LIQUID FUELS PRODUCTION
FROM BIOMASS

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Section 1

Annual 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 to 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.
6. Design processes for converting 3 tons/day and 1000 tons/day of biomass to liquid hydrocarbon fuels and perform an economic analysis for the 1000 ton/day design.

The accomplishments in this program for the first year of work are as follows:

A coenzyme M analogue, 2-bromoethanesulfonic acid has been shown to be an effective suppressor of methane in nonsterile anaerobic fermentation of cellulosic substrates. As a result the primary substrate in this investigation has been changed from Chondrus crispis to Hydrilla, a freshwater aquatic weed. A recent Hydrilla fermentation experiment in the 300 liter fermentor using 2-bromoethanesulfonic acid gave less than 2.5% conversion of carbon to methane. Work is continuing in the area of methane suppression of carbon to methane. Work is continuing in the area of methane suppression to identify other techniques which may be more suitable in large scale fermentations.

A tapered auger device has been designed and built which has been demonstrated on the bench to be effective for adding substrate and removing residue in a continuous manner from a fixed packed bed fermenter.

A solvent extractor system using kerosene as the nonaqueous phase has been constructed and is currently in operation in series with the 300 liter fixed packed bed fermenter.

Although additional work is required to optimize the electrolysis process the electrolytic oxidation of organic acids produced in the 300 liter fixed packed bed fermenter is operating with a favorable energy balance of 6/1 based on the applied potential.

As stated earlier the liquid-liquid extractor system is operating in line with the 300 liter fixed packed bed fermentor. The other components of an integrated continuous system, the continuous feed device and the Kolbe electrolysis cell are operating satisfactorily out of line on a scale compatible with the 300 liter fixed packed bed fermentor.

An economic analysis for a 1000 ton per day plant has been performed and has been improved and updated based on additional experimental results.

Currently a cost based on utility financing including a reasonable return on investment of \$5.48/million BTU is estimated, making the process fully competitive with the most favorable estimates from other processes for producing liquid fuels from renewable resources.

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 had been accomplished using the membrane separation process described previously (Ref. 2). Briefly, the process used a silicone rubber membrane swollen with Freon TF. However, it was anticipated that for production of aliphatic hydrocarbons a liquid-liquid extraction procedure using the product aliphatic hydrocarbons as the water immiscible phase would 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 has been in operation for the past three months.

Ultimately, the acids are extracted from the water immiscible phase into aqueous sodium hydroxide. The products in this form are 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 of the electricity required for the electrolysis in a fuel cell. As side products in the electrolysis, C₂-C₅ olefins are produced. These are also valuable products with large markets.

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

where I = Current, V = Voltage

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 fermentor 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 fermentor.
6. Design processes for converting 3 tons per day and 1000 tons per day of biomass to liquid hydrocarbon fuel and perform an economic analysis for the 1000 ton per day design.

LIQUID HYDROCARBONS FROM BIOMASS --- PROCESS FLOWSHEET

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Section 3

Static Fermentations

The effort to obtain high conversions of biomass into organic acids has been pursued. As it was mentioned in the previous report, (Report No. 7), the loss of organic acids produced during fermentation due to methane production has been prevented. From the chemicals tested for methane suppression, Bromoethanesulfonic acid performed the best at a $1-5 \times 10^{-4}$ M concentration.

3.1 Improvement on the Conversions

Pretreatment of the fermentation residues - According to the preliminary results in Figure 3.3, (p.17-18, Report No. 7), the residual Hydrilla from a regular fermentation cannot be further digested. This residue represents approximately 50% of the total initial substrate. It is therefore important to find a means of further utilizing the carbon available in this biomass.

3.1.1 Preparation of the Residue

The washed and partially dried residue was treated with sodium hydroxide (4g/100g solids) at 25°C for 3 days and at 110°C for one hour. After the treatment, the pH was adjusted to 6-6.5. Sewage digester effluent was added as inoculum along with CaCO_3 (1g/100ml) and 5×10^{-4} M bromoethane sulfonic acid. The results for the fermentation of the heated residue are illustrated in Figure 3.1.2. It is observed that only the high temperature treated residue became a suitable substrate for the production of acids. The concentration of acids produced amounts for an extra 12% conversion on the 33%-38% accomplished in the first fermentation step before the pretreatment.

3.1.2 Acid Treatment

Another portion of the washed and partially dried residue was

Figure 3.1

Pretreatment procedure for the residue of a Hydrilla fermentation

Figure 3.2 Acid production from *Hydrilla* fermentation residues at 37°C following NaOH (4g/100g solids) treatment @ : A) 25°C for 3 days; B) 110°C for 1 hour. After pretreatment the pH was adjusted with H_2SO_4 to 6.4-6.5. The inoculum used was sewage sludge. $1 \times 10^{-5}M$ Bromoethanesulfonic acid was added for methane suppression.

Figure 3.3 Acid production from *Hydrilla* fermentation residues at 37°C following H_2SO_4 (1% w/v final) treatment @: A) 25°C for 3 days; B) 110°C for 1 hour. After pretreatment the pH was adjusted with NaOH to 6.4-6.5. The inoculum used was sewage sludge. $1 \times 10^{-5}M$ bromoethane sulfonic acid was added for methane suppression.

treated with sulfuric acid (1% w/v final concentration) at 25°C for 3 days and at 110°C for one hour. The preparation of the fermentation system was the same as described for the alkali treated samples.

The results of the fermentation of the acid pretreated residue are illustrated in Figure 3.3. The increased digestibility after the high temperature acid treatment is very similar to that of the high temperature alkali treatment.

