewage sludge at temperatures between 435°F and 475°F (234-246°C). Ploos Van Amstel's results show that residence time has the greatest effect at higher temperatures. At 290°C residence time has greatest effect at 20 minutes or less. After 40 minutes, the effect is negligible. Lockheed varied residence time from 90 minutes to 20 minutes at 288°C and 2200 psig; conversion decreased from 96 to 88% which is a greater effect than Ploos Van Amstel observed.

The Barber-Coleman Company also found an effect of pH on reaction rate (1). A pH between 1 and 5 is supposed to produce an additional 10% reduction in COD according to Fassell and Bridges of Barber-Coleman Company. Lockheed used a ruthenium trichloride catalyst to suppress formation of ammonia in the wet oxidation of urine and feces. As a result of using this catalyst, the environment in the reactor was very

acidic. The reduction in TOC was greater with the catalyst. Lockheed workers attributed it to the catalytic effect of ruthenium but it could have been due to the acidity in the reactor.

Wet oxidation has an effect on the chemical composition of wastes besides the effect on carbon. According to Sommers et al total nitrogen levels in sewage sludge decreases by more than 50%. Other components: P, Co, Zn, Ni, Cd and Pb increase or remain unchanged. The concentration of soluble total phosphorous decreases and phosphorous in the particulate phase increases from 90 to more than 99%. According to Modell et al (8) all mineral nutrients including nitrogen are expected to stay in aqueous solutions from which heavy metal ions (Ca, Mg, Fe, Cu, Zn, Mn, etc.) will precipitate as insoluble phosphates and/or sulfates. Little carbonate precipitation should occur in the presence of these ions and loss of fixed N_2 should be small. Lockheed analyzed the liquid effluent samples for many elements but only analyzed the feed for C, H, N, O, S, and P. For the elements present in small amounts (N, S, and P) the error in analysis was great. More of these elements were always detected in the effluent than were present in the feed. Qualitatively, most of the carbon and nitrogen in the effluent was in the gas phase and most of the sulfur and phosphorous was in the liquid phase. Lockheed's results are different from what was expected.

III. Objectives and Approach

The general objective of this thesis is to fill in gaps in the literature and provide useful information to help build a CELSS. Specifically, the objectives are:

1. Build a wet oxidation system to oxidize a slurry of urine and feces.
2. Determine effects of operating conditions upon efficiency of oxidation using past research to define suitable operating conditions.
3. Close the material balance on carbon.
4. Determine effects of wet oxidation on other components of urine and feces.

The approach used to look at the effects of operating conditions on the efficiency of oxidation was to design a reactor without gas-liquid mass transfer effects. This goal could be achieved with a one phase system in which the dissolved oxygen at reactor conditions and the feed concentration are in stoichiometric proportion. The temperatures and residence times were chosen based on the work of previous researchers. The pressures were chosen based on those employed by previous researchers as well but were increased so that the oxygen flow rate at standard temperature and pressure would be reasonable and the liquid/oxygen flow rate would be large. Henry's law was used to determine solubility of oxygen in water. The stoichiometric feed concentration was determined from this oxygen solubility. The original list of experiments is found in Appendix G, Selection of Experiments.

IV. Apparatus and Procedure

The apparatus used for the experiments was a flow system. The feed, a slurry of urine and feces, hot water, and oxygen, was pumped up to pressure and the volume of the feed and water were measured with respect

to time. The water passed through a coiled length of tubing in a furnace to preheat it to reactor temperature or higher. The hot water, feed, and oxygen were then mixed together and passed through a Hastelloy reactor kept hot by another furnace. There the oxidation reaction occurred. The reactor effluent then passed through a heat exchanger to be cooled and a solid product collector to have suspended solids removed. The stream then passed through a back pressure regulator and upon expanding the phases were separated. The gas phase went to an on-line gas chromatograph which periodically analyzed a sample. The liquid passed to a collection bottle. Grab samples were periodically taken to be subsequently analyzed for total carbon, inorganic carbon, total organic carbon, and several inorganic components.

A. Apparatus

The flow system is pictured in Figure 4-1. Its description is divided into the following sections: Feed, Preheating, Mixing, Reactor, Separation, Pressure Measurement and Control, Temperature Measurement and Control, Safety, Tubings and Fittings, and Analytical. Each piece of equipment is numbered in Figure 4-1 and referred to in the text by the corresponding number.

1. Feed System

A dual-head American Lewa pump (1), Type HKM-2 was used to feed the water and slurry. The single diaphragm head with ruby balls and tungsten carbide seats in the check valves pumped the water. The double diaphragm head with Hastelloy C balls and seats in the check valves was used for the slurry. Both heads had pressure ratings of 5000 psig. The motor provided a horsepower of 1/2 at 1725 rpm. The water was pumped from a polypropylene Nalgene bottle (2) through a 50 cc buret (3) which was used to

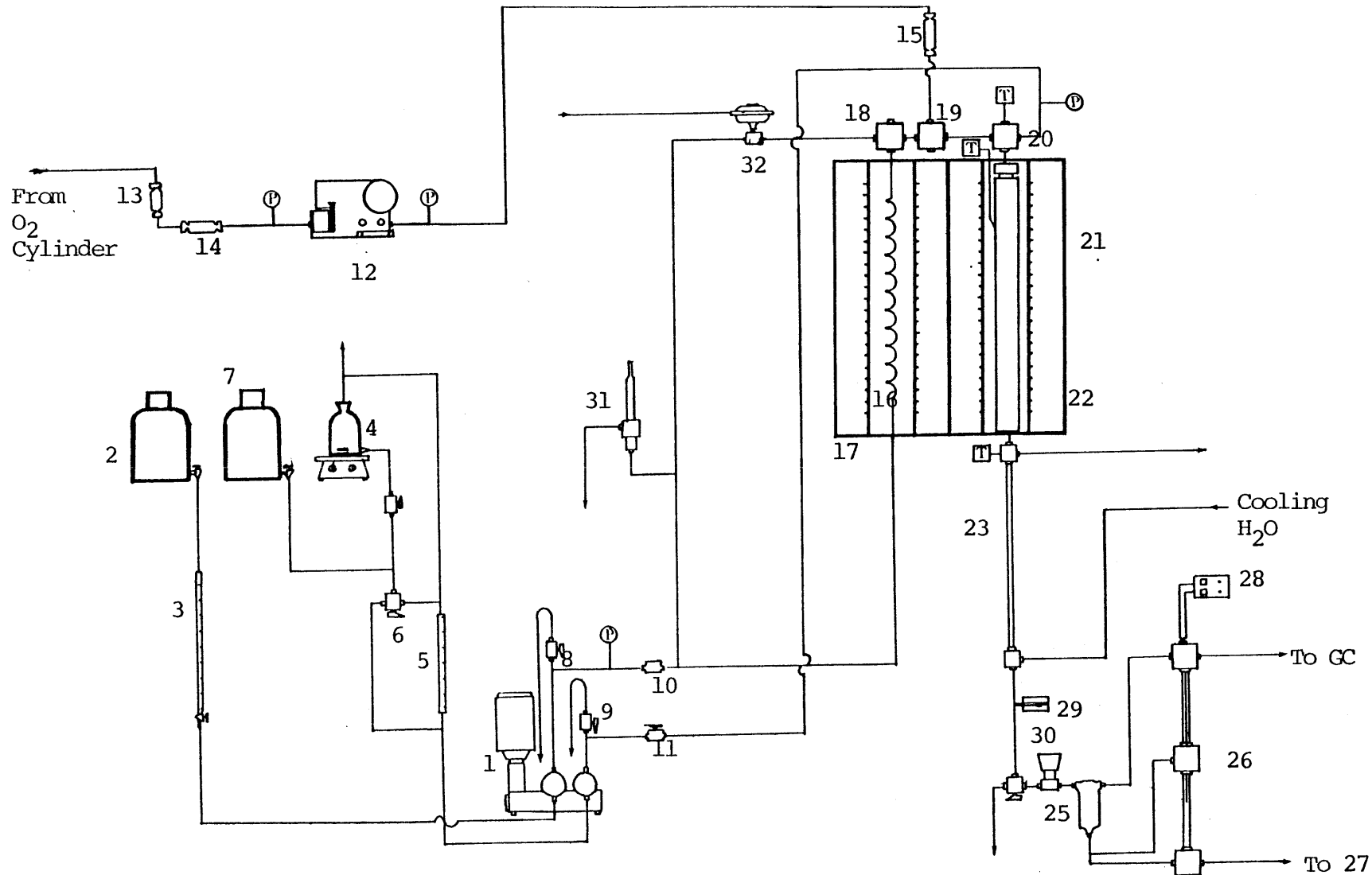


Figure 4-1. System Schematic

measure flow rate. The slurry was pumped from a 1000 cc pyrex aspirator bottle (4) through a 1 cc pipet (5) whose tip had been cut off. The pipet was used to measure flow rate. When slurry was not being pumped, a Hoke three-way ball valve (6) allowed switching to water contained in a Nalgene bottle (7). The water used was distilled water treated with a Barnsted Water Purification Nanopure A system equipped with four cartridges: two mixed-resin cartridges using cation and strong base anion resins for deionization, one cartridge for removal of organics and chlorine, and one cartridge containing a $.2\mu$ filter for removal of sub-micron particulates. Water with a resistance as high as 18 megaohm-cm could be obtained.

After each pump head was a Hoke two-way ball bleed valve (8, 9) used to rid the head of air which may have gotten trapped. Directly downstream of the single diaphragm head was a Hoke check valve (10) to prevent any of the system contents from backing up when the bleed valve was opened. Downstream of the double-diaphragm pump was another two-way ball valve (11) which served the same purpose as the check valve after the single diaphragm head.

The oxygen compressor (12) was an American Instrument Company (AMINCO) motor driven diaphragm compressor Model No. J46-13411. It has a compression ratio of 14 to 1 and a 10,000 psi pressure rating. An oxygen compatible fluorinated oil was used to pulse the diaphragm. The motor put out 1 HP at 1800 rpm. Wetted materials were 316 SS for the valves and 302 SS for the diaphragm.

