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LIQUID FUELS PRODUCTION
FROM BIOMASS

Progress Report No. 7

Period Covered - January 1 to March 31, 1979

Contract No. FG-77-C-02-4388-7
Dynatech Project No. DOE-2
Dynatech Report No. 1889

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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 broth 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 have shown that the electrolysis of organic acids produced by fermentation to liquid hydrocarbon fuels is already operating with a favorable energy balance of 6/1 based on the applied potential and over 10/1 based on the working potential. 2-Bromoethanesulfonic acid, a coenzyme M analogue, has been shown to be an effective methane suppressor, and the program is being rapidly expanded to include biomass substrates other than marine algae. In addition, considerable effort has been directed toward refining the process design and economic analysis presented previously.

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 has 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. It has now been demonstrated that 2-Bromoethanesulfonic acid is an effective methane inhibitor for Hydrilla, and it is anticipated that this compound will also suppress methane formation from other substrates as well.

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. The design and construction of a liquid-liquid extractor system for use with the 300 liter fixed packed bed fermentor is complete and will be put into operation shortly. Ultimately, the acids are extracted from the water immiscible

Figure 2.1 Liquid Hydrocarbon Fuels from Biomass -- PIA Process Flowsheet

TDF

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 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 in a fuel cell. 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 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.

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Section 3

Suppression of Methane

In attempts to obtain the highest conversions possible of Hydrilla carbon into acids, continuing efforts have been made to prevent any carbon from converting to methane. As it was mentioned in the previous report (October 1 to December 31, 1978), an important pathway in methane formation is the reduction of CO_2 with molecular hydrogen. There is also proven methanogenesis from acetate (Ref. 1,2), a phenomenon which is deleterious to the Hydrilla fermentation, since the desired products are higher acids whose most important precursor is acetate. Other processes which require hydrogen are lipid and protein synthesis, biohydrogenation of unsaturated fatty acids and the production of propionic acid. Therefore, a methanogenic inhibitor must not interfere with these processes nor with the normal metabolism of non-methanogenic microorganisms. For the purpose of methane suppression, the inhibitors can be classified into two groups. The first group includes those chemicals that act as alternative electron receptors, i.e., sulfates, propanediol, etc. The second consists of specific inhibitors of particular methanogenic steps.

A thorough search of alternative means of suppressing methane was made, and a summary is presented as follows.

3.1 Group I - Alternative Electron Acceptors

3.1.1 Viologen Dyes

Wolin, Wolfe, and Wolin (Ref.4) discovered that low concentrations of methyl or benzyl viologen inhibited in vitro formation of CH_4 from ethanol and CO_2 by washed cells of Methanobacillus omelianskii. Hydrogen, normally formed from ethanol, accumulated in the medium in greater quantities when CH_4 formation was suppressed. Electrons which are normally used for both H_2 production and CO_2 reduction are used only for the former in the

presence of viologen dyes. Therefore, the viologens are not responsible for the production of hydrogen, only the inhibition of methane production (Ref.4). However, the extent of inhibition could not be duplicated in a culture of mixed rumen bacteria (Ref. 5).

3.1.2 Long-Chain Fatty Acids

Methanogenic bacteria are particularly sensitive to the presence of fatty acids of high molecular weights, especially those in the series C_{10} to C_{18} . Apparently fatty acids do not inhibit methane production by suppressing the fermentation of soluble carbohydrates since the apparent digestibility is not decreased to the same extent as methane production when the fats are added to the diet. Rather it was concluded that the effect of long chain fatty acids occurs at a later stage in the fermentation process because the fatty acids act specifically on gram positive bacteria (Ref. 6).

The number of double bonds in the fatty acid affects its degree of toxicity since less linolenate (C_{18} , 3 double bonds) than linoleate (C_{18} , 2 double bonds) is needed to effect the same reduction in methane production. Also, it is necessary that a free carboxyl group be present in the acid for it to retain its inhibitory nature. Substitution of a hydroxyl for the carboxyl group or the introduction of a second alkyl chain will lessen or even abolish its effect on methanogenesis (Ref. 7).

3.1.3 Propanediol and Sodium Sulfite

Two other substances that have been shown to have the ability to reduce methane fermentation are propanediol and sodium sulfite. Sodium sulfite acts to inhibit acetate production and to increase the percentage of propionate and butyrate formed. The mechanism of its action has not yet been determined. Treatment with propanediol decreased methane production from 22 to 35% (depending upon concentration and other conditions) and had no effect on the apparent digestibility of dry matter. However, the propanediol concentration fell off quickly within the rumen, leaving investigators to conclude

that it was either absorbed or metabolized (Ref. 6).

3.2 Group II - Specific Methane Inhibitors

3.2.1 Methane Analogues and Similar Compounds

Halogen-substituted analogues of methane, such as chloroform, carbon tetrachloride, bromochloromethane, and chloral hydrate, are powerful inhibitors of methane production under both in vitro and in vivo conditions. They belong to the second group of inhibitors, those that inhibit specific steps in the methanogenic process. Their activity is probably due to the formation of halogen analogues of methyl-cyanocobalamin from reduced cyanocobalamin (Ref. 7,8,9).

The alkyl halides that were tested were active in vitro in μM concentrations. Simple halomethanes were so potent that less than 10 ppm were required for complete in vitro inhibition (Ref.10). Much higher levels, however, were required to produce changes in vivo. This would suggest that the halides were either detoxified or rapidly removed (Ref. 6).

Of the simple alkyl halides, CCl_4 was the most powerful. 50% inhibition was accomplished at concentrations as low as 1.4 μM . Bromochloromethane caused complete inhibition also at very low concentrations. Chloral hydrate was less potent than the others, but they all acted to reduce methane and acetate formation and to stimulate propionate and butyrate production (Ref. 5,6,7).

Because most halomethanes are volatile liquids, they are not suitable for methane suppression in cattle rumen. Therefore, the use of such non-volatile compounds as hemi-acetal or chloral (trichloroacetaldehyde) and trichloroacetamide is preferred over the use of chloroform or bromochloromethane.

Czerkawski and Brekenridge (Ref.8) tried to combine long chain fatty acids and poly-halogen compounds into a single substance in order to

achieve the advantages of each. They showed that 2,2,2 trichloroethanol (TCE) was a strong inhibitor and that TCE pivalate was as active as TCE itself. Experiments with halogen-substituted alcohols and their esters showed that the number and types of halogen atoms proved to be important for methane inhibition. In most cases, alcohols were 3 to 4 times as potent as inhibitors than were their pivalate esters. The most potent pair was tribromoethyl alcohol and its ester, with the alcohol being more active (Ref. 8,9).

3.2.2 Rumensin

The Elanco Products Company (a division of Eli Lilly) instituted a search program to identify compounds that act to inhibit methane production in the cattle rumen. One of the most effective that they found was rumensin, the trade name for monensin, a fermentation product from Streptomyces cinnamonensis. Monensin (actually monensin sodium since monensin is changed to the sodium salt during the manufacturing process) was originally used as an anticoccidial agent in poultry (Ref. 11,12,13).

Although rumensin has moderate in vitro activity against gram positive organisms, its antibiotic activity is very limited. Rather, it works by altering the metabolic products of microbes in the rumen of cattle. The improvement in the efficiency of converting dietary energy into carcass energy is due to the shift in the rumen volatile fatty acids toward more propionic acid (Ref.14). Since there is no change in the total VFA production, there is no change in the energy content of the carcass, only in its form (Ref. 13,3).

Because cattle normally eat only enough to satisfy their energy needs, rumensin does not act to increase their daily weight gain, but it does reduce their consumption by slightly greater than 10%. Since the normal balance of VFA's is restored after a few days when the monensin treatments are stopped, the drug does not permanently alter the proportions of the rumen microbes. Rumensin also does not affect the quality of the beef carcasses, and it degrades rapidly when it is released into the soil as manure (Ref. 14).

3.2.3 Salinomycin

The use of another anticoccidial agent, salinomycin, has been shown to reduce the amount of methane produced in cattle. Like rumensin, salinomycin is a fermentation product that has been used to control coccidiosis in poultry. Although there is little literature on salinomycin as an inhibitor of methane production, it has been reported to be active at the dosage of 100 mg/day (Ref. 12).

