ACETIC ACID PRODUCTION
FROM MARINE ALGAE

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3. Modification of the process economics presented in Progress Report #1 to include isolation and purification, with emphasis on electrolyzing the mixed organic products to aliphatic hydrocarbons.

Section 2

INTRODUCTION

The objects of this work are to develop an economically competitive process for producing acetic acid from biomass, to evaluate marine algae as a biomass, and to demonstrate the feasibility of running fermentations which produce inhibitory liquid products in a fixed packed bed fermenter. It is known that in the anaerobic digestion of organic matter to methane that acetic acid is an intermediate, and conversion will stop at the organic acid stage unless careful control of the digester is exercised.

The anaerobic fermentation of cellulosic material to acetic acid by sewage sludge flora has been studied by Jeris and McCarty (Reference 1) who showed by radioactive tracer studies that the process is best described as:

presumably proceeding through pyruvate via the Embden-Myerhoff Pathway. It was shown in these tracer studies that approximately 70% of the methane formed in anaerobic digestion processes derived from acetic acid.

Anderson et al (Reference 2) have shown that Clostridium thermoaceticum can produce three acetates from each glucose molecule, two by the route just described and the third by the reduction of the CO_2 formed to formate, which is further reduced by intermediates of the tetrahydrofolate pathway. Ultimately carboxylation occurs to give acetate. The overall reaction is shown as:

These workers were able to obtain an actual yield of 2.5 acetates per glucose molecule. It is likely, however, that in the mixed culture anaerobic fermentation under study that acetic acid is produced according to equation 2.1, and that the hydrogen produced or the precursors to hydrogen formation are utilized to form higher acids according to the following stoichiometry:

One of the most significant results of the current program is that greater than 85% of the available reducing equivalents in several marine algal species have been incorporated into organic acid products.

Section 3

BIOMASS EVALUATION

3.1 Introduction

The primary task in evaluating Chondrus crispus and other potential biomass species is the determination of the total available reducing equivalents. The total available reducing equivalents (R) is obtained from the equation:

$$R = A + 1.75 P + 2.5 B + 3.25 V + 4.0C$$

where A, P, B, V, and C are the measured concentrations of acetic, propionic, butyric, valeric, and caproic acids, respectively.

The basis for this equation is the following set of reactions:

The percent conversion (% C) is then calculated by multiplying R (in meq/l) by 0.06 g/meq and then dividing by the substrate concentration (S) in g/l on a total solids basis:

$$\% C = 0.06 R/S$$

In order to estimate the maximum available reducing equivalents in Chondrus crispus and several other aquatic plants, elemental analyses were obtained. The results of these determinations are shown in Table 3.1. It is interesting to note that the marine algae are only about 17% carbon whereas the fresh water weeds, Duckweed and Hydrilla have nearly twice the carbon. If one assumes that all of the carbon in these plants is fermentable and is in the same oxidation state as the carbon in cellulose, then a maximum % conversion can be calculated for each of these plants. Table 3.2 presents these estimates of the maximum conversions. For the marine algal species the estimated maximum conversion is 43-45%, assuming each hexose molecule is converted to three acetic acid molecules. As a lower estimate of potential conversion one might subtract 10% of the carbon for conversion to cell mass and convert the rest of the carbon to acetic acid at three carbon atoms per acetic acid as through a pyruvic acid intermediate. These assumptions give the minimum estimated conversion percentages listed in Table 3.2. The minimum estimates for the marine algal species run around 25% whereas for the fresh water species the estimates are around 50%.

3.2 Static Fermentations

In order to determine the total reducing equivalents available for organic acid production from the substrates of interest a variety of fermentation conditions have been investigated. In general, the best results have been obtained in static fermenters containing 5% total solids, using sewage sludge as inoculum at a level of about 2% of total solids, controlled at a pH of 5.5-6.0 using calcium carbonate and phosphoric acid, as appropriate, to maintain this pH range. Table 3.3 presents the results of the acid analyses for a fermenter containing Chondrus crispus run in this manner. The results opposite $T = \infty$ are estimates of the ultimate conversion percentages for each acid product obtained from the plots of each acid concentration vs. time in Figure 3.1. The percent conversion is 40% of the total solids, indicating essentially complete conversion of substrate

Table 3.1
ELEMENTAL ANALYSES*

<u>Sample</u>	<u>Weight %</u>			
	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>
1. <u>Hydrilla</u>	33	4.0	2.4	0.3
2. <u>Gracilaria</u>	17	2.6	2.0	3.6
3. <u>Duckweed</u>	34	5.3	6.7	0.7
4. <u>Ulva lactuca</u>	17	3.0	0.7	6.2
5. <u>Chondrus crispus</u>	18	3.1	1.8	2.2

*Galbraith Laboratories, Knoxville, Tenn.