Upstream of the compressor was a 316 SS High Pressure Company (HIP) surge valve (13), model number 30-41HF5-E, used as a safety precaution in case the cylinder regulator failed. A 5μ dry type filter (14), an

AMINCO model number J49-14405, was also put in line upstream of the compressor to protect the compressor diaphragm from particles. It was rated at 30,000 psig and could handle 2.5 scfh of air with a pressure drop of 5 psig. It could not be used with a pressure drop greater than 250 psig without deforming the sintered filter elements. Downstream of the oxygen compressor immediately before oxygen was mixed with the other stream was a HIP oxygen check valve (15), model number 10-41AF4-T which served the purpose of preventing any back flow into the oxygen lines.

2. Preheating

To preheat the feed, water from the single diaphragm head at a flow rate ratio of 2 to 1 or higher to the slurry was passed through a coil (16) in a Lindberg Laboratory single zone tube furnace (17), model number 55451 controlled by a model number 58121 control console. The water was heated to a temperature hot enough to insure that the temperature after the water and slurry were mixed was close to the reactor temperature.

3. Mixing

From 7/8/80 to 9/6/80 the slurry was mixed into the water through a tube in the middle of a 1/4" high-pressure tee (18) and then the oxygen was introduced into this mixed stream similarly but in a Hastelloy C-276 1/4" high-pressure tee (19). The final mixture then went directly to the reactor.

Due to clogging by deposited solids in the tees where mixing took place the method of mixing was changed for the 9/22 run. A tube through which undiluted slurry entered was put directly into the reactor. The slurry mixed with previously mixed oxygen and water. The tube was of very small ID and it soon clogged with solids as well. The tube was

removed for subsequent runs but the slurry came in at the same place. The mixture of O_2 and water was then mixed with slurry before entering the reactor in a Hastelloy tee (20) (without a tube in the middle of the stream). The latter set-up caused clogs at the reactor exit. The clogs occurred long enough after a run began such that data could be gathered.

4. Reactor System

The reactor (21) was designed by Hydropak. It was made from Hastelloy C-276 and rated at 5000 psi and 1000°F (538°C). Its maximum pressure rating is 11,000 psi at 100°F maximum. Hastelloy C-276 was chosen as the material of construction because corrosion tests by researchers at Lockheed (7) showed it to be the best material when compared to E-Brite 26, MP35N, Inconel 625, Zirconium, Zircaloy 2, Elgiloy, Tantalum, and Tantalum-40% Columbium. Inconel 625 was the second choice. The reactor design was an empty cavity without baffles or agitation, 1.25" ID by 25.12" long. The seal was a modified Bridgeman single end which after use did not work very well. The system was down many times due to leaks at the seal. The reactor inlet and exit were made for 1/4" high pressure fittings. The reactor was kept heated with a three-zone Lindberg Laboratory Tube Furnace (22), model 55453, with a control console, model number 58321.

Immediately following the reactor was a tube-in-tube heat exchanger (23). Inconel was chosen for the inside tube because of its availability. The dimensions of the tube were 1/4" OD by 3/8" ID. The reactor effluent stream was cooled to room temperature to quench the reaction and to protect subsequent pieces of equipment from extremely hot temperatures. Water from the tap was used for cooling and passed through the annulus of the heat exchanger countercurrent to the reactor effluent.

5. Separation

The cooled stream leaving the heat-exchanger entered a solid product collector (24). This consisted of a vertical tube with a dip tube inside. The effluent entered through the annulus; the solids were supposed to settle to the bottom and the resulting clean stream went up the inside of the dip tube. Very few solids made it to the solid product collector and some of those that did were so small in particle diameter they did not settle. They stayed in the liquid product. The effluent from the solids separator went to a 304 SS Wright Austin gas liquid separator (25) which worked on a principle similar to a cyclone: by centrifugal force and gravity. The separator was rated for 500 psi at 200°F.

The separator was connected to a liquid-level controller (26). The liquid level controller consisted of two 9/16" OD vertical tubes connected at the top to the gas outlet, at the bottom to the liquid outlet, and at the middle to the liquid outlet of the Wright Austin separator. A wire was inserted a quarter of the length of both tubes into the tube from the top. It was connected to an Asco 2-way normally closed solenoid valve which was connected to a HIP air actuated valve (27). When the liquid level rose to touch the wire, the solenoid valve was energized. It opened and let air or nitrogen leave the cylinder, pass through the solenoid valve and open the air-actuated valve. The air-actuated valve was in the liquid effluent line and remained open until the level dropped below the wire. When the liquid level did drop, the solenoid valve was deenergized. It closed cutting off flow of air or N₂ to the air-actuated valve causing the latter to close. The valve stayed closed until the liquid level rose again and the cycle was repeated. Air or N₂

at 30 psig was used to actuate the valve. The solenoid valve had a control box (28) which provided main power and had a switch which could be used to bypass the automatic mode and open the solenoid valve.

6. Tubings and Fittings

All tubing used in the cold part of the system and in the hot parts which were exposed to water only was 316 SS but the dimensions varied depending upon the part of the system. In the O₂ feed system, the tubing was 1/4" OD by 1/8" ID. In the water and slurry feed system downstream of each pump head the tubing was 1/8" OD by .06" ID. The tubing used for the coil in the preheating section was 1/8" OD by .04" ID high pressure tubing as was the tubing leading from the coil to the first mixing tee. High pressure 1/4" Hastelloy tubing 1/4" OD by .083" ID was used in the hot part of the system where O₂ was present from the O₂-water mixing tee to the Inconel heat exchanger. The tubing from the solid product collector to the analytical equipment was 1/4" OD by 1/8" ID or larger. It was still capable of standing pressures greater than 5000 psig at low temperatures.

Fittings in the low temperature part of the system were Swagelok or low-pressure fittings from HIP, HEX, or Autoclave Engineers. Fittings in the high-temperature part of the system were coned and threaded medium or high pressure from HEX, HIP, or Autoclave Engineers. This included couplings, tees, crosses, and adapters. The solid product collector and liquid level controller were made from 9/16" OD medium pressure fittings and 9/16" OD medium pressure tubing.

7. Pressure Measurement and Control

Four pressure gauges were used to monitor pressure and are represented by the letter P in Figure 4-1: a 1000 psi US Gauge gauge upstream

of the compressor, a 5000 psi US Gauge gauge immediately downstream of the single diaphragm head, a 5000 psi Acco Helicoid Gauge on the slurry line before the mixing tee, and a 5000 psi gauge immediately downstream of the compressor. For the October 19 run, a pressure transducer (29), BLH Electronics model STD-H, and a digital transducer indicator, BLH Electronics model 450A, with a 10,000 psi range was installed after the solid separator and before the back pressure regulator.

The back pressure regulator (30) controlled system pressure. It was a spring loaded manually operated Tescom regulator which controls pressure up to 6000 psi at a maximum temperature of 425°F.

8. Temperature Measurement and Control

Temperatures were monitored using Omega Type K thermocouples, one Omega model 2160A digital temperature readout with a model 2161 multi-point selector, and two Omega model 4002KC temperature controllers and readouts. The furnaces were equipped with thermocouples and the temperature controlled by the respective control console.

There were a total of six thermocouples: in-line before the reactor, in-line after the reactor, middle of the reactor on the surface, reactor thermowell, on the surface of the mixing tee before the reactor and in-line after the heat exchanger. Usually just four or five of the six thermocouples were used during a particular run. The thermocouples are represented by the letter T in Figure 4-1.

Briskheat flexible electric heating tapes were used on the lines between the preheater furnace and the reactor to prevent cooling. Variacs were used to control the power to the heating tapes so the temperature of the mixed stream before the reactor could be controlled.

9. Safety Precautions

There were two safety precautions built into the system: a HIP safety relief valve (31) with a 5500 psi rating and a furnace bypass. The furnace bypass consisted of an Asco 2-way normally closed solenoid valve connected to one of the Omega temperature controller-readouts and to a HIP normally closed air actuated valve (32). When the temperature at the reactor outlet which was indicated on the Omega temperature controller/readout reached a temperature equal to a set point temperature, the controller energized the solenoid valve. It opened allowing nitrogen at 30 psig to open the actuated valve. When this happened, cold water from the single diaphragm head bypassed the furnace and went through the line containing the actuated valve directly to the furnace. This was protection against an uncontrolled temperature rise. The safety relief was protection against uncontrolled pressure rises.

10. Analytical Equipment

Liquid samples were analyzed for total carbon, inorganic carbon, and total organic carbon on a Beckman Tocamaster Total Organic Carbon Analyzer. Solid samples were analyzed for carbon, hydrogen, and nitrogen on a Perkin Elmer elemental analyzer. Standard procedures recommended by the manufacturer were used. Liquid and solid samples were analyzed at Georgia Institute of Technology for inorganic components using Inductively Coupled Plasma Emission Spectroscopy (ICPES).

Gas samples were analyzed using a Perkin Elmer Sigma 1B gas chromatograph. The columns used were a 12', 1/8" OD, Porapak T and a 3', 1/8" OD, Molecular Sieve 5A, connected through a Valco 10-port Hastelloy valve in series. The gas sample was injected onto the Porapak T. After H₂, O₂, N₂, CH₄ and CO eluted off the porapak onto the molecular sieve the

order of the columns was resequenced using the valve. Any gases left on the porapak went to the detectors after elution. The other gases, separated by the molecular sieve, eluted back on to the porapak before going to the detectors. A thermal conductivity detector (TCD) was used to detect CO, CO₂, O₂, N₂, CH₄, and H₂. A flame ionization detector in series with the TCD was used to analyze hydrocarbons. Appendix B, Analysis of Gaseous Products explains how peak areas and concentrations were determined.

B. Procedure

1. Feed Preparation

Freeze dried feces from GIT batch GF1, Sample No. 5 was ground to 170 mesh or smaller using a Tekmar model no. A-10S laboratory grinder. The feces used for the August 8 run had only been ground small enough to pass through an 80 mesh sieve but that run indicated the particle size had to be smaller for the slurry to be pumped smoothly and 170 mesh was small enough.