3.2.4 Bromoethane Sulfonic Acid ($\text{BrCH}_2\text{CH}_2\text{SO}_3^-$)

This is a potent inhibitor of growth and uptake of the coenzyme-M, 2 mercapto-ethane sulfonic acid, (HS-CoM). Coenzyme-M is found predominantly as $\text{CH}_3\text{-S-Co-M}$ and $(\text{S-CoM})_2$ forms in the cells. Presumably the former is the final precursor of methane fermentation in the cell. In the presence of the inhibitor, the final step is blocked and methane biosynthesis is suppressed. As it is indicated in Table 3.1, $1\ \mu\text{M}$ of $\text{BrCH}_2\text{CH}_2\text{SO}_3^-$ is enough to exert 100% inhibition of HS-CoM uptake (Ref. 15).

3.3 Experimental Results

3.3.1 Hydrilla Fermentations

The need for a methane suppressor in Hydrilla fermentation for acid production has been made clear by results shown in a previous report (July 1st - Sept. 30, 1978).

After a literature review was made in search for methods for methane suppression, some alternatives were experimentally tested for the Hydrilla system. In the first set of experiments salinomycin, chloroform and sulfide were tested. The results, illustrated in Figure 1, indicated that the addition of:

- a. salinomycin, an anticoccidial agent, effectively suppressed methane in the period of time tested. However, the percent conversion of Hydrilla into acids achieved (20-23%) suggested

Table 3.1. Effect of Metabolic Inhibitors^a and
Uncoupling Agents on HS-CoM Uptake. (Ref. 16)

Inhibitor	Final Concn	Inhibition (%)
Sodium azide	10 mM	95
Potassium cyanide	10 mM	0
2,4-Dinitrophenol	1 mM	69
Iodoacetate	100 μ M	88
BrCH ₂ CH ₂ SO ₃ ⁻	1 μ M	100
Br(CH ₂) ₃ SO ₃ ⁻	10 μ M	0
DCCD ^b	1 mM	0
CCCP ^b	10 μ M	0
Valinomycin	10 μ M	20

^a Inhibitor was added to cells 3 min prior to addition of 0.5 μ M H³⁵S-CoM. Uptake rate was determined from 0.5-, 1.0-, and 1.5-min time points. Rate is expressed relative to a control which contained no inhibitor.

^b DCCD (N,N'-dicyclohexylcarbodiimide) and CCCP (carbonyl cyanide-m-chlorophenyl hydrazone) dissolved in methanol. A 10- μ l portion was added to 1 ml of cell suspension to give the final concentration indicated. No inhibition was observed by addition of methanol alone.

Figure 3.1. Effect of Methane Inhibitors on Production of Acids from Hydrilla (5% w/v). Sewage Sludge Used as Inoculum.

that acidogenic bacteria might have been altered in their acid production capabilities. However, no methane was produced.

- b. chloroform, a methane analogue, resulted in very low conversions into acids (15-20%). The low conversions could not be attributed to methane production since none was detected. However, acidogenic bacteria could have been damaged by the presence of the chemical, given its intrinsic properties (i.e. solvent for fats).
- c. sodium sulfide, a proven repressor of methane production, resulted in very attractive conversions (35-38%). However, after approximately 20 days of fermentation significant amounts of acetic acid were lost from the solution with the concomitant production of methane.

This first set of experiments ruled out the utilization of methane analogues for methane suppression since very low conversions were obtained. Out of the other two tested which looked promising, one resulted in low conversions (i.e. salinomycin), and the other in methane formation after "stimulating" higher conversions with respect to control runs (Figure 1D).

At this point a very specific methane suppressor (i.e. bromoethane sulfonic acid) was tested. The results, illustrated in Figure 2, determined that this chemical was more likely to solve the problem. On one hand the conversions achieved were significantly higher than the control (35-40%) when the methane inhibitor was added, versus 25-29% in the control. On the other hand, at 60 days fermentation when practically all the acids would have been consumed for methane formation in flasks containing no inhibitor, (Figure 3.2), 100% of the acids produced still remain in solution. After duplicating the results with bromoethane sulfonic acid addition, the problem of methane formation was considered solved.

Figure 3.2. Effect of the Addition of Bromoethane Sulfonic Acid (Coenzyme M Analogue) on the conversion of Hydrilla (3% w/v) into acids. Sewage sludge used as inoculum.

Once the problem of methane formation was solved, a new question arose. Typically numbers ranging from 35-40% conversion of substrate into acids have been obtained. Theoretically, higher conversions could be achieved, assuming that all the carbon is available for the acidogenic bacteria. Some alternative answers could be:

- a. The residual substrate is not available for fermentation with the population and environmental conditions available, in which case the substrate may have to be pretreated to increase conversion.
- b. The acidogenic bacteria are product-inhibited and/or there is a metabolite formed that alters their metabolism.

Experiments are in progress to test whether the low conversions obtained are due to either of those potential causes. The procedure used for the analysis of the first potential cause of low conversion consisted of washing thoroughly the solid residue from a 60-day old fermentation. After drying at 100°C overnight, the substrate was resuspended and inoculated with fresh sewage digester effluent. Along with this substrate, a fresh Hydrilla fermentation was initiated. Preliminary information indicates (Figure 3.3) that the residual substrate as it is cannot be further utilized for acid production. Efforts will be made in the determination of whether a pretreatment of the substrate is necessary in order to increase the conversion and if so, which set of conditions is more adequate for the purpose.

3.3.2 Acid Production from Agricultural Residues

In the initial phase of expanding the biomass substrates into agricultural and industrial residues, onion and garlic waste was tested. Preliminary results show (Figure 3.4) that onion and garlic residues can be successfully converted into acids by the microbial population present in the dairy manure used as inoculum. An interesting feature of this substrate is that no methane is formed as part of the products. Since this substrate

Figure 3.3 Production of acids from fresh substrate and solid residue from a 60-day old fermentation. 3% w/v of substrate was inoculated with sewage digester effluent.

Figure 3.4 Acid Formation from Onion-Garlic Residues and Hydrilla. Dairy Manure Used as Inoculum.

is known to contain some antibacterial components (Ref.17), it is apparent that only methanogenic bacteria are affected by their presence. As Figure 4 indicates, addition of onion-garlic residues to Hydrilla fermentation is a potential preventive measure of methane formation. This peculiar character could be exploited by using onion-garlic residues along with other substrates in order to prevent methane formation.

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Section 4

KOLBE ELECTROLYSIS

4.1 Introduction

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 hydrocarbon. Kolbe's important discoveries in the mid-nineteenth century led to the establishment of the principles of electrolytic oxidation and reduction (Ref. 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:

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 (Ref. 2):

In an aqueous medium, hydrocarbon formation occurs to an appreciable extent only at a smooth platinum or iridium anode. Using a platinum electrode, the Kolbe dimerization is favored by high concentrations of carboxylate, current densities over 0.25 amps/cm^2 , low temperature (below 50°C), low pH (~ 6) and the absence of foreign anions (Ref. 3). The most important competing reaction is the formation of olefin possessing half the carbon atoms of the Kolbe electrolysis product. Esters and alcohols have also been observed as electrolysis products.

When carboxylic acid mixtures are electrolyzed, "cross coupling" occurs in addition to the usual Kolbe reaction (Ref. 3):

Higher fatty acids give satisfactory yields of the Kolbe dimer, and alkanes up to $\text{C}_{34}\text{H}_{70}$ have been prepared by this method (Ref. 2).

4.2 Reaction Mechanism

Electrolysis of monobasic aliphatic organic acids generates paraffins, olefins, esters, alcohols, and carbon dioxide at the anode and hydrogen gas at the cathode. The mechanism of the anode reaction is not well understood, but a likely scheme is presented in Figure 4.1. Carboxylate is adsorbed to the anode surface and oxidized to form an acid radical. The acid radical decomposes to form CO_2 and an alkyl radical which can react with another radical to form the Kolbe dimer, or disproportionate to form alkene and alkane with half the carbon atoms of the Kolbe dimer. The alkyl radical can also be further oxidized to a carbonium ion which subsequently forms alcohol, alkene or ester.

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

Figure 4.1

Anodic Oxidation of Carboxylates
Reaction Mechanism

From Ref. 3, p. 801.

