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. 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

DYNATECH R/D CO		
SCALE: NONE	APPROVED BY:	DRAWN BY: MPB
DATE: 4/6/78		
LIQUID FUEL FROM BIOMASS		
REVISIONS: NONE		

gas is a valuable co-product in itself or may be used to generate part or perhaps 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.

In this report three topics are covered, a discussion of methane suppression, initial results on Kolbe Electrolysis, and preliminary economical analysis of the process.

Section 3

SUPPRESSION OF METHANE

In the anaerobic fermentation of sugars by mixed populations, a series of compounds are found as products. Organic acids, ethanol and higher alcohols, CO_2 and H_2 are among the fermentation products. Acetate, methanol, formate, CO_2 and H_2 are substrates for the formation of methane according to the following reactions⁽¹⁾:

It is considered by several investigators that the chief pathway of methane formation is the reduction of CO_2 with molecular hydrogen⁽²⁾. Since there is experimental evidence⁽³⁾ that hydrogen is an intermediate in methanogenesis, alternative metabolic uses of hydrogen have to be considered if methane formation is to be avoided.

In the present program, the production of methane is undesirable and has become a major problem in the fermentation of Hydrilla, as stated in the previous report (July 1 - September 30, 1978).

Since keeping low pH values does not prevent methanogenesis, alternative methods for methane suppression have to be analyzed.

3.1 Electron Sinks in Anaerobic Metabolism

Sulfate, thiosulphate and sulfite are known to act as electron sinks in anaerobic metabolism⁽⁴⁾. The presence of sulfate of up to a 0.85 mM

concentration appears necessary for anaerobic degradation of cellulose by mixed cultures. However, concentrations higher than 1.75 mM affected the ratio of cellulose degraded to methane formed after 3 weeks of incubation. Since sulfate is reduced to sulfide (as it's generally agreed on), the inhibition occurring at a higher concentration of sulfate, noted after 3 weeks of incubation and not after one week of incubation, may be due to the accumulation of sulfide in the medium. At a 9 mM concentration, the inhibitory concentration on cellulose degradation increases in the following order:

sulfate < thiosulphate < sulfite < sulfide

Sulfite and H_2S have the greatest inhibitory effect on methanogenesis⁽⁴⁾. There is a very high tolerance for sulfate in the ecosystem which is probably due to the presence of hydrogen in the initial stages of the fermentation and presence of acetate after the start of cellulose degradation, both of which have been shown to prevent sulfate inhibition of methanogenesis.

Competition for both acetate and H_2 appears to be responsible for inhibition of methane production by sulfate⁽⁵⁾.

3.2 Methane Analogues

Inhibition of methanogenesis in anaerobic digestion by extremely low concentrations of chloroform, carbon tetrachloride and methylene chloride has been demonstrated⁽⁶⁾. The concentrations required to produce 50% inhibition of the rumen methanogenesis are 1.4 μM CCl_4 , 7.8 μM $CHCl_3$, and $2.4 \times 10^3 \mu M$ CH_2Cl_2 ⁽²⁾.

3.3 Others

Viologen dyes have a depressing effect on the rate of CH_4 formation, while the rate of hydrogen production is increased⁽²⁾.

Bromo-ethane sulfonic acid is known to be a methane suppressor (G. Zerkus, personal communication) acting on the last step of the methane formation.

Possible pathways of methane formation⁽⁷⁾.

In future experiments, the compounds mentioned before will be tested for methane suppression. However, how these compounds may affect acid formation has to be carefully considered in order to maintain high conversions to acids and prevent any carbon from being reduced to CH_4 .

Section 3

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Section 4

KOLBE ELECTROLYSIS

4.1 Introduction - History and Mechanism

The potential for use of electricity as an oxidizing or reducing agent was realized early in the nineteenth century by Rheinold and Erman who electrolyzed dilute aqueous solutions of alcohol. Lüdersdorff in 1830 was the first to undertake a detailed study of the products obtained in the oxidation of alcohol using different electrodes. Faraday first realized the potential for using electric current to synthesize or decompose a compound. As early as 1834, he observed that electrolysis of an acetate solution yielded some hydro-carbon. Kolbe's important discoveries in the mid-nineteenth century led to the establishment of the principles of electrolytic oxidation and reduction (Reference 4.1).

Kolbe completely replaced the chlorine with hydrogen in chloromethylsulphonic acid by electrolytic means in 1845. He observed that trichloromethylsulphonic acid was completely decomposed in an aqueous solution at a platinum electrode, stating: "This acid, which is stable to the strongest oxidizing media, breaks down with little difficulty at a platinum anode." Kolbe then studied the anodic oxidation of organic compounds. Electrolysis of an alkali-metal acetate was shown to evolve ethane and two volumes of carbon dioxide: $2\text{CH}_3\text{COO} \rightarrow 2\text{CO}_2 + \text{C}_2\text{H}_6 + 2\text{e}^-$. (4.1)

Further investigation of this reaction by Kolbe and others demonstrated the feasibility of hydrocarbon synthesis by electrolysis of other monobasic aliphatic acid salts. The Kolbe reaction proceeds by the oxidative removal of CO_2 from the acid anion, with subsequent dimerization of the remaining alkyl radical. For example, valeric acid (pentanoic acid) forms octane according to the following equation (Reference 4.2):

In an aqueous medium, hydrocarbon formation occurs to an appreciable extent only at a smooth platinum or iridium electrode. Using a platinum

electrode, the most favorable results are obtained at temperatures lower than 50°C, and anode current densities over 0.25 amps/cm². High acid concentrations also favor this reaction. Paraffins and olefins possessing only half the carbon atoms of Kolbe electrolysis products are formed at low anode current densities. Esters and alcohols have also been observed as electrolysis products.

Higher fatty acids give satisfactory yields of the Kolbe dimer and alkanes up to C₃₄H₂₀ have been prepared by this method (Reference 4.2).

4.2 Reaction Mechanisms

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 CO₂ and the alkyl radical as in 4.3 below. Two alkyl radicals then combine to form the Kolbe product 4.4.

As the anode reaction occurs, hydrogen ions are reduced at the cathode, forming hydrogen gas 4.5.