Table 3.2
ESTIMATED CONVERSION PERCENTAGES

<u>Substrate</u>	<u>% C</u>	<u>Maximum % Conversion</u>	<u>Minimum % Conversion</u>
<u>Hydrilla</u>	33	83	49
<u>Gracilaria</u>	17	43	26
Duckweed	34	85	51
<u>Ulva lactuca</u>	17	43	26
<u>Chondrus crispus</u>	18	45	27

Table 3.3

ORGANIC ACID CONCENTRATION VS. TIME

Expt. #00354-1 - 5% Chondrus crispus, Controlled pH, 37°C

Time, Day	pH	A ⁽¹⁾	P	B	V	C	Total	A/T	R ⁽²⁾	% ⁽³⁾ Conv.
0	---	0	0	0	0	0	0	---	0	0
1	---	25	10.5	6	0	0	41.5	60%	58	7%
2	4.5	14.5	8.5	7.5	6	0	36.5	40%	68	8%
5	---	29	4	17.5	3	0	53.5	54%	90	11%
6	---	33	14.5	24	15	~1	81.5	38%	171	20%
7	---	25.5	8	20	6.5	0	60	43%	111	13%
8	5.3	28	7	27.5	4	5	71.5	39%	142	17%
12	5.2	70	15	26	5	0	116	60%	178	21%
19	5.2	46	8.5	13	6	30	103.5	44%	233	28%
26	5.9	45	6	28	4	31	114	39%	263	32%
33	5.9	68	9	29.5	6.5	32.5	145.5	47%	309	37%
41	6.0	51	7	24	4	13	99	52%	188	23%
47	5.9	124	25	33.5	3	3	188.5	66%	273	33%
54	5.9	53	7	23.5	5.5	25.5	116.5	45%	249	30%
61	---	55	11	28	7	33	134	41%	299	36%
68	6.1	58	14	29	10	34	145	40%	324	39%
75	5.8	59	5	28	7	34	133	44%	297	36%
81	6.2	60.5	9	29	12	43	154	39%	360	43%
89	5.7	64	4	28	10	47	153	42%	362	43%
96	5.8	60	12	45	19	42	178	34%	422	51%
103	5.7	56	6.5	33	12.5	35	143	39%	331	40%

Average final concentrations

∞	---	60	10	32	12	35	149	40%	336.5	40%
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(1) A = Acetic, P = Propionic, B = Butyric, V = Valeric,
C = Caproic Acid Concentration in meq/l.

(2) R = Total reducing equivalents = A + 1.75P + 2.5B + 3.25V + 4.0C

(3) % Conv., % Conversion based on total solids.

Figure 3.1

ORGANIC ACIDS CONCENTRATION VS. TIME
EXPT. #02354-1 5% CHONDRUS CRISPUS 37°C

on a three acetic acid equivalents per hexose unit basis. The results of fermentations of Gracilaria, Ulva lactuca, and Hydrilla run under the same conditions are presented in Tables 3.4-3.6.

Table 3.4

RUN #00354-3; 5% Gracilaria; Controlled pH 37°C

	A	P	B	V	C	T	A/T	R	% Conversion
0 Day	1	1	0	1	0	1.5	33%	3	0.36%
1	37.5	9	7	0	0	53.5	70%	71	8.5%
2	15	9.5	2	0	0	26.5	57%	37	4.4%
5	65	19	10.5	1	0	95.5	68%	128	15.3%
6	46	12.5	10	3	0	71.5	64%	103	12.3%
7	45	14	13.5	2	0	74.5	60%	110	13.2%
8	39.5	5	8	1	0	52.5	75%	68	8.19%
12	55	12	9	0	0	76	72%	98.5	11.8%
19	72.5	17.5	29.5	2	.5	122	59%	185	22.3%
26	114	20	31	7	0	172	66%	249	29.9%
33	80	9.5	12.5	1	0	102	78%	128	15.4%
41	182.5	31	47	4	1	264.5	69%	367.5	44.1%
47	59.5	7	34.5	7.5	37	145.5	41%	330	40%
54	94.5	15	15.5	0.5	0	125.5	75%	161	19%
61	115	22.5	24	7	0	169	68%	237	28%
68	106	17.5	24.5	5	1	154	69%	218	26%
75	98	11.5	16	0.5	0	126	78%	160	19%
82	119	17	21	2	0	159	75%	208	25%
88	110	12	30	2	0	154	71%	213	26%
96	104	14	23	7	2	150	69%	217	26%
103	125	14	23	8	0	170	73%	233	28%
110	92	12	19.5	1	0	125	74%	165	20%
117	101	13.5	21.5	4.5	2	143	71%	201	24%
124	129	16.5	23	2	.5	171	75%	224	27%
131	140	24	34	4	2	204	69%	288	35%

