LIQUID FUELS PRODUCTION
FROM BIOMASS

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Section 1

SUMMARY

The current program to convert biomass into liquid hydrocarbon fuels is an extension of the previous program to ferment marine algae to acetic acid. In that study, it was found that marine algae could be converted to higher aliphatic organic acids and that these acids could be readily removed from the fermentation both by membrane or liquid-liquid extraction. It was then proposed to convert these higher organic acids to aliphatic hydrocarbons via Kolbe Electrolysis, which may be used as a diesel fuel.

The specific goals for the current program are:

1. Establish conditions under which substrates other than marine algae may be converted in good yield to organic acids. The primary task in this regard is methane suppression.
2. Modify the current 300 liter fixed packed bed batch fermenter to operate in a continuous mode.
3. Change from membrane extraction of organic acids to liquid-liquid extraction.
4. Optimize the energy balance of the electrolytic oxidation process. The primary task in this regard is to reduce the working potential required for the electrolysis while maintaining an adequate current density.
5. Scale the entire process up to match the output of the 300 liter fermenter.

The accomplishments in this program are on schedule. Substantial progress has been made on the problem of methane suppression through the use of sulfide addition and the identification of bromoethane-sulfonic acid as a specific inhibitor of methanogenesis. A conceptual design of a continuously fed fixed packed bed fermenter is presented. Experimental results show that the electrolysis of organic acids produced by fermentation to liquid hydrocarbon fuels already have a favorable energy balance of 6/1 based on the applied potential and over 10/1 based on the working potential.

Section 2

INTRODUCTION

As an extension of the work on anaerobic fermentation of biomass to organic acids undertaken previously under DOE sponsorship, a program for the production of liquid hydrocarbon fuels from biomass was initiated. The process, as presented in Figure 2.1, consists of non-sterile anaerobic fermentation of the biomass to mixed organic acids, extraction of the higher organic acids (primarily butyric, valeric, and caproic acids) and electrolytic oxidation (Kolbe Electrolysis) of these acids to aliphatic hydrocarbons, primarily hexane, heptane, octane, nonane, and decane. The fermentation process to convert marine algae to organic acids was developed in the previous program, giving rapid rates and high conversion yields (Ref. 1) However, in the course of this work, it was found that when other substrates were used methane formation was a serious competitive process. Work in the current program in the fermentation area is concentrated on the suppression of methane so that the fermentation process can be broadened to include other sources of biomass, particularly fresh water aquatic weeds and agricultural residues.

Removal of the product acids is currently being accomplished using the membrane separation process described previously (Ref. 2). Briefly, the process uses a silicone rubber membrane swollen with Freon TF. It is anticipated that for production of aliphatic hydrocarbons a liquid-liquid extraction procedure using the product aliphatic hydrocarbons as the water immiscible phase will be most suitable. Ultimately, the acids are extracted from the water immiscible phase into aqueous sodium hydroxide. The products in this form may be then electrolytically oxidized to the aliphatic hydrocarbon product, regenerating the sodium hydroxide in the process. The cathode product in the electrolytic oxidation is hydrogen. The hydrogen

Figure 2.1

Process to Produce Liquid Hydrocarbon Fuels from Biomass

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gas is a valuable co-product in itself or may be used to generate part or all of the electricity required for the electrolysis. As side products in the electrolysis, C_2-C_5 olefins are produced. These are also valuable products with large markets.

In short, the overall process under development may be expressed:

In order to maximize the efficiency of this process, it is necessary to minimize the amount of reactants used and to maximize the amount of valuable products produced. To accomplish this goal, it is necessary to:

1. Maximize the conversion of biomass to organic acids.
2. Minimize the electric power (IV) required in the electrolysis. Since the valuable products produced, paraffins, olefins, and hydrogen are stoichiometrically related to the current (I), then minimization of the electric power requirements is equivalent to minimizing the voltage (V) required for the electrolysis.

The specific goals for the current project are:

1. Establish conditions under which substrates other than marine algae may be converted in good yield to organic acids. The primary task in this regard is methanol suppression.
2. Modify the current 300 liter fixed packed bed batch fermenter to operate in a continuous mode.
3. Change from membrane extraction of organic acids to liquid-liquid extraction.