Since the Kolbe product results from a bimolecular reaction, high concentration of the alkyl radical will favor this dimerization. High concentration of the alkyl radical may be attained at high acid concentration, and anode current density equivalent to the acid anion diffusion currents at the potential required for acid oxidation (Reference 4.3). Diffusion current is defined as the current required to oxidize all acid as it diffuses to the anode. Acid oxidation will cause species depletion at the anode surface, and a boundary layer between both solution concentration and concentration at the anode surface will be established. The rate at which a species diffuses to

the anode would fix the diffusion current and rate of hydrocarbon production.

Allen (Reference 4.3) reports that the diffusion boundary layer at an electrode will be approximately 0.05 cm thick in a stagnant solution, and approximately 0.001 cm thick in a well-stirred electrolytic cell. 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, the organic acid diffusion coefficient will have a value in the range of $6 \text{ to } 10 \times 10^{-6} \text{ cm}^2/\text{sec}$. The diffusion current density can be estimated from the formula:

$$I_{\text{max}} = \frac{ZF D A C_0}{\alpha} \quad 4.6$$

where Z = ionic charge = 1.6×10^{-19} coul/ion or electron for monobasic aliphatic carboxylic acids

F = 1 faraday = 96,490 coulombs/equivalent

D = diffusion coefficient = $6 \text{ to } 10 \times 10^{-6} \text{ cm}^2/\text{sec}$

C_0 = acid concentration = $4.89 \times 10^{-4} \text{ mole/cm}^3 = 5\% \text{ w/v}$

α = diffusion boundary layer thickness
 = 0.05 cm (stagnant fluid)
 to
 0.001 cm (well stirred)

Table 4.1 lists the approximate diffusion current density for a number of electrolysis conditions. Examination of Table 4.1 reveals that diffusion current density is less than 1 amp/cm^2 for all conditions, and ranges from 0.005 to 0.02 Amps/cm^2 for unstirred conditions.

Allen (Reference 4.3) reports an anode potential of about + 2.2 volts vs. Standard Calomel Electrode (S.C.E.) for acetate oxidation to ethane, and + 1.8 volts vs. S.C.E. for acetate oxidation to methanol. Preferential production of alcohols is known as the Hofer-Moest reaction, and is favored by use of an alkaline solution and by addition of inorganic salts such as perchlorates, sulphates and bicarbonates.

Experimental results have shown that electrolysis proceeds at very low electrolysis potentials. A half-wave potential of less than 0.5 volts

TABLE 4.1

LIMITING CURRENT DENSITY FOR FLAT PLATE ELECTRODE

(Coulombs/ion) Z	(Coul/equiv) F	(cm ² /sec) D	(mol/cm ³) Co	(cm) α	I _{max} /A	
1.6×10^{-19}	96,490	6×10^{-6}	4.89×10^{-4}	0.05	5.7×10^{-3}	unstirred
			= 5% w/v	1×10^{-3}	0.28	stirred
		1×10^{-5}		0.05	9.4×10^{-3}	
				1×10^{-3}	0.47	
		6×10^{-6}	9.8×10^{-4}	0.05	0.02	
			= 10% w/v	1×10^{-3}	0.98	
		1×10^{-5}		0.05	0.019	
				1×10^{-3}	0.95	

was obtained when current was measured as a function of potential in a stagnant 10% w/v valeric acid solution, buffered to pH6 (Figure 4.1). 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 is probably due to electrolysis of water. The observation of a potential on the order of 0.5 v for the reaction:

is consistent with the thermodynamics of the process. Table 4.2 presents the free energy for this reaction and for the analogous reactions of other aliphatic organic acids in kilocalories/mole and in electron volts based on heats of combustion to liquid water and gaseous CO_2 . All of the calculated potentials are less than the 0.5 v observed for valeric acid, although the difference between the observed and calculated values does not appear to allow sufficient potential to generate fully developed free alkyl radical intermediates. The inconsistent variation in the $\Delta\Delta\text{Hc}$'s for these reactions is probably not real as these values are small differences between large measured values.

No oxygen was evolved as would be expected from water electrolysis when potential was increased to 23 volts. This phenomenon merits further mechanistic examination. Water electrolysis proceeds by the anodic oxidation of water to hydroxyl radicals and hydrogen ions. Hydroxyl radicals then combine to form water and molecular oxygen. Hydrogen ions are reduced at the cathode to molecular hydrogen.

Figure 4.1
VOLTS VS. CURRENT
10% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ @ pH 6.0 w/o STIRRING

TABLE 4.2
OXIDATION POTENTIALS OF ORGANIC ACIDS
BASED ON HEATS OF COMBUSTION

<u>Acid</u>	<u>$\Delta G(\sim \Delta \Delta H_c)$ Kcal/mole</u>	<u>E Volts</u>
Acetic	+ 9	0.39 V
Propionic	+ 11	0.48 V
Butyric	+ 5	0.22 V
Valeric	+ 4	0.17 V
Caproic	+ 8	0.35 V

In the Kolbe cell, however, very little molecular oxygen is evolved, and evolution of Kolbe and other products increases with voltage and current. A mechanism which might explain the experimental lack of oxygen generation in high-voltage Kolbe electrolysis was suggested by Glasstone and Hickling and is referenced as the "Hydrogen Peroxide Theory" (Reference 4.4). 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. Radicals then combine as in equations 4.3 and 4.4 to yield alkane and carbon dioxide.

or

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. Insufficient concentration of organic acid anions due to low current density or low bulk acid concentration also results in poor yields of the Kolbe product, and formation of alkenes, alkanes with half the number of carbon atom in Kolbe product, esters and alcohols by the reactions presented in equations 4.11, 4.12, 4.13 and 4.14 respectively, predominates.

Alkenes are obtained from the alkyl radical intermediate by elimination of a hydrogen atom from the β - carbon atom of the acid. For example, propionic acid would produce a propyl radical intermediate, and the alkene, propene, would form:

The alkyl radical intermediate could react with an organic acid molecule to yield alkane and an organic acid radical (4.12) which is subsequently oxidized to carbon dioxide and water, or an ester, and an hydrogen radical (4.13) which is oxidized to an hydrogen ion (4.14).