The ground feces and the urine from batch GF1, Sample No. 1 were weighed on a Mettler Type H6 Analytical balance and put in a blender. A 500 cc graduated cylinder was used to measure enough purified water. A 1000 cc volumetric flask was used once to make the solution but the slurry foamed so much it was hard to measure. Water from the cylinder was added to the blender and the slurry mixed a few seconds on a medium speed.

After mixing the slurry was poured into a 1000 cc Pyrex aspirator bottle. A magnetic stirrer and bar were used to keep the particles suspended in the slurry and to maintain homogeneity.

2. Start-up Procedure

The start-up procedure was the following:

1. Calibrate GC before run if necessary.
 2. Turn on heat exchanger cooling water.
 3. Turn on power to the thermocouples.
 4. Turn on power to the liquid level controller.
 5. Open gas cylinders that operate each valve and set correct pressure on regulator (30 psig).
 6. Turn on pumps. Set at flow rates specified for the run.
 7. Adjust back-pressure regulator to the pressure specified for the run.
 8. When system reaches operating pressure, turn on heaters and heating tapes, turning up slowly.
 9. Measure flow rates in and out to help indicate presence of system leaks.
 10. When system reaches operating temperature, take a blank liquid sample.
 11. Turn on O₂ compressor using calibration charts as approximate guide for inlet pressure (The O₂ flow rate is fixed by the inlet and outlet pressure so it could be varied by adjusting the pressure of O₂ leaving cylinder).
 12. Measure O₂ outlet flow using a 100 cc soap bubble flow meter. If not in the right range, adjust compressor suction pressure accordingly.
 13. If in the right range, switch feed to waste slurry.
3. Run and Shutdown Procedure
1. Record and monitor temperatures and pressures, and water, feed, and gas product flow rates frequently.
 2. Record and monitor liquid effluent flowrates a few times to in-

insure absence of leaks.

3. Take a gas sample every 20 minutes. (Each analysis took 20 minutes.)
4. Take small liquid samples frequently (1 oz. polyethylene bottles make good containers) for carbon analysis. Label with date, time, and sample type.
5. Take a few large liquid samples (16 oz.) for ICPES analysis.
6. If temperatures, pressures, or flow rates change significantly, adjust appropriate piece of equipment: furnace set points, variacs to heating tapes, back pressure regulator or pumps.
7. When all the feed is exhausted, switch back to water.
8. When a GC trace shows 99% O₂ then most of feed is through the system and O₂ compressor can be turned off.
9. Slowly cool the system down by slowly lowering the set point on the furnace controllers and the settings on the heating tape variacs. When the variacs are down to zero and furnace controllers are down to 150°C, turn off the power to them.
10. Turn off pumps.
11. Turn off detectors on GC.
12. Close all cylinders which operate actuated valves.
13. Turn off power to liquid level controllers.
14. Turn off power to thermocouples.

V. Results

A. Residence Times

During each run, liquid flow rates were measured and recorded. They are tabulated in Appendix A, Flow Rate Data. The flow rates were averaged and their standard deviations and the 95% confidence limits using the t-distribution were calculated. (See Appendix H, Error Analysis) From the liquid flow rates and the density of water at reactor conditions, the residence times are calculated. (See Appendix F, Residence Time Determination) These residence times are reported in Table 5-4.

B. Gaseous Results

Gas composition with time was recorded for all runs. The gas compositions for the period the system was at steady state are reported in Appendix B, Analysis of Gaseous Products. The average concentration for each component is reported in Table 5-1 for each run. The gas is assumed to be saturated with water so the gas compositions were normalized to account for the 2.3% water vapor present. The gas flow rates for each run are listed in Appendix A, Flow Rate Data. The average flow rates along with the 95% confidence limits are reported in Table 5-1.

C. Liquid Results

Table 5-2 presents the liquid results. Total carbon in the feed, inorganic carbon in the liquid effluent, and organic carbon in the liquid effluent are reported in units of moles of carbon per minute (moles C/min) and parts per million (ppm). Appendix D, Carbon Content of Feed shows how the total carbon in the feed was obtained using the results of the waste analysis in Appendix C and the liquid flow rate data in Appendix A. The inorganic and organic carbon are the average amount of carbon in ppm

TABLE 5-1

Gas Results

Date	Flow rate (cc/min)	%C	Gas Composition (% by Volume)						
			H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ S
7/8	180.3 + 99.2	46.553	.037	35.559	50.773	.341	.000	10.982	.0123
8/8	47.9 + 16.2	8.029	.105	8.011	88.851	.552	.000	.018	.008
8/11	56.6 + 28.2	9.912	.075	9.680	87.072	.641	.008	.232	.008
8/14	97.9 + 11.9	7.084	.014	6.961	89.654	.373	.008	.133	.008
8/24	87.1 + 22.1	3.041	.055	2.868	94.517	.088	.008	.173	.008
9/1	141.1 + 6.8	27.708	.260	17.314	69.221	.577	.045	10.219	.065
9/6	123.3 + 5.7	31.161	.291	21.608	65.762	.800	.019	9.458	.038
9/22	135.7 + 11.3	17.234	.339	11.149	79.874	.287	.025	6.018	.021
9/24	127.1 + 4.8	3.575	.112	.309	93.313	.717	.014	3.222	.015
10/19 ^a	171.0 + 13.2	22.364	.557	12.381	74.434	.414	.405	9.426	.076

a 10/19 run also had C₃s with a concentration of .015.

TABLE 5-2

Liquid Results

Date	Feed Flow rate Total $\frac{\text{cc}}{\text{min}}$	Feed Flow rate moles $\frac{\text{C}}{\text{min}}$	Total Carbon in Feed (ppm)	Organic Carbon in Liq. Effluent (ppm)	Organic Carbon moles $\frac{\text{min}}$	Inorganic Carbon in Liq. Effluent (ppm)	Inorganic Carbon moles $\frac{\text{min}}$
7/8	16.79 $\pm .97$	0.00604 $\pm .00050$	4316 ± 450	1876 ± 493	0.00262 $\pm .00075$	36 ± 38	0.00005 $\pm .000056$
8/8	16.18 $\pm .74$	0.00100 $\pm .00010$	742 ± 108	27 ± 129	0.000037 $\pm .00018$	102 ± 28	0.00014 $\pm .000041$
8/11	16.31 $\pm .66$	0.00092 $\pm .00014$	678 ± 110	318 ± 261	0.00043 $\pm .00037$	144 ± 9	0.00020 $\pm .000021$
8/14	16.38 $\pm .89$	0.00112 $\pm .00015$	819 ± 115	150 ± 5	0.00020 $\pm .000007$	130 ± 4	0.00018 $\pm .000014$
8/24	16.19 $\pm .79$	0.00117 $\pm .00021$	870 ± 149	170 ± 6	0.00023 $\pm .000018$	133 ± 4	0.00018 $\pm .000014$
9/1	25.32 $\pm .49$	0.00352 $\pm .00013$	1670 ± 76	207 ± 14	0.00044 $\pm .000038$	415 ± 22	0.00088 $\pm .00006$
9/6	25.96 $\pm .55$	0.00380 $\pm .00026$	1755 ± 121	201 ± 8	0.00044 $\pm .000027$	423 ± 21	0.00092 $\pm .000065$
9/22	19.28 $\pm .27$	0.00284 $\pm .00016$	1766 ± 118	139 ± 20	0.00022 $\pm .00003$	353 ± 100	0.00057 $\pm .00017$
9/24	26.11 $\pm .47$	0.00146 $\pm .00009$	713 ± 51	51 ± 11	0.00011 $\pm .000026$	386 ± 64	0.00084 $\pm .000015$
10/19	25.82 ± 1.25	0.00356 $\pm .00028$	1653 ± 168	202 ± 21	0.00043 $\pm .000066$	229 ± 137	0.00049 $\pm .00032$

calculated from the analysis of individual samples listed in Appendix E, Analysis of Carbon Content in Liquid Effluent- Organic and Inorganic. This average number was then multiplied by the average total flow rate to obtain the result in moles C/min for each run.

The liquid product from the glucose run of 7/8/80 was slightly yellow but yellowed even more after storage. The concentration of carbon was still greater than 2000 ppm which is higher than the starting material in subsequent runs. The liquid products from the urine and feces runs were clear and had a slight odor. Some of the samples contained a white particulate. The samples from the 10/19 run had a small amount of brown particulate which settled after the sample sat for a while. During the 8/14 run, O₂ flow was lost and the liquid product was brown with brown particulates. Some of the liquid products were analyzed for inorganic components by ICPES (Inductively Coupled Plasma Emission Spectroscopy). This data is reported in Table 5-3.

D. Carbon Conversion and Carbon Balance

Carbon Conversion was calculated from the change in organic carbon concentration:

$$\% \text{ Conversion} = \left(1 - \frac{\text{ppm TOC effluent}}{\text{ppm TOC feed}}\right) \times 100 \quad (\text{Eqn. 5-1})$$

The carbon in the feed, carbon in the product, and conversion are tabulated in Table 5-4.