Further studies will be made at intermediate temperature and chemical concentrations in order to optimize the conversion of the biomass into organic acids.

3.2 Product Inhibition

The possibility of having a product inhibited system in the Hydrilla fermentation has been explored. However, no clearcut results have been obtained to date and further experimentation will be pursued.

3.3 Acid Production from Agricultural Residues

As reported before, the residues from onion-garlic industrial processing result in very high accumulation of acids. A very interesting feature of the anaerobic fermentation of these residues is that no methane is produced. Allyl-sulfoxides contained in onion and garlic are known to be antibacterial agents (Ref. 17, Report No.7). Experiments have been started using (+) S-methyl-L-cysteine sulfoxide which is one of the components of intact onion in order to define which of the sulfoxides is (are) responsible for the prevention of methane formation.

Two concentrations of this commercially available chemical were tested. The results illustrated in Figure 3.4 indicate that lower concentrations (10^{-4} M) stimulate acid production in the first stage of fermentation, but after 15 days methane fermentation becomes evident. However, the higher concentration (10^{-2} M) does not show a sharply different pattern

from a control run. Efforts on the detection of naturally active anti-bacterial components from onion and garlic will be pursued.

Figure 3.4 - Effect of the addition of (+) S-Methyl-L eysteine sulfoxide on the acid production from a 5% (w/v) Hydrilla fermentation.

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 Derman 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 (Re. 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. A layer of adsorbed carboxylate may cover 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	17.8	-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

The cell potential, V , versus current density, i , in an electrolysis cell may be represented by an equation of the form:

$$V = E_R + N_A + N_C + IR \quad (4.7)$$

where E_R = the thermodynamic, reversible potential given by equation 4.5

N_A and N_C = the anodic and cathodic overpotentials which may be expressed by the Tafel equation of the form:

$$N = a + b \ln i \quad (4.8)$$

Tafel plots were obtained for a 0.5 N caproic acid solution at pH 7; these are shown in Figure 4.2.

From these results:

$$N'_A = 2.32 + 0.090 \ln i \quad (4.9)$$

and

$$N'_C = 1.03 + 0.105 \ln i \quad (4.10)$$

where

$$N'_A + N'_C = E_R + N_A + N_C \quad (4.11)$$

Overall,

$$V = 3.35 + 0.195 \ln i + IR \quad (4.12)$$

Previous results have indicated that, in an electrolysis cell:

1. Low temperatures favor paraffin formation.

2. High flow rates over the electrodes favor paraffin formation.

3. Increasing chain length favors paraffin formation.

These results are consistent with results reported in the literature.

Figure 4.2

Tafel Plots for 0.5 N Carpoic Acid at pH 7
(Platinum Anode and Monel Cathode)

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Section 5

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, the percentage of organics which are degradable must be multiplied by the percentage which actually convert to acids under plant conditions. For example, a yield of 75% would be obtained if 90% of the organics were biodegradable and 83% of those converted to acids. It is important to note as background 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.

The cellulose equivalent material converts to acetic acid by the reaction:

Higher aliphatic acids may be formed from acetic acid by the following set of disproportionation reactions:

The approximate yield of product alkanes (depending on the exact plant operating conditions) will be 5.0×10^5 lb/day with a heating value of 10^{10} Btu/day, equivalent to 1700 bbl/day 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 overall process economics. The volume of the digester (at a cost of \$1.50/ft³) 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:

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

where t = retention time (days),

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

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

A theoretical model, fit to experimental data, determines the rate constant as a function of hydrogen ion concentration:

$$k = \frac{0.195}{(3.1 \times 10^5)([H^+]) + 1}$$

where $[H^+] = 10^{-pH}$

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:

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = \frac{F_A M_A}{\rho_A} dC_A \quad (5.3)$$

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 (5.3) can be simplified to:

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = 1 \times 10^{-3} V_A dC_A \quad (5.4)$$

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

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

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = N_A dh \quad (5.5)$$

where N = rate of diffusion of the acid (meq/sec-cm²),

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:

$$N = 1 \times 10^{-3} K_L (C_A - C_A^*) \quad (5.6)$$

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)

$$C_A^* = \frac{C_H}{P}$$

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

p = partition coefficient

Substituting N from equation (5.6) into equation (5.5) yields:

$$\frac{\text{moles of acid transferred}}{(\text{time}) (\text{cross-sectional area})} = 1 \times 10^{-3} K_L a (C_A - C_A^*) dh \quad (5.8)$$

Setting equation (5.8) equal to equation (5.4) and rearranging produces:

$$dh = \frac{V_A}{K_{La}} \frac{dC_A}{(C_A - C_A^*)} \quad (5.9)$$

Integrating both sides of equation (5.9) defines the height of

the extractor:

$$h = \frac{V_A}{K_L a} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(C_A - C_A^*)} \quad (5.10)$$

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:

$$\frac{1}{K_L} = \frac{1}{k_{LA}} + \frac{m}{k_{LH}} \quad (5.11)$$

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):

$$k_o = 2 \frac{DV}{\pi d} \quad (5.12)$$

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

d = drop diameter (cm), and

D = diffusivity of acid (cm^2/sec)

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

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

where μ_C = viscosity of continuous phase (poise) and

μ_D = viscosity of disperse phase (poise)

It can be observed from equations (5.12) and (5.13) 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:

$$d_C = 0.33 \rho_C^{-0.14} \Delta \rho^{-0.43} \mu_C^{0.30} \gamma^{0.24} \quad (5.14)$$

where γ = interfacial tension (dyn/cm),

ρ_C = density of continuous phase (g/cm^3), and

$\Delta \rho$ = density difference of phases (g/cm^3)