Alcohols may form due to reaction of hydrogen radicals with alkyl radicals during electrolysis. For example, propyl alcohol may be formed from propyl radical:

Mixtures of organic acids will yield products containing constituents of the various size organic acids present. Yields of product paraffin, olefin and esters from Kolbe electrolysis of aliphatic monobasic carboxylic acids presented in reference 4.3 are given in Table 4.2.

The data in this table on valeric acid, isovaleric acid, trimethyl acid, methyl ethyl acetic acid, lauric, myristic, palmitic and stearic acids are from the work of Julius Petersen (reference 4.2). Basically, his method was to electrolyze a 33% solution of the subject acid as its potassium salt at a constant current of 0.5 amp at 0°C. Voltages and electrode areas are not specified. The electrolyses were run for long times to provide for substantial quantities of products. The liquid products were removed from the top of the cell and were separated into several fractions based on boiling ranges. Each fraction was saponified to determine its ester content.

The gaseous products were brominated and the brominated products were fractionally distilled. By this procedure in the case of isovaleric acid out of 800g of acid consumed in the electrolysis, 731g were accounted for in the isolated products. With careful control of voltage and current density and proper cell design it is likely that improved paraffin yields will be obtained.

TABLE 4.3

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	—	—

In summary, 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:

According to Glesstone and Hickling (op cit.) and consistent with current findings, Kolbe Electrolysis is normally run along Path (1), the oxidation of water to hydroxyl radicals. This process is the anode process in the electrolysis of water and is known to require a working potential of about 1.4 v, depending somewhat on the electrode composition. However, in the presence of organic acids and in the absence of materials which catalyze the decomposition of hydrogen peroxide, oxygen is not produced at the anode, but rather the hydroxyl radicals oxidize the organic acid to its corresponding radical⁽³⁾. The radical decarboxylates to an alkyl radical which may:

1. Dimerize to give the Kolbe product, aliphatic hydrocarbon⁽⁵⁾.
2. Eliminate to give olefin⁽⁶⁾.
3. React with other radical species to give alcohol⁽⁷⁾ or ester⁽⁸⁾.

However, another route to the organic acid radical⁽³⁾ is the direct oxidation of the organic acid at the electrode surface, Path (2). Proceeding by this route has a number of advantages:

1. The potential required for this path is less than for Path (2) since hydroxide ions spontaneously oxidize organic acids to organic acid radicals.
2. The possibility of producing alcohol products⁽⁷⁾ is eliminated.

The primary disadvantage to this approach is that at practical concentrations of organic acid, the current density available by this path is too low to produce sufficient quantities of alkyl radical⁽⁴⁾ to dimerize to aliphatic hydrocarbons⁽⁵⁾, as discussed earlier.

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 4.2. This cell consists of a 0.075" I.D. platinum 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. This cell is a revised version of the one discussed in Progress Report No. 5 in that a platinum cathode replaces the stainless steel one. No change in operating characteristics have been observed. Another change is the angle of the inlet and outlet parts have been reduced from 90° to the electrode axis to about 40°. This change affected a significant reduction in the pressure drop of the cell.

The results to date have been quite promising. Table 4.4 presents the results of an electrolysis experiment using this type of 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

Figure 4.2
ELECTROLYSIS CELL

Table 4.4
ELECTROLYSIS DATA SHEET

Run No. 02392
Date: 10/22/78

	Measured Value	Calculated Value	Final Results
I. Electrolysis Solution			
A. Acid used fermentation product	8		
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 ρ)		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			5.9/1

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 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 4.3. 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 4.4. 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.

Another series of electrolysis experiments has been run using solutions of pure organic acids in an attempt to determine the effects of:

1. Temperature,
2. Flow rate,
3. Acid composition, and
4. Current density.

on the products compositions (paraffin/olefin ratio) and on the working potential. These experiments have not been entirely conclusive. The major difficulty with this set of experiments has been in the isolation of the olefinic products. The moles of olefins produced can be determined indirectly from the coulombs consumed and the carbon dioxide produced (or the organic acid consumed) in the following manner.

Figure 4.3

Liquid Electrolysis Products

Run No. 02392

Figure 4.4

Gaseous Electrolysis Products

Run No. 02392

$$E = 2 (O + P)$$

$$CO_2 = A = 2P + O$$

$$\therefore E - CO_2 = 0$$

That is to say, since both olefin (O) plus paraffin (P) required two coulombs (E)/molecule formed and the formation of paraffin consumes two molecules of acid (A), thereby releasing two molecules of CO_2 whereas olefin formation results in the release of only one molecule of CO_2 , then the coulombs consumed minus the CO_2 released equals the molecules of olefin formed, assuming paraffin and olefin are the only products. This final assumption appears to be valid since in some cases this relationship holds to over 90% and other possible products, ester and alcohol, have been analyzed for and not formed.

In early experiments, the primary loss of olefin was found to occur via diffusion through the silicone rubber tubing used in the recirculation system. Changing to Tygon tubing improved the material balance drastically, but diffusion through the tubing walls is still the most likely source of product loss. The quantity of paraffin isolated generally correlates well with the coulombs consumed and the CO_2 produced. Another point that should be mentioned is that pH control is necessary during the course of the electrolysis in order to obtain a proper CO_2 balance. As acid is consumed, the pH of the electrolysis solution will tend to rise, and the solubility of CO_2 will increase, resulting in an apparent loss of CO_2 . As described earlier, additional acid is added during the course of the electrolysis experiment to maintain a constant pH, usually pH6.