To do a carbon balance, the amount of carbon in the gas phase and liquid phase products in units of moles C/min are added and checked against the moles of carbon in the feed in the same units:

TABLE 5-3

Inorganic Components in Liquid Products^d

Sample Number	Ca	P	K
9-24 #1 Blank ^a	<.001	N.D. ^e	<.009
9-24 #4	≤.001	0.8	.041
9-24 #5	<.001	7.0	.054
9-24 #6	<.001	12.0	1.058
9-24 #7	<.001	15.0	.075
10-19 #3 ^b	<.001		.081
10-19 #4	<.001		.091
10-19 #2 ^c	<.001		.047
10-19 #3	<.001		.055

^a white solids filtered with 5 micron filter

^b brown solids filtered

^c brown solids digested with concentrated HNO₃ and 3% H₂O

^d units are mg/gm; multiply by 1000 to get ppm

^e N.D. - not detected

TABLE 5-4

Carbon Conversion

Date	P (psig)	T (°C)	θ (min)	Feed (moles C/min)	Feed (ppm)	Total Organic Carbon (TOC) Liquid Effluent (ppm)	Liquid Effluent (moles C/min)	% Conversion
7/8	2275	277	23.2 ± 1.4	0.00604 ± 0.0005	4316 ± 450	1876 ± 428	0.00262 ± 0.00075	56.5 ± 18.8
8/8	2375	303	23.7 ± 0.9	0.00100 ± 0.0001	742 ± 108	27.2 ± 129	0.000037 ± 0.00018	96.3 ± 474.4
8/11	2275	292	23.3 ± 1.3	0.00092 ± 0.00014	678 ± 110	318 ± 261	0.00043 ± 0.00037	53.1 ± 52.2
8/14	3200	289	23.8 ± 1.3	0.00112 ± 0.00015	819 ± 115	150 ± 5	0.00020 ± 0.00007	81.7 ± 14.1
8/24	2550	295	23.9 ± 1.1	0.00117 ± 0.00021	870 ± 149	170 ± 5.6	0.00023 ± 0.00018	80.5 ± 16.4
9/1	4050	409	4.1 ± 0.1	0.00352 ± 0.00013	1670 ± 76	207 ± 14	0.00044 ± 0.00038	87.6 ± 9.9
9/6	3825	400	3.8 ± 0.1	0.00380 ± 0.00026	1755 ± 121	201 ± 8	0.00044 ± 0.00027	88.5 ± 9.6
9/22	3825	404	5.1 ± 0.1	0.00284 ± 0.00016	1766 ± 118	139 ± 20	0.00022 ± 0.00003	92.1 ± 19.4
9/24	3825	402	3.7 ± 0.1	0.00155 ± 0.00009	713 ± 51	51 ± 11	0.00011 ± 0.000026	92.8 ± 26.6
10/19	3850	443	2.4 ± 0.1	0.00356 ± 0.00028	1653 ± 168	202 ± 21	0.00043 ± 0.00007	87.7 ± 18.0

$$\text{Carbon material balance closure(\%)} = \frac{\text{Gas phase C, moles} + \text{Liq. phase IC, moles} + \text{Liq. TOC, moles}}{\text{Feed Carbon, moles}} \times 100 \quad (\text{Eqn. 5-2})$$

These results are reported in Table 5-5.

E. Solid Results

Solid products deposited at many places in the system. The solids collected on 9/6/80 came from that run and all preceding runs. The others are from the run indicated. Inorganic constituents were analyzed using ICPES and organic constituents using an elemental analyzer. The solids were not weighed and therefore are not useful in the carbon balance. The results are presented in Table 5-6.

VI. Discussion of Results

A. Wet Oxidation System

One goal of this thesis was to build a wet oxidation flow system to oxidize a slurry of urine and feces. This goal was accomplished but problems in the operation of the system led to errors in the results.

Temperature control was not very good. There was no way of measuring the temperature inside the reactor. The temperatures indicated by the thermocouples placed before the reactor inline, on the reactor surface in the middle, in the thermowell in the bottom of the reactor, and after the reactor inline were usually different from each other. The furnace used to heat the reactor and the insulation used did not keep the reactor isothermal. The temperatures did remain constant during the period the system was at steady state.

Pressure control was better. Pressure fluctuations averaged about

TABLE 5-5

Carbon Balance

Date	Gas Flow rate (moles $\frac{C}{min}$)	% of Feed C	Feed (moles $\frac{C}{min}$)	Liquid Effluent		Carbon Accounted For (%)
				(moles $\frac{IC}{min}$)	(moles $\frac{TOC}{min}$)	
7/8	.0038 <u>+ .0021</u>	62.1 <u>+34.9</u>	.00604 <u>+ .0005</u>	.00005 <u>+ .000056</u>	.00262 <u>+ .00075</u>	106.3 <u>+56.9</u>
8/8	.00017 <u>+ .00006</u>	17.0 <u>+ 8.7</u>	.00100 <u>+ .0001</u>	.00014 <u>+ .000041</u>	.000037 <u>+ .00018</u>	34.7 <u>+22.3</u>
8/11	.00025 <u>+ .00012</u>	27.2 <u>+21</u>	.00092 <u>+ .00014</u>	.00020 <u>+ .000021</u>	.00043 <u>+ .00037</u>	95.6 <u>+33.9</u>
8/14	.00031 <u>+ .00004</u>	27.7 <u>+ 6.7</u>	.00112 <u>+ .00015</u>	.00018 <u>+ .000014</u>	.00020 <u>+ .000007</u>	61.6 <u>+13.5</u>
8/24	.00012 <u>+ .00003</u>	10.3 <u>+ 3.9</u>	.00117 <u>+ .00021</u>	.00018 <u>+ .000014</u>	.00023 <u>+ .000018</u>	45.3 <u>+13.4</u>
9/1	.00175 <u>+ .00008</u>	49.7 <u>+ 4.6</u>	.00352 <u>+ .00013</u>	.00088 <u>+ .00006</u>	.00044 <u>+ .000038</u>	87.2 <u>+ 8.4</u>
9/6	.00172 <u>+ .00008</u>	45.3 <u>+ 3.1</u>	.00380 <u>+ .00026</u>	.00092 <u>+ .000065</u>	.00044 <u>+ .000027</u>	81.8 <u>+10.1</u>
9/22	.00104 <u>+ .00009</u>	36.6 <u>+ 5.4</u>	.00284 <u>+ .00016</u>	.00057 <u>+ .00017</u>	.00022 <u>+ .00003</u>	64.4 <u>+13.7</u>
9/24	.00020 <u>+ .00001</u>	12.9 <u>+ 1.0</u>	.00146 <u>+ .00009</u>	.00084 <u>+ .000015</u>	.00011 <u>+ .000026</u>	78.8 <u>+ 8.1</u>
10/19	.00171 <u>+ .00013</u>	48.0 <u>+ 7.3</u>	.00356 <u>+ .00028</u>	.00049 <u>+ .00032</u>	.00043 <u>+ .00066</u>	73.9 <u>+18.2</u>

TABLE 5-6

Organic and Inorganic Composition of Feed and Solid Products^a

Sample	Ca	K	Mg	Mn	P	C	H	N	S	Total
Urine	.21	2.42	.083	.0002	1.2	19.76	4.7	20.50	1.77	50.64
Feces	.40	.91	.19	.0038	.71	46.61	6.82	4.44	.5	60.08
9-6-1 ^b	5.8	<.0009	3.6	.087	16.0	1.46	.26	.06		27.27
9-6-2 ^c	2.2	<.0009	1.2		7.0	1.52	.35	.14		12.41
9-6-3 ^d	5.5	<.0009	3.0	.12	15.0	.38	.1	.03		24.13
9-22-1 ^e	13.4	<.0009	5.0			1.43	.21	.02		20.06
9-22-2 ^f						2.34	.44	.16		2.94
10-19 ^g	4.2		2.9							7.10

^aunits- weight %

^bsolids deposited in fittings before reactor

^csolids collected in solid separator

^dsolids deposited on reactor walls

^fsolids washed out of the system after run was completed and collected at solid separator; supernatant liquid was yellow and allowed to evaporate off without washing solids

^{e,g}solids washed out of the system at end of run

4% except for the runs on 8/14/80 and 9/1/80 when the pressure fluctuations were 22% and 10% respectively. In both these cases the pressures increased greatly such that on 8/14 the back pressure regulator had to be turned down and on 9/1 the pumps had to be turned off. Later it was discovered that clogs in the lines caused this behavior.

The diaphragm pump which pumped deionized water was very stable and errors in water flowrates are due mostly to errors in measurement. The double diaphragm pump used to pump the slurry was not as reliable. To pump the slurry smoothly the particle size had to be 170 mesh or smaller. This was the case for all runs except the 8/8 run where the particle size was less than 80 mesh. The flow of feed was not steady and ceased completely twice. This explains some of the error for this run. The particle size was smaller for the 8/11 run but the feed flowrate was still not steady although better than the 8/8 run. The errors in measurement for the slurry are greater than those for the water because of the one cc pipet which was used to measure volume pumped in a given time. The flowrate was fast enough to make it difficult to read the pipet.

Most of the errors in the gas phase were due to changing gas flowrates. No errors in measurement could account for the large differences in gas flowrates observed (See Appendix A, Flowrate Data) in some of the runs. The gas chromatograph accurately analyzed the gas but to close the carbon balance the flowrate was very important. The flowrates for the runs at supercritical conditions did not vary as much as those at subcritical conditions (See Appendix A, Table 9-2).

There were also problems with the equipment which caused a shutdown or prevented start-up. These were clogs in the system at various places

which could cause the pressure to go out of control and prevent the continuation of a run or leaks in the reactor which prevented start-up. The reactor was the limiting factor in determining the number of runs which could be completed. When the reactor was disassembled for cleaning it always leaked after reassembly. Attempts at making it leak-free usually had a temporary effect. The reactor might remain leak-free until it was disassembled again or just until the next run. Each time something different was tried. The sealing surface was polished well, grooves were put in the sealing ring, and the ring was even silverplated. Nothing worked permanently. This problem still exists.

The problem with the leaking reactor was the main reason the original set of experiments was not completed. Another reason was the oxygen flowrates. The ones specified were too low for proper operation of the compressor, therefore higher flowrates were used and later higher carbon concentration in the feed. The subcritical runs were not smooth and the conversions were low. The decision was made to run at supercritical conditions to increase conversion and to achieve smoother operation.

B. Efficiency of Oxidation

At subcritical conditions, 289–295°C and 2550–3200 psig, conversions as high as 81% were obtained. At 292°C and 2275 psig the conversion was only 56%. There was so much error in the 8/8 run that I have chosen to disregard the result. To see how error was calculated, see Appendix H, Error Analysis. At 288°C and 2200 psig Lockheed achieved a conversion of 88% with a residence time of 19 minutes. Longer residence times gave higher conversions (see Table 6-1). This appears to be better than the results obtained in this thesis. There are several differences between the Lock-

TABLE 6-1

Lockheed Wet Oxidation Results

P (psig)	T (°C)	Residence Time (min)	% Reduction TOC
2200	288	45	94
2200	288	45	92
2200	288	30	91
2200	288	19	88
1795	288	45	86
940	243	90	90

heed wet oxidation experiments and these results. Lockheed utilized agitation. Although they conclude that agitation was not necessary, only one set of data was presented where agitation was not used, the material balance run at a temperature of 243°C, a pressure of 940 psig, and a 90 minute residence time.