Yields of product paraffin, olefin and ester from Kolbe electrolysis of aliphatic monobasic carboxylic acids presented in Ref. 3 are given in Table 4.1. 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 (Ref. 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 reaction conditions and proper cell design it is likely that improved paraffin yields will be obtained.

Oxygen is not produced when aqueous carboxylic acid solutions are electrolyzed. This is noteworthy because the potential at which water electrolysis occurs (1.5V) is less than that at which Kolbe electrolysis normally occurs (~2V). Presumably, a layer of adsorbed carboxylate covers the electrode surface (Refs. 3,4) inhibiting water electrolysis by preventing the adsorption of water.

4.3 Reaction Thermodynamics

In electrolysis, the Gibbs free energy of reaction, ΔG , can be interchanged with electrical energy at constant temperature and pressure. This relationship can be represented by the equation:

Table 4.1
KOLBE ELECTROLYSIS OF ALIPHATIC MONOBASIC CARBOXYLATES

Acid	Solvent	Yield of Dimer %	Current Yield %	Major Side Products (%)
$\text{CH}_3\text{CO}_2\text{H}$	H_2O		90	
$\text{CH}_3\text{CO}_2\text{H}$	MeOH		93	
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	H_2O	40		$\text{CH}_2:\text{CH}_2$ (32)
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	H_2O		8	$\text{CH}_2:\text{CH}_2$ (66, current yield)
$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$	H_2O	60		
$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$	H_2O		14.5	$\text{CH}_3\text{CH}:\text{CH}_2$ (53, current yield)
$\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$	H_2O		50	$\text{CH}_3\text{CH}_2\text{CH}:\text{CH}_2$ (18, current yield)
$\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	33		C_4H_8 alkenes (42)
$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	H_2O	86		
$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$	H_2O		75	$\text{CH}_3(\text{CH}_2)_2\text{CH}:\text{CH}_2$ (7, current yield)
$\text{CH}_3(\text{CH}_2)_5\text{CO}_2\text{H}$	H_2O	—		
$\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	58		
$\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$	H_2O	—		
$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$	$\text{EtOH}/\text{H}_2\text{O}$	90	45	
$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	69		
$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$	$\text{EtOH}/\text{H}_2\text{O}$	89	34	

$$\Delta G = -nFE \quad (4.5)$$

where n is the number of electrons transferred per molecule, F is the Faraday value (96,520 coulombs/g - equivalent) and E is the potential difference in volts. (ΔG , in these units, is in joules/mole. 1 joule = 2.390×10^{-4} kcal.)

The enthalpy of the reaction, ΔH , is related to ΔG by the equation

$$\Delta H = \Delta G + T\Delta S \quad (4.6)$$

where ΔS is the change in entropy. This entropy change is not convertible to electricity; it must be liberated as heat (for a negative ΔS) and can be supplied as either heat or electricity (for a positive ΔS). Only ΔG must be supplied as electricity.

The enthalpies and free energies of reaction for the Kolbe reaction and for olefin formation are shown in Table 4.2. All products with five or fewer carbon atoms are considered to be gaseous. All products with greater than five carbon atoms (from the Kolbe electrolysis of butyric, valeric, and caproic acids) are considered to be in the liquid state. Solution effects are not considered; assuming regular solution thermodynamics for the acid-water mixture (0.5N acid) shows little change in the ΔH 's but adds approximately +4 kcal/mole to the ΔG 's for both paraffin and olefin.

For the Kolbe reaction, ΔG is slightly negative and ΔH is positive. This means that the reaction is spontaneous, requiring the addition of heat but not electricity. Theoretically, the Kolbe reaction could be run in a fuel cell, requiring heat but producing a small amount of electricity.

The electrical input to Kolbe electrolysis is necessary for kinetic rather than thermodynamic reasons. This suggests that a suitable catalyst, if discovered, could greatly reduce the energy requirements

Table 4.2
ENTHALPY AND FREE ENERGY (WITH CORRESPONDING
OXIDATION POTENTIALS) FOR ELECTROLYSIS OF ORGANIC ACIDS

Kolbe Reaction

ACID	ΔH		ΔG	
	kcal/mole	volts	kcal/mole	volts
Acetic	9.0	-0.39	-4.4	0.19
Propionic	10.8	-0.47	-4.6	0.20
Butyric	4.8	-0.21	-5.1	0.22
Valeric	3.9	-0.17	-5.8	0.25
Caproic	8.3	-0.36	-6.5	0.28

Elimination Reaction

ACID	ΔH		ΔG	
	kcal/mole	volts	kcal/mole	volts
Propionic	38.3	-0.83	13.7	-0.30
Butyric	26.2	-0.57	10.3	-0.22
Valeric	36.2	-0.79	10.5	-0.23
Caproic	44.2	-0.96	10.0	-0.22

The ΔH 's and ΔG 's presented above were obtained from the enthalpic and free energies of formation of the products and reactants. References 5, 6, and 7 were used as sources of thermodynamic data.

of this process. Olefin production is not spontaneous, but the thermodynamic requirements of this reaction are satisfied at potentials far lower than those at which Kolbe electrolysis is conventionally run.

4.4 Experimental Results

In order to achieve high current densities without applying larger overpotentials, the present approach is to perform 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 4.3 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 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 hydro-

Figure 4.2
ELECTROLYSIS CELL

Table 4.3
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 ($B \times C \times M_w$)		13.0 g	
E. Amount of acid added ($Vol \times \rho$)		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 ($B \times C / 96,500$)			0.065 Moles
E. Power ($A \times B \times C$) 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 ($A1 \times A2$)		3.73 ml/min.	
4. Total hydrogen ($A3 \times IIC$)		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 ($A1 \times C1 \times IIC$)		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 ($D3/M_w$)			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 $E3/M_w$			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 $F4/M_w$			0.5 Moles
V. Yields			
A. Current yield ($2(IVD4 + IVE4)/IID$)			92%
B. % Paraffin $IVE4/(IVD4 + IVE4)$			67%
C. Energy ($230 \times IVA5 + (IVD3 + IVE3)/45$)(1054)/IIE)			5.9/1

carbon 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

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

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

$$\therefore E - CO_2 = 0$$

Figure 4.3
Liquid Electrolysis Products
Run No. 02392

Figure 4.4

Gaseous Electrolysis Products

Run No. 02392

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 found.

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 4.4. From these data some conclusions may be drawn:

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.

TABLE 4.4
RESULTS OF ELECTROLYSIS EXPERIMENTS

Run No.	Acid		Current Density	Temperature	Flow Rate	Working Potential	% Paraffin
			A/cm ²	°C	cm/sec	Volts	
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%

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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. 1 through 6. 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. 1.
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:

With these assumptions, yield of product alkanes 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 Packed Bed Digester

The size of the reactor required to carry out the conversion of biomass is an important factor in the overall process economics. The volume of the digester is determined by the total amount of solids loaded, the solid fraction, and the average retention time. The retention time is described by the equation:

$$t = - \frac{\ln(1-x)}{k} \quad (5.1)$$

where t = retention time (days),

x = fractional conversion of D.A.L.F. solids, and

k = rate constant for the biomass degradation.
(days⁻¹)

It is a common assumption that the rate limiting step in the formation of carboxylic acids is the same as that for the production of methane; solubilization of organic matter. Thus, the rate constants for both processes should be equivalent. Ashare et al. (Ref. 2) observed a rate constant in the order of 0.12 day⁻¹ for the anaerobic digestion of various substrates to methane. However, a correction factor for the inhibition of product formation by the presence of product acids in the reactor must be applied. Assuming that product inhibition reduces the rate by 75% results in a value of 0.03 day⁻¹ for the rate constant. The inhibition reduction factor is large since high product acid concentrations and low pH are necessary to facilitate the generation and removal of higher acids (discussed later).

A further assumption is that solids loading in the packed bed digester is 15% by weight. At this initial solids loading, with an input feed of 1333 tons/day (75% D.A.L.F.), and a residue retention time of 60 days, the total reaction volume requirement is 17.1×10^6 ft³. This volume is equal to the space offered by 56 typical sewage treatment digesters (90'D x 50'H). The cost for such equipment, including covers and piping, is approximately \$1.50/ft³, or \$25,600,000 for all the digesters.

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.