Table 3.5

RUN #00354-4; 5% Buffered Ulva lactuca

	A	P	B	V	C	T	A/T	R	% Conversion
0 Day									
2	5	2.5	2	<1	0	10	50%	16	1.9%
5	16	8	1	<1	<<1	25.5	63%	34.5	4.1%
6	13	13	2	1	<1	29.5	44%	46	5.5%
7	12.5	13	2.5	<1	<<1	28.5	44%	44	5.3%
8	25	10	1.5	1.5	1	39	64%	55	6.6%
12	144	47	16	5.5	0	212.5	68%	284	34.1%
19	40	15	3	2	2.5	62.5	64%	90	10.8%
26	70	19	10	~0	2	101	69%	136	16.4%
33	98	30.5	12	0	3	143.5	68%	193	23.2%
41	112	30	11.5	<<1	2	155.5	72%	201	24.12%
47	65	25.5	10	< .5	0	101	64%	136	16%
54	75	26	6.5	0	0	107.5	70%	137	16%
61	72	42	11.5	9	6	141	51%	228	27%
68	61	40.5	12	4	4	122	50%	191	23%
75	38	28.5	6	0.5	0	73	52%	105	13%
81	47	32.5	14.5	1	0	95	49%	140	17%
89	25	40	12.5	2.5	0	80	31%	134	16%
96	31	52	13	1	0	97	32%	158	19%
103	13	46	11.5	7	0	78	17%	145	17%
110	14	48	10.5	2	0	75	19%	131	16%
117	18	40	7	1	0	56	14%	99	12%
124	23.5	60.5	14	4	1	103	20%	181	22%
131	27	73	10	1.5	0	112	24%	185	22%

Table 3.6

RUN #00355-5; 5% Buffered Hydrilla

	A	P	B	V	C	T	A/T	R	% Conversion
0 Day	<1	<1	0	0	0	~1	50%	~1	0.16%
2	22.5	21	7	2	0	52.5	43%	83	10%
5	73	50	14.5	12	0	149.5	49%	236	28%
6	49	33	8	7	0	97	51%	149.5	18%
7	54	36	8	4	0	102	53%	150	18%
8	56	38	5.5	4	0	103.5	54%	149	18%
12	97.5	53	27	12.5	0	190	51%	298	36%
19	96	30	19	9.5	0	154.5	62%	227	27%
26	127	76	24.5	11	0	238.5	53%	357	43%
33	89.5	59.5	13	6	0	168	53%	246	29%
41	5	64.5	13	7	0	89.5	6%	173	21%
47	21	65.5	7	1.5	0	95	22%	158	19%
54	14	70	0	.5	0	84.5	17%	138	17%
61	7	64	6	6.5	0	84	8%	155	19%
68	8	67	6.5	8	0	90	9%	168	20%
75	0	60	1	1	0	62	0	66	8%
82	0	61	0	2.5	0	64	0	115	14%
88	0	69	3	3.5	0	76	0	140	17%
96	0	56	1	1	0	58	0	62	7%
103	0	61	0	3	0	64	0	117	14%
110	0	53	0	4.5	0	50	0	107	13%
117	0	41	0	2	0	44	0	79	9%
124	0	25	0	1	0	26	0	28	3%
131	0	61.5	0	2.5	0	64	0	116	14%

Section 4

THERMOPHILIC FERMENTATION

A series of static thermophilic fermentations were run to determine the effect of increased temperature ($\sim 55^\circ$) on conversion percentage, conversion rate, and product composition. These fermentations were run at 5% total solids using 2% of solids sewage sludge as inoculum. Initially 1g/100 ml CaCO_3 was added to help maintain the pH of the fermenters at a desirable level. The results of fermentation of Chondrus crispus, Gracilaria, and Ulva lactuca are presented in Tables 4.1-4.3, respectively.

