340

4-25-78

LH. 2042

HCP/T4388-02

Acetic Acid Production from Marine Algae

Progress Report No. 2

MASTER

Period Covered - September 30 to
December 31, 1977

March 1978

Prepared For

U.S. Department of Energy

Assistant Secretary for Energy Technology

Division of Solar Technology

Under Contract No. EG-77-C-02-4388-2

*Dynatech Corp.
Cambridge, MA*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report was prepared by Dynatech R/D Company as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Acetic Acid Production from Marine Algae

Progress Report No. 2

Period Covered - September 30 to
December 31., 1977

March 1978

Prepared For
U.S. Department of Energy
Assistant Secretary for Energy Technology
Division of Solar Technology

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1	SUMMARY	1
2	INTRODUCTION	3
3.	BIOMASS EVALUATION	6
	3.1 Introduction	6
	3.2 Static Fermentations	7
4	FIXED PACKED BED FERMENTATIONS	24
	4.1 Study of Extraction Methods	24
	4.2 Large Fixed Packed Bed Fermenter	28
5	PROGRAM FOR THE THIRD QUARTER	31
6	REFERENCES	32

Section 1

SUMMARY

The acetic acid production from Marine Algae program has had three goals.

1. To develop an economically competitive process for producing acetic acid from biomass for the purpose of sparing petroleum for other uses.
2. To evaluate marine algae as a potential source of biomass.
3. To document the feasibility of running fermentations in fixed packed bed fermenters.

Recently, an additional goal has been added to the program:

4. To determine the feasibility of producing liquid fuels from dilute solutions of organic acids, such as are produced by anaerobic fermentation.

Preliminary results on the production of acetic acid from marine algae by anaerobic fermentation indicates that the rate is quite fast. First order rate constants of 0.77 day^{-1} have been observed. This rate constant gives a half-life of less than one day. In other words, with a properly designed product removal system a five day retention time would yield 98% of theoretical conversion. Determination of the theoretical conversion of marine algae to acetic acid is the subject of much experimentation. The production of one acetic acid molecule (or equivalent in higher organic acids) for each three carbon atoms in the substrate has been achieved; but it is possible that with a mixed culture more than one acetic acid molecule may be produced for each three carbons in the substrate. Work is continuing to improve the yield of acetic acid from marine algae.

Marine algae has been found to be rather low in carbon, but the carbon appears to be readily available for fermentation. It, therefore, lends itself to the production of higher value chemicals in relatively expensive equipment, where the rapid conversion rate is particularly cost effective.

Fixed packed bed fermenters appear to be desirable for the production of liquid products which are inhibitory to the fermentation from coarse substrates. The inhibitory products may be removed from the fermentation by extraction during recirculation. This technique lends itself to either conventional processing or low capital processing of substrates which require long retention times.

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 reaction for conversion of a hexose to acetic acid may be represented as:

However, it has been demonstrated that certain anaerobic bacteria (e.g., *Clostridium Thermoaceticum*) convert hexose to acetic acid according to the reaction:

It is also known that anaerobic bacteria exist which convert CO_2 and hydrogen to methane:

and that acetic acid can be detected in the liquid phase. It has not been demonstrated that acetic acid is an intermediate in this reaction, but it is likely. It is, therefore, likely that even with a mixed culture of bacterial anaerobes that more than two acetic acid molecules will be

obtained from each hexose molecule, and percent yields are calculated based on three acetic acid molecules/hexose as 100%.

It was anticipated that since acetic acid is an intermediate in methane formation that its rate of production would be greater than or equal to methane formation. This anticipation has been borne out by initial experiments, which will be discussed in more detail later.

It was also anticipated that because of its higher yield and selling price on a weight basis that distinct economic advantages are available to acetic acid production over methane production provided relatively inexpensive isolation techniques could be employed. A comparison of results to date with the economic assumptions made in the previous quarterly report is presented.

Marine algae (seaweed) is a very interesting form of biomass. In addition to having high yields per acre of otherwise relatively unproductive area, their organic matter consists largely of water-soluble polysaccharides instead of the cellulose of land-based biomass. In fact, Chondrus Crispus a red alga contains only 2% cellulose. These polysaccharides should be readily available to the required hydrolytic enzymes if present. It is thought that cellulose hydrolysis is the rate-limiting step in fermentation or digestion of land-based biomass. It is, therefore, likely that improved rates may be obtained from marine algae over land-based biomass.