Assuming that the aqueous phase is continuous, and substituting the appropriate values into equation (5.14) determines a critical diameter of 0.36 cm. At drop diameters less than the critical diameter the relative velocity of relative velocity of the two phases can be calculated by:

$$V = 38.3 \rho_C^{-0.45} \Delta \rho^{0.58} \mu_C^{-0.11} d^{0.70} \quad (5.15)$$

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 (5.12) and (5.13) produces

values of 2.28×10^{-2} and 2.79×10^{-2} and 2.79×10^{-2} for k_o (or k_{LH}) and k_1 (or k_L) respectively. Substituting these numbers and the appropriate values of $M(I/P)$ -- See Table 5.1) into equation (5.11) 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 (5.10) yields:

$$h = 0.191 \frac{K_A}{K_L} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(C_A - C_A^*)} \quad (5.16)$$

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 (5.15) can now be integrated to:

$$h = 0.191 \frac{V_A}{K_L} \frac{C_A - C_A^*}{(C_A - C_A^*)_{lm}} \quad (5.17)$$

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

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:

$$C_A = \Delta C_A \frac{[H^+]}{[H^+] + k_i}$$

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.

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

Now that the governing equation for the system has been determined, the type of continuous contact equipment (cocurrent or counter-current) to be employed must be chosen. This decision depends on the plant operating conditions. After the type of exchanger has been selected the velocity of each phase can be determined from equations (5.15) and (5.19):

$$\frac{S_H}{S_A + S_H} = \frac{\frac{Q_H}{V_H}}{\frac{Q_H}{V_H} + \frac{Q_A}{V_A}} = \theta \quad (5.19)$$

where S = cross-sectional area required for the specific phase to flow (cm^2),

θ = void fraction

Q = volumetric flow (cm^3/sec)

V = velocity (cm/sec)

A or H = aqueous or hydrocarbon phase

The dimensions of the extractor can now be determined (equations (5.17) and (5.19)) as functions of volumetric flow out of the digesters, the type of extractor, and the void fraction. Extractor cost is estimated to be \$50/ft³.

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 cocurrent 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 CO_2 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 hydrocarbons 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 by the electrolysis step (to be discussed later), the amount of acid reacted and transferred to this phase is determined from the constraint $Q_A \Delta C_A = -Q_H \Delta C_H$. 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}) and the log-mean driving force are now set. Employing a cocurrent¹ extractor with the hydrocarbon phase continuous results in a relative velocity (equation 5.15) of 18 cm/sec. Following the same procedures as in Section 5.4.2 determines the dimensions of the extractor.

5.6 Extraction of Excess Water from the Packed Bed Digester

The excess water (contained in the wet biomass) which is continuously being added to the digesters 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). The same procedure (Section 5.4.2) is used to calculate the size of the extractors.

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 product distribution is listed in Table 5.4.

5.7.2 Optimum Current Density and Sizing of the Electrodes

From Table 5.4, 33.4 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 6.44×10^6 amps.

Table 5.4

ELECTROLYSIS PRODUCTS

Product	Average Molecular Weight	$\frac{\text{Moles}}{\text{sec}}$ produced	$\frac{\text{g}}{\text{sec}}$ produced
Alkanes	110	19.1	2093
Alkenes	48	14.3	690
CO ₂		52.4	2306
H ₂		33.4	67

As discussed in Section 4 (equation 4.12).

$$V = 3.35 + 0.20 \ln i + IR \quad (5.20)$$

where V = applied voltage,

i = current density in amps/cm²,

I = current (6.44×10^6 amps), and

R = resistance of the cell in ohms

The 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 cm²,

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

where R is in ohms and

$$IR = 0.76i \quad (5.22)$$

$$\text{Then, } V = 3.35 - 0.20 \ln i + 0.76 i \quad (5.23)$$

The optimum current density is obtained by balancing the increased capital cost of greater electrode area with the decrease in operating cost (from lower current density and, therefore, lower voltage) from greater electrode area. Operating and capital costs are related by the American Gas Association Method for Synthetic Fuels equation (to be explained in Section 5.12). By taking the derivative of product cost with respect to current density and setting the result equal to zero, one obtains the optimum current density. The result is:

$$i_{\text{optimum}} = \frac{-0.263 + (0.069 + 4 F)^{\frac{1}{2}}}{2}$$

where

$$F = \frac{1370 C_{EC}}{3.4 \times 10^7 C_E + 978 C_T}$$

C_{EC} = the capital cost of the electrolysis cell system in \$/ft² of electrode area (\$140/ft²)

C_E = the cost of electricity in \$/kWh (\$0.035/kWh) and,

C_T = the capital cost of the transformer rectifier system in \$/kW (\$140/kW).

The optimum current density for the current system is, therefore, 0.27 amps/cm², the required electrode area is 2.39×10^7 cm², and the voltage (from equation 5.23) is 3.15V.

5.7.3 Electrolysis Cell Design

The electrolysis 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, will be required.

For 240V line current, each filter press unit will be comprised of 240V/3.15V/cell) = 76 cells. If the anode area of each cell is 18,200 cm² (the size of the Lurgi water electrolysis cell), 17-18 such units will be required. If the electrodes are square, each will be 135 cm on a side.