From these data three observations can be made:

1. The fermentations are slow, but this may be a result of a low population of thermophilically active bacteria in the mesophilic sewage sludge used as an inoculum.
2. None of the fermenters have exceeded the minimum percent conversions listed in Table 3.2, although the Gracilaria fermenter is getting close.
3. The ratio of acetic acid to total acid is extraordinarily high, averaging 81% over all measurements on all three fermenters and averaging 92% on the Chondrus crispus fermenter alone.

Table 4.1

RUN #00398-1, 5% Chondrus crispus, Buffered, 55°C

Day	A	P	B	V	C	T	A/T	R	%C
0	~0	0	0	0	0	0	0	0	0
1	5	0	0	5	0	6	91%	7	1%
2	19	0	~1	0	0	20	95%	22	3%
4	67	0	0	0	0	67	100%	67	8%
5	34	0	0	0	0	34	100%	34	4%
7	37	0	0	0	0	37	100%	37	4%
8	29	0	0	0	0	29	100%	29	3%
13	66	0	<1	0	0	67	99%	67	8%
16									
20	65	0	15	0	0	80	81%	103	12%
27	63	3	5	0	0	71	89%	81	10%
34	61	15	7	0	0	83	73%	105	13%
41	44	<<1	1	0	0	45	98%	47	6%
48	84	7	5	2	0	98	86%	115	14%
55	103	8	5	2.5	0	119	87%	138	17%

Table 4.2

RUN #00398-2, 5% Gracilaria, Buffered, 55°C

Day	A	P	B	V	C	T	A/T	R	% Conv.
0	~0	0	0	0	0	0	0	0	0
1	10	3	0	0	0	13	77%	15	2%
2	17	1	0	0	0	18	94%	19	2%
3	14	2	5	0	0	21	67%	30	4%
4	37	4.5	8	0	0	50	75%	65	8%
5	22	2	5	0	0	29	76%	38	5%
7	31	5	8	0	0	44	70%	60	7%
8	33	4.5	6	0	0	44	76%	56	7%
13	65.5	6	8	4	0	84	78%	109	13%
20	71	5	18	0	0	94	76%	125	15%
27	95	7.5	12.5	4	0	119	80%	152	18%
34	92	11	18	4	0	125	74%	169	20%
41	74.5	7.5	10	2	0	94	79%	119	14%
48	120	16	18	7	0	161	75%	216	26%
55	138	17	16	5	0	176	78%	224	27%

Table 4.3

RUN #01153-3, 5% Ulva lactuca, Buffered, 55°C

Day	A	P	B	V	C	T	A/T	R	% Conv.
0	0	0	0	0	0	0	0	0	0
2	8	2.5	0	0	0	11	76%	12	1%
3	21	9.5	0	0	0	31	69%	38	5%
4	21	15	0	~0	0	36	58%	47	6%
5	29	4	<<1	3	<1	37	79%	48	6%
6	35	6	<<1	0	0	41	85%	46	6%
7	41	9.5	5	0	5	61	68%	90	11%
8	42.5	17	8	2.5	2	72	59%	108	13%
15	52	12.5	2.5	7	7	81	64%	131	16%
22	47.5	6	3	2.5	0	59	81%	74	9%
29	58	9	2	0	0	69	84%	79	9%
36	83	10.5	9	7	6	116	72%	171	20%
43	64	4	4	1.5	6	80	81%	110	13%
50	140	11	95	8	11	180	78%	253	30%

Section 5

EXTRACTION PROCESSES

Concurrent with the fermentation process an extraction process is required. The extraction process should be designed to:

1. Maintain an acid concentration in the digester to give a desired product mix at a rate as rapid as possible.
2. Concentrate the acids to the desired level for further processing.
3. Remove the desired products preferentially.

It is clear that the choice of extraction method as well as the fermentation condition depends on the product mix desired. Some possible extraction methods are listed in Table 5.1. Of these ion exchange with conventional elution, solvent extraction with recovery by re-extraction and diffusion membrane processes have been investigated.