Another point to consider is the absence of lignin in marine algae. Lignin in land-based biomass impedes cellulose hydrolysis as well as being refractory to these processes itself.

Some of the negative aspects of marine algae as biomass are that many have high ash contents, which make disposal a chore as well as may effect bacterial action because of hypertonicity. The biggest negative aspect is that no estimate of the production cost of marine algae is currently available.

The species of marine algae selected for initial study is Chondrus Crispus, a red ~~alg~~ae of commercial interest because of its carrageenan content. Carrageenan is a sulfonated polygalactose which is used commercially as a thickening agent. The primary advantage of Chondrus Crispus (Irish moss) over other marine algae species is that it is available in commercial quantities on the East Coast.

In the current quarter some preliminary studies have been run with two other marine algal species, Gracilaria, another red algae, and Ulva Lactuca, a green algae, and with Hydrilla, a fresh water weed which grows wild in inland waters in the southeastern part of the United States. All of these species exhibit higher growth rates than Chondrus Crispus.

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:

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

where A. P. B. and V are the measured concentrations of Acetic, Propionic, Butyric, and Valeric 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

*In the first quarterly report conversions were determined on a volatile solids basis.

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

The initial fermentations in unstirred reactors (results presented in Progress Report No. 1) were run using 10% or more sewage sludge as an inoculum. Although conversions as high as 24% (based on total solids) were observed, it is not clear how many reducing equivalents obtained were from the sludge. Subsequent experiments were run with less than 2% sewage sludge and more often with only effluent from another fermenter as inoculum.

One exception to this statement is the operation of a 50 liter continuous stirred tank reactor (CSTR) which was fed equal amounts of Chondrus Crispus and sewage sludge. The reducing equivalents from the sludge were accounted for by running a control digester which was fed only sewage sludge. This experiment was run to determine the total available reducing

Table 3.1
ELEMENTAL ANALYSES

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

Table 3.2

ESTIMATED CONVERSION PERCENTAGES

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

equivalents in Chondrus Crispus via conversion to methane. The results of this experiment, run on a 28 day retention time at 37°C, are shown in Figure 3.1. The methane production in excess of the control represents a 14% conversion based on total solids. Subsequently, methane production dropped to insignificant levels. The gaseous product was found at this time to contain 2.1% hydrogen sulfide. Hydrogen sulfide fermentation has been observed previously in the anaerobic digestion of marine algal species containing sulfonated polysaccharides.¹ Hydrogen sulfide production has not been observed in acetic acid fermentation of these species.

The results of fermentation of Chondrus Crispus and the other aquatic biomass materials mentioned previously in static reactors have generally exceeded the 14% conversion obtained in the digestion experiment, although to date none of the fermentations have been shown unequivocally to have gone to completion. The primary impediment is the product inhibition of the process. The results of a successful experiment are presented in Table 3.3 and in Figure 3.2. This experiment was run using 13.5% Gracilaria and 1.5% effluent from the Chondrus Crispus digester. The final conversion was 22% based on the Gracilaria solids or 20% based on total solids. The first order rate constant for this conversion is 0.62 day⁻¹, comparable to the 0.77 day⁻¹ reported in the first quarter for Chondrus Crispus. These rate constants give a half life for acid production on the order of 1 day provided acid can be removed as fast as it is formed. Development of a process for rapid acid removal will be discussed later.

Fermentations in static reactors using calcium carbonate as a buffer have provided substantially higher conversions. Table 3.4-3.7 present the results for Chondrus Crispus, Hydrilla, Ulva Lactuca, and Gracilaria, respectively, buffered with 10 g/l CaCO₃ at 5% total solids using 2% inoculum, either sewage sludge or digester effluent. In the case of the marine algal species the minimum conversions presented in Table 3.2 have been exceeded.