The results of a series of experiments using caproic and butyric acids are presented in Table 4.5. From these data some conclusions may be drawn:

TABLE 4.5

RESULTS OF ELECTROLYSIS EXPERIMENTS

<u>Run No.</u>	<u>Acid</u>	<u>Current Density</u>	<u>Temperature</u>	<u>Flow Rate</u>	<u>Working Potential</u>	<u>% Paraffin</u>
		<u>A/cm²</u>	<u>°C</u>	<u>cm/sec</u>	<u>Volts</u>	
02365	Caproic 2M	0.8	18	50	---	59%
02380	" 2M	0.8	30	100	---	46%
02367	" 2M	0.8	72	100	1.9	24%
02394	Butyric 2M	0.8	30	15	2.5	5%
02395	" 2M	0.8	30	100	2.6	20%
02396	" 2M	0.8	10	15	2.4	3%
02397	" 2M	0.8	15	100	1.8	23%
02398	" 2M	0.8	10	100	---	35%
02349	" 2M	0.2	15	100	2.3	33%
03801	" 2M	0.2	15	100	2.2	33%

1. The caproic acid data indicate that low temperatures favor paraffin formation.
2. The butyric acid data indicate that high flow rates favor paraffin formation.
3. Comparison of the caproic acid data with the butyric acid data indicates that chain length favors paraffin formation, as reported in the literature. No conclusions concerning current density and working potential may be drawn at this time. Work in progress is designed to elucidate these points and to confirm the conclusions already drawn.

Section 4

REFERENCES

1. Sanderson, J.E. and Wise, D.L., Acetic Acid Production from Marine Algae, Report No. C-02-4388-4, August 28, 1978.
2. Sanderson, J.E. and Wise, D.L., Acetic Acid Production from Marine Algae, Report No. C-02-4388-3, pp. 19-24.
3. Allen, M.J., Organic Electrode Processes, Reinhold, New York (1958).
4. Glasstone and Hickling, J. Chem. Soc., 1878 (1934).

Section 5

PRELIMINARY PROCESS DESCRIPTION AND ECONOMIC ANALYSIS

5.1 Process Description

A process to produce liquid hydrocarbon fuels from biomass was presented in Figure 2.1. Analysis will be based on concepts and experiments summarized in earlier publications from Dynatech outlined in Refs. 5.3-5.8. The following basic unit operations will be required:

1. Collection of selected biomass at a receiving station.
2. Shredding of the selected biomass. This shredding step is necessary to provide a material suitable for packed bed fermentation. Because of the nature of biomass, it is anticipated that shredding be accomplished by equipment similar to the secondary shredders of Ref. 5.3.
3. Fermentation of biomass in a packed bed fermenter. Acids formed during fermentation will be continuously removed in an external subsystem and converted to liquid hydrocarbon fuels. Aqueous phase is recycled to the packed bed system after the acid removal step.
4. Return of the spent residue, containing nutrients, to the biomass growth system.

5.2 Material Flows, Process Performance and Yield

As the basis for evaluating the performance of a full-scale facility for generation of liquid hydrocarbons and a selected biomass, it is assumed that biomass input to the facility will be on a common 1000 tons/day on a dry, lignin and ash-free, (D.A.L.F.) basis. In this manner, by selecting a common basis, the economic analysis is independent of the particular biomass selected. Thus, if the biomass contains 25% lignin then ≈ 1333 tons/day

of the selected biomass must be delivered (dry basis). Similarly, should the biomass contain 25% ash as is found with aquatic biomass, then 1333 tons/day will also need to be delivered (dry basis). It is further noted that both low moisture and high moisture biomass may be considered in this analysis. This nominal plant size and input are similar to those chosen for evaluating other alternative energy from biomass processing systems.

In estimating organic acid yield, it will be assumed that 75% by weight of fermentable organic input (lignin and ash free) to the facility will be converted to acids. This yield would be obtained, for example, if 90% of organics were biodegradable and 83% were actually converted to acids under plant conditions. It is important to note as background with this yield assumption that volatile solids reductions for Hydrilla have shown values of up to 62%. For Chondrus crispus close to quantitative (> 90%) conversions of available carbon have been obtained. With a 1000 ton/day D.A.L.F. biomass input, and 75% conversion on a dry basis of a material equivalent to cellulose by:

a yield of 2.78×10^4 lb·mols/day acetic acid (or the equivalent in other acids as discussed below) is obtained. This product acid will disproportionate to higher acids by reactions of the type:

As part of this analysis it is assumed here that the acid product is caproate, which is converted to n-decane as discussed in Section 5.9. With these assumptions, yield of product n-decane will be 5.0×10^5 lb/day with a heating value of 10^{10} BTU/day, equivalent to 1720 bbl/day oil in heating value. Additionally, the reaction stoichiometry dictates the generation of 1.25×10^6 ft³ H₂/day with a heating value of 4.23×10^8 BTU/day.

5.3 Estimate of Packed Bed Digester Size

A critical factor in the over-all economics of acid production will be the size of reactor required to carry out the conversion. Reactor size is fixed by the volumetric productivity and the desired output rate. For purposes of this evaluation, it will be assumed that the value for productivity which can be attained is that implicit from kinetic information presented by Ashare, et al in Ref. 2. A correction factor is applied for inhibition of product formation by the presence of acid product in the reactor. A rate constant in the order of 0.12 day^{-1} is observed in Ref. 2 for anaerobic digestion of various substrates to methane. It is assumed that product inhibition in the acid generation step will reduce rates and this rate constant by 75%, to 0.03 day^{-1} (high product acid levels and low pH will be necessary to facilitate the necessary generation and removal of higher product acids, as discussed later). With this rate constant, the time requirement for 83% conversion of biodegradable solids will be 60 days. Note that this choice of rate constant is conservative in view of constants as high as 0.77 day^{-1} attained with acid generation from marine algae as a model biomass in the experimental program.

A further assumption is that solids loading in the packed bed digesters will be 15% (D.A.L.F.) by weight. At this initial solids loading, with an input feed of 1000 tons/day and a residence time of 60 days (necessary to accomplish the desired degree of conversion) the total reaction volume requirement is readily computed to be $12.8 \times 10^6 \text{ ft}^3$.

The packed bed digester costs are a prime concern since this is the largest single item of capital equipment. Because this reactor may be of simple construction, that is, simple large tanks through which liquid circulates or perhaps even lined, covered pits, the cost is estimated at $\$1.00/\text{ft}^3$, or $\$12,800,000$.

5.4 Extraction of Organic Acids from Aqueous Phase

As part of the process organic acids must be continuously extracted from the aqueous product of the packed bed digestion step. Here, one tentative

design for the extraction step is presented with a performance estimate. Also presented is a discussion of how changes in values of parameters could affect this estimated performance. Though there are uncertainties, it appears that solvent extraction with hydrocarbon will be practical.