To generate 0.27 amps/cm² of current, 2.2×10^{-6} $\frac{\text{moles}}{\text{cm-sec}}$ of acid must diffuse to the electrode. For a fluid containing a species A flowing over a flat plate on which A is consumed,

$$N_A = -(0.664 D_{AB} C_{AO} / L) (V_O L / \nu)^{1/2} (\nu / D_{AB})^{1/3} \quad (5.26)$$

where N_A = the mass flux of A (acid) in moles/cm²-sec = -2.2×10^{-6} ,

D_{AB} = the diffusivity of acid in water = 8×10^{-6} cm²/sec,

C_{AO} = the bulk acid concentration = 5×10^{-4} moles/cm³,

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 = 8.6×10^{-3} cm²/sec.

Equation 5.25 is derived in Appendix A. 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), $L = 2.7$ cm. This means that the desired flux cannot be achieved for electrodes of length greater than 2.7 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 4.5×10^{-4} moles/cm³. If this value of C_{AO} is placed in equation (5.25) $L = 2.4$ cm. This means that the grooves should be spaced not more than 2.4 cm apart.

5.7.4 Molten Carbonate Fuel Cell

The electrolysis step will produce hydrogen at the rate of 33.4 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 opera-

ting 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 6850 kw of electricity at an estimated capital cost of \$200/kw. It will also generate 3.74×10^8 Btu/day of high temperature heat which will produce steam sufficient to provide 1370 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 \$0.35/MMBtu saving in the cost of the final product (assuming a value of \$3/MMBtu for the H_2/CO_2 mixture, 6850 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 \$1,890,000 at the power requirement of 13.47 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 (approximately \$5,520,000). 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 Computer Optimization

Two HP-97 programs were used to calculate the product cost (\$/MMBtu) and optimum plant operating conditions.

Program 1 - Fermentation Output and Constant

This program calculates two constants, W and E, to be placed in protected registers 0 and 1 of program 2. W is the number of pounds of hydrocarbon product per pound of acetic acid equivalents produced by fermentation (i.e. propionic acid is two acetic acid equivalents, caproic acid is five). W ranges from 0.25 (for 100% acetic acid) to 0.30 (for 100% caproic acid). The calculation of W assumes that the following reactions are at thermodynamic equilibrium:

A CO_2 partial pressure (and activity) of one atmosphere was assumed for these calculations, and the total acetic acid equivalents/liter in the fermenters was assumed to be a constant (0.281 - stored in register E). The major variable is pH, with lower pH shifting the equilibria of the above reactions to the right. The ΔG values were modified slightly (less than 1 kcal per mole higher acid) to conform to the acid concentrations at pH 4.75 listed on page 53 of Progress Report 7 (acetic-42.0 meg/l; propionic - 12.5 meg/l; butyric - 62.0 meg/l; valeric - 10.5 meg/l; caproic - 7.0 meg/l). This modification is not unreasonable because G values calculated from free energies of formation (as these were) are the differences between large numbers and are subject to errors of a few kcal/mole.

Because W is actually dependent on the acid distribution in the electrolysis cell rather than in the fermenters, the calculation of W involves the hydrocarbon/water partition coefficients of the acids (acetic and propionic - 0; butyric - 0.4; valeric - 2.0; caproic - 4.0) as well as the acid concentrations.

E is a constant by which the amount of electricity required is multiplied. It reflects the increased electricity per Btu of product necessary to electrolyze lower molecular weight acids. E is calculated directly from W by the empirical relationship

$$E = -20W + 6.78$$

The program steps are as follows:

- Step 2 Stores guess for concentration of acetic acid plus acetate.
- Steps 3-32 Calculates the equilibrium concentration of propionic acid plus propionate, given the acetic acid concentration in register 2 and the hydrogen ion concentration in register 0. Stores result in register 3.
- Steps 33-54 Calculates equilibrium concentration of butyric acid plus butyrate. Stores result in register 7.

Steps 55-78. Calculates equilibrium concentration of valeric acid plus valerate. Stores result in register 8.

Steps 79-100 Calculates equilibrium concentration of caproic acid plus caproate. Stores result in register 9.

Steps 101-176 Checks whether the total number of acetic acid equivalents calculated from the above equilibria are equal to the constant stored in register E. If not, iterations are performed, using Newton's method, until equality is attained.

Steps 177-209 Calculates and prints W using the previously calculated acid concentrations.

Steps 210-219 Uses W to calculate E. Prints E.

Inputs and Outputs

Register	Input
0	Hydrogen ion concentration
1	1.74×10^{-5}
6	0
B	9.68
C	58.65
D	136.8
E	Acetic Acid equivalents/ liter (0.281)