4. Optimize the energy balance of the electrolytic oxidation process.
The primary task in this regard is to reduce the working potential required for the electrolysis while maintaining an adequate current density.
5. Scale the entire process up to match the output of the 300 liter fermenter.

Section 3

METHANE SUPPRESSION

Suppression of methane formation is a task which received only a minor amount of attention in the previous program since methane formation is relatively unimportant in the mesophilic fermentation of Chondrus crispus, the primary substrate in that study. Results have also shown that methane formation during mesophilic fermentation of Gracilaria and Ulva lactuca at pH 5.5-6.0 is somewhat more prevalent, but still not a serious problem. However, methane formation under these conditions is a serious problem when Hydrilla, a freshwater aquatic plant, is fermented. Figure 3.1 presents the results of one such fermentation. From these data it is seen that the total acid peaks and then declines, with the decline of acetic acid most important.

Additional fermentations using rice straw as the substrate gave similar results. Results of one such fermentation are presented in Table 3.1. Methane production was observed beginning on day 13. On day 20, the organic acid concentration peaked. It appears that methane formation is a serious competing reaction even at pH 5.5-6.0 with many, if not all, biomass substrates where cellulose is the primary fermentable material.

A series of experiments were performed in which Hydrilla was fermented at pH 5.0-5.5. Table 3.2 presents the data (plotted in Figure 3.1) from a pH 5.5-6.0 Hydrilla fermentation. Table 3.3 presents the data from a subsequent Hydrilla fermentation using effluent from the aforementioned fermentation as inoculum. This fermentation was run at a pH of 5.0-5.5. Conversion to acids never exceeded about 20%, and methane production began in earnest after about two weeks. It appears that low pH is no panacea for methane suppression.

Another approach to methane suppression, which appears more promising, is the addition of sulfide to the fermentation broth. Run No. 02740 (Table 3.4) was set up using Hydrilla as substrate and secondary sewage sludge as inoculum with the addition of sodium sulfide at a 1% solids level. This fermentation was the fastest Hydrilla fermentation to date using a sewage inoculum and went to about 38% conversion in four weeks time. Shortly thereafter, methane formation was observed in substantial quantities. On the 57th day, an additional 1% sodium sulfide was added, whereupon methane formation ceased. However, acid formation has not yet resumed. One explanation for the observed results is that sulfide is effective in suppressing methane formation but the sulfide is lost as H_2S over a period of time at pH 5.5-6.0. This experiment will be continued in order to test this hypothesis.

Another approach to methane suppression is the use of bromoethane sulfonic acid, which is reputed to be a specific inhibitor for methanogenesis.* This material is on order and will be tested as soon as it arrives. In summary, it is anticipated that the methane suppression problem is close to solution.

*Professor Gregory Zeikus, Private Communication.

Figure 3.1

Acid Production Vs. Time
 Expt. # 01185-D - Hydrilla
 5% Solids - 37°C
 Inoculum - Effluent from 00354-1

● Total Reducing Equivalents
 ○ Acetic

Reducing
 Equivalents
 (in eq./l)

% Conversion
 (based on Total
 Solids)

Table 3.1

ORGANIC ACID CONCENTRATION VS. TIME
 Expt. #02725 - 5% Rice Straw - 37°C - pH 5.5-6.0
 Inoculum - Sewage Sludge

Time, Day	% CH ₄	A	P	B	V	C	T	A/T	R	%C
1		12	5	0	0	0	17	71%	21	2%
2		8.5	2.5	2	0	0	13	65%	18	2%
3		11	3	1.5	0	0	16	71%	20	2%
6	0%	23	7.5	6.5	7	0	44	52%	75	9%
8		20.5	7	4.5	3.5	0	36	58%	55	7%
10	0%	20.5	7	3.5	1.5	0	33	63%	46	6%
13	37%	32	12	6	2	.5	53	61%	77	9%
20	36%	47	16	10	1.5	2	77	61%	113	14%
27	65%	21	12.5	7.5	3.5	1	46	46%	77	9%
34	55%	8.5	18.5	6.5	5	1.5	40	21%	79	10%
41	15%	15	11	3.5	2.5	<<1	32	47%	51	6%
48	12%	17	13.5	6	5.5	.5	43	40%	76	9%
52	12%									
55	11%	21	15	3	5.5	1	46	46%	77	9%
57	7%									
59	12%									
62	12%	20.5	12.5	1	1.5	1	37	56%	54	6%
64	8%									