Figure 3.1
CSTR DIGESTION OF CHONDRUS CRISPUS

Key: ■ Digestor #9 (Chondrus)
 ○ Digestor #2 (Control)

Table 3.3

Run #30517-4. 15% Solids, 90% Gracilaria/10% Digester Effluent

<u>Time</u>	<u>Acetic</u>	<u>Propionic</u>	<u>Butyric</u>	<u>Valeric</u>	<u>Total</u>	<u>Red. Eq.</u>	<u>% Conv.</u>
0 Hrs.	2	1.5	.5	0	4	6	
3 Hrs.	2	1.5	.5	0	4	6	
20 Hrs.	32.5	7	9.5	.5	49.5	70	
27 Hrs.	69.5	10	11.5	1	92	119	
48 Hrs.	110	15.5	20.5	2	148	195	
72 Hrs.	134.5	17	23	2	176.5	228	
130 Hrs.	162.5	19	29	5	215.5	285	
205 Hrs.	237	26	40	7	310	405	
274 Hrs.	173	20	43	3	239	325	
346 Hrs.	240	26.5	54	4.5	325	436	
514 Hrs.	232	22	68	0	322	440.5	
682 Hrs.	285	18	60	1.0	373	499	20% ¹ 22% ²

(1) on total solids including digester effluent

(2) on Gracilaria total solids

Figure 3.2

Table 3.4

RUN #31168-B, 98% Chondrus Crispus, 1% Sewage Sludge, 1% Digester Effluent

			A	P	B	V	T	A/T	R	%C
0 Hrs.	12/22	3:30	0	0	0	0	0	0	0	0
	12/23		15	3	0	0	18	83%	20	2.4%
	12/24									
	12/25	10:30	27.5	10.5	8.5	0	46.5	59%	67	8.0%
	12/26		35	26	18	0	79	44%	125.5	15.0%
	12/27	10:00	40	26	17.5	0	73.5	54%	129	15.5%
	1/3		40	19	16	3	78	51%	123	14.7%
	1/9	11:30	101	45	30	5	181	56%	271	32.5%
	1/16	2:00	131	45.5	27.5	6	210	62%	299	35.8%
	1/23	2:00	71	24.5	17.5	2	115	62%	164	19.7%
	1/30	3:30	40	30	23	12	106	38%	193	23.1%

Table 3.5

RUN #31170-3; 5% T.S., 98% Hydrilla, 2% Sewage Sludge, 1g/100 ml CaCO_3

			A	P	B	V	T	A/T	R	C
0 Hrs.	12/28	9:30	5	0	0	0	5	100%	5	0.60%
	12/29		29	15	4	~0	48	60%	65	7.8%
	12/30		17	8	3	0	28	61%	38.5	4.6%
	12/31		52	23	11	3	89	58%	129.5	15.5%
	1/1		48	10	6	4	64.5	74%	82	9.8%
	1/2		72.5	20	13	5	110.5	66%	156	18.7%
	1/3		80.5	27.5	22	4.5	134.5	60%	198	23%
	1/4		62.5	20	18.5	6.5	107.5	58%	165	19.8%
	1/9	11:30	100	35	23	6	164	51%	238	28.6%
	1/23	2:00	66	37	18	12	133	50%	215	25.8%
	1/30	3:30	25	32.5	15.5	10	83.5	30%	155	18.6%

Table 3.6

RUN #31170-4; 5% T.S., 98% *Ulva Lactuca*, 2% Sewage Sludge, 1 g/100 ml CaCO_3

			A	P	B	V	T	A/T	R	C
0 Hrs.	12/28	9:30	3	0	0	0	3	100%	3	0.36%
	12/29		4	2.5	~0	~0	6.5	62%	8	1.0%
	12/30		~0	<1	<1	<1	~1.5	0%	4	0.45%
	12/31		10	7	<1	<0	~17.5	57%	23.5	2.8%
	1/1		12	9	~0	~0	21	57%	28	3.3%
	1/2		0	0	0	0	0	0%	0	0
	1/3		33	20	1.5	0	54.5	61%	72	8.6%
	1/4		53	27	1.5	0	81.5	65%	104	12.5%
	1/9	11:30	95	57.5	12	0	164.5	58%	226	27.0%
	1/23	2:00	104	65	24	10.5	203.5	51%	312	37.4%
	1/30	3:30	91.5	58	15	1.5	166	55%	235	28.3%