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 continuous-contacting mass transfer equipment in which the aqueous stream is mixed 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.	$P = \left(\frac{CF}{CI} \right) = \frac{\text{Concentration in Freon}}{\text{Concentration in Water}}$
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 Extractor

The moles of a diffusing component transferred per time per cross-sectional area can be defined by two different concepts, a material balance and a mass transfer equation. For equipment involving the continuous-contact between two immiscible phases, these two equations may be combined and the resulting expression integrated to provide a defining relation for the height of the reactor.

The mass balance for an acid over the differential length dh is described by:

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = \frac{F_A M_A}{\rho_A} dC_A \quad (5.2)$$

where F_A = molar flow of aqueous phase (g-moles/sec-cm²),

M_A = molecular weight of aqueous phase (g/g-mole),

ρ_A = density of aqueous phase (g/cm³), and

dC_A = differential change in the concentration of acid being transferred in the aqueous phase (meq/l)

Equation (5.2) can be simplified to:

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = 1 \times 10^{-3} V_A dC_A \quad (5.3)$$

where V_A = velocity of the aqueous phase (cm/sec)

The mass transfer of an acid in the differential length dh is defined by:

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = Ndh \quad (5.4)$$

where N = rate of diffusion of the acid (meq/sec-cm^2),

a = interfacial area per unit volume of extractor (cm^{-1}), and

dh = differential height (cm)

Assuming a constant mass-transfer coefficient and steady-state transfer of acid, the rate of diffusion of acid towards the interface of the phases can be described by:

$$N = 1 \times 10^{-3} K_L (C_A - C_A^*) \quad (5.5)$$

where K_L = overall mass-transfer coefficient, based on a liquid concentration driving force (cm/sec),

C_A = bulk concentration of acid in aqueous phase (meq/l), and

C_A^* = concentration of acid in the aqueous phase in equilibrium with the concentration in the hydrocarbon phase (meq/l)

$$C_A^* = \frac{C_H}{P} \quad (5.6)$$

where C_H = concentration of acid in hydrocarbon phase (meq/l) and

P = partition coefficient

Substituting N from equation (5.5) into equation (5.4) yields:

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = 1 \times 10^{-3} K_L a (C_A - C_A^*) dh \quad (5.7)$$

Setting equation (5.7) equal to equation (5.3) and rearranging produces:

$$dh = \frac{V_A}{K_L a} \frac{dC_A}{(C_A - C_A^*)} \quad (5.8)$$

Integrating both sides of equation (5.8) defines the height of the extractor:

$$h = \frac{V_A}{K_L a} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(C_A - C_A^*)} \quad (5.9)$$

where h = height of extractor (cm),

C_{A1} = acid concentration in aqueous phase influent (meq/l), and

C_{A2} = acid concentration in aqueous phase effluent (meq/l)

The overall capacity coefficient, K_L , is a combination of the individual phase resistances:

$$\frac{1}{K_L} = \frac{1}{k_{LA}} + \frac{m}{k_{LH}} \quad (5.10)$$

where m = Henry's law constant, $\frac{1}{P}$,

k_{LA} = aqueous phase resistance (cm/sec), and

k_{LH} = hydrocarbon phase resistance (cm/sec)

The individual coefficients can be determined from two simple equations. The first (Higbie equation) is for the fluid surrounding the drop (continuous phase):

$$k_o = 2 \frac{DV}{\pi d} \quad (5.11)$$

where V = relative velocity of rise or fall (cm/sec),

d = drop diameter (cm), and

D = diffusivity of acid (cm²/sec)

The second equation (Perry's 4th ed., 14-65) is for the fluid within the drop:

$$k_i = 0.00375 \frac{V}{1 + (\mu_D/\mu_C)} \quad (5.12)$$

where μ_C = viscosity of continuous phase (poise) and

μ_D = viscosity of disperse phase (poise)

It can be observed from equations (5.11) and (5.12) that a high relative velocity and small drop diameter will produce the largest mass transfer coefficients. However, the smaller the drop diameter, the slower the relative velocity. Therefore, the greatest relative velocity at the smallest possible drop diameter is desired. This drop size defines the critical diameter:

$$d_C = 0.33 \rho_C^{-0.14} \Delta \rho^{-0.43} \mu_C^{0.30} \gamma^{-0.24} \quad (5.13)$$

where γ = interfacial tension (dyn/cm),

ρ_C = density of continuous phase (g/cm³), and

$\Delta \rho$ = density difference of phases (g/cm³)

Assuming that the aqueous phase is continuous, and substituting the appropriate values into equation (5.13) determines a critical diameter of 0.36 cm. At drop diameters less than the critical diameter the relative velocity of the two phases can be calculated by:

$$V = 38.3 \rho_C^{-0.45} \Delta \rho^{0.58} \mu_C^{-0.11} d^{0.70} \quad (5.14)$$

Using hydrocarbon drops of 0.35 cm diameter results in a relative velocity of 14.3 cm/sec. Substituting this velocity, along with an assumed diffusivity of $1 \times 10^{-5} \text{ cm}^2/\text{sec}$ into equations (5.11) and (5.12) produces values of 2.28×10^{-2} and 2.79×10^{-2} for k_o (or k_{LH}) and k_i (or k_{LA}) respectively. Substituting these numbers and the appropriate values of M ($1/P$ -- see Table 5.1) into equation (5.10) gives the overall mass transport coefficient for different acids.

Table 5.2
MASS TRANSFER COEFFICIENTS FOR VARIOUS ACIDS
(Aqueous-Continuous)

Acid	P	K_L
Acetic	0	0.0
Propionic	0.05	1.10×10^{-3}
Butyric	0.4	6.87×10^{-3}
Valeric	2.0	1.73×10^{-2}

The surface area of a 0.35 cm diameter drop is 0.385 cm^2 . Assuming a void fraction of 0.30, there exists 0.30 cm^3 of hydrocarbon bubbles (each drop having a volume of 0.022 cm^3) in 1.0 cm^3 of extractor volume. Therefore, there are 13.6 hydrocarbon drops per cm^3 of extractor. Consequently, there are 5.24 cm^2 of interfacial area per cm^3 of extractor ($a = 5.24 \text{ cm}^{-1}$). Substituting this value into equation (5.9) yields:

$$h = 0.191 \frac{V_A}{K_L} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(C_A - C_A^*)} \quad (5.15)$$

Although this equation is solved by a graphical integration procedure in most practical design calculations, in the present case it is possible to use a much simpler equation based upon a logarithmic mean driving force. Since the two contacting streams are relatively dilute, the equilibrium and operating concentrations may be considered to vary

linearly with time, and consequently with height in the extractor. Under these conditions, the driving force $(C_A - C_A^*)$ changes linearly with column height. Equation (5.14) can now be integrated to:

$$h = 0.191 \frac{V_A}{K_L} \frac{C_A - C_A^*}{(C_A - C_A^*)_{1m}} \quad (5.16)$$

$$\text{where } (C_A - C_A^*)_{1m} = \frac{(C_A - C_A^*)_1 - (C_A - C_A^*)_2}{\ln \frac{(C_A - C_A^*)_1}{(C_A - C_A^*)_2}}$$

An initial assumption is that the driving force is provided by the undissociated acid component only. Therefore, the concentration of undissociated acid in the aqueous phase is:

$$C_A = \Delta C_A \left(\frac{[H^+]}{[H^+] + k_i} \right) \quad (5.17)$$

where ΔC_A = total acid concentration (meq/l),

$[H^+]$ = concentration of hydronium ions (moles/l), and

k_i = ionization constant of the acid

Table 5.3 lists $C_A/\Delta C_A$ at two pH's.