Program 1

001	*LBLA	21 11	057	.	-62	113	5	05
002	ST02	35 02	058	2	02	114	x	-35
003	RCL1	36 01	059	5	05	115	+	-55
004	÷	36 00	060	Y*	31	116	RCL3	36 03
005	÷	-24	061	1	01	117	1	01
006	1	01	062	6	06	118	.	-62
007	+	-55	063	2	02	119	7	07
008	÷	-24	064	1	01	120	5	05
009	ST01	35 46	065	x	-35	121	x	-35
010	1	01	066	1	01	122	+	-55
011	.	-62	067	.	-62	123	RCL2	36 02
012	7	07	068	3	03	124	+	-55
013	5	05	069	8	08	125	RCL5	36 15
014	Y*	31	070	EEX	-23	126	-	-45
015	6	06	071	5	05	127	RCL6	36 06
016	.	-62	072	CHS	-22	128	1	01
017	0	00	073	RCL0	36 00	129	ST06	35 06
018	9	09	074	÷	-24	130	X=Y?	16-33
019	x	-35	075	1	01	131	ST0C	22 13
020	1	01	076	+	-55	132	R4	-31
021	.	-62	077	x	-35	133	R4	-31
022	3	03	078	ST08	35 08	134	ST04	35 04
023	2	02	079	RCL1	36 46	135	RCL2	36 02
024	EEX	-23	080	4	04	136	ST05	35 05
025	5	05	081	Y*	31	137	1	01
026	CHS	-22	082	1	01	138	.	-62
027	RCL0	36 00	083	9	09	139	0	00
028	÷	-24	084	3	03	140	0	00
029	1	01	085	0	00	141	0	00
030	+	-55	086	0	00	142	1	01
031	x	-35	087	x	-35	143	x	-35
032	ST03	35 03	088	1	01	144	ST0A	22 11
033	RCL1	36 46	089	.	-62	145	*LBLC	21 13
034	.	02	090	4	04	146	0	00
035	.	-62	091	1	01	147	ST06	35 06
036	5	05	092	EEX	-23	148	R4	-31
037	Y*	31	093	5	05	149	R4	-31
038	5	05	094	CHS	-22	150	R4	-31
039	1	01	095	RCL0	36 00	151	RCL4	36 04
040	2	02	096	÷	-24	152	-	-45
041	x	-35	097	1	01	153	RCL2	36 02
042	1	01	098	+	-55	154	RCL5	36 05
043	.	-62	099	x	-35	155	-	-45
044	5	05	100	ST09	35 09	156	÷	-24
045	1	01	101	4	04	157	RCL4	36 04
046	EEX	-23	102	x	-35	158	X*Y	-41
047	5	05	103	X*Y	-41	159	÷	-24
048	CHS	-22	104	3	03	160	ST04	35 04
049	RCL0	36 00	105	.	-62	161	CHS	-22
050	÷	-24	106	2	02	162	RCL5	36 05
051	1	01	107	5	05	163	+	-55
052	+	-55	108	x	-35	164	ST02	35 02
053	x	-35	109	+	-55	165	.	-62
054	ST07	35 07	110	RCL7	36 07	166	0	00
055	RCL1	36 46	111	2	02	167	0	00
056	3	03	112	.	-6	168	1	01

Program 1 (continued)

169	X	-35
170	ABS	16 31
171	RCL4	36 04
172	ABS	16 31
173	X&Y?	16-35
174	GT08	22 12
175	RCL2	36 02
176	GT0A	22 11
177	*LBL8	21 12
178	RCL8	36 12
179	RCL7	36 07
180	X	-35
181	RCLC	36 13
182	RCL8	36 08
183	X	-35
184	+	-55
185	RCLD	36 14
186	RCL9	36 09
187	X	-35
188	+	-55
189	8	08
190	8	08
191	RCL7	36 07
192	X	-35
193	.	-62
194	4	04
195	X	-35
196	2	02
197	0	00
198	4	04
199	RCL8	36 08
200	X	-35
201	+	-55
202	4	04
203	5	05
204	6	06
205	RCL9	36 09
206	X	-35
207	+	-55
208	÷	-24
209	PRTX	-14
210	2	02
211	0	00
212	X	-35
213	CHS	-22
214	6	06
215	.	-62
216	7	07
217	8	08
218	+	-55
219	PRTX	-14
220	R/S	51

Register	Output
2	Concentration of acetic acid plus acetate
3	Concentration of propionic acid plus propiate
7	Concentration of butyric acid plus butyrate
8	Concentration of valeric acid plus valerate
9	Concentration of caproic acid plus caproate

Registers 4, 5 and I are used in the program. Register A is free. The program will first print W, then E. W should be placed in protected register 0 of program 2; E should be placed in protected register 1. The calculator should be reset to the unprotected registers before running program 2.

To use the program, type a guess for the acetic acid concentration (0.05 is a good guess) and hit "A".

Program 2- Determination of Product Cost

This program determines the liquid hydrocarbon production cost as a function of the following registers:

RCL 0 = Hydronium Ion Concentration

RCL 1 = Electricity Cost (\$/kwh)

RCL 2 = Cost of Electrodes (\$/ft²)

RCL 3 = Rectifier - Transformer Cost (\$/kw)

RCL 4 = Solids Loaded (tons/day)

RCL 5 = Retention Time (days)

RCL 6 = Fraction of Biomass which is Solids

RCL 7 = Labor Cost (\$/yr.)

RCL 8 = Fraction of Solids which are Organic and Degradable

RCL 9 = Biomass Cost (\$/ton)

The protected registers are defined as:

RCL 0 = W

RCL 1 = E

RCL 2 = Fraction of Hydrogen Produced in the Kolbe Cell

RCL 3 = Fraction of Hydrogen Produced in the Digester

RCL 4 = A constant employed in the program

Steps 2-36 The optimum current density (STO A) is determined as a function of electrode cost, electricity cost, and transformer - rectifier cost (see Sec. 5.7.2)

Steps 37-52 The applied voltage (STO B) is calculated from the optimized current density (equation 5.20).

Steps 53-74 The rate constant (equation 5.2) and conversion (equation 5.1) of biomass to carboxylic acids is determined as a function of hydronium ion concentration and retention time.

Steps 75-144 The total capital requirement (STO D) for the facility is computed.

- Steps 75-82 determine the digester costs.