5.4.1 Solvent Extraction with Hydrocarbon

For best process energetics it is most desirable to selectively withdraw and electrolyze the higher organic acids to liquid hydrocarbon product. (This must be associated with return of the raffinate aqueous acid mix to the packed bed fermentation system to close the cycle.) This can be accomplished by countercurrent extraction of the aqueous stream with solvent whose partition behavior is such that the higher acids are selectively extracted. Table 5.1 presents measured partition coefficients of organic acids in Freon-113; it is seen that this set of partition coefficients favors higher acids. As a first approximation it will be assumed that the solvent utilized is a hydrocarbon having these properties. An additional property necessary for the solvent is that it have minimal solubility in the aqueous phase in order to minimize solvent losses. Freon 113 (solubility $\approx$ 50 PPM) and any of a wide range of hydrocarbons will fall into this category.

Table 5.1

DETERMINATION OF PARTITION COEFFICIENTS OF ACETIC,
PROPIONIC, BUTYRIC, AND VALERIC ACIDS WITH FREON TF

Acid	Initial Conc.	Final Conc.	$P = \left(\frac{CI - CF}{CI} \right)^* = \frac{\text{Concentration in Freon}}{\text{Concentration in Water}}$
Acetic	0.173 M/l	0.173 M/l	0
Propionic	0.134 M/l	0.128 M/l	0.047
Butyric	0.110 M/l	0.079 M/l	0.392
Valeric	0.093 M/l	0.031 M/l	2.00

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

5.4.2 Mass Transfer and Sizing of Reactor

It will be assumed here that the dispersed phase in the counter-current extraction step is hydrocarbon, which rises countercurrently through the aqueous phase. For situations in which the partition coefficient (as expressed in Table 5.1) is above .03, the limiting resistance will be on the aqueous side of the aqueous-hydrocarbon interface (Perry's Handbook, 9th ed. p. 14-65), in which the governing equation for the dispersed hydrocarbon phase is:

$$\frac{dC_H}{dt} = \frac{k_L a}{v} (C_A^* - C_A) \quad (5.1)$$

where: k_L = mass transfer coefficient, cm/sec
 a/v = area/unit volume of disperse phase, cm^{-1}
 C_A^* = bulk concentration in aqueous phase
 C_A = concentration in aqueous phase in equilibrium with C_H below
 C_H = concentration in hydrocarbon phase

$$\text{and } C_A = C_H/P \quad (5.2)$$

Further, estimates, based on information in Perry's Handbook (pp. 14-64, 5-62) are that the hydrocarbon disperse phase has an average drop size of 0.5 cm and that the rise velocity is 0.7 ft/sec (.22 cm/sec) relative to the aqueous phase. Other assumptions necessary to size the extractor are the relative volumetric flow of aqueous phase downward (Q_A) through the extractor, to the hydrocarbon going up (Q_H) which is taken to be 2.0, and the void fraction of the disperse phase, assumed to be 0.1. With these assumptions, the downward velocity of aqueous phase in the extractor will be 0.15 ft/sec (~ 5 cm/sec) and the net upward velocity of hydrocarbon droplets will be 0.55 ft/sec (16 cm/sec).

The relation giving the mass transfer coefficient in such an extraction system is that for the aqueous phase surrounding the drop:

$$k_{\ell} = 2 \sqrt{\frac{D_{\ell} v}{\pi d}} \quad (5.3)$$

where:

k_{ℓ} = mass transfer coefficient, cm/sec

D_{ℓ} = diffusivity of acid in aqueous phase, cm^2/sec

d = drop diameter, cm

v = velocity

If D_{ℓ} is taken as $10^{-5} \text{ cm}^2/\text{sec}$, then substitution gives $k_{\ell} = 2 \times 10^{-2} \text{ cm/sec}$. For $d = 0.5 \text{ cm}$, a/v for the dispersed hydrocarbon phase is $12 \text{ cm}^2/\text{cm}^3$ (or, $12,000 \text{ cm}^3/\ell$) and $\frac{k_{\ell} a}{v} = .24 \text{ sec}^{-1}$. Substituting in Eq. 5.1,

$$\frac{dC_H}{dt} = 0.24 (C_A^* - C_A) \quad (5.4)$$

With this introduction, and making the substitution of Eq. 5.2 a trial-and-error process may be carried out to size the extractor. A constraint, set by the relative volumetric flows is that the material balance $Q_H \Delta C_H = -Q_A \Delta C_A$ over any height increment in the reactor (where ΔC_A is the sum of dissociated and undissociated acid species in the aqueous phase).

An initial assumption (about which more comment later) is that the driving force is provided by the undissociated acid component only; thus the driving force, ΔC will be $\Delta C_A (H^+ / (H^+ + k_i))$ where k_i is the ionization constant of the acid in question. Withdrawal of undissociated acid will also change the pH, and adjustment must be made for this. The pH change may be estimated assuming a constant net cation concentration which will be equal to the total normality of dissociated acid anions. Thus, for an individual acid, $H^+ = (k_i A^-) / A$ where A^- = dissociated acid (constant) and A is the remaining undissociated acid.

The initial composition (influent aqueous phase) used for the trial and error sizing is shown in Table 5.2. This is a typical experimentally determined composition. By trial and error, initial and final concentrations were selected (with compensation for pH effects) such that:

$$\Delta C_H = \Delta C_{lm(A)} \Delta t \quad (5.5)$$

where: ΔC_H = concentration in hydrocarbon phase
 $\Delta C_{lm(A)}$ = log mean concentration difference (undissociated) in aqueous phase, $\Delta C_{in} - \Delta C_{out} / \ln(\Delta C_{in} / \Delta C_{out})$
 Δt = rise time of droplet, 55 sec with assumed 30 foot high column

Table 5.2

RESULTS OF MASS TRANSFER COMPUTATION FOR COUNTERCURRENT EXTRACTION
(milliequivalents per liter)

	<u>Aqueous Phase</u>		<u>Hydrocarbon Extraction Phase</u>	
	<u>Initial Influent Composition (Total Acid)</u>	<u>Final Effluent Composition (Total Acid)</u>	<u>Initial Influent</u>	<u>Final Effluent</u>
Acetic	42	42	0 ↓	0
Propionic	12.5	12.5		< .1
Butyric	6.2	55.3		13.5
Valeric	10.5	5.4		10.2
Caproic	7.0	1.5		11
	pH = 4.75	pH = 4.90		

Two assumptions made in Table 5.2 are that the column height is 30 feet, and that caproic acid has a partition coefficient of $P = 4.0$ in the rising hydrocarbon phase (butyric = 0.4 and valeric = 2.0).