Now that the governing equation for the system has been determined, the type of continuous contact equipment (cocurrent or countercurrent) to be employed must be chosen. In most industrial applications a countercurrent extractor is more desirable since: (1) more acid can be removed in a single pass, (2) a higher concentration of acid can be achieved in the hydrocarbon stream, and (3) for the same amount of acid transferred the countercurrent has a larger average driving force and consequently shorter residence times and smaller volumes. However, in our system we have a large volumetric flow and only desire to extract a small percentage

Table 5.3

FRACTION OF TOTAL ACID WHICH IS UNDISSOCIATED AS
A FUNCTION OF pH

Acid	k_i	$\frac{C_A}{\Delta C_A}$	
		pH = 4.75	pH = 5.00
Acetic	1.74×10^{-5}	0.505	0.365
Propionic	1.32×10^{-5}	0.574	0.431
Butyric	1.51×10^{-5}	0.541	0.398
Valeric	1.38×10^{-5}	0.563	0.420
Caproic	1.41×10^{-5}	0.558	0.415

of the acids (15%). Since the maximum velocity of any phase in counter-current flow is the relative velocity, which is quite low, a very large cross-sectional area is required to accommodate the high volumetric flow. The small fraction of acids to be extracted requires a short residence time and extractor height. The above two factors are in agreement with calculations (Appendix A) which show that running the liquids countercurrently produces a short, very wide, and consequently inefficient extraction system. However, by running the process cocurrently, there are no individual restrictions on the phase velocities (only their relative velocities). This fact allows a tall, narrow, and efficient tower to be built. Even though the volume required for a cocurrent extractor is slightly greater, the advantages of good mixing and physical convenience more than outweigh the relatively minimal extra expense.

It is assumed that the dispersed aqueous phase occupies three-tenths of the total extractor volume (void fraction = 0.30) meaning that:

$$\frac{S_H}{S_A + S_H} = \frac{\frac{Q_H}{V_H}}{\frac{Q_H}{V_H} + \frac{Q_A}{V_A}} = 0.30 \quad (5.18)$$

where S = cross-sectional area required for the specified phase to flow (cm²),

Q = volumetric flow (cm³/sec)

V = velocity (cm/sec)

A or H = aqueous or hydrocarbon phase

The volumetric flow of the aqueous phase can be determined from information on the digesters. It leaves the digesters at a velocity of 8.5×10^{-3} cm/sec (1.0 ft/hr) and passes through a cross-sectional area of 3.31×10^8 cm², resulting in a flow of 2800 l/sec. It is suggested ((Ref. that the hydrocarbon flow be half that of the aqueous (1400 l/sec). With knowledge of Q_A, Q_H, and a relationship between V_A and V_H

(equation 5.14), equation (5.18) can be solved for the aqueous phase velocity ($V_A = 85.8$ cm/sec). Substituting this value into equation (5.16) yields:

$$h = \frac{16.4}{K_L} \frac{C_{A1} - C_{A2}}{(C_A - C_A^*)_{1m}} \quad (5.19)$$

After the application of constraints on the system, the above equation can be solved by a trial and error iteration procedure. The first constraint is the material balance $Q_H \Delta C_H = Q_A \Delta C_A$ over any height increment in the reactor. The second is that it is only desirable to extract 3700 g acid/sec. If more than this amount is taken out, the recycle stream returning to the extractor has a lower acid concentration. Consequently, the acid concentration in the digester will drop and less higher chain acids will be produced. The iteration procedure for determining the dimensions of an extractor for a given influent stream is:

- (1) For the highest chain acid assume an exit concentration in the hydrocarbon phase.
- (2) Determine $(C_{A1} - C_{A2}) / (C_A - C_A^*)_{1m}$ from equation (5.16) and the first constraint.
- (3) Using the K_L value from Table 5.1 and substituting it into equation (5.19) solve for the height of the extractor.
- (4) For each of the other acids (rearrange equation 5.16) solve for the concentration driving force in terms of $hK_L a / V_A$.
- (5) Using equation (5.18) and the first constraint determine the concentration of each of the other acids in the hydrocarbon effluent stream.

- (6) Calculate the total amount of acid being extracted per unit time.
- (7) If this number is greater than 3700 g/sec, go to step (1) and assume a lower exit concentration. If the number is less than 3700 g/sec assume a higher concentration. Repeat steps (1-6) until approximately 3700 g/sec are being extracted.
- (8) The cross-sectional area of the extractor can be determined from the denominator of equation (5.18).

Table 5.4 shows the results of these calculations.

Table 5.4
RESULTS OF MASS TRANSFER COMPUTATION FOR COCURRENT EXTRACTION
(milliequivalents per liter)

Acid	Aqueous Phase		Hydrocarbon Extraction Phase	
	Influent (Total Acid)	Effluent (Total Acid)	Influent	Effluent
Acetic	42.0	42.0	0.0	0.0
Propionic	12.5	12.5	0.0	0.0
Butyric	62.0	56.0	0.0	11.8
Valeric	10.5	6.7	0.0	7.4
Caproic	7.0	3.4	0.0	7.2

Height = 50.2 ft Diameter = 8.0 ft

It should be noted that the use of an undissociated acid concentration gradient results in a minimum mass transfer. In the ionic mix considered here, ionized species will also contribute to transport. Actual aqueous side transfer coefficients will be improved by a factor of two or more when ionic transport is taken into account. The calculation of extractor dimensions is therefore a maximum.

An estimated cost for the extractor is \$50/ft³, considered conservative since it will be of relatively simple design, an 8' diameter, 55' high tank (allowing for distributors, etc.) and a settling chamber. At approximately 2,750 ft³ the total cost is projected at \$140,000.

5.5 Extraction of Product Acids from 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. A co-current extraction with aqueous base is envisioned; base is continuously withdrawn, acid anions are removed by Kolbe electrolysis, and the base returned in a closed loop. Depending on base concentration (a consequent 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 the chemical reaction:

All resistance to mass transfer is in the hydrocarbon phase. The equilibrium concentration of acid in this phase is zero (equivalent to an infinite partition coefficient). Since the volumetric flow of the aqueous phase is specified ($Q_A = 500$ l/sec) by the electrolysis step (to be discussed later), the amount of acid reacted and transferred to this phase is determined from the constraint $Q_A \Delta C_A = -Q_H \Delta C_H$ to be 75 meq/l. A minimal aqueous effluent concentration of 0.5N is desired in order to maintain a low cell resistance in the electrolysis step. The influent aqueous phase concentration ($C_{A1} = 425$ meq/l) and the log-mean driving force (D.F. = 7.7) are now set. Employing a cocurrent extractor with the hydrocarbon phase continues results in a relative velocity (equation 5.14) of 18 cm/sec. Assuming a void fraction of 0.20 and employing equation (5.18) determines the individual phase velocities ($V_A = 60$ cm/sec, $V_H = 42$ cm/sec). Following the same procedures as in Section 5.4.2 produces an

extractor which is 55 ft tall and 7.5 ft in diameter. At a height of 60 feet (allowing for distributors, etc.) the volume required is $2,700 \text{ ft}^3$. The total cost at $\$50/\text{ft}^3$ of extractor V volume is $\$135,000$.

5.6 Extraction of Excess Water from the Packed Bed Digester

The 80 l/sec of water (contained in the wet biomass) which is continuously being added to the digester must be removed in an overflow stream. A second extraction series is required to remove the acids from the water and send them to the electrolysis step. Since it is desirable to extract all the acids in a single pass, the aqueous phase will be contacted against a stream of 20% Trioctylphosphine oxide (TOPO) in hydrocarbon (all the acids have a high partition coefficient in TOPO ~ 4). Using two countercurrent extractors (due to the small volumetric flow) and assuming that 90% of the acids are removed, the dimensions of the extractors using the methods of the previous two sections are:

Aqueous Phase Extraction Column

Height = 15 ft (includes distributors)

Diameter - 7 ft

Volume - 575 ft^3

$Q_A = 80 \text{ l/sec}$ (continuous)

$Q_H = 80 \text{ l/sec}$ (disperse)

Drop Diameter = 0.35 cm

$V_A = 3 \text{ cm/sec}$

$V_H = 10 \text{ cm/sec}$

Alkali Extraction Column

Height - 20 ft (includes distributors)

Diameter - 4 ft

Volume = 250 ft^3

$Q_A = 21 \text{ l/sec}$ (disperse)

$Q_H = 80 \text{ l/sec}$ (continuous)

Drop Diameter = 0.35 cm

$V_A = 9 \text{ cm/sec}$

$V_H = 9 \text{ cm/sec}$

At a price of \$50/ft³ the cost of the second extraction series is \$41,000.

5.7 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 and oxidized to aliphatic hydrocarbons, carbon dioxide, and hydrogen gas. Olefins are the major side product.