The Lockheed reactor also was designed with baffles which aid contacting if two phases are present. Lockheed reports the reduction in TOC but gives no indication of how much error is present in the result. They did say that for all their runs they mixed the same amount of urine, feces, and water but the TOC of the resulting slurry varied widely, how widely is not known. For the material balance test they got a conversion of 91% based on TOC in and TOC out. They also provide a carbon balance and if those numbers are used conversion is 88%. The results for the carbon balance were obtained similarly to the way the results for this thesis were obtained. The slurry and liquid effluent were freeze-dried and the carbon analyzed by an elemental analyzer. The error in this number is due to the presence of inorganic carbon. Since the conversion obtained by two different methods is close, the error involved in calculating conversion from TOC is small at least for this run. The error in their other runs may or may not be as small.

The flowrate of oxygen used by Lockheed was much more in excess than that used in this thesis. Since Lockheed presented data which shows that conversion increased with an increase in oxygen flowrate this may be one reason their conversions are higher.

Lockheed also used a catalyst to suppress ammonia formation. The catalyst also enhanced oxidation. This may be due to the acidic environment caused by the catalyst, RuCl_3 , rather than a real catalytic effect

since other researchers have seen positive effects on oxidation when the pH in the reactor is less than five. Either way no catalyst was used in this thesis nor was anything added to lower the pH.

One other difference is the characteristics of the feed. Lockheed always used more urine than feces, about fifteen times as much. Using the data from the material balance run, the amount of carbon in their urine and feces can be calculated. They freeze-dried a standard slurry and analyzed the resulting solid residue for carbon. It was 28% carbon. In this thesis equal amounts of freeze-dried urine and feces were used. The mixed urine and feces was 41% carbon.

The wet oxidation solid product obtained by Lockheed had a higher percentage of carbon, hydrogen, and nitrogen, 7.92%, 1.32%, and 1.7% respectively. The solid products obtained in this research had less than 2.5% C, .5% H, and .2% N. This difference can probably be attributed to the longer residence time of the latter solids which deposited and remained in the reactor until the run was over up to three hours later.

Most other researchers obtained better results also, although the feed used was usually sewage sludge. Some of these results are tabulated in Table 6-2. Some of the difference can probably be attributed to reactor design or type. Ploos Van Amstel (9) used a semi-batch type reactor with agitation. The Barber-Coleman Company employed a compartmentalized reactor with agitation in each compartment. Besides agitation the only other factor may be residence time. Some workers used lower pressures and temperatures but the residence times were longer.

TABLE 6-2

Other Wet Oxidation Results

Researcher	Feed	P (psig)	T (°C)	Residence Time (min)	%Reduction in TOC
McDonald	Sewage	350-1800	190-280	45	43
Tenwolde	Sewage sludge		180-190	30	67.4
Otlergraf	Sludge	338	160	60	76
			180	60	80
			200	60	76
Barber-Coleman	Ship-board sewage	600	215-250	20	70
				40	70
				60	73
				80	75
Ploos Van Amstel	Sewage sludge	1100	185	90	69
				300	77
		1400	290	20	90
				6	75
				60	94
				80	94

C. Effect of Operating Conditions on Oxidation

The results show an effect of pressure:

TABLE 6-3

Effect of Pressure on Conversion

	<u>P (psig)</u>	<u>T (°C)</u>	<u>Residence Time (min)</u>	<u>% Conversion</u>
8/11	2275	292	23.3	53.1
8/24	2550	295	23.8	80.5
8/14	3200	289	23.8	81.7

Conversion increases with pressure. This result is exactly what Ploos Van Amstel observed in his studies. As Pruden and Le(11) predicted, the effect of pressure decreases as pressure increases. The increase in conversion is greatest at the lower pressure. Since the data follows the equations presented by Pruden and Le, some liquid phase resistance to diffusion of oxygen must exist. There are two phases present, but if the resistance is small kinetics will still control.

According to Henry's law, when pressure increases at constant temperature, the partial pressure of oxygen increases and the oxygen concentration at saturation increases as the following table demonstrates:

TABLE 6-4

Effect of Pressure on Oxygen Solubility

	<u>P (psig)</u>	<u>T (°C)</u>	<u>P_{H₂O} (psig)</u>	<u>H (m³atm/kg)</u>	<u>C* (ppm)</u>	<u>Feed C (ppm)</u>
8/11	2275	290	1088	7.63	3968	678
8/24	2550	290	1088	7.63	4888	819
8/14	3200	290	1088	7.63	7061	870

Since conversion and oxygen solubility increase with pressure then the

rate of oxidation must depend upon the oxygen concentration in solution. In all three runs above the oxygen concentration at saturation is greater than stoichiometric so the conversion should be as great as that obtained from a two-phase system with enough agitation to keep the dissolved oxygen at a level sufficient for oxidation. The conversions were less than those obtained by other researchers at similar conditions, therefore the actual dissolved oxygen must have been less than the oxygen concentration at saturation. Equilibrium was not reached. Further evidence to this being the case is data on the time it takes the oxygen concentration to reach equilibrium at various pressures. Taylor(15) presents times on the order of hours, therefore all the oxygen did not have time to dissolve within the twenty minute residence time of a run.

The supercritical runs had higher conversions. Compared to the subcritical runs pressures and temperatures were higher. Because the density of water is low at these conditions, the residence times are shorter. The conversions are probably higher due to the increased temperatures. The reaction also probably was not limited by the solubility of oxygen. According to Pray(10) , at supercritical conditions oxygen must be infinitely soluble in water and the Henry's law constant becomes relatively small. Wet oxidation of other feeds at supercritical conditions has produced conversions greater than 99%. The results reported here are less than that. The error in the results does not explain the lower conversions. The feed was about 1700 ppm carbon and the effluent 200 ppm. If 200 ppm in effluent represented a 99% reduction in carbon, the feed would have to have had a carbon concentration of 20,000 ppm. The error in the determination of carbon in the feed is not that large. It would have to be greater than 1000%. The residence times are shorter than those at which other feeds, e.g. glucose, were oxidized. That may be the reason for the different

conversions observed although no effect of residence time is apparent in the urine and feces results.

D. Effects of Wet Oxidation on Inorganic Components of Urine and Feces

Comparing the inorganic composition of the urine and feces feed and the solid products gives some qualitative information about the effects of wet oxidation on the inorganic components. Calcium, phosphorous, magnesium, and manganese have higher concentrations in the solid product than in the feed. The concentration of potassium decreased. This is the expected result. All mineral nutrients are expected to stay in the aqueous solutions from which the heavy metal ions (Ca, Mg, Fe, Cu, Zn, Mn, etc) will precipitate as insoluble phosphates and/or sulfates. This result differs with Lockheed's whose material balance test showed most of the phosphorous in the liquid phase.

The only conclusion to be drawn from the liquid product results are that calcium precipitates out as expected. Very little was in the liquid phase and a lot was in the solid phase. This was true for all samples. Since the concentration of inorganics in the feed slurry was not known not much more can be said about the effect of oxidation on inorganics in the liquid phase.

E. Carbon Balance Results

The results of a carbon balance for each run presented in Table 5-5 indicate that a lot of the carbon in the feed remains unaccounted for. Only one run gave a closure greater than 90%. One reason the carbon balance does not close is that absorbed CO_2 in the liquid product desorbs before TOC analysis is done.

VII. Conclusions

1. Conversion obtained at a similar pressure, temperature, and residence time was less than that obtained by Lockheed. The difference may be due to differences in pH, reactor configuration, oxygen flowrate, feed, and the presence of a catalyst. Also due to errors in both investigators' results the differences in conversion may not be so great.
2. The wet oxidation system is capable of oxidizing waste but contains several design deficiencies which cause errors in the results.
3. At subcritical conditions pressure increases lead to increases in conversion and liquid phase resistance to oxygen diffusion exists.
4. An increase in temperature caused an increase in conversion.
5. Wet oxidation of urine and feces produces a clear liquid product with a slight odor even at conversions as low as 56%.
6. Wet oxidation of urine and feces at the conditions tested produces a solid product with a higher content of calcium, magnesium, manganese, and phosphorous than in the feed.
7. Most of the nitrogen, carbon, hydrogen, and potassium do not remain in the solid phase after oxidation.
8. The residence time of the solid precipitate is longer than that of the fluid passing through the reactor because it builds up in the reactor.

VIII. Recommendations

1. Reduce error in the results through changes in the experimental system:
 - a. Devise a way to collect solid products so that they can be weighed and used to close the material balance. Also devise a way to prevent the lines from clogging with the solid precipitate. Perhaps put a solid product collector before the reactor.
 - b. Modify the reactor heating system to make the reactor more isothermal. Either use something other than a furnace or eliminate the heat losses at the ends of the present one.
 - c. Develop a way to measure the temperature inside the reactor.
 - d. Replace the one cc pipet with a larger one to reduce error in waste flow measurement.
 - e. Hook up the oxygen rotameter with a pulsation dampener before the compressor to get accurate oxygen flowrates.
 - f. Obtain a larger feed container so that a run can last longer than two hours and more data can be collected.
2. After the design deficiencies in the system have been corrected check the results in this thesis.
3. If better and acceptable results are obtained then pursue the answers to other questions about wet oxidation of urine and feces:
 - a. Close the material balance so that the effect of oxidation on inorganic components can be studied quantitatively.
 - b. Refine the gas chromatographic analysis to account for other gases, especially nitrogen and sulfur compounds.

- c. Analyze the liquid products to see what organic species are present.
4. If the conversions do not improve try one of the following:
 - a. Increase residence times.
 - b. For subcritical runs increase pressure.
 - c. Increase oxygen flowrates.
 - d. Lower pH to the acidic range in the reactor.
 - e. Devise a way to insure the pure water and oxygen are in equilibrium before either enters the reactor.

IX. APPENDIX

A. Flowrate Data

The flowrates for the water and waste feeds were measured using a 50 cc buret and a 1 cc pipet respectively. The time elapsed for a specific volume of fluid or slurry to be pumped was recorded. The flowrate was calculated from the following equation:

$$\text{Flowrate} = \frac{\text{Volume}}{\text{Time}} \quad (\text{Eqn. 9-1})$$

A 100 cc soap bubble flowmeter and a dry test meter were used to measure gaseous effluent flow rates. The same equation was applicable. Liquid effluent flowrates were only measured intermittently to insure the operator of a leak-free system.