Table 3.2

ORGANIC ACID CONCENTRATION VS. TIME

Expt. #01185-D - 5% Hydrilla - 37°C - pH 5.5-6.0Inoculum - #00354-1 (Chondrus) Effluent

<u>Time, Day</u>	<u>% CH₄</u>	<u>A</u>	<u>P</u>	<u>B</u>	<u>V</u>	<u>C</u>	<u>T</u>	<u>A/T</u>	<u>R</u>	<u>%C</u>
0		12	1	4	1.5	4	23	53%	45	5%
3		53	11	18	1	4	87	61%	137	16%
4		82	15.5	27	1.5	3.5	130	63%	196	23%
5		100.5	21	41	2	4	169	60%	262	31%
12		109	34	46	4	4	197	55%	313	38%
13		123	38	59.5	5.5	6.5	233	53%	382	46%
14		100	31	52	5	6.5	195	51%	327	39%
17		121	42	52.5	12	10	238	51%	405	49%
21	5%									
26		83	24.5	34.5	3	2.5	148	56%	232	28%
30		95	27	41.5	5	4.5	173	55%	280	34%
38	11%	*145	54	61	8	9	277	52%	454	54%
47	18%	110	38	39.5	2.5	2.5	193	57%	293	35%
48	0%									
52	7%	78.5	27.5	35.5	4	4	150	53%	244	29%
59	77%	11	32	44	9	5.5	102	11%	228	27%
66	66%	18	24	7.5	5.5	1	56	32%	101	12%
73	43%	13	53.5	0	4	0	71	18%	120	14%
80	47%	9	50.5	7.5	5	0	72	13%	132	16%
87	9%	1.5	36	<<1	1	0	39	4%	68	8%
94	37%									
101	48%	0	11.5	0	3	0	15	0%	30	4%
109	50%	10.5	13	0	0	0	24	45%	33	4%
115	0%									
122	7%									

Table 3.3

ORGANIC ACID CONCENTRATION VS. TIME

Expt. #01971-D - 5% Hydrilla - 37°C - pH 5.5-6.0

Inoculum - #01185-D Effluent

Time, Day	% CH ₄	A	P	B	V	C	T	A/T	R	%C
0		43	15	9	0	0	67	64%	92	11%
1		23	0	8	0	0	31	74%	43	5%
2		20	4	10	0	0	34	59%	52	6%
3		25.5	8.5	13.5	0	0	48	54%	74	9%
6		49	15	22.5	1	0	88	56%	135	16%
7	5%	65	22	24.5	2	0	114	57%	171	21%
8		51.5	16	20	.5	0	88	59%	131	16%
13	37%	58.5	17.5	16.5	.5	0	93	63%	132	16%
21	20%	62	17.5	15	1	0	96	65%	133	16%
27	21%	72	23.5	23.5	3	.5	123	59%	184	22%
34	48%	53	21	20	3.5	2	100	53%	159	19%
41	50%									
48	37%	0	29	17.5	3	0	50	0%	104	13%
56	44%	5.5	33.5	17.5	4.5	.5	62	9%	125	15%
62	61%	13	36	11	11.5	3	75	17%	153	18%
69	58%	3	21.5	.5	1	0	26	12%	45	5%
76	62%	1.5	32	0	2	0	36	4%	64	8%
83	29%	3.5	28.5	0	1.5	0	34	10%	58	7%
90	13%	0	27.5	0	5	0	33	0%	64	8%

Table 3.4

ORGANIC ACID CONCENTRATION VS. TIME
 Expt. #02740 - 5% Hydrilla w/Na₂S (1%)
 37°C - pH 5.5-6.0
 Inoculum - Sewage Sludge