- Steps 83-88 takes the capital for other equipment

Program 2

001	*LBLA	21 11	058	ENT1	-21	115	RCL1	36 01
002	1	01	059	1	01	116	x	-35
003	3	03	060	1	01	117	P2S	16-51
004	7	07	061	EEX	-23	118	+	-55
005	0	00	062	5	05	119	RCLC	36 13
006	RCL2	36 02	063	RCL0	36 00	120	2	02
007	x	-35	064	x	-35	121	1	01
008	3	03	065	+	-55	122	4	04
009	4	04	066	=	-24	123	EEX	-23
010	EEX	-23	067	.	-62	124	4	04
011	6	06	068	5	05	125	x	-35
012	RCL1	36 01	069	X2Y	-41	126	+	-55
013	x	-35	070	Yx	31	127	RCL0	36 00
014	9	09	071	1	01	128	1	01
015	7	07	072	X2Y	-41	129	7	07
016	8	08	073	-	-45	130	4	04
017	RCL5	36 03	074	STOC	35 13	131	EEX	-23
018	x	-35	075	7	07	132	CHS	-22
019	+	-55	076	6	06	133	7	07
020	=	-24	077	RCL4	36 04	134	+	-55
021	4	04	078	x	-35	135	RCL0	36 00
022	x	-35	079	RCL5	36 05	136	=	-24
023	.	-62	080	x	-35	137	1	01
024	0	00	081	RCL6	36 06	138	6	06
025	6	06	082	=	-24	139	5	05
026	9	09	083	5	05	140	EEX	-23
027	+	-55	084	5	05	141	3	03
028	JX	54	085	2	02	142	x	-35
029	.	-62	086	EEX	-23	143	+	-55
030	2	02	087	4	04	144	STOD	35 14
031	6	06	088	+	-55	145	.	-62
032	3	03	089	1	01	146	0	00
033	-	-45	090	4	04	147	3	03
034	2	02	091	7	07	148	8	08
035	=	-24	092	EEX	-23	149	3	03
036	STOA	35 11	093	4	04	150	x	-35
037	LN	32	094	RCLC	36 13	151	3	03
038	.	-62	095	x	-35	152	2	02
039	2	02	096	RCLA	36 11	153	8	08
040	x	-35	097	=	-24	154	5	05
041	RCLA	36 11	098	+	-55	155	EEX	-23
042	.	-62	099	1	01	156	2	02
043	7	07	100	3	03	157	RCL9	36 09
044	6	06	101	7	07	158	x	-35
045	x	-35	102	5	05	159	+	-55
046	+	-55	103	EEX	-23	160	RCL7	36 07
047	3	03	104	3	03	161	+	-55
048	.	-62	105	RCLB	36 12	162	5	05
049	2	02	106	x	-35	163	3	03
050	1	01	107	1	01	164	9	09
051	+	-55	108	5	05	165	EEX	-23
052	STOB	35 12	109	EEX	-23	166	5	05
053	RCL5	36 05	110	5	05	167	RCLB	36 12
054	3	03	111	-	-45	168	x	-35
055	.	-62	112	RCLC	36 13	169	P2S	16-51
056	5	05	113	x	-35	170	RCL1	36 01
057	5	05	114	P2S	16-51	171	x	-35

Program 2 (continued)

172	RCL2	36 02
173	RCL1	36 01
174	x	-35
175	RCL3	36 03
176	+	-55
177	RCL4	36 04
178	x	-35
179	P2S	16-51
180	-	-45
181	RCLC	36 13
182	x	-35
183	RCL1	36 01
184	x	-35
185	+	-55
186	STOE	35 15
187	RCL4	36 04
188	RCL8	36 08
189	x	-35
190	RCLC	36 13
191	x	-35
192	1	01
193	5	05
194	0	00
195	0	00
196	0	00
197	x	-35
198	P2S	16-51
199	RCL0	36 00
200	P2S	16-51
201	x	-35
202	STOI	35 46
203	RCLC	36 15
204	1	01
205	.	-62
206	0	00
207	0	00
208	1	01
209	6	06
210	x	-35
211	.	-62
212	1	01
213	2	02
214	RCLD	36 14
215	x	-35
216	+	-55
217	RCL1	36 46
218	÷	-24
219	PRTX	-14
220	R/S	51

items into account (see Sec. 5.8).

- Steps 89-98 calculate the electrode cost
- Steps 99-118 determine the transformer - rectifier cost
- Steps 119-126 adds the cost of the fuel cell onto the total capital
- Steps 127-144 calculate extractor costs by the methods of Section 5.4.2

Steps 145-186 The yearly operating cost (STO E) for the facility is computed.

- Steps 145-150 take a percentage of the plant capital to allot for plant maintenance, taxes, and insurance
- Steps 151-159 add on the biomass cost (at \$30/ton)
- Steps 160-161 cover labor
- Steps 162-186 determine the total electricity cost for the Kolbe cell.

Steps 187-202 The total product produced in MMBtu/yr (STO I) is calculated.

Steps 203-219 The American Gas Association Method (see Section 5.12) is used to determine the liquid hydrocarbon production cost in \$/mmBtu.

The initial values of the registers are:

RCL 0 = Hydronium Ion Concentration (1×10^{-5})

RCL 1 = Electricity Cost (\$0.035/kwh)

RCL 2 = Cost of Electrodes ($\$140/\text{ft}^2$)

RCL 3 = Rectifier - Transformer Cost ($\$140/\text{kw}$)

RCL 4 = Solids Loaded (1333 tons/day)

RCL 5 = Retention Time (60 days)

RCL 6 = Fraction of Biomass which is Solids 0.15

RCL 7 = Labor Cost ($\$824,000/\text{yr}$)

RCL 8 = Fraction Solids which are Organic and Degradable (0.68)

RCL 9 = Biomass Cost ($\$30/\text{ton}$)

Protected Registers:

RCL 0 = W (.2883)

RCL 1 = E (1.0139)