The flowrates reported in Table 9-1 are those measured during the period the system was considered at steady state.

TABLE 9-1

Flow Rate Data

7/8	Water	Glucose	Gas
	12.06	4.21	121.80
	12.24	4.26	254.96
	12.66	4.19	121.80
	<u>12.90</u>	<u>4.67</u>	121.80
	12.46 s = .38	4.33 s = .23	339.90
		<u>121.80</u>	
		180.34 s = 94.59	
8/8	Water	Waste	Gas
	12.57	3.96	41.31
	12.63	3.81	54.24
	12.73	3.25	<u>46.24</u>
	<u>12.47</u>	<u>3.30</u>	47.26 s = 6.53
	12.60 s = .11	3.58 s = .36	
8/11	Water	Waste	Gas
	12.30	4.29	50.10
	12.40	3.68	49.90
	12.50	3.41	<u>69.69</u>
	<u>12.44</u>	3.48	56.56 s = 11.37
	12.41 s = .08	3.38	
		3.35	
		5.00	
	<u>4.59</u>		
	3.90 s = .64		
8/14	Water	Waste	Gas
	12.50	4.09	110.90
	12.18	4.14	91.60
	<u>12.44</u>	<u>3.79</u>	70.59
	12.37 s = .17	4.01 s = .19	101.50
			110.67
			114.80
			92.28
		109.40	
		<u>79.60</u>	
		97.93 s = 15.47	

TABLE 9-1 cont.

	Water	Waste	Gas
8/24	12.44	4.63	84.00
	12.37	4.21	80.13
	12.73	3.10	<u>97.09</u>
	12.63	4.00	87.07 s = 8.89
	<u>12.77</u>	2.89	
	12.58 s = .18	2.70	
		3.82	
		<u>3.56</u>	
		3.61 s = .68	
9/1	18.18	7.62	134.20
	17.87	7.33	144.90
	17.64	7.40	126.10
	<u>17.96</u>	7.44	141.50
	17.91 s = .22	7.44	148.50
		<u>7.22</u>	144.60
		7.41 s = .13	150.80
			<u>138.20</u>
			141.10 s = 8.1
9/6	17.80	8.21	130.72
	17.70	8.00	119.05
	17.80	8.70	122.95
	18.00	7.65	118.58
	18.10	8.00	115.60
	<u>18.00</u>	<u>7.80</u>	122.20
	17.90 s = .15	8.06 s = .37	136.05
			<u>121.20</u>
			123.29 s = 6.79

TABLE 9-1 cont.

	Water	Waste	Gas
9/22	13.20	5.81	193.5
	13.25	5.65	144.0
	13.25	4.97	128.5
	13.33	5.71	122.0
	13.30	6.11	118.6
	13.33	6.00	124.5
	13.25	6.22	120.2
	13.21	5.55	135.4
	13.25	5.72	113.6
	13.21	6.00	129.3
	<u>13.30</u>	6.21	191.0
	13.26 s = .05	6.82	147.0
		6.22	124.0
		6.00	135.1
		6.68	143.9
		6.00	117.2
		<u>6.67</u>	124.5
		6.02 s = .46	<u>129.9</u>
			135.7 s = 22.7
9/24	Water	Waste	Gas
	18.2	7.70	115.8 133.3
	18.5	7.65	123.2 <u>120.5</u>
	18.4	7.50	143.5 127.5 s = 12.0
	<u>18.5</u>	<u>8.00</u>	138.3
	18.4 s = .14	7.71 s = .21	140.8
			129.9
			103.1
			137.3
			133.3
			136.4
			126.8
			114.9
			101.0
			114.9
			129.9
			127.7
			108.3
			112.8
			134.2
			136.4
			126.6
			129.9
			133.3
			140.5
			139.2

TABLE 9-1 cont.

10/19	Water	Waste	Gas
	17.60	7.70	182.9
	18.07	7.70	172.9
	<u>18.20</u>	6.54	174.9
	17.96 s = .32	6.67	174.4
		6.84	174.4
		9.79	<u>146.3</u>
		8.22	170.97 s = 12.6
		8.00	
		7.44	
		8.13	
		8.93	
		7.50	
		9.00	
		7.29	
		7.10	
		8.22	
		<u>8.68</u>	
		7.87 s = .89	

TABLE 9-2

Average Flowrates and 95%
Confidence Limits

	Water	Waste	Gas
7/8	12.46 \pm .60	4.33 \pm .37	180.34 \pm 99.24
8/8	12.60 \pm .17	3.58 \pm .57	47.26 \pm 16.21
8/11	12.41 \pm .13	3.90 \pm .53	56.56 \pm 28.23
8/14	12.37 \pm .42	4.01 \pm .47	97.93 \pm 11.91
8/24	12.58 \pm .22	3.61 \pm .57	87.07 \pm 22.07
9/1	17.91 \pm .35	7.41 \pm .14	141.10 \pm 6.76
9/6	17.90 \pm .16	8.06 \pm .39	123.29 \pm 5.67
9/22	13.26 \pm .03	6.02 \pm .24	135.70 \pm 11.29
9/24	18.40 \pm .16	7.71 \pm .33	127.10 \pm 4.76
10/19	17.96 \pm .79	7.86 \pm .46	170.97 \pm 13.22

B. Analysis of Gaseous Products

The peak areas of a chromatograph trace were automatically calculated by the Perkin-Elmer Sigma 1B microprocessor using directions specified by the user in the data processing section of a method generated by the user. The directions also include response factors previously calculated by the Sigma 1B using calibration standards. These response factors were then used by the Sigma 1B to calculate concentrations. The calibration was checked before each run and if it was necessary the calibration was repeated. The standards used contained the following gases and corresponding concentrations (volume %):

TCD	H ₂	1.00	FID	C ₂ H ₆	1.000
	CO ₂	15.00		C ₂ H ₄	1.000
	CO	7.04		CH ₄	1.000
	CH ₄	4.50		C ₂ H ₂	1.000
	N ₂	63.50			
	O ₂	10.00			

For runs on October 19 and after the standards were:

TCD	H ₂	1.00	FID	C ₂ H ₆ , C ₂ H ₄	10.1 ppm
	CO ₂	15.00		CH ₄ , C ₂ H ₂	10.2
	CO	7.04		C ₃ H ₈ , C ₃ H ₆	9.92
	CH ₄	4.50		Propyne	15.5
	N ₂	66.50		I-butane	9.67
	O ₂	7.00		N-butane	9.60

The calibration standards for the FID were changed because previous runs produced unidentified hydrocarbons although in very small amounts.

The gas compositions were normalized to 100% to account for changes in sample volume. Any gases not detected within the analysis time were not taken into account. Other gases may have been present such as other hydrocarbons with longer residence times and products from oxidation

of sulfur and nitrogen in the feed. Such hydrocarbons make a small contribution to the total amount of gas. The columns and analysis conditions were either not suitable for detection of nitrogen and sulfur compounds or the compounds were in concentrations too small to be detected by the thermal conductivity detector. Water was accounted for in the gas compositions reported in Table 9-3. The gas was assumed to be saturated with H_2O . Its vapor pressure at $20^{\circ}C$ and 760 mm mercury is 17.535 mm of mercury which is a concentration of 2.3%. So the compositions in Table 9-3 add up to 97.7%.

The gas compositions reported were only those believed to represent the system at steady state. Figure 9-1 is a sample of the method used. The method was the same for each run except for the response factors which could change if the system was recalibrated. Figure 9-2 shows a typical report from an analysis performed by the Sigma 1B.

TABLE 9-3

Gas Compositions

7/8	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.043	27.760	56.894	.397	.000	12.594	.0110
2	.042	47.619	39.156	<.002	.000	10.868	.0146
3	.056	18.785	68.286	.000	.000	10.563	.0104
4	.059	51.073	34.411	.000	.000	12.157	.0229
5	.021	47.635	41.068	.000	.000	8.961	.0150
6	<u>.000</u>	<u>20.481</u>	<u>64.821</u>	<u>1.647</u>	<u>.000</u>	<u>10.750</u>	<u>.0000</u>
AVG	.037	35.559	50.773	.341	.000	10.982	.0123
s =	.02	13.549	13.155	.002	.000	1.177	.0068
8/8	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.110	8.998	87.828	.540	.000	.224	<.008
2	<u>.100</u>	<u>7.024</u>	<u>89.874</u>	<u>.565</u>	<u>.000</u>	<u>.137</u>	<u><.008</u>
AVG	.105	8.011	88.851	.552	.000	.018	<.008
s =		1.396	1.447	.018	.000	.062	
8/11	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.081	10.162	86.512	.727	<.008	.218	<.008
2	.077	9.718	87.055	.600	<.008	.250	<.008
3	<u>.068</u>	<u>9.161</u>	<u>87.648</u>	<u>.596</u>	<u><.008</u>	<u>.227</u>	<u><.008</u>
AVG	.075	9.680	87.072	.641	<.008	.232	<.008
s =	.007	.502	.568	.074		.016	
8/14	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.002	6.694	90.633	.262	<.008	.111	<.008
2	.042	6.943	90.197	.397	<.008	.121	<.008
3	<u>.002</u>	<u>7.247</u>	<u>88.133</u>	<u>.461</u>	<u><.008</u>	<u>.137</u>	<u><.008</u>
AVG	.014	6.961	89.654	.373	.008	.123	<.008
s =	.02	.226	1.09	.083		.011	

TABLE 9-3 cont.