The use of a conventional strong anion exchange resin with quarternary ammonium sites was considered for use as an acid removal technique. The hydroxylated resin is inserted in the recirculation loop of the fixed packed bed reactor. The hydroxyl ions are displaced by the organic acid anions. When the resin is spent (as indicated by no pH change across the resin) it is removed and replaced by fresh resin. The spent resin is then eluted with an equivalent amount of mineral acid to remove the organic acids collected. The resin is then regenerated by eluting with alkali.

Use of strong anion exchange resins is unsuitable in this application for several reasons. First, replacement of anions in the fermentation broth such as acetate, butyrate, and bicarbonate tends to

Table 5.1

EXTRACTION METHODS

1. ION EXCHANGE

- a. Conventional Elution
- b. Methanol Elution

2. SOLVENT EXTRACTION

- a. Recovery by Distillation (Hydrosciences process)
- b. Recovery by Re-Extraction

3. MEMBRANES

- a. Diffusion
- b. Electrodialysis

increase the pH of the fermenter to the pK of the resin. The fermentation does not function at pH's above about 8.0. Secondly, the resin will reduce the phosphate level and the levels of other nutritive anions to very low levels. Thirdly, one equivalent of mineral acid and more than one equivalent of alkali are required to generate each equivalent of organic acid. More than one equivalent of alkali is required because the equilibrium constant for the reaction:

is less than 1. However, weak anion exchange resins with equilibrium constants greater than 1 are available and are under investigation for their utility in this application.

Solvent extraction of organic acids from aqueous solution is a technique which has been under consideration for some years. In fact, Goering is credited for suggesting ethyl acetate as an extractant for acetic acid in 1833 (Reference 3). Ethyl acetate, along with diethyl ether, continued to be the most efficient extraction medium at low acid concentrations (Reference 4) until recently when novel solvent extraction media were developed. This new technology is based on the use of trioctylphosphine oxide in combination with other solvents, the details of which are proprietary to Hydrosiences, Inc. (Reference 5).

An alternate approach to conventional solvent extraction followed by distillation is solvent extraction followed by re-extraction into aqueous base. The organic acids are accumulated in the aqueous base as salts, and when their concentration reaches say 25% by weight they are neutralized with mineral acid and distilled. This approach requires only one equivalent each of acid and base to concentrate the organic acid product from 1-3% in the fermenter to 20 or 25%.

Although some difficulty has been experienced in the use of this technique in the laboratory (such as emulsion formation) it appears that this approach is the most suitable for use on a large scale. The problems are not fundamental in nature but rather are those which are generally amenable to engineering solutions, and, in fact, may have already been solved by Hydrosiences, Inc.

It was found that an extraction medium of this type could be incorporated into a membrane consisting of a cellulose acetate gel supported by stainless steel screen. Membranes under investigation for some time and reported previously were prepared by dissolving 6% by weight of cellulose triacetate in acetic acid. The screen was then impregnated with this solution and immersed in water to gel the cellulose triacetate. The water was changed periodically to remove as much of the acetic acid as possible. The membrane was then checked for leaks, and when present they were plugged with more of the cellulose triacetate solution and re-equilibrated with water. The membrane was then exchanged with isopropanol to remove the water, then with Freon TF to remove the isopropanol. The final step was to equilibrate the membrane with Freon TF containing 10% by weight of trioctylphosphine oxide.

Membranes prepared in this way diffuse organic acids at approximately the same rate as would be expected for an equal thickness of the Freon-TOPO mixture itself and did not pass appreciable quantities of ionic species under osmotic pressures of 1100 pounds per square inch. It appears that for experimental purposes that this membrane extraction procedure will prove more useful than solvent extraction although for commercial purposes potential stability problems in the presence of base and anaerobic bacteria may limit the useful lifetime of the membrane to an extent which will make this approach unattractive economically.

More recently, another membrane system has been developed which appears to have potential on a commercial scale. It is a hollow fiber membrane device consisting of silicone rubber tubing swollen with Freon TF and soaked in a 20% TOPO in Freon solution. A membrane of this composition consisting of a 40 foot length of 3/8" i.d., 1/2" o.d. silicone rubber tubing is currently in operation with the lab/pilot fixed packed bed fermenter and is performing well.

In principle, a membrane of this type could be constructed from any polymeric, preferably partially crosslinked, tubing which may be swollen by a solvent for TOPO or which has a favorable partition coefficient for organic acids against water. These systems have the promise of being sufficiently resistance to alkali and biological attack as well as being sufficiently durable to mechanical fatigue to be suitable for use in a commercial process.