RCL 2 = 0.691

RCL 3 = 0.309

RCL 4 = 5.89×10^7

In order to determine the best plant operating conditions the optimum pH and retention time must be found. A converging iterative procedure is employed. First the pH is held constant while the retention time is varied. A plot of retention time verse product cost is made. The retention time corresponding to the minimum cost is then determined. pH is now varied (new E and W calculated by Program 1 for each pH) at the new retention time. This procedure is continued till it converges (no decrease in product cost). The absolute minimum is $\$5.48/\text{MMBtu}$ and it occurs at the following operating conditions:

pH = 5.75

Retention time = 22 days

Program 2 also determines:

Current Density = 0.27 amps/cm²

Applied Voltage = 3.15 Volts

Total Capital = \$33,000,000

Total Operating = \$16,030, 000/yr

Total Product = 3,650,000 MMBtu/yr

Product Cost = \$5.48/MMBtu

5.10 Computation of Capital Costs

Estimated capital costs are presented in Table 5.5 showing a total capital requirement of 33.0 million dollars for the facility. A brief discussion of the sensitivity of this capital cost to various changes is presented later.

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 5.6. A total operating cost of \$15.03 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.

Table 5.5

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	100,000
Shredding	300,000
Screw Conveyors	600,000
Packed Bed Digestion	9,840,000
Acid Extraction System	1,190,000
Electrolysis	3,240,000
Transformer/Rectifier System	1,890,000
Fuel Cell	1,280,000
Separation and Storage	1,000,000
Instrumentaion	300,000
Pumps and Piping	500,000
Building	<u>300,000</u>
Subtotal Plant Investment	20,840,000
Contractor's Overhead, Profit (12%)	2,500,000
Engineering and Design (6%)	<u>1,250,000</u>
Subtotal Palnt Investment	24,590,000
Project Contingency (15%)	3,689,000
Development Contingency (7%)	<u>1,721,000</u>
Total Plant Investment	30,000,000
Interest During Construction (10%; 1.5 years)	<u>3,000,000</u>
	\$33,000,000

Table 5.6

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>
<u>Total Labor</u>	\$ 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)	450,000
<u>Local Taxes and Insurance</u>	
(.027 Total Plant Investment)	809,000
<u>Electric Power @ \$0.035/kwh</u>	3,638,000
Royalty on Electrolysis @ 10% of Electrolytic Power Use	<u>364,000</u>
<u>Total Operating Cost/Yr.</u>	<u>\$16,030,000</u>

5.12 Computation of Liquid Hydrocarbon Product Cost

The cost of generating liquid hydrocarbon product is computed in Table 5.7 using the American Gas Association synthetic gas cost calculation method modified for the acid production process. The computation assumes a 75%/25% debt/equity ration, 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 3.65×10^{12} Btu/yr of liquid hydrocarbon fuel yearly is computed to be \$5.48/MMBtu @ \$30/ton biomass.

5.13 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

Table 5.7

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.	16,030,000
	C = Total capital requirement	33,000,000
	W = Working capital (1 mo. op. cost)	1,336,000
	P = Annual product, MMBtu/yr.	3,650,000
	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 = \$5.48/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.

system will be 59 hp.

The power requirement for the electrolytic cell is determined by:

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

where $\bar{v}$ = 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 ($\bar{v}$ = 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).

Table 5.8

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 = 20,320

Electrical Output of Fuel Cell = 6,850 kw

Total Power Requirement for Electric Needs = 13,470 kw

Total Energy Requirement (including inefficiency of electrical generation)
= 13,470 kw x 24 hrs/day x 365 days/yr x 0.9 service factor x 3413 Btu/kwh
x 1/0.3 efficiency = 1.21×10^{12} 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 = 1.11×10^{10} Btu/day x 365 days/yr x 0.9 service factor
= 3.65×10^{12} Btu/yr.

Energy Balance = Output/Input = 0.60

Energy Balance (excluding energy in biomass) = 3.02

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 3.15 V supplied to the electrolysis, only 0.3 V is necessary to supply the enthalpy of reaction and 2.85 V will appear as heat. At 5.16×10^6 amps, the heat generated is 1.2×10^9 Btu/day, more than enough to heat the incoming material.

With this information, the power consumption is as shown in Table 5.8. A net energy balance (energy output/energy input) of 0.60/1 is obtained, (with the heat of combustion of the biomass included in the energy inputs). If the energy in the biomass is not included as an input the overall balance is 3.02/1.

5.14 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.

A significant point is that processing cost with the assumptions used is about half of the total product cost. The balance is for biomass which, at \$30/ton D.A.L.F., contributes \$2.72/MMBtu to the liquid hydrocarbon product. The contribution of other factors to product cost is summarized in Table 5.9.

FIGURE 5.1

COST OF LIQUID FUEL PRODUCED AS A FUNCTION
OF BIOMASS COST

Table 5.9

BREAKDOWN OF TOTAL HYDROCARBON PRODUCT COST BY COMPONENT

	<u>Cost, \$/MMBtu</u>
Biomass @ \$30/ton D.A.L.F.	2.72
Labor and labor-related costs	.22
Capital and capital-related costs	1.00
Electric Power and Royalty	1.23
Taxes & other operating costs	<u>.31</u>
Total Cost, \$/MMBtu	5.48 @ \$30/ton biomass

Figure 5.1 shows the effect of biomass cost on the product cost.

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.

The sensitivity of the assumption that the biomass in the digester is 15% solids is shown in Figure 5.2. The effect of the fraction of solids which are organic and degradable on the product cost is shown in Figure 5.3. The approximation of electrical costs of \$0.035/kwh is not valid in some geographical locations. The sensitivity of the product cost on this assumption is illustrated in Figure 5.4.