8/24	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.089	2.788	94.641	<.002	<.008	.182	<.008
2	.000	2.912	94.366	.264	<.008	.158	<.008
3	<u>.075</u>	<u>2.903</u>	<u>94.543</u>	<u><.002</u>	<u><.008</u>	<u>.179</u>	<u><.008</u>
AVG	.055	2.868	94.517	.088	<.008	.173	<.008
s =	.039	.056	.114			.011	
9/1	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.236	16.488	71.138	.499	.041	9.237	.061
2	.266	17.821	68.113	.621	.045	10.765	.068
3	<u>.277</u>	<u>17.632</u>	<u>68.412</u>	<u>.610</u>	<u>.048</u>	<u>10.654</u>	<u>.067</u>
AVG	.260	17.314	69.221	.577	.045	10.219	.065
s =	.017	.589	1.361	.055	.003	.696	.003
9/6	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.290	20.508	67.061	.749	.018	9.037	.036
2	.286	20.217	67.365	.760	.018	9.018	.036
3	.308	22.962	63.167	.912	.021	10.309	.042
4	<u>.293</u>	<u>21.645</u>	<u>65.456</u>	<u>.780</u>	<u>.019</u>	<u>9.469</u>	<u>.038</u>
AVG	.294	21.608	65.762	.800	.019	9.458	.038
s =	.008	1.121	1.665	.065	.001	.523	.002
9/22	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.330	6.985	88.053	.05	.009	2.313	.001
2	.436	6.560	84.957	.245	.023	5.633	.019
3	.412	10.804	79.342	.173	.027	6.917	.025
4	.286	19.120	70.438	.442	.038	7.341	.034
5	<u>.328</u>	<u>12.276</u>	<u>76.581</u>	<u>.576</u>	<u>.028</u>	<u>7.884</u>	<u>.026</u>
AVG	.339	11.149	79.874	.287	.025	6.018	.021
s =	.046	4.546	.621	.202	.009	1.996	.011

TABLE 9-3 cont.

9/24	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₂ H ₆ + C ₂ H ₄
1	.102	.273	93.268	.617	.011	3.413	.015
2	.144	.302	93.615	.712	.012	2.903	.013
3	.147	.308	93.965	.555	.012	2.708	.013
4	.095	.331	92.640	.866	.019	3.732	.018
5	<u>.073</u>	<u>.332</u>	<u>93.076</u>	<u>.836</u>	<u>.014</u>	<u>3.353</u>	<u>.016</u>
AVG	.112	.309	93.313	.717	.014	3.222	.015
s =	.029	.022	.453	.121	.003	.369	.0019

10/19	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO	C ₃	C ₂ H ₆ + C ₂ H ₄
1	.272	11.250	78.825	.256	.147	6.950	--	----
2	.446	12.183	71.131	.375	.146	13.350	.012	.057
3	.556	11.893	73.693	.592	.146	10.746	.014	.060
4	<u>.955</u>	<u>14.196</u>	<u>74.087</u>	<u>.432</u>	<u>1.181</u>	<u>6.658</u>	<u>.020</u>	<u>.131</u>
AVG	.557	12.381	74.434	.414	.405	9.426	.015	.076
s =	.251	1.101	2.778	.121	.448	3.211	.003	.040

FIGURE 9-1

Method 200

ANALYZER CONTROL

INJ TEMP 200
 DET ZONE 1.2 150 150
 AUX TEMP 105
 FLOW A,B 20 20
 INIT OVEN TEMP, TIME 80 3

TEMP	RATE	TIME
96	3.0	0
130	40.0	1
140	40.0	4

DATA PROC

STD WT, SMP WT 0.0000 1.0000 0
 FACTOR, SCALE 1 0
 TIMES 13.43 0.00 4.50 7.50 9.90 13.00
 SENS-DET RANGE 100 4 0.00 2 0 0
 UNK,AIR 1.000 0.00
 TOL 0.0020 0.050 1.0
 REF PK 0.000 0.00 0.00 0.00
 STD NAME

RT	RF	CONC	NAME
3.20	2.637	1.0000	HYDROGEN
5.35	0.515	149.9968	CARBON DIOXIDE
6.35	0.658	100.0992	OXYGEN
7.02	0.596	634.4960	NITROGEN
9.15	0.709	45.0000	METHANE
11.29	0.613	70.4000	CARBON MONOXIDE

EVENT CONTROL

FIGURE 9-1 cont.

ATTN-CHART-DELAY 10 1 0.20

TIME	DEVICE	FUNCTION	NAME
0.00	EXT	X -7	TCD
0.00	NO INT	NI 1	NO INT
0.01	EXT	X 1	INJECT
0.03	EXT	X -1	BLEED
0.50	NO INT	NI 0	INT
• 0.60	CHART	C 10	CHART
0.70	ATTN	A 2	ATN
3.50	NO INT	NI 1	NO
3.51	EXT	X 2	RESEQ
3.53	EXT	X -2	BLEED
3.80	ZERO	Z 2	ZERO
3.85	NO INT	NI 0	INT
3.95	ATTN	A 6	ATN

FIGURE 9-2

Sigma 1B Analysis Report

ANAL 1 DET 2 METH 201 200 FILE 161
 RUN 2 11 : 14.5 9/6/80
 SENSITIVITIES 100 4

TIME	AREA	BC	RRT ^a	RF ^b	C ^c	NAME
2.78	0.0050		0.278	26.370	0.0668	HYDROGEN:
5.39	58.0505	T	0.539	0.515	14.9179	CARBON DIOXIDE:
6.30	30.4243	T	0.630	0.658	9.9894	OXYGEN:
6.90	213.6985		0.690	0.596	63.5537	NITROGEN:
8.97	12.6041		0.897	0.709	4.4592	METHANE:
10.79	22.9273		1.079	0.613	7.0131	CARBON MONOXIDE:

a
Relative retention time

b
Response factor

c
Concentration (vol %)

C. Waste Analysis

The urine, Batch GF-1 Sample No. 1, and feces, Batch GF-1 Sample No. 5 were shipped from Georgia Institute of Technology where they had been collected and freeze-dried. The urine and feces were analyzed at Georgia Tech for several elements including C, H, N, S, Ca, and Mn. At MIT a Perkin-Elmer Elemental Analyzer was used for analysis of C, H, and N in the urine and feces. The Georgia Tech and MIT results are both reported, but only the MIT results are used in determination of the C, H, and N content of the waste for use in further calculations. The MIT data was obtained from analysis of ground (< 170 mesh) and unground ($170 <$ particle size < 10 mesh) freeze-dried feces. The results agree well. Table 9-4 tabulates the results.

TABLE 9-4

Waste Analysis

FECES - MIT

C	H	N
46.21%	6.89	4.00
46.73	6.83	4.36
46.65	6.67	4.27
46.20	6.77	4.27
47.09	6.92	4.81
<u>46.80</u>	<u>6.91</u>	<u>4.94</u>
46.61	6.83	4.44
s = .35	.10	.36
95% C.L. <u>±.37</u>	<u>±.10</u>	<u>±.38</u>

FECES - GIT

C	H	N	S
45.93	6.57	4.15	<.5
46.02	6.64	4.01	<.5
<u>45.63</u>	<u>6.62</u>	<u>4.07</u>	<u><.5</u>
45.86	6.61	4.08	<.5
s = .20	.04	.07	
95% C.L. <u>±.50</u>	<u>±.10</u>	<u>±.17</u>	

URINE - MIT

C	H	N
19.52	4.61	20.44
20.18	4.70	20.75
<u>19.57</u>	<u>4.80</u>	<u>20.31</u>
19.76	4.70	20.50
s = .37	.10	.23
95% C.L. <u>±.92</u>	<u>±.25</u>	<u>±.57</u>

URINE - GIT

C	H	N	S
19.13	5.19	19.97	1.59
19.50	5.30	19.86	1.84
<u>18.98</u>	<u>5.06</u>	<u>20.34</u>	<u>1.89</u>
s = .27	.12	.25	.16
95% C.L. <u>±.67</u>	<u>±.30</u>	<u>±.62</u>	<u>±.40</u>

D. Carbon Content of Feed

For purposes of calculating conversion knowledge of the carbon content of the feed stream in units of moles carbon/min is necessary. This was obtained in the following way: For each run urine and feces were weighed and a known volume of solution was made by adding deionized H₂O. From the results of the C, H, N analysis in Appendix C, the carbon content of the solution was calculated. Then the following equation was used to calculate moles/min:

$$\begin{aligned} (\text{gC/liter}) \times (1 \text{ liter}/1000 \text{ cc}) \times (\text{waste flowrate, cc/min}) \times (1 \text{ mole}/12 \text{ gC}) \\ = \text{moles C/min} \end{aligned} \quad (\text{Eqn. 9-2})$$

Table 9-5 lists the amounts of urine and feces used in each run, total Carbon, the volume of resulting solution, the corresponding flowrate from Table 9-1, Appendix A, and the result of application of the above equation.

Conversion was also measured in units of parts per million (ppm). Total carbon in the feed in ppm was calculated from the following equation:

$$\text{ppm} = \frac{\text{mg carbon in feed}}{\frac{(\text{water flowrate}) (\text{vol. of feed sol'n})}{(\text{waste flowrate}) (\text{in liters})} + \text{vol. of feed sol'n in liters}} \quad (\text{Eqn. 9-3})$$

This is also reported in Table 9-5.

TABLE 9-5

Carbon Content of Feed

Date	Urine(gm)	Feces(gm)	Total Carbon(gm)	Solution Volume (liters)	Waste Flowrate (cc/min)	Waste Flowrate (moles C/min)	Feed Carbon (ppm)
7/8	--	--	35.42 ^a	2.116	4.33 ± .37	.00604 ± .0005	4316 ± 450
8/8	5.3999	5.5000	3.63 ± .07	1.082	3.58 ± .57	.00100 ± .00018	742 ± 108
8/11	4.3556	4.2378	2.84 ± .06	1.000	3.90 ± .53	.00092 ± .00014	678 ± 110
8/14	5.1641	4.9890	3.35 ± .07	1.000	4.01 ± .47	.00112 ± .00015	819 ± 115
8/24	5.0378	6.2366	3.90 ± .07	1.000	3.61 ± .57	.00117 ± .00021	870 ± 149
9/1	8.5388	8.6199	5.71 ± .11	1.0000	7.41 ± .14	.00352 ± .00013	1670 ± 76
9/6	8.5310	8.4791	5.65 ± .11	1.0000	8.06 ± .39	.00380 ± .00026	1755 ± 121
9/22	8.5988	8.4863	5.65 ± .11	1.0000	6.02 ± .24	.00284 ± .00016	1766 ± 118
9/24	11.4936	--	2.27 ± .05	1.0000	7.71 ± .33	.00146 ± .00009	713 ± 51
10/19	8.4763	8.0585	5.43 ± .11	1.0000	7.86 ± .46	.00356 ± .00028	1653 ± 168

a. glucose 97.4 gm monohydrate = 88.55 gm glucose = 35.42 gm carbon

E. Analysis of Carbon Content in Liquid Effluent:
Organic and Inorganic

The liquid products were analyzed for total carbon and inorganic carbon on a Beckman Tocamaster Total Organic Carbon Analyzer. The total organic carbon is the difference between total and inorganic carbon. Some of the samples were analyzed for total carbon soon after collection. They were also later analyzed again for total carbon and for inorganic carbon. In the interim the samples were stored in the freezer or refrigerator. Table 9-6 shows any changes in total carbon. Table 9-7 lists results of all samples along with averages, standard deviations, and 95% confidence limits.