None of the processes described will remove acetic acid preferentially from a dilute organic acid mixture. Strong anion exchange resins will remove organic acids indiscriminately. Some selectivity for acetic acid may be obtained with weak ion exchange resins based on acid strength* but the difference in acid strengths of the product acids is small.

Extraction with organic solvents will generally remove higher acids in preference to lower ones because the partition coefficients of aliphatic organic acids are proportional to chain length, as expected.

A possible exception to this statement is trioctylphosphine oxide, which appears to remove organic acids relatively indiscriminately (see Section 6). However, this compound is a solid at mesophilic temperatures and has therefore been used in solution in organic solvents. The organic solvents used in this work, aliphatic and fluorinated hydrocarbons (selected on the basis of their compatibility with the fermentation process)

*This phenomenon is expected to favor acetic acid.

are solvents for organic acids themselves and therefore these systems remove higher acids preferentially. If TOPO were dissolved in a non-solvent for all of the product acids indiscriminate acid extraction may be obtained, but no such solvent comes immediately to mind. Other possibilities are to operate the extraction at elevated temperatures with pure TOPO, which should be compatible with thermophilic fermentations, to use a lower molecular weight phosphine oxide or a mixture of two phosphine oxides that are liquid at mesophilic temperatures.

The membrane processes investigated give the same selectivity as the extraction processes because they are driven by the same partition coefficients. In principal, however, it should be possible to construct a membrane which favors the lower acids based on higher diffusion coefficients of smaller molecules. However, as this effect is proportional to the cube root of molecular weight, the selectivity would be expected to be minor.

In summary, if acetic acid is the desired product it is best to run the fermentation to favor this product. The preferred conditions appear to be low acid concentrations and thermophilic operation. The preferred extraction method is to use one extraction which favors the higher acids followed by an indiscriminate extraction. The product of the second extraction may then be distilled to yield glacial acetic acid. The product of the first extraction may be:

1. Fractionally distilled to give higher organic acids.
2. Electrolyzed to give olefins or aliphatic hydrocarbons.
3. Fed back into the digester where they may be converted to additional acetic acid.

Section 6

FIXED PACKED BED FERMENTATIONS

The lab/pilot fixed packed bed fermenter was loaded with 20.6 lbs. unshredded Chondrus crispus, 0.2 lbs. sewage sludge solids, and 296 liters of water. Five days later the products were tabulated, and a comparison was made between the amount of carbon dioxide produced and the amount expected based on the other products produced. The organic acids found in the fermenter are shown in Table 6.1. Those found in the extractor are shown in Table 6.2. It is interesting to note from these data that the ratios of acid concentration in the extractor to the acid concentration in the fermenter appear to obey a relationship of the form:

$$\frac{C_E}{C_F} = aK + b \quad 6.1$$

where K is the partition coefficient between water and Freon TF as presented in Table 6.3 and a and b are constants. Values of $a = 1$ and $b = 0.1$ give calculated values of C_E/C_F quite close to the observed values, at least for the lower acids, as shown in Table 6.4. An extraction medium consisting of a mixture of two materials acting independently would be expected to obey a relationship of the form:

$$C_E/C_F = aK_1 + bK_2 \quad 6.2$$

where K_1 and K_2 are the partition coefficients of the two materials against water. The attempt to fit the data to an equation of the form of 6.1 suggests that K_2 is the same for all of the acids, that is to say, TOPO removes acids indiscriminately. Deviations from 6.1 for the higher acids suggests that K_2 may vary inversely with acid length. Further data will be required to clear up this point. Table 6.5 presents the gaseous products from Run No. 00354. In addition 2.8 gram moles or 0.25 lbs. of carbon dioxide were removed by the extractor. From these data the degree of conversion for the first five days of this experiment may be calculated as follows:

Table 6.1

Organic Acid Composition Run No. 00437 - Fermenter

<u>Acid</u>	<u>Concentration</u>	<u>Amount</u>	
		<u>Weight</u>	<u>g. Moles</u>
Acetic	30.5 meq/l	1.2 lbs.	9.0
Propionic	10 meq/l	0.5 lbs.	3.0
Butyric	20 meq/l	1.1 lbs.	6.0
Valeric	2 meq/l	0.1 lbs.	0.6
Caproic	<u>1.5 meq/l</u>	<u>0.1 lbs.</u>	<u>0.5</u>
Total	64.0 meq/l	3.0 lbs.	19.1 g. Moles