5.7.1 Electrolysis Products

Based on the results of Section 4.4, alkanes (Kolbe dimer), alkenes, carbon dioxide, and hydrogen are assumed to be the sole electrolysis products. The anticipated products and reactants are listed in Table 5.5. The relative amounts of each acid reacting to form alkane and alkene were obtained from Table 4.1. Cross coupling (Sec. 4.1) and the usual Kolbe reactions were assumed to occur with equal frequency.

5.7.2 Sizing of the Electrodes

From Table 5.5, 26.8 moles/sec of hydrogen are produced by electrolysis. Since each hydrogen molecule requires two electrons, the electric current required to produce this hydrolysis (which is the total current required for electrolysis) is 5.16×10^6 amps.

For the electrolysis cell

$$V - V_A = IR \quad (5.20)$$

V is the applied voltage. V_A is a constant determined by the thermodynamics and kinetics of the reaction (for very low current densities V_A is a function of current density). V_A for the Kolbe reaction is about 2V. I is the current (5.16×10^6 amps). R is the resistance of the cell. The

Table 5.5
ELECTROLYSIS REACTANTS AND PRODUCTS

	<u>Moles</u> <u>sec.</u> reacting	<u>Moles</u> <u>sec.</u> produced	<u>g/sec</u>
Acetic acid	1.6		96
Propionic acid	0.5		37
Butyric acid	18.9		1663
Valeric acid	10.8		1102
Caproic acid	10.3		1195
Ethane		0.04	1.2
Propane		0.01	0.4
Butane		0.6	35
Pentane		0.5	36
Hexane		2.7	232
Heptane		3.0	300
Octane		4.5	513
Nonane		2.4	307
Decane		1.5	213
Ethylene		0.2	5.6
Propene		7.6	319
Butene		2.8	157
Pentene		0.9	63
CO ₂		42.0	1848
H ₂		26.8	54

resistivity of a 0.5 N caproic acid solution was found, with a conductivity bridge, to be 47 ohm-cm at 23°C. This was corrected to 23 ohm-cm at 60°C (the approximate temperature of cell operation). For an electrode spacing of 0.033 cm (the closest spacing deemed practical) the cell resistance will be approximately $23 \text{ ohm-cm} \times 0.033 \text{ cm} = 0.76 \text{ ohm-cm}^2$. If A is the anode area in cm^2 ,

$$R = 0.76/A \quad (5.21)$$

where R is in ohms. Combining equations 5.20 and 5.21 gives

$$V - 2.0 = 5.16 \times 10^6 \times 0.76/A \quad (5.22)$$

Equation 5.22 shows the trade-off between operating cost (voltage) and capital cost (electrode area). Based on conversations with a major chlor-alkali manufacturer, the installed cost of the electrodes is estimated at \$140/ft² of anode.

Operating and capital costs are related by the American Gas Association Method for Synthetic Fuels equation (to be explained in Section 5.12). The product cost, as obtained from this equation, is shown as a function of current density in Figure 5.1. The minimum occurs at a current density of 0.32 amps/cm². Since

$$\rho = I/A = 5.16 \times 10^6/A \quad (5.23)$$

where ρ is the current density, the required anode area is $1.61 \times 10^7 \text{ cm}^2$. Combining equations (5.22) and (5.23) gives the voltage

$$V - 2.0 = 0.76\rho \quad (5.24)$$

$V=2.2$ volts when $\rho=0.32 \text{ amps/cm}^2$. At this voltage, the power requirement for electrolysis is 11,560 kw.

Figure 5.1 Cost of Liquid Fuel Produced as a Function of Electrolysis Current Density

5.7.3 Electrolysis Cell Design

The electrolysis cell is to be of the filter press design; the series arrangement of the electrodes will allow the use of high voltages, minimizing resistance losses. The electrolysis units will be similar to those used for water electrolysis. No diaphragm, however, would be required.

For 240V line current, each filter press unit will be comprised of $240\text{V}/(2.2\text{V/cell}) = 109$ cells. If the anode area of each cell is $18,200\text{ cm}^2$ (the size of the Lurgi water electrolysis cell), 10 such units will be required. If the electrodes are square, each will be 135 cm on a side.

To generate 0.32 amps/cm^2 of current, $2.6 \times 10^{-6} \frac{\text{moles}}{\text{cm}^2\text{-sec}}$ of acid must diffuse to the electrode. For a fluid containing a species A flowing over a flat plate on which A is consumed,

$$N_A = -(0.664 D_{AB} C_{AO}/L) (V_0 L/\nu)^{1/2} (\nu/D_{AB})^{1/3} \quad (5.25)$$

where N_A = the mass flux of A (acid) in $\text{moles/cm}^2\text{-sec} = 2.6 \times 10^{-6}$,

D_{AB} = the diffusivity of acid in water = $8 \times 10^{-6} \text{ cm}^2/\text{sec}$,

C_{AO} = the bulk acid concentration = $5 \times 10^{-4} \text{ moles/cm}^3$,

L = the electrode length (in the direction of fluid flow) in cm,

V_0 = the fluid velocity far from the plate = 150 cm/sec, and

ν = the kinematic viscosity = $8.6 \times 10^{-3} \text{ cm}^2/\text{sec}$.

Equation 5.25 is derived in Appendix B. This equation is valid for laminar flow. With an electrode spacing of 0.33 cm, the Reynolds number = 1150, in the laminar flow region.

To satisfy equation (5.25), $L = 1.9$ cm. This means that the desired mass flux cannot be achieved for electrodes of length greater than 1.9 cm and suggests short electrodes covering a large area. A more practical solution is to place grooves in the electrodes to allow mixing of the solution. The grooves would destroy any concentration boundary layers and reestablish the bulk acid concentration close to the anode. Because acid will be consumed, the bulk acid concentration will not remain at 5×10^{-4} moles/cm³. About 21% of the acid will be consumed during a pass through the electrolysis cell, so the average bulk acid concentration will be 0.45 moles/cm³. If this value of C_{AO} is placed in equation (5.25), $L = 1.5$ cm. This means that the grooves should be spaced not more than 1.5 cm apart.

5.7.4 Molten Carbonate Fuel Cell

The electrolysis step will produce hydrogen at the rate of 26.8 moles/sec. Laboratory results have indicated that an additional 12 moles/sec will be produced by the fermentation step. In both cases the hydrogen is mixed with carbon dioxide which would have to be extracted before the hydrogen could be sold.

An alternative to purifying, compressing, and selling the hydrogen is using it to produce electricity in a molten carbonate fuel cell operating at 60% efficiency and a temperature of 650°C. An H_2/CO_2 mixture is ideal for the application because the fuel cell requires carbon oxides as well as hydrogen.

The fuel cell will generate 5630 kw of electricity at an estimated capital cost of \$200/kw. It will also generate 3.07×10^8 Btu/day of high temperature heat which would produce steam sufficient to provide 1130 kw (assuming 30% efficiency) at a cost of \$60/kw. The electricity produced would meet almost half of the requirements of Kolbe electrolysis while the steam would be more than sufficient to supply all of the pumping and mechanical power required by the plant (see Sec. 5.10).

A single fuel cell will produce electricity at 0.75 V. If 320 smaller fuel cells are lined up in series, the electricity produced will be at 240 V.

Using a molten carbonate fuel cell results in a \$0.29/MMBTU saving in the cost of the final product (assuming a value of \$3/MMBTU for the H_2/CO_2 mixture, 5630 kw of electricity produced, and all mechanical power requirements are met by steam produced by the fuel cell. The use of a molten carbonate fuel cell will be assumed in all subsequent economic calculations.

5.7.5 Other Electrolysis Equipment and Costs

Rectification is necessary before utility current can be used in the electrolysis cell. In addition, transformers will be required. A cost for the necessary D.C. power supply of \$140/kw is extrapolated from manufacturers' cost data, giving a total capital cost of \$830,000 at the power requirement of 5.93 megawatts. A licensing fee on a sliding scale but near 1/10 the electric power cost may also be expected.

5.8 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. 1. 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.

5.9 Computation of Capital Costs

Estimated capital costs are presented in Table 5.6 showing a total capital requirement of 53.5 million dollars for the facility. A brief discussion of the sensitivity of this capital cost to various changes is presented later.