TABLE 9-6

Analysis of Carbon in Liquid Products:
Changes in TC with Storage Time

SAMPLES	ANALYSIS DATES	
	9/17/80	11/14/80
8/8/80 LE 3	TC 94.8	TC 99.5 IC 82.9 TOC 16.6
8/11/80 LE 3	TC 421	TC 441 IC 144 TOC 297
8/14/80 LE 7	TC 290	TC 281 IC 130 TOC 150
8/24/80 LE 3	TC 289	TC 302 IC 133 TOC 170
9/1/80 Blank w/o O ₂	TC .5	TC 2.97 IC .06 TOC 2.91
9/1/80 LE 3	TC 406	TC 425 IC 252 TOC 174
9/1/80 LE 5	TC 557	TC 613 IC 399 TOC 215
9/1/80 LE 7	TC 589	TC 647 IC 426 TOC 221
9/1/80 LE 11	TC 55.1	TC 54.8 IC 49.2 TOC 5.6

TABLE 9-6 cont.

SAMPLES	ANALYSIS DATES	
	9/17/80	11/14/80
9/6/80 LE 3	TC 660	TC 604 IC 401 TOC 203
9/6/80 LE 3B	TC 645	TC 624 IC 426 TOC 198
9/6/80 LE 5A	TC 673	TC 642 IC 459 TOC 194
9/6/80 LE 5B	TC 679	TC 646 IC 426 TOC 220
9/6/80 LE 7	TC 379	TC 342 IC 201 TOC 141

TABLE 9-7

Analysis of Carbon in Liquid Products-
Inorganic and Organic

7/8/80			1	2	3	4				
Total Carbon, TC			1678	1635	2128	2208				
Inorganic Carbon, IC			68.5	24.8	39.2	13.0				
Total Organic Carbon, TOC			1609	1610	2088	2195				
Avg TOC = 1876		s = 310	95% C.L. \pm 493							
Avg IC = 36.4		s = 24	95% C.L. \pm 38							
8/8/80	1	2	Avg	S.D.	95% C.L.					
TC	99.5	159	129.2	42.1	378					
IC	82.9	122	102.4	27.6	240					
TOC	16.6	37.7	27.2	14.9	129.6					
8/14/80	1									
TC	281									
IC	130									
TOC	150									
8/24/80	1									
TC	302									
IC	133									
TOC	170									
9/1/80										
	1	2	3	4	5	Avg	S.D.	95% C.L.		
TC	613	594	647	620	638	622	21	29		
IC	399	397	426	420	434	415	16	22		
TOC	215	197	221	200	204	207	10	14		
9/6/80										
	1	2	3	4	5	6	7	Avg	S.D.	95% C.L.
TC	604	593	624	653	642	646	607	624	23	21
IC	401	394	426	459	445	426	410	423	23	21
TOC	203	199	198	194	197	220	197	201	9	8

TABLE 9-7 cont.

9/24/80								
	1	2	3	4	5	6	7	8
TC	306	381	473	423	516	385	442	521
IC	242	320	430	377	484	319	380	487
TOC	64.3	61.3	43.2	47	31.8	66.5	62.5	34.5
	9	10	Avg	S.D.	95% C.L.			
TC	536	386	437	75	54			
IC	507	319	386	89	64			
TOC	29	66.8	51	15	11			
10/19/80								
	1	2	3	4	Avg	S.D.	95% C.L.	
TC	339	478	518	391	432	81	129	
IC	133	260	331	191	229	86	137	
TOC	206	217	187	199	202	13	21	

F. Residence Time Determination

Residence time was calculated from the following equation:

$$\text{Residence Time}(\theta) = \frac{\text{Reactor volume, cc}}{\text{Flowrate, cc/min}} \quad (\text{Eqn. 9-4})$$

Reactor volume is 513 cc and flowrates are tabulated in Table 9-1. At reactor conditions the density of water changes so that the flowrates are different from those listed in Table 9-1. The actual flowrate at reactor conditions is:

$$F_{\text{actual}} = F_{\text{at room T \& P}} \times \frac{\text{density of water at room T \& P}}{\text{density of water at reactor conditions}} \quad (\text{Eqn. 9-5})$$

Table 9-8 lists the measured flowrates, density of water at corresponding reactor conditions, actual flowrate, and residence times for each run.

The density of water is taken to be 1 gm/cc at ambient conditions.

TABLE 9-8

Residence Time Determination						
DATE	T (°C)	P (psig)	F _{measured} (cc/min)	ρ H ₂ O ^a (g/cc)	F _{actual} (cc/min)	Θ (min)
7/8	277	2275	16.79 \pm .97	.76	22.09 \pm 1.28	23.22 \pm 1.35
8/8	303	2375	16.18 \pm .66	.73	22.16 \pm .90	23.15 \pm .94
8/11	292	2275	16.31 \pm .89	.74	22.04 \pm 1.20	23.28 \pm 1.27
8/14	289	3200	16.38 \pm .89	.76	21.51 \pm 1.17	23.85 \pm 1.29
8/24	295	2550	16.19 \pm .79	.75	21.59 \pm 1.05	23.76 \pm 1.13
9/1	409	4050	25.32 \pm .49	.2	126.60 \pm 2.45	4.05 \pm .08
9/6	400	3825	25.96 \pm .55	.19	136.63 \pm 2.89	3.75 \pm .08
9/22	404	3825	19.28 \pm .27	.19	101.47 \pm 1.42	5.06 \pm .07
9/24	402	3825	26.11 \pm .47	.19	137.42 \pm 2.47	3.73 \pm .11
10/19	443	3850	25.82 \pm 1.25	.12	215.17 \pm 10.42	2.38 \pm .11

a Holzer and Kennedy (2,3).

G. Selection of Experiments

The original set of experiments were selected based on the criteria that dissolved O_2 be greater than stoichiometric, and the liquid / O_2 flowrate ratio at reactor conditions be high. The concentration of feed was selected after O_2 flowrate was selected using the criteria above. Henry's Law was used to determine oxygen solubility. The Henry's law constant was obtained from Pray et al (10) and Ploos Van Amstel and Rietema (9). Table 9-9 lists the Henry's law constants at several temperatures. Henry's Law states:

$$C^* = \frac{P - P_{H_2O}^0}{H} \quad (\text{Eqn. 9-6})$$

where P is total pressure, $P_{H_2O}^0$ is the vapor pressure of water, C^* is the equilibrium concentration of oxygen at saturation and H is Henry's Law constant.

For ease of experimentation it was decided to keep the feed concentration a constant as well as the equilibrium concentration of oxygen. Since $H = f(T)$ only, the equilibrium concentration for all runs would have to be equal to the highest that can be attained at lowest temperature (180°C). Using Henry's law and the maximum system operating pressure (3700 psig) this concentration was calculated to be 3.17×10^{-4} moles O_2 /cc which was enough for 3800 mg Carbon/liter. Table 9-10 lists the original set of experiments. The oxygen flowrates chosen gave a liquid/ O_2 ratio of 100:1 at 180°C and 3700 psi. This was enough oxygen for a feed of 824 mg C/liter.

TABLE 9-9

Henry's Law Constant

T (°C)	$P_{H_2O}^o$ (psia)	H (m ³ atm/kg)
180	147	23.81
200	220	19.23
220	338	16.39
240	470	14.08
255	617	11.36
270	808	9.01
290	1088	7.63

TABLE 9-10

Wet Oxidation Experiment Set

Residence Time(min)	Temp. (°C)	P (psig)	O ₂ flowrate (cc/min at STP)
15	180	3700	50.7
30	180	3700	25.3
45	180	3700	16.8
60	180	3700	12.6
15	220	2784	50.7
30	220	2784	25.3
45	220	2784	16.8
60	220	2784	12.6
15	255	2313	50.7
30	255	2313	25.3
45	255	2313	16.8
60	255	2313	12.6
15	290	2227	50.7
30	290	2227	25.3
45	290	2227	16.8
60	290	2227	12.6

H. Error Analysis

All results were averaged, the standard deviations calculated, and the 95% confidence limits determined from the t-distribution. Standard deviations were calculated using a function on a Hewlett-Packard 34C calculator. The equation used by the calculator was:

$$s = \sqrt{\frac{n\sum x^2 - (\sum x)^2}{n(n-1)}} \quad (\text{Eqn. 9-7})$$

where x is the data point and n is the total number of data points. The 95% confidence limits were calculated from the standard deviations using the following equation:

$$95\% \text{ C.L.} = ts/\sqrt{N} \quad (\text{Eqn. 9-8})$$

where N is the number of data points and s is the standard deviation.

Values for t were obtained from the Laboratory Techniques Manual, Volume 1, Undergraduate Chemistry Laboratory, MIT Department of Chemical Engineering c 1974, page 3-12.

The following rule was used when calculating errors on values which were calculated from one or more measured values. When adding or subtracting two numbers, absolute errors were added and when multiplying or dividing, relative errors were added.

The error in the subcritical urine and feces runs is higher than in the supercritical. Only two liquid effluents were analyzed which were not very close in TOC for the 8/8 and 8/11 runs. These two runs did not last long and large samples were used. The more samples there are the less the error. The error in the 8/14 and 8/24 runs look lower but the error is probably higher. Only one sample was analyzed for TOC so no average could be taken. It is possible the samples were not representative.

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