Table 6.2

Organic Acid Composition Run No. 00437 - Extractor

Acid	Concentration	Amount	
		<u>Weight</u>	<u>g. Moles</u>
Acetic	3 meq/l	0.003 lbs.	0.02
Propionic	2 meq/l	0.002 lbs.	0.01
Butyric	22.5 meq/l	0.027 lbs.	0.14
Valeric	2.5 meq/l	0.004 lbs.	0.02
Caproic	<u>3 meq/l</u>	<u>0.005 lbs.</u>	<u>0.02</u>
Total	33 meq/l	0.041 lbs.	0.21 g. Moles

Table 6.3
Partition Coefficients of Acetic, Propionic,
Butyric, and Valeric Acids with Freon TF

<u>Acid</u>	<u>Initial Conc.</u>	<u>Final Conc.</u>	$P = \frac{CI - CF}{CI} * \frac{\text{Concentration in Freon}}{\text{Concentration in Water}}$
Acetic	0.173 M/	0.173 M/	0
Propionic	0.134 M/	0.128 M/	0.047
Butyric	0.110 M/	0.079 M/	0.0392
Valeric	0.093 M/	0.031 M/	2.00

where: P = partition coefficient
 CI = concentration in water
 CF = concentration in Freon

Table 6.4
Comparison of Calculated and Observed Ratios
Of CE/CF* Run No. 00437

<u>Acid</u>	<u>CE</u>	<u>CF</u>	<u>CE/CF Observed</u>	<u>CE/CF Calculated</u>
Acetic	3 meq/l	30.5 meq/l	0.098	0.1
Propionic	2 meq/l	10 meq/l	0.20	0.19
Butyric	22.5 meq/l	20 meq/l	1.13	0.88
Valeric	2.5 meq/l	2 meq/l	1.25	4.1
Caproic	3 meq/l	1.5 meq/l	2.00	>4.1

*CE = Concentration in extractor
CF = Concentration in fermenter

Table 6.5

Gaseous Products - Run. No. 00437

<u>Gas</u>	<u>Volume (STP)</u>	<u>g. Moles</u>	<u>Weight</u>
Hydrogen	4.8 ft. ³	6.1	0.03 lbs.
Methane	5.4 ft. ³	6.8	0.2 lbs.
Carbon Dioxide	<u>12.4 ft.³</u>	15.7	<u>1.5 lbs.</u>
Total	22.6 ft. ³		1.7 lbs.

$$\% \text{ Conversion} = \frac{\text{Total Products}}{\text{Total Reactants}} = \frac{3.0 \text{ lbs.} + 0.04 + 1.7 + 0.25}{20.8} = 25\% \quad 6.3$$

In addition, an oxidation-reduction balance may be made for the fermentation. Since carbon dioxide is the only oxidized product relative to the hexose starting material (acetic acid is in the same oxidation state as hexose), the quantity of carbon dioxide produced should correlate with the amount of reduced products formed on a reducing equivalent basis. Table 6.6 presents these results. The total amount of carbon dioxide expected based on the amounts of other products formed is 19.3 gram moles. The amount actually obtained was 15.7 gram moles removed as a gas and 2.8 gram moles removed by the extractor or a total of 18.5 moles for a 96% recovery.

Table 6.6

Carbon Dioxide Production - Run No. 00354

Source	Quantity	Stoichiometry	Ratio	Moles CO ₂
Hydrogen	6.1 moles	$C_6H_{12}O_6 \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$	1:2	3.1
Methane	6.8 moles	$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$	1:1	6.8
Propionic	3.0 moles	$7 CH_3COOH \rightarrow 4 CH_3CH_2COOH + 2CO_2 + 2H_2O$	1:2	1.5
Butyric	6.0 moles	$5 CH_3COOH \rightarrow 2 CH_3(CH_2)_2COOH + 2CO_2 + 2H_2O$	1:1	6.0
Valeric	0.6 moles	$13 CH_3COOH \rightarrow 4 CH_3(CH_2)_3COOH + 6CO_2 + 6H_2O$	3:2	0.9
Caproic	0.5 moles	$4 CH_3COOH \rightarrow CH_3(CH_2)_4COOH + 2CO_2 + 2H_2O$	2:1	1.0
Total				19.3 Moles

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