<u>Time, Day</u>	<u>% CH₄</u>	<u>A</u>	<u>P</u>	<u>B</u>	<u>V</u>	<u>C</u>	<u>T</u>	<u>A/T</u>	<u>R</u>	<u>%C</u>
0		5	2.5	.5	.5	0	9	59%	12	1%
1		20	7.5	8	1.5	0	37	54%	58	7%
3	1%	45.5	20.5	13.5	3.5	0	83	55%	127	15%
6	8%	74.5	40.5	22	7.5	1	146	51%	229	27%
7		57.5	36	17.5	7	.5	119	49%	189	23%
8	0%	65.5	42.5	20.5	8.5	1	138	47%	223	27%
9		73	44.5	26	8.5	1	153	48%	248	30%
13	19%	68	45	19	5	1	138	49%	215	26%
20	40%	77	46	22	13	5	163	47%	275	33%
24	0%	87.5	51	26	14.5	.5	180	49%	291	35%
27	0%	94	59.5	27.5	12.5	2.5	196	48%	318	38%
29	0%									
31	0%									
34	5%	75	47	22	9	2.5	156	48%	252	30%
36	0%									
38	14%									
41	56%	71.5	47	21	11	.5	151	47%	244	29%
48	57%	19.5	45	15	13.5	0	93	21%	180	22%
51	54%									
55	61%	11	50.5	3	8.5	0	73	15%	135	16%
57	Na ₂ S addition (1%)									
63	7%	10	47	3	7.5	0	68	15%	124	15%
65	0%									

Section 4

FIXED PACKED BED FERMENTATION

The lab/pilot fixed packed bed fermenter was loaded with 40 lbs. unshredded Chondrus crispus, 0.4 lbs. sewage sludge solids, and 318 liters of water. After one hundred days at 37°C 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 4.1.

The gaseous products consisted only of carbon dioxide and hydrogen. Unlike the fermentation reported in Progress Report No. 3 (Dynatech Report No. 1767, p. 25), where approximately equal amounts of hydrogen and methane were produced, no methane was detected in the present experiment. The gaseous products of the fermentation are presented in Table 4.2.

From these data, the percent conversion based on total solids for the experiment may be calculated as follows:

$$\% \text{ Conversion} = \frac{\text{Total Products}}{\text{Total Reactants}} = \frac{7.28 + 6.4}{36.16} = 37.8\%$$

In addition, an oxidation-reduction balance may be made for the fermentation. Since carbon dioxide is the only oxidation 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 6.3 presents these results. The total amount of carbon dioxide expected based on the amounts of other products formed is 49.5 gram moles. The amount actually obtained was 64.5 gram moles for a 130% recovery. The extra carbon dioxide recovered may be partly a result of aerobic fermentation at the beginning of the experiment when oxygen was present in the fermenter.

Table 4.1

ORGANIC ACID PRODUCTION - RUN NO. 02357

Acid	Fermenter		1st Extraction		2nd Extraction		Total	
	Wt.	G Moles	Wt.	G Moles	Wt.	G Moles	Wt.	G Moles
Acetic	1.44	10.88	0.02	0.17	0	0		11.05
Propionic	0.52	3.20	0.02	0.14	0.03	0.19		3.53
Butyric	1.27	6.56	0.24	1.23	0.24	1.26		9.05
Valeric	0.43	1.92	0.11	0.5	0.13	0.58		3.00
Caproic	<u>0.86</u>	<u>3.36</u>	<u>1.05</u>	<u>4.11</u>	<u>0.56</u>	<u>2.19</u>		<u>9.66</u>
TOTAL	4.52	25.92	1.44	6.15	0.96	4.22	7.28	36.29

Table 4.2

GASEOUS PRODUCTS - RUN NO. 02357

<u>Gas</u>	<u>Volume (STP)</u>	<u>g. Moles</u>	<u>Weight</u>
Hydrogen	25.3 ft. ³	29.3	0.1 lbs.
Methane	0 ft. ³		0 lbs.
Carbon Dioxide	<u>51.1 ft.³</u>	<u>64.6</u>	<u>6.3 lbs.</u>
TOTAL	58.4 ft. ³		6.4 lbs.