5.10 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 net head through which the liquid up-flow must be pumped is 1.25 ft H₂O. Since the recirculation rate is 100 ft³/sec, the power requirement for pumping of the aqueous phase through a pressure drop of 1.25 ft of water (0.55 psi) will be 15 horsepower, which is minimal.

The net pressure loss for hydrocarbon circulating at 50 ft³/sec (1400 l/sec) in the aqueous phase extraction column (main series) may be demonstrated to be about 2 psi which will also be the loss in the alkali extraction column. For the aqueous extractor in the second series there is a pressure drop of approximately 1 psi in the column for the hydrocarbon recycling at 3 ft³/sec. Total pumping losses for the closed-loop hydrocarbon circulation will be 54 hp. Calculating on a similar basis, the net pressure loss in circulating aqueous phase through the extraction system will be 59 hp.

The power requirement for the electrolytic cell is determined by:

$$W = \Delta \frac{1}{2} \langle \bar{v} \rangle^2 + g \Delta h + \int_{P_2}^{P_1} \frac{1}{\rho} dp + \sum_i \left(\frac{1}{2} \langle \bar{v} \rangle^2 \frac{L}{R_h} f \right)_i + \sum_i \left(\frac{1}{2} \langle \bar{v} \rangle^2 e_v \right), \quad (5.26)$$

Table 5.6
ESTIMATE OF CAPITAL REQUIREMENT FOR FACILITY
TO MANUFACTURE LIQUID HYDROCARBON FUELS FROM BIOMASS

Item	Installed Cost
Site Preparation	\$ 300,000
Receiving Area	100,000
Shredding	300,000
Screw Conveyors	600,000
Packed Bed Digestion	25,600,000
Acid Extraction System	326,000
Electrolysis	2,440,000
Transformer/Rectifier System	830,000
Fuel Cell	1,180,000
Separation and Storage	1,000,000
Instrumentation	300,000
Pumps and Piping	500,000
Building	<u>300,000</u>
Subtotal Plant Investment	33,800,000
Contractor's Overhead, Profit (12%)	4,060,000
Engineering and Design (6%)	<u>2,030,000</u>
Subtotal Plant Investment	39,890,000
Project Contingency (15%)	5,984,000
Development Contingency (7%)	<u>2,792,000</u>
Total Plant Investment	48,666,000
Interest During Construction (10%; 1.5 years)	<u>4,867,000</u>
	\$53,533,000

where $\langle \bar{V} \rangle$ = average velocity (cm/sec),

g = gravitational acceleration (cm/sec²),

p = pressure (g/cm-sec²),

L = length of the cell (cm),

R_h = hydraulic radius (cm),

f = friction factor,

e_v = friction-loss factor, and

w = work done by pump (cm²/sec²)

$$P = 3.34 \times 10^{-5} W Q \rho$$

where P = power (hp),

ρ = density (lbm/ft³), and

Q = volumetric flow (ft³/sec)

Only the third and fourth terms of equation (5.26) are significant. Upon substitution of the appropriate values ($\langle \bar{V} \rangle = 100$ cm/sec, $f = 0.015$, and $R_h = 0.017$) the power required is determined to be 65 hp.

The power requirement for the shredder (Ref. 1) is estimated at 300 hp. Other pumping and miscellaneous energy requirements are approximated at 200 hp.

The total power requirement for mechanical equipment is 693 hp (520 kw). The entire requirement can be met by the steam output of the molten carbonate fuel cell, which can provide up to 1500 hp (1130 kw).

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 is that required to raise 6700 TPD input material ($C_p = 1$) from a baseline temperature of 70°F (assuming typical areas where biomass will be grown) to 98°F or 3.75×10^8 Btu/day. This process heat will be met by the electrolysis. Of the 2.2 V supplied to the electrolysis, only 0.3 V is necessary to supply

the enthalpy of reaction and 1.9 V will appear as heat. At 5.16×10^6 amps, the heat generated is 8.03×10^8 Btu/day, more than enough to heat the incoming material.

With this information, the power consumption is as shown in Table 5.7. A net energy balance (energy output/energy input) of 0.58/1 is obtained. The heat of combustion of the biomass is included in the energy inputs.

5.11 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. 1, with salaries updated to 1979 wage scales. Other operating costs follow as shown in Table 5.8. A total operating cost of \$13.97 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.

5.12 Computation of Liquid Hydrocarbon Product Cost

The cost of generating liquid hydrocarbon product is computed in Table 5.9 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 estimated previously. The cost of generating 3.17×10^{12} Btu/yr of liquid hydrocarbon fuel yearly is computed to be \$6.42/MMBtu @ \$30/ton biomass.

5.13 Commentary on Sensitivity

The preceding analysis of the process to produce liquid hydrocarbon fuels from biomass is preliminary and clearly has the usual undertainties inherent in such exercises. Its significance lies in the

Table 5.7
ESTIMATED ENERGY BALANCE OF PROCESS FOR CONVERTING
BIOMASS TO LIQUID HYDROCARBON FUELS

<u>Mechanical Equipment</u>	<u>Power Requirement, hp (Time - Average)</u>
Shredder	300
Packed Bed Digestion	15
Hydrocarbon Circulation	54
Aqueous Circulation through Hydrocarbon	59
Circulation through Electrolysis Cell	65
Pumping and Miscellaneous	<u>200</u>
Total	693 hp = 520 kw

Steam Output of Fuel Cell = 693 hp = 520 kw

Total Power Requirement for Electrolysis = 11,560 kw

Electrical Output of Fuel Cell = 5,630 kw

Total Power Requirement for Electric Needs = 5,930 kw

Total Energy Requirement

= 5,930 kw x 24 hrs/day x 365 days/yr x 0.9 service factor x 3413 Btu/kwh
x 1/0.3 efficiency = 5.32×10^{11} Btu/yr.

Energy in Cellulose (Biomass) = 2×10^6 lbs/day x 365 days/yr x 7500 Btu/lb
x 0.9 service factor = 4.92×10^{12} Btu/yr.

Total Output = 9.65×10^9 Btu/day x 365 days/yr x 0.9 service factor
= 3.17×10^{12} Btu/yr

Energy Balance = Output/Input = 0.58

Table 5.8
ESTIMATED OPERATING COST FOR FACILITY TO PRODUCE
LIQUID HYDROCARBON FUELS FROM BIOMASS

	<u>Cost/Year</u>
<u>Raw Materials</u>	
Biomass @ \$30/ton	\$ 9,855,000
<u>Labor</u>	
Process Operating Labor - 16 men @ \$9/hr.	299,520
Maintenance Labor - 12 men @ \$9/hr.	244,640
Supervision - 4 men @ \$12/hr.	<u>99,840</u>
Total	\$ 644,000
<u>Administration and General Overhead</u>	
(60% of Process Operating Labor)	179,700
<u>Supplies</u>	
Operating (30% of Process Operating Labor)	89,900
Maintenance (.015 of Total Plant Investment)	507,000
<u>Local Taxes and Insurance</u>	
(.027 Total Plant Investment)	912,600
<u>Electric Power @ \$0.035/kwh</u>	1,636,000
<u>Royalty on Electrolysis @ 10% of Electrolytic Power Use</u>	<u>164,000</u>
Total Operating Cost/Yr.:	<u><u>\$13,988,000</u></u>

Table 5.9
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. 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.	\$13,988,200
C = Total capital requirement	53,533,000
W = Working capital (1 mo. op. cost)	1,230,000
P = Annual product, MMBtu/yr.	3,170,000
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 = \$6.42/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.

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, the capital cost of the fermentation unit comprises 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 several-fold reactor size and cost reduction; also reactor designs are plausible such that unit costs might be reduced severalfold.

Figure 5.2 shows the effect of digester retention time (assuming a rate constant of 0.03 day^{-1}) on product cost. The minimum price (\$6.35/MMBtu) occurs at a retention time of 75 days, which corresponds to a conversion of 89% (this is greater than our assumed conversion of 83%-60 days). Therefore, if the percentage of organics that degrade can be increased, the product cost will be cut slightly.

Accomplishment of a capital cost reduction of 75% in this item 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 5.3 presents the cost of liquid fuel produced as a function of applied voltage. An applied voltage of greater than 4 V may be used before a cost of \$7.00/MMBtu is reached. The slope change at approximately 1.5 V occurs because at this potential sufficient resistance heating in the electrolysis is reached to supply all of the process heat requirements.