Table 3.7

RUN #31170-5; 5% T.S., 98% Gracilaria, 2% Sewage Sludge, 1 g/100 ml CaCO_3

			A	P	B	V	T	A/T	R	C
0 Hrs.	12/28	9:30	0	0	0	0	0	0	0	0
	12/29		13	6	2	~0	21	62%	28.5	3.4%
	12/30		35.5	9	10	~0	54.5	65%	76	9.1%
	12/31		35	15	9	<1	59.5	59%	85	10.2%
	1/1		43	11	12	<1	66.5	65%	94	11.3%
	1/2		28	14	8.5	0	50.5	55%	74	8.85%
	1/3		83	17	12	0	112	74%	143	17.1%
	1/4		38	4	4	0	46	83%	55	6.60%
	1/9	11:30	107	18	20	~1	146	73%	192	23.0%
	1/16	2:00	112	26	21	0	159	70%	210	25.2%
	1/23		152.5	27	33.5	10.5	223.5	68%	318	38.1%
	1/30	3:30	120	19.5	30.5	7	177	68%	253	30.4%

It is interesting to note that once maximum conversion is reached, the total reducing equivalents tend to decrease with time. In the tables just presented this phenomenon is quite pronounced, but these do not represent the worst case. The worst case is the 5% solids static fermenter containing 99% Hydrilla and 1% digester effluent, unbuffered presented in Table 3.8. The conversion, after peaking at 18% after seven days drops to approximately 1% after 60 days. This phenomenon has happened sufficiently often that it is unlikely that its cause is artifactual. Two possible causes currently under investigation are:

1. Methane formation.
2. Formation of acids higher than caproic, which do not elute from the gas chromatography column in the time of the analysis.

The fear of methane formation from the flasks buffered with calcium carbonate motivated an additional set of experiments. These were run using phosphoric acid or calcium carbonate addition initially and at the time of sampling to control the pH between 5.5 and 6.0. This pH range should favor acid production over methane production. The results to date are presented in Tables 3.9 - 3.12. In each case to date conversion has exceeded 24% based on total solids and in the case of Chondrus Crispus and Gracilaria the minimum conversion levels have been exceeded and the maximum theoretical conversion levels have been approached.

Table 3.8

RUN #31147-5 (Hydrilla 5%; 99:1)

0 Hrs.		A	P	B	V	T	A/T	R	C
	12/1	8.5	4	1.5	3	17	50.00%	29	3.5%
	12/2 4:00	35.5	6	7	5	53.5	66.36%	80	9.6%
	12/3	22	2	5.5	1	30	73%	40	4.8%
	12/4	38	3	12	1	54	70.37%	76.5	9.2%
	12/5 9:30	40	5	14	2.5	61.5	65.04%	92	11.1%
	12/6 11:00	56	5.5	18	4	83.5	67.07%	124	14.9%
	12/7 2:00	58	3	12	1	74	78.38%	96.5	11.6%
	12/8 2:00	53	8.5	26.5	6	94	56.38%	154.	18.5%
	12/19 11:30	52.5	4.5	13	1	71	74%	96	11.5%
	1/9 11:30	5.5	12.5	0	1	19	29%	31	3.68%
	1/23 2:00	13	10.5	0	0	23.5	55%	31	3.77%
	1/30 3:30	5	2.5	0	0	7.5	67%	9	1.13%

Table 3.9

RUN #00354-1; 5% Buffered Chondrus

0 Hrs.			A	P	B	V	Other	T	A/T	R	C
			0	0	0	0	0	0	0	0	0
	1/11	1:30									
	1/12	9:00	25	10.5	6	0	0	41.5	60%	58	7.0%
	1/13	9:30	14.5	8.5	7.5	6	0	36.5	40%	684.5	8.1%
	1/16	9:15	29	4	17.5	3	0	53.5	54%	89.5	10.7%
	1/17	9:00	33	14.5	24	15	1	87.5	38%	171	20.5%
	1/18	9:15	25.5	8	20	6.5	0	60	43%	111	13.3%
	1/19	11:30	28	7	27.5	4	5	71.5	39%	142	17.0%
	1/23	2:00	70	15	26	5	0	116	60%	177.5	21.3%
	1/30	3:30	46	8.5	13	6	30	103.5	44%	233	27.9%
	2/6	9:00	45	6	28	4	31	114	39%	262.5	31.5%
	2/13	12:15	68	9	29.5	6.5	32.5	145.5	47%	309	37.0%
	2/21	1:45	51	7	24	4	13	99	52%	188	23%
	2/27	10:45	124	25	33.5	3	3	188.5	66%	273	33%
	3/6	10:30	53	7	25.5	5.5	25.5	116.5	45%	249	30%