Table 4.3

CARBON DIOXIDE PRODUCTION - RUN NO. 02357

	Quantity	Stoichiometry		Ratio	Moles CO ₂
Hydrogen	29.3 moles → C ₆ H ₁₂ O ₆	2CH ₃ COOH + 2CO ₂ + 4H ₂	1:2	14.7	
Propionic	3.5 moles → 7 CH ₃ COOH	4 CH ₃ CH ₂ COOH + 2CO ₂ + 2H ₂ O	1:2	1.8	
Butyric	9.1 moles → 5 CH ₃ COOH	2 CH ₃ (CH ₂) ₂ COOH + 2CO ₂ + 2H ₂ O	1:1	9.1	
Valeric	3.0 moles → 13 CH ₃ COOH	4 CH ₃ (CH ₂) ₃ COOH + 6CO ₂ + 6H ₂ O	3:2	4.5	
Caproic	9.7 moles → 4 CH ₃ COOH	CH ₃ (CH ₂) ₄ COOH + 2CO ₂ + 2H ₂ O	2:1	<u>19.4</u>	
					49.5 Moles

Section 5

CONTINUOUS FIXED PACKED BED FERMENTATIONS

A part of the current program is to design and build a fixed packed bed fermenter into which biomass can be fed continuously and from which residue may be removed continuously. This work is currently in the conceptual design stage. The most promising conceptual design is presented in Figure 5.1. Both biomass feed and residue withdrawal are accomplished using tapered shaft augers similar to the screws used in polyethylene injection molding. Initial laboratory experiments indicate that devices of these type are capable of feeding biomass solids out of a slurry.

The ability to feed solids out of a slurry is a desirable property both for loading and unloading. In the loading operation, it is desirable to slurry the biomass in water before it is added to prevent introduction of air to the fermenter. At the same time, it is desirable to minimize the amount of additional liquid added to the fermenter. Likewise it is desirable to be able to remove biomass residue from the fermenter without removing an excessive amount of fermentation broth. Both of these tasks may be accomplished using a tapered shaft auger, which has the ability of squeezing the liquid from the solid matter. The plan is to construct a model of the proposed device of approximately 10 gallons capacity to test the concept and to generate operating parameters before modifying the 300 liter fermenter to operate with continuous feed.

Figure 5.1

Continuous Fixed Packed
Bed Fermenter

Section 6

KOLBE ELECTROLYSIS

Electrolysis of monobasic aliphatic organic acids generates paraffins olefins, esters, alcohol and carbon dioxide at the anode, and hydrogen gas at the cathode. Anode reactions occur via different mechanisms. The Kolbe reaction at an anode consists of the reduction of acid anion at the electrode surface to form an acid radical, which subsequently decomposes to form CO_2 and the alkyl radical as in 6.1 below. Two alkyl radicals then combine to form the Kolbe product 6.2

As the anode reaction occurs, hydrogen ions are reduced at the cathode, forming hydrogen gas 6.3

Since the Kolbe product results from a bimolecular reaction, high concentration of the alkyl radical will favor this dimerization. For an electrolytic process the requirement of high alkyl radical concentration at the electrode surface means a high current density. A current density of 0.25 amps/cm^2 is considered the lower limit for aliphatic hydrocarbon formation (Reference 3). This current density is well above the current density anticipated from diffusion. The current density estimated from Fick's law is:

$$\frac{I}{A} = .02 c \quad 6.4$$

where c is in moles/liter. However, stirring has been shown to reduce the effective boundary layer thickness and thereby to increase the current

density by up to a factor of 20, which will give a current density in the right range at a concentration of about 1 mole/liter.

Experimental results have shown that electrolysis proceeds at very low electrolysis potentials. A half-wave potential of less than 0.5 volts was obtained when current was measured as a function of potential in a stagnant 10% w/v valeric acid solution, buffered to pH6 in a solution containing a much higher concentration of depolarizer than electroactive species, so that diffusion of acid anions is not affected by electrode-ion attractions (Figure 6.1). The electrolysis current displayed a plateau from 0.7 to 1.3 volts, corresponding to the diffusion current, but increased as the electrolysis potential increased above 1.3 volts. The increased current was due to electrolysis of water. However, no oxygen evolved as would be expected from water electrolysis, when potential was increased to 23 volts.

A mechanism which might explain the experimental lack of oxygen generation in high-voltage electrolysis was suggested by Glasstone and Hickling and is referred to as the "Hydrogen Peroxide Theory" (Reference 4). These investigators suggest that hydrogen peroxide, formed at the anode from hydroxyl radicals, or the hydroxyl radicals themselves prior to dimerization, react with organic acid anions to form organic acid radicals (6.6). Radicals then combine as in equations 6.1 and 6.2 to yield alkane and carbon dioxide.