Two comments are in order with respect to this computation. First, it will be noted that the use of undissociated acid concentration gradient results in a minimum mass transfer. In the ionic mix considered here,

ionized species will also contribute to transport. Actual liquid side transfer coefficients will be improved by a factor of 2 or more when ionic transport is taken into account. Secondly, use of an extraction solvent with a more favorable partition coefficient would result (depending on coefficients which can be attained) in much more efficient extraction in terms of space velocity within the extraction vessel. The calculation presented is therefore conservative. However, it is evident that the extraction step is one needing considerable further analysis.

With this concentration of acids in the hydrocarbon solvent from the extraction step, (representing the equivalent of 137 meq/l acetic acid) it may be established in conjunction with acid yield assumptions made earlier that liquid hydrocarbon flow is 37.6 ft³/sec. At a net upward flow of .55 ft/sec over 10% of the tower cross sectional area, 684 or ~ 700 ft² of extraction column area will be required, which, at a total height of 35 feet (allowing for distributors, etc.) will be 25,000 ft³ of volume. An estimated cost for the extractor is \$50/ft³, considered conservative since it may be of relatively simple design, (perhaps consisting in the limit, of a single 30' diameter tank, 35' high, with the necessary pipes, distributors, and perhaps baffles or perforated plates to damp vertical mixing and maintain countercurrent flow). At \$50/ft³, this will represent a cost of \$1.25 million.

5.5 Extraction of Product Acids for Hydrocarbon Solvent into Alkali

The extraction of product acids from the hydrocarbon stream represents a much simpler analysis than the extraction of product acids from the aqueous phase because of simplifying boundary conditions. Envisioned is countercurrent extraction with aqueous base; base is continuously withdrawn, acid anions are removed by Kolbe electrolysis, and the base returned in a closed loop. Depending on base concentration (a consequence of CO₂ evolution in the Kolbe step is that base will consist of a mix of acid salts and alkali carbonates) the transfer of acids from hydrocarbon to the aqueous phase will be augmented by chemical reaction:

and with a reasonable base concentration of > 1 molar, acid reaching the surface of the liquid drop will react immediately upon reaching the surface. Available concentration gradients with base (> 1000 mmol/l) are such that enough will always be able to diffuse to the hydrocarbon drop surface and react with all acid released. An estimate for the cost of the unit to strip acids from the hydrocarbon is $1/5$ that of the cost for aqueous extraction, or \$250,000.

It is to be noted that in the above processing step, that concentrations of the pure acid is not required at any stage, and heat requirements and distillation are avoided. Because of these factors energy consumption is minimized.

5.6 The Electrolysis Step

As outlined in Section 4 the product acids are to be subjected to Kolbe electrolysis. In the electrolysis step circulating base containing acid anions is brought through electrolytic cells operated at current densities up to 1.0 amp/cm^2 . As the basis for sizing electrodes it will be assumed that current densities of 1 A/cm^2 and 0.25 Ampere/cm^2 are obtained, and further that decane is the product. (Kolbe electrolytic production of decane requires 2 Faradays/g.mol.)

The projected plant output will require 4.33×10^6 amps and depending on current density $4.33 \times 10^6 \text{ cm}^2$ of electrode area at 1 amp/cm^2 or $1.73 \times 10^7 \text{ cm}^2$ at 0.25 amp/cm^2 . For purposes of estimating power requirement a total applied voltage of 1 volt is assumed. (A working voltage of 0.6 volt has been observed in the experimental program. Resistance losses with a solution of $1 \Omega/\text{cm}$, which is the anticipated range, may for example be kept below 0.1 v @ 1 amp/cm^2 with an electrode separation of $< 1 \text{ mm}$. No diaphragm is necessary, and this is judged not to be a serious constraint.)

Based on conversations with a major chlor-alkali manufacturer, it is estimated that the installed cost of the electrolysis unit will be about $\$140/\text{ft}^2$ of anode. (Since the electrode system to be used is outside the

manufacturer's experience the cost could range from 30% less than this figure to as much as 50% more. A lower value is more likely, because product is not corrosive and because the diaphragm may be omitted.) At the power requirement of 3.5 megawatts, a cost for the necessary D.C. power supply of \$140/kw is extrapolated from the manufacturer's cost data, giving a total capital cost of \$500,000 for the D.C. power source. A licensing fee (specific to the chlor-alkali industry) on a sliding scale but near 1/10 the electric power cost is also to be expected, if licensing procedures are similar to those obtaining in that industry.

With the baseline cost of \$140/ft² the cost of electrodes will range from 2.2 million at 0.25 amp/cm², to \$550,000 at 1 amp/cm².

5.7 Other Equipment Items

A number of auxiliary equipment items will be common to both the process for hydrocarbon fuels operation and to processes presented in the references. These include the receiving area, and such items as pumps, piping, electrical (other than the electrolysis power source) and instrumentation where applicable. The costs for these are taken from Ref. 5.3. It is assumed that spent material from the fermentation process may be returned to the biomass growth system after the conversion process. Thus a vacuum filter will not be required.

Separation of product and product storage (or, alternatively, a pipeline) will present additional costs. These are uncertain but for purposes of estimation the installed capital costs are assumed to total one million dollars.

5.8 Computation of Capital Costs

Estimated capital costs are presented in Table 5.3, showing a total capital requirement of 34.1 million dollars for the facility. A brief discussion of the sensitivity of this capital cost to various changes is presented later.