Table 3.10

RUN #00355-5; 5% Buffered Hydrilla

			A	P	B	V	Other	T	A/T	R	C
0 Hrs.	1/11	1:30	<1	<1	0	0	0	~1	50%	~1	0.16%
	1/13	9:30	22.5	21	7	2	0	52.5	43%	83	10%
	1/16	9:15	73	50	14.5	12	0	149.5	49%	236	28%
	1/17	9:00	49	33	8	7	0	97	51%	149.5	18%
	1/18	9:15	54	36	8	4	0	102	53%	150	18%
	1/19	11:30	56	38	5.5	4	0	103.5	54%	149	18%
	1/23	2:00	97.5	53	27	12.5	0	190	51%	298	36%
	1/30	3:30	96	30	19	9.5	0	154.5	62%	227	27%
	2/6	9:00	127	76	24.5	11	0	238.5	53%	357	43%
	2/13	12:15	89.5	59.5	13	6	0	168	53%	246	29%
	2/21	1:45	5	64.5	13	7	0	89.5	6%	173	21%
	2/27	10:45	21	65.5	7	1.5	221	95	22%	158	19%
	3/6	10:30	14	70	0	.5	00	84.5	17%	138	17%

Table 3.11

RUN #00354-4; 5% Buffered Ulva

			A	P	B	V	Other	T	A/T	R	C
0 Hrs.	1/11	1:30									
	1/13	9:30	5	2.5	2	<1	0	10	50%	16	1.9%
	1/16	9:15	16	8	1	<1	<<1	25.5	63%	34.5	4.1%
	1/17	9:00	13	13	2	1	<1	29.5	44%	46	5.5%
	1/18	9:15	12.5	13	2.5	<1	<<1	28.5	44%	44	5.3%
	1/19	11:30	25	10	1.5	1.5	1	39	64%	55	6.6%
	1/23	2:00	144	47	16	5.5	0	212.5	68%	284	34.1%
	1/30	3:30	40	15	3	2	2.5	62.5	64%	90	10.8%
	2/6	9:00	70	19	10	~0	2	101	69%	136	16.4%
	2/13	12:15	98	30.5	12	0	3	143.5	68%	193	23.2%
	2/21	1:45	112	30	11.5	<<1	2	155.5	72%	201	24.12%
	2/27	10:45	65	25.5	10	<.5	0	101	64%	136	16%
	3/6	10:30	75	26	6.5	0	0	107.5	70%	137	16%

Table 3.12

RUN #00354-3; 5% Gracilaria; buffered

			A	P	B	V	Other	T	A/T	R	C
0 Hrs.	1/11	1:30	<1	<1	0	<1	0	1.5	33%	3	0.36%
	1/12	9:00	37.5	9	7	0	0	53.5	70%	71	8.5%
	1/13	9:30	15	9.5	2	0	0	26.5	57%	37	4.4%
	1/16	9:15	65	19	10.5	1	0	95.5	68%	128	15.3%
	1/17	9:00	46	12.5	10	3	0	71.5	64%	103	12.3%
	1/18	9:15	45	14	13.5	2	0	74.5	60%	110	13.2%
	1/19	11:30	39.5	5	8	<<1	0	52.5	75%	68	8.19%
	1/23	2:00	55	12	9	0	0	76	72%	98.5	11.8%
	1/30	3:30	72.5	17.5	29.5	2	~.5	122	59%	185	22.3%
	2/6	9:00	114	20	31	7	0	172	66%	249	29.9%
	2/13	12:15	80	9.5	12.5	<<1	0	102	78%	128	15.4%
	2/21	1:45	182.5	31	47	4	<<1	264.5	69%	367.5	44.1%
	2/27	10:45	59.5	7	34.5	7.5	37	145.5	41%	330	40%
	3/6	10:30	94.5	15	15.5	0.5	0	125.5	75%	161	19%