It is significant to note that anodes consisting of substances which are catalysts or which are oxidized to substances which are catalysts for hydrogen peroxide decomposition do not produce the Kolbe product.

FIGURE 6.1

VOLTS VS. CURRENT

10% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ @ pH 6.0 w/o STIRRING

Electrolysis of organic acids has been found to give a mixture of products, including olefins, alcohols, and esters as well as aliphatic hydrocarbons presumably from the following set of reactions:

Table 6.1 lists the product composition from the electrolysis of a number of organic acids (Reference 3).

One may speculate from this reaction scheme that to maximize aliphatic hydrocarbon the preferred conditions are:

1. Low voltage to minimize hydroxyl ion formation, thus minimizing alcohol formation and perhaps reducing olefin formation.
2. High current density to maximize $\text{R}^\bullet$ concentration, favoring bimolecular product. In order to obtain high current densities at low voltages, it is necessary to have high stirring rates. Use of depolarizers (supporting electrolytes) is counterproductive.

This is accomplished most economically by run at extremely low working voltages and large electrode areas. It is interesting to note that if voltages are kept below that required to electrolyze water, then platinum electrodes should not be necessary. Furthermore, sufficient hydrogen is produced by these processes to supply the required current at a potential of 0.7V from a state-of-the-art fuel cell. As this potential is on the plateau region of Figure 6.1 it is likely that when optimized the olefin electrolysis and perhaps the paraffin electrolysis as well may be run with no external energy requirement. It should also be noted that in Table 6.1 propionic and butyric acids tend to favor olefin formation, i.e., ethylene and propylene, whereas valeric and caproic acids tend to give alkanes. That is to say, the unoptimized electrolysis process tends to give the desired products.

In order to achieve high current densities without applying larger overpotentials, the present approach is to perform the electrolytic oxidation in a flow-through cell, such as the one shown in Figure 6.2. This cell consists of a 0.075" I.D. 316 stainless steel tube for a cathode, a 0.05" diameter platinum wire in the center of the cathode as anode, and an additional 0.05" diameter platinum wire as a reference cathode. The aqueous solution of organic acid anions flows through the cell in order to minimize the thickness of the diffusion layer at the anode surface.

The results to date have been quite promising. Table 6.2 presents the results of an electrolysis experiment using this apparatus. The electrolysis solution was the product obtained from the first extraction of fermentation Run No. 02357. The aqueous alkaline solution of organic acids was adjusted to pH6 using the organic acid mixture obtained by acidifying an additional sample of the extraction solution with mineral acid and separating the organic layer. The electrolysis solution was maintained at pH6 by adding an additional quantity of this organic acid layer during the course of the electrolysis. The electrolysis was run

TABLE 6.1

KOLBE ELECTROLYSIS OF ALIPHATIC MONOBASIC CARBOXYLATES

ACID	STRUCTURE	PERCENTAGE YIELD		
		PARAFFIN	OLEFIN	ESTER
Acetic	CH_3COOH	8 ₅	2	2
Propionic	$\text{C}_2\text{H}_5\text{COOH}$	8	66	5
<i>n</i> -Butyric	$\text{C}_3\text{H}_7\text{COOH}$	14 [•] 5	53	10
<i>iso</i> -Butyric	$(\text{CH}_3)_2\text{CHCOOH}$	trace	62	10
<i>n</i> -Valeric	$\text{C}_4\text{H}_9\text{COOH}$	50	18	4
<i>iso</i> -Valeric	$(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$	43	42	5
Methyl Ethyl acetic	$\begin{array}{c} (\text{CH}_3) \\ \diagdown \\ \text{CHCOOH} \\ \diagup \\ (\text{C}_2\text{H}_5) \end{array}$	10	42	10
Trimethyl acetic	$(\text{CH}_3)_3\text{C COOH}$	13	52	0
Caproic	$\text{C}_5\text{H}_{11}\text{COOH}$	75	7	1 [•] 5
Lauric	$\text{C}_{11}\text{H}_{23}\text{COOH}$	45	—	—
Myristic	$\text{C}_{13}\text{H}_{27}\text{COOH}$	33 [•] 7	—	—
Palmitic	$\text{C}_{15}\text{H}_{31}\text{COOH}$	30	—	—
Stearic	$\text{C}_{17}\text{H}_{35}\text{COOH}$	27 [•] 6	—	—