Table 5.3

ESTIMATE OF CAPITAL REQUIREMENT FOR FACILITY
TO MANUFACTURE LIQUID HYDROCARBON FUELS FROM BIOMASS

<u>Item</u>	<u>Installed Cost</u>
Site Preparation	300,000
Receiving Area	120,000
Shredding	300,000
Screw Conveyors	600,000
Packed Bed Digestion	12,800,000
Acid Extraction	1,250,000
Acid Resorption into Alkali	250,000
Electrolysis*	2,200,000
Transformer/Rectifier System	500,000
Separation and Storage	1,000,000
Instrumentation	300,000
Pumps and Piping	500,000
Building	<u>300,000</u>
Subtotal Plant Investment	20,420,000
Contractor's Overhead, Profit (12%)	2,456,000
Engineering and Design (6%)	<u>1,228,000</u>
Subtotal Plant Investment	24,154,000
Project Contingency (15%)	3,623,000
Development Contingency (7%)	<u>1,691,000</u>
Total Plant Investment	29,468,000
Interest During Construction (10%; 1.5 yrs)	<u>4,420,000</u>
	<u><u>33,838,000</u></u>

*At 0.25 amp/cm²

5.9 Energy Consumption of the Process

Figures for total electrolytic power consumption for the process were presented earlier. In order to compute total energy consumption for the process, it is necessary to estimate a number of other energy requirements, particularly for pumping and heating.

In order to calculate pumping requirements for recirculation of liquid through the packed bed fermenter, it will be assumed that the aqueous phase retention time is one day, which with assumptions presented earlier will dictate a recirculation rate of $127 \text{ ft}^3/\text{sec}$. The net head through which this liquid up flow must be pumped in the packed bed is assumed to be 1.25 ft H_2O . (At a 50 foot bed height, 15% solids loading and $\rho = 1.5$, a pressure equal to 2.5 feet of water head would totally lift the solid material in the bed.) The power requirement for pumping $127 \text{ ft}^3/\text{sec}$ of aqueous phase through a pressure drop of 1.25 ft of water (0.55 psi) will be 14 horsepower, which is minimal.

The net pressure loss for hydrocarbon circulating at $72 \text{ ft}^3/\text{sec}$ in the aqueous phase extraction column may be demonstrated to be about 2 psi which will also be the loss in the alkali extraction column. Total pumping losses for the closed-loop hydrocarbon circulation will be 75 hp. Calculating on a similar basis, the net pressure loss in circulating aqueous phase through the extraction column will be 37 hp.

The power requirement for the shredder, from Ref. 3 is estimated at 300 hp. Other pumping and miscellaneous energy requirement is estimated at 200 hp.

Based on experience with solid waste fermentation to methane, the sole significant process heat requirement will be that to heat the incoming material to the process temperature. The process heat required for acid generation is that needed to raise 6700 TPD input material ($C_p = 1$) from a baseline temperature of 70°F (assumed typical of areas where biomass will be grown) to 98°F , or $3.75 \times 10^8 \text{ BTU/day}$.

Much of this process heat requirement will be met by the electrolysis. Note that:

which means that the Kolbe electrolysis process is slightly endothermic. The heat absorption will be essentially zero; which means that the energy spent in electrolysis will appear as heat. At a total electrode potential of 1 v, the net energy available will be 46 kcal -16 or 30 kcal/g.mol, which on the basis of a 3.5 megawatt power consumption, means that electrical heating will contribute 1.9×10^8 BTU/day. Additional heat required will be 1.85×10^8 BTU/day.

With this information, the power consumption is as shown in Table 5.4. A net energy balance of 8.0/1 is obtained.

5.10 Operating Costs

Operating costs are broken down into the three major categories of labor-related, capital-related (primarily maintenance, local taxes, and insurance) and energy. As an estimate it is assumed that process operating labor will be equal to that required to operate an alternative fermentation plant as described in Ref. 3, with salaries updated to 1978 wage scales. Other operating costs follow as shown in Table 5.5. A total operating cost of \$13.35 million is obtained. Raw material cost is estimated at near zero except for biomass at \$30/ton DAF since no chemical is consumed and process liquid may be recycled.

5.11 Computation of Liquid Hydrocarbon Product Cost

The cost of generating liquid hydrocarbon product is computed in Table 5.6 using the American Gas Association synthetic gas cost calculation method modified for the acid production process. The computation assumes a 75%/25% debt/equity ratio, 9% interest on debt, 15% return on equity, and 20 year straight-line amortization. Capital and operating costs are as

Table 5.4

ESTIMATED ENERGY BALANCE OF PROCESS FOR CONVERTING
BIOMASS TO LIQUID HYDROCARBON FUELS

Mechanical Equipment <u>Item</u>	Power Requirement, hp <u>(Time - Average)</u>
Shredder	300
Packed Bed Digestion	14
Hydrocarbon Circulation	75
Aqueous Circulation through Hydrocarbon	37
Pumping and Miscellaneous	<u>200</u>
Total	626 hp = 470 kw

Total Power Requirement for Electrolysis = 3520 kw

Total Power Requirement for Electric Needs

= 4220 kw x 24 hrs/day x 365 days/yr x 0.9 service factor x 3413 BTU/kwh
x 1/0.3 efficiency = 3.78×10^{11} BTU/yr.

Heat Requirement = 1.85×10^8 BTU/day x 365 days/yr. x 0.9 service factor
x 1/.85 efficiency = 7.15×10^{10} BTU/yr.

Total Energy Requirement = 4.49×10^{11} BTU/yr.

Total Output = 1.066×10^{10} BTU/day x 365 days/yr x 0.90 service factor
= 3.5×10^{12} BTU/yr.