Section 4

FIXED PACKED BED FERMENTATIONS

4.1 Study of Extraction Methods

Fixed packed bed fermentations have been run to evaluate techniques for removing the acidic products as they are formed. Table 4.1 lists some of the extraction methods that may be used for this purpose. Of these ion exchange with conventional elution, solvent extraction with recovery by re-extraction, and hydrogel membrane processes have been investigated.

The use of a conventional strong anion exchange resin with quarternary ammonium sites may have use as an acid removal technique for experimental purposes. The hydroxylated resin is inserted in the recirculation loop of the fixed packed bed reactor as in Figure 4.1. 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.

For experimental purposes it is sometimes convenient to elute the spent resin with alkali, then neutralize the eluent with mineral acid. In either case, however, one equivalent of mineral acid and more than one equivalent of alkali has been 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.

Table 4.1

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. Hydrogels

b. Electrodialysis

Figure 4.1
Continuous Flow Packed Bed Fermenter

Use of strong anion exchange resin with conventional elution is economically noncompetitive because other methods of extraction require only one equivalent of alkali although the use of weak anion exchange resins may be satisfactory and will be investigated.

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 1833.²

Ethyl acetate, along with diethyl ether, continued to be the most efficient extraction medium at low acid concentrations³ 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.⁴

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 currently under investigation were prepared by dissolving 6% by weight of cellulose triacetate in acetic acid. The screen is then impregnated with this solution and immersed in water to gel the cellulose triacetate. The water is changed periodically to remove as much of the acetic acid as possible. The membrane is then checked for leaks, and if any are present they are plugged with more of the cellulose triacetate solution and re-equilibrated with water. The membrane is then exchanged with isopropanol to remove the water, then with Freon TF to remove the isopropanol. The first step is to equilibrate the membrane with Freon TF containing 10% by weight of trioctylphosphine oxides.

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 does 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 to be 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.

4.2 Large Fixed Packed Bed Reactor

Until recently fixed packed bed fermentations were run in columns 3" in diameter and 4' long. Construction of a larger fixed packed bed fermenter has recently been completed. It is constructed of 12" diameter glass tubing and is 15' in height (see Figure 4.2). It is supported by a triangular framework of 1-1/4" pipe and is enclosed with plywood and plexiglass. The temperature is controlled at 100°F by circulating warm air inside the enclosure. A flow rate of 3 gallons per hour

Figure 4.2
Large Fixed Packed Bed Fermenter

is sufficient to fluidize the Chondrus Crispus initially at 10% solids in the reactor to reduce the operating pressure at the pump (approximately 7 feet below the top of the column) to 3 PSIG. Installation of a 1.2 ft² membrane extraction system for use with this reactor will be complete shortly.

Section 5

PROGRAM FOR THE THIRD QUARTER

1. Static Reactor Experiments

Current static reactor experiments will be continued until no more acids are produced. Residues will be analyzed for volatile solids in order to close mass balances.

2. Development of an Acid Removal System

Work will continue to optimize acid removal systems now under investigation for experimental purposes.

3. Operation of the Large Fixed Packed Bed Fermenters

The large fixed packed bed fermenter will be operated with continuous acid removal in order to minimize residence time in the fermenter.

4. Process Economics

The process economics presented in progress report #1 will be expanded to include isolation and purification and will be updated in the light of recent experimental results affecting yields and rates.

REFERENCES

1. Augenstein, D.C., "Production of Nutrient Material for Cultivation of Aquatic Biomass." Dynatech Progress Report No. 1686, prepared for Woods Hole Oceanographic Institute, March 16, 1977.
2. Jones, E.L., Chem. & Ind., 1590 (1967).
3. Brown, W.V., Chem. Eng. Progr. 59 10 (1963).
4. Helsel, R.W., Chem. Eng. Progr., (1977).

* U. S. GOVERNMENT PRINTING OFFICE : 1978 261-325/511