Figure 5.2

Cost of Liquid Fuel Produced as a Function of Retention Time

Fig. 5.3

Cost of Liquid Fuel Produced as a Function of Electrolysis Voltage

What is significant is that processing cost with the assumptions used about half the total product cost. The balance is for biomass which, at \$30/ton D.A.L.F., contributes \$3.12/MMBtu to the liquid hydrocarbon product. The contribution of other factors to product cost is summarized in Table 5.10.

Table 5.10
BREAKDOWN OF TOTAL HYDROCARBON PRODUCT COST BY COMPONENT

<u>Component</u>	<u>Cost, \$/MMBtu</u>
Biomass @ \$30/ton D.A.F.	3.12
Labor and Labor-Related Costs	.29
Capital and Capital-Related Costs	2.01
Electric Power and Royalty	.63
Taxes & Other Operating Costs	.37
Total Cost, \$/MMBtu	6.42 @ \$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.

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 10.4 million from this source alone. Liquid hydrocarbon production would still be 4.5×10^5 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.

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ACKNOWLEDGMENTS

We would like to thank Dr. John Ryther of the Woods Hole Oceanographic Institute for supplying samples of some of the aquatic plants used in this study. The background of Kolbe Electrolysis was compiled by Mr. Carl Sharon. Much of the experimental work was performed by Ms. Sara Molyneaux and Mr. Merer Klonowski.

APPENDIX A

If the extraction in Section 5.4.2 was run countercurrently, a very wide and short tower would be required. Assuming the same volumetric flows ($Q_A = 2800 \text{ l/sec}$, $Q_H = 1400 \text{ l/sec}$), a void fraction of 0.20, and a relative velocity of 14.3 cm/sec (equation 5.14), the individual phase velocities are determined by equation 5.18 to be: $V_A = 4.8 \text{ cm/sec}$ and $V_N = 9.5 \text{ cm/sec}$. Using the same drop diameter and overall mass transfer coefficients results in an extractor (for the same amount of acid transferred as in the cocurrent case) which is 2.2 ft tall and 33 ft in diameter. It is obvious that this tower would not be very efficient since the length to diameter ratio is so small. For this reason, a cocurrent extractor is used.

Appendix B
CONCENTRATION DISTRIBUTION IN A FLUID IN
LAMINAR FLOW PAST A FLAT PLATE

$$\begin{aligned}
 \text{Mass in through top of element:} & \quad N_{A_x} / x \Delta y \Delta z \\
 \text{Mass out through bottom of element:} & \quad N_{A_x} / (x + \Delta x) \Delta y \Delta z \\
 \text{Mass out through side of element:} & \quad N_{A_y} / (y + \Delta y) \Delta x \Delta z \\
 \text{Mass in through side of element:} & \quad N_{A_y} / y \Delta x \Delta z
 \end{aligned}$$

Steady State: Mass in--Mass out = 0

$$N_{A_x} / x \Delta y \Delta z - N_{A_x} / (x + \Delta x) \Delta y \Delta z + N_{A_y} / y \Delta x \Delta z - N_{A_y} / (y + \Delta y) \Delta x \Delta z = 0$$

Divide by $\Delta x \Delta y \Delta z$ and take as Δx and Δy approach zero.

$$- \frac{dN_{A_x}}{dx} - \frac{dN_{A_y}}{dy} = 0 \quad (B.1)$$

$$\text{Fick's Law: } N_{A_x} = -D_{AB} \frac{\partial C_A}{\partial x} + x_A (N_{A_x} + N_{B_x})$$

(x-direction)

It can be assumed that in the x-direction most of the flux is due to bulk flow:

$$N_{A_x} \approx x_A (N_{A_x} + N_{B_x}) \approx C_A V_x \quad (B.2)$$

$$\text{Fick's Law: } N_{A_y} = -D_{AB} \frac{\partial C_A}{\partial y} + x_A (N_{A_y} + N_{B_y}) \quad (B.3)$$

(y-direction)

Substituting equations (B.2) and (B.3) into equation (B.1) yields

$$- \frac{d}{dx} (C_A v_x) - \frac{d}{dy} (-D_{AB} \frac{C_A}{y} + C_A v_y) = 0$$

$$- v_x \frac{dC_A}{dx} + D_{AB} \frac{d^2 C_A}{dy^2} - v_y \frac{dC_A}{dy}$$

$$v_x \frac{dC_A}{dx} + v_y \frac{dC_A}{dy} = D_{AB} \frac{d^2 C_A}{dy^2} \quad (B.4)$$

Boundary Conditions: $v_x = 0$ at $y = 0$

$v_y = 0$ at $y = 0$

$v_x = v_o$ at $y = \infty$

$C_A = C_{A_o}$ at $y = \infty$

$C_A = C_{A_s}$ at $y = 0$

Equation of Continuity $\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$

This equation is satisfied by a stream function, ψ ,

$$v_x = \frac{\partial \psi}{\partial y} \quad v_y = - \frac{\partial \psi}{\partial x}$$

Redefinition variables

$$\xi = 1/2 \sqrt{\frac{v_o}{v}} \frac{y}{\sqrt{x}}$$

$$v_x \frac{dv_x}{dx} + v_y \frac{dv_y}{dy} = v \frac{d^2 v}{dy^2} \quad (B.5)$$

$$\rho(\xi) = \frac{\psi}{\sqrt{v v_o}} \frac{1}{\sqrt{x}}$$

$$\phi(\xi) = \frac{C_A - C_{A_s}}{C_{A_o} - C_{A_s}}$$

$$\frac{d \rho(\xi)}{d \xi} = \frac{2}{v_o} \frac{\psi}{y}$$

$$v_x = \frac{d\psi}{dy} = 1/2 v_o \frac{d\rho(\xi)}{d\xi} \quad (B.6)$$

$$v_y = - \frac{d\psi}{dx} = 1/2 \sqrt{v_o} \frac{1}{\sqrt{x}} \left(\xi \frac{d\rho(\xi)}{d\xi} - \rho(\xi) \right) \quad (B.7)$$

Substitute equations (B.6) and (B.7) into equations (B.4) and (B.5):

$$\frac{d^3 \rho(\xi)}{d\xi^3} + \rho(\xi) \frac{d\rho(\xi)}{d\xi} = 0$$

Boundary Conditions: $\rho = 0 \quad \frac{d\rho(\xi)}{d\xi} = 0 \text{ for } \xi = 0$

$$\frac{d\rho(\xi)}{d\xi} = 2 \text{ for } \xi = \infty$$

Blasius solved this equation (1908--Table B.1)

$$\frac{d^2 \rho(\xi)}{d\xi^2} + \frac{v}{D_{AB}} \rho(\xi) \frac{d\rho(\xi)}{d\xi} = 0$$

Polhausen solved $\frac{d\rho(\xi)}{d\xi} \bigg|_{\xi=0} = 0.664 \sqrt{\frac{v}{D_{AB}}} \quad (B.8)$

Mass transfer to wall is:

$$N_A = - D_{AB} W \int_{x=0}^{x=L} \left(\frac{\partial C_A}{\partial y} \right)_{y=0} dx$$

$$= D_{AB} W (C_{A_o} - C_{A_s}) \frac{1}{2} \sqrt{\frac{v_o}{v}} \frac{d\rho(\xi)}{d\xi} \bigg|_{\xi=0} \int_{x=0}^{x=L} x^{-1/2} dx$$

$$= D_{AB} W (C_{A_s} - C_{A_o}) \frac{1}{2} \sqrt{\frac{v_o}{v}} \frac{d\rho(\xi)}{d\xi} \bigg|_{\xi=0} 2L^{-1/2}$$

$$= D_{AB} W (C_{A_s} - C_{A_o}) \sqrt{\frac{v_o L}{v}} \frac{d\rho(\xi)}{d\xi}$$

Using equation (B.8):

$$N_A = -D_{AB}^{WC} A_o \sqrt{\frac{V_o L}{v}} \quad 0.664 \sqrt{\frac{v}{D_{AB}}}$$

$$N_A = -0.664 D_{AB}^{WC} A_o \sqrt{\frac{V_o L}{v}} \sqrt{\frac{v}{D_{AB}}}$$