Table 6.2
ELECTROLYSIS DATA SHEET

Run No. 02392
Date: 10/22/78

	Measured Value	Calculated Value	Final Results
I. Electrolysis Solution			
A. Acid used fermentation product	g		
B. Concentration	1.12 M/l		
C. Volume	0.1 l		
D. Amount of acid (BxCxMw)		13.0 g	
E. Amount of acid added (Vol x p)		8.3 g	
F. Total amount of acid (D+E)			21.3 g
II. Electricity			
A. Voltage (applied)	4.65 v		
B. Current	0.5 amps		
C. Time	12600 sec.		
D. Moles of Electrons (BxC/96,500)			0.065 Moles
E. Power (AxBxC) watts		3×10^4 watt sec.	
F. Voltage (working)	2.65 v		
III. Conditions			
A. Anode area	1.36 cm ²		
B. Current density (IIB/A)		0.38 amp/cm ²	
C. Temperature	22°C		
D. Electrode spacing	0.013 in		
E. Flow rate (tubing size)	41 unit		
F. pH	6.0		
IV. Products			
A. Hydrogen			
1. Gas flow rate	8.56 ml/min.		
2. % Hydrogen	41.6%		
3. Hydrogen flow rate (AlxA2)		3.73 ml/min.	
4. Total hydrogen (A3xIIC)		7.83 ml	
5. Moles of H ₂ (experimental (A4/24450))			0.037 Moles
6. Moles H ₂ (theoretical (IID/2))			0.032 Moles
7. % Hydrogen yield (A-5/A-6)			100%
B. Oxygen			
1. % Oxygen	0%		
2. % Nitrogen	0%		
3. Net % oxygen (B1-B2/4)			0%
C. Carbon Dioxide			
1. % CO ₂	53.8%		
2. Total CO ₂ (AlxC1xIIC)		1014 ml	
3. Moles CO ₂ (C2/24458) experimental			0.041 Moles
4. Moles CO ₂ (theoretical)(IID)			0.065 Moles
5. % yield (C3/C4)			63%
D. Olefin			
1. Trap Tare	GC g		
2. Final trap weight	GC g		
3. Weight olefin (D2-D1)		0.7 g	
4. Moles of olefin (D3/Mw)			0.01 Moles
E. Hydrocarbon			
1. Tare - first ether extraction	GC g		
2. Final weight of jar	GC g		
3. Weight of hydrocarbon (E2-E1)		2.86 g	
4. Moles hydrocarbon E3/Mw			0.02 Moles
F. Acid			
1. Tare 2nd ether extraction	GC g		
2. Final weight of jar	GC g		
3. Final weight of acid (F2-F1)		6 g	
4. Net weight of acid consumed (IF-F3)		6 g	
5. Moles of acid consumed F4/Mw			0.5 Moles
V. Yields			
A. Current yield (2(IVD4 + IVE4))/IID			92%
B. % Paraffin IVE4/(IVD4 + IVE4)			67%
C. Energy (230 x IVA5 + (IVD3 + IVE3)45)(1054)/IIE)			5.9/l

Figure 6.2

Electrolysis Cell

for 3-1/2 hours at an applied voltage of 4.65 volts and a working voltage of 2.65 V (the difference being IR drop in the electrolysis cell). The hydrocarbon layer was then separated and analyzed by gas chromatography using a chromasorb 101 column at 125°C. The liquid product spectrum is shown in Figure 6.3. The gases were analyzed for hydrogen and carbon dioxide using a Fisher Gas Partitioner using argon and helium carrier gases, respectively. The gases were then analyzed by Gas Chromatography on the same column at 80°C to determine the volatile products, primarily olefins. These products are shown in Figure 6.4. The current yield for this experiment was 92% and the % paraffin product was 67%. The energy balance (products isolated/electricity consumed) was approximately 6/1 based on the applied potential and over 10/1 based on the working potential. It is clear that even when the inefficiency of electricity generation is considered, a positive energy balance for the electrolysis process has already been obtained.

Figure 6.3

Liquid Electrolysis Products

Run No. 02392

Figure 6.4

Gaseous Electrolysis Products

Run No. 02392

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