Energy Balance = Output/Input = 8.0/1

Table 5.5

ESTIMATED OPERATING COST FOR FACILITY TO
PRODUCE LIQUID HYDROCARBON FUELS FROM BIOMASS

	<u>Cost/Yr.</u>
Raw Materials:	
Biomass @ \$30/ton*	9,855,000
Labor:	
Process Operating Labor - 16 men at \$9/hr.	299,520
Maintenance Labor - 12 men at \$9/hr.	244,640
Supervision - 4 men at \$12/hr.	<u>99,840</u>
Total	624,000
Administration and General Overhead (60% of Process Operating Labor)	374,400
Supplies:	
Operating (30% of Process Operating Labor)	89,900
Maintenance (.015 of Total Plant Investment)	442,000
Local Taxes and Insurance (.027 Total Plant Investment)	801,500
Electric Power at 0.035/kwh*	1,164,000
Royalty on Electrolysis at 10% of Electrolytic Power Use	120,000
Heat at \$5/MMBTU	357,500
Credit: Hydrogen at \$3/MMBTU*	<u>(515,400)</u>
Total Operating Cost/Yr.:	<u><u>13,320,000</u></u>

Table 5.6

COST OF PRODUCING LIQUID HYDROCARBON

The cost for generating hydrocarbon is computed using the American Gas Association Method for Synthetic Fuels as utilized in Ref. 5.1 adapted to the cost of producing hydrocarbons.

$$\text{Average Production Cost} = \frac{N + 0.05 (C - W) + 0.005 \left[p + \frac{48}{52} (1 - d) r \right] (C + W)}{P}$$

where: N = Yearly operating cost; \$/Yr.	13,320,000
C = Total capital requirement	33,838,000
W = Working capital (1 mo. op. cost)	1,110,000
P = Annual product, MMBTU/yr.	3,335,000
p = Return on base rate $d(i) + (1 - d)r$, %/yr.	10.5
d = Fraction debt	0.75
r = Return on equity, %/yr.	15
i = Interest on debt, %/yr.	9

Average Production Cost = 5.22/MMBTU @ \$30/ton biomass (90% Plant Service Factor).

The first term on the right-hand side represents the total net cost of operating the facility. The second term is the 5% per year straight-line depreciation on the total capital requirement excluding the working capital. The last expression includes terms for both the return on rate base and the federal income tax. The sum of all these terms is the total yearly revenue requirement, which, when divided by the annual production in MMBTU yields the average production cost in \$/MMBTU.

estimated previously. The cost of generating 3.33×10^{12} BTU/yr of liquid hydrocarbon fuel yearly is computed to be \$5.22/MMBTU @ \$30/ton biomass. In Figure 5.1 is shown the cost of liquid fuel produced as a function of biomass (on the dry ash/lignin free basis of this analysis). Some commentary on the sensitivity of this cost to various possible factors follows.

5.12 Commentary on Sensitivity

The preceding analysis of the process to produce liquid hydrocarbon fuels from biomass is preliminary and clearly has the usual uncertainties inherent in such exercises. Its significance lies in the fact that a processing scheme can be devised which has favorable economics and energetics. There does not appear to be a priori any serious obstacle which would preclude the process.

It is certain that there are cost factors which have not been foreseen. On the other hand, a deliberate attempt has been made to cost major capital items conservatively. For example, combined capital costs of the electrolysis and fermentation unit together comprise about 3/4 of the total capital. A choice of higher rate constant for acid generation (as noted, rate constants much higher than 0.03 day^{-1} could probably be obtained) could lead to a severalfold reactor size and cost reduction; also reactor designs are plausible such that unit costs might be reduced severalfold. Additionally, the assumption of a current density of 1 amp/cm^2 rather than 0.25 could reduce the electrolysis capital cost by a factor of 4. Accomplishment of a capital cost reduction of 75% in these two items alone which is within the realm of possibility, would halve the total capital requirement for the facility. Thus while some costs including those unforeseen, may be higher than anticipated, others could be lower than projected here. Additionally, contingencies or safety factors, totalling 22% are added in during the computation of total capital requirement to take care of escalation and unforeseen factors.

Energetics are critically dependent on the efficiency of the electrolysis process. Figure 5.2 presents the cost of liquid fuel produced

Figure 5.1

COST OF LIQUID FUEL PRODUCED AS A FUNCTION OF BIOMASS COST
(See Text for Assumptions)

Figure 5.2

COST OF LIQUID FUEL PRODUCED AS A FUNCTION OF ELECTROLYSIS VOLTAGE

as a function of applied voltage. An applied voltage of nearly 4v may be used before a cost of \$6.00/MMBTU is reached. The slope change at approximately 1.5v occurs because at this potential sufficient resistance heating in the electrolysis is reached to supply all of the process heat requirements.

One possibility not discussed but deserving strong future consideration is that product hydrogen could be used in fuel cells to generate up to 100% of the necessary D.C. electric power (depending on requirements and efficiency) needed for the electrolysis. Recent communications with organizations familiar with fuel cell technology indicate that the H_2/CO_2 off gas would be ideal for a molten carbonate fuel cell which has an energetic efficiency of 60% electrical/thermal and an installed cost less than \$200/kw. This would about halve electric power costs.

What is significant is that processing cost with the assumptions used is less than half the total product cost. The balance is for biomass which, at \$30/ton D.A.L.F., contributes \$3.00/MMBTU to the liquid hydrocarbon product. The contribution of other factors to product cost is summarized in Table 5.7.

Table 5.7

BREAKDOWN OF TOTAL HYDROCARBON PRODUCT COST BY COMPONENT

<u>Component</u>	<u>Cost, \$/MMBTU</u>
Biomass @ \$30/ton D.A.F.	2.96
Labor and Labor-Related Costs	.33
Capital and Capital-Related Costs	1.60
Electric Power and Royalty	.38
Heat	.10
Hydrogen Credit	- 0.15
Total Cost, \$/MMBTU	\$5.22 @ \$30/ton biomass

It is clear that the parameter biomass cost/yield must be low in order to give an acceptable final product cost. This will be true, incidentally of all biomass conversion processes. With respect to processing costs exclusive of feedstock, a doubling of any other particular component would be tolerable. Likewise, as noted, a doubling in energy consumption would still leave an acceptable energy balance, through not understanding, of 4/1.

No side product credits were taken in the analysis, and it is of interest to observe that if 10% of the product heating value were diverted to acetic acid, total revenue at current market of 18¢/lb acid would be \$9.8 million from this source alone. Liquid hydrocarbon production would still be 1550 lb/day but feedstock cost would be completely defrayed at \$30/ton D.A.L.F. and the liquid fuel cost component would be solely that for processing, probably in the range of \$3.00/MMBTU if similar assumptions are made.

Section 5

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