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

FIGURE 5.2

PRODUCT COST AS A FUNCTION OF WEIGHT-FRACTION
SOLIDS IN THE DIGESTER

FIGURE 5.3

LIQUID FUEL PRODUCTION COST AS A FUNCTION
OF THE FRACTION OF SOLIDS WHICH ARE ORGANIC AND DEGRADABLE

FIGURE 5.4

PRODUCT COST AS A FUNCTION OF ELECTRICITY
COST

still be 4.9×10^5 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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Appendix A
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 the limit as Δx and Δy approach zero.

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

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

(x-direction)

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

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

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

(y-direction)

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

$$\begin{aligned}
& - \frac{d}{dx} (C_A v_x) - \frac{d}{dy} (-D_{AB} \frac{C_A}{y} + C_A v_y) \\
& - v_x \frac{dC_A}{dx} + D_{AB} \frac{d^2 C_A}{dy^2} - v_y \frac{dC_A}{dy} \\
& v_x \frac{dC_A}{dx} + v_y \frac{dC_A}{dy} = D_{AB} \frac{d^2 C_A}{dy^2} \quad (A.4)
\end{aligned}$$

Boundary Conditions:

$$\begin{aligned}
v_x &= 0 \text{ at } y = 0 \\
v_y &= 0 \text{ at } y = 0 \\
v_x &= v_o \text{ at } y = \infty \\
C_A &= C_{A_o} \text{ at } y = \infty \\
C_A &= C_{A_s} \text{ at } y = 0
\end{aligned}$$

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

$$\xi = 1/2 \sqrt{\frac{v_o}{v}} \frac{y}{\sqrt{x}} \quad v_x \frac{dv_x}{dx} + v_y \frac{dv_y}{dy} = v \frac{d^2 v}{dy^2} \quad (A.5)$$

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

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

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

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

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

Substitute equations (A.6) and (A.7) into equations (A.4) and (A.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

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

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

Mass transfer to wall is:

$$\begin{aligned} N_A &= -D_{AB} W \int_{x=0}^{x=L} \left(\frac{\partial C_A}{\partial y} \right)_{y=0} dx \\ &= D_{AB} W (C_{A_0} - C_{A_s}) \frac{1}{2} \sqrt{\frac{v_o}{v}} \frac{d\rho(\xi)}{d\xi} \bigg|_{\xi=0} \int_{x=0}^{x=L} x^{-1/2} dx \\ &= D_{AB} W (C_{A_s} - C_{A_0}) \frac{1}{2} \sqrt{\frac{v_o}{v}} \frac{d\rho(\xi)}{d\xi} \bigg|_{\xi=0} 2L^{-1/2} \\ &= D_{AB} W (C_{A_s} - C_{A_0}) \sqrt{\frac{v_o L}{v}} \frac{d\rho(\xi)}{d\xi} \end{aligned}$$

Using equation (A.8):

$$N_A = -D_{AB} W C_{A_o} \sqrt{\frac{v_o L}{v}} \cdot 0.664 \sqrt{\frac{v}{D_{AB}}}$$

$$N_A = -0.664 D_{AB} W C_{A_o} \sqrt{\frac{v_o L}{v}} \sqrt{\frac{v}{D_{AB}}}$$

Section 6

CONTINUOUS PACKED BED FERMENTATION

One of the goals of the present program is to convert the current 300 liter fixed packed bed fermenter to operate in a continuous mode. This will involve designing systems for adding fresh biomass to the fermenter as well as removing spent solids. The prime requirement for both systems is the ability to remove just solids from a solid/liquid mixture while maintaining anaerobiosis. In the case of the feed mechanism, solids will be introduced into the fermenter from a preparation tank in which the biomass has been pre-soaked in water to exclude air. Minimizing the amount of concomitant water addition will be desirable since it will prevent unproductive dilution of the fermenter contents. In a similar way, the residue removal system must remove only those portions of the fermentation mix which are unwanted, namely the spent solids (fermenter liquid contains organic acids and is therefore valuable).

As a first step in implementing continuous mode operation, tests have been performed to assess the viability of tapered auger devices for the addition and removal of solids from the fermenter. Such a system is shown conceptually in Figure 6.1. Each unit would consist of a tapered-shaft auger inside a hollow tube. The solid/liquid mixture would feed in at the end where the shaft is narrowest. As the mixture is pushed along the tube by the rotating blades of the auger, the widening shaft will gradually compress it. This will, in principle, squeeze the liquids from the solids and force them to percolate back down the tube into the original vessel. Thus, only the solid fraction will reach the end of the tube where the shaft is widest, and the compression greatest. They will then be expelled through an appropriate opening.

A bench-scale test unit was designed and built to evaluate the suitability of tapered auger devices. It consists of a modified 4 inch diameter earth boring auger encased in a plexiglass tube. The auger shaft

was tapered by wrapping it with successive strips of 1/8" rubber, in a step-wise fashion. Shaft diameter ranges from 1" at the narrow end to 2 1/2" at the wide end. The auger is supported at each end on pillow block bearings and drive for the unit is provided with a hand crank. Aluminum end plates seal the two ends of the tube. The test mixture of seaweed and water is fed in at the narrow-shaft end through an opening in the tube onto which a feed hopper has been built. Dewatered weed exits at the other end of the unit through slots cut in the end plate. A sealing plate can be positioned over the exit slots to prevent leakage when the unit is not operating.

The unit had been tested using a slurry of shredded Chondrus crispus as the feed material (approximately 5% solids). With the sealing plate initially in position, the auger was slowly turned. The slurry could be seen gradually filling the tube, becoming compressed as it went. When the tube was full the sealing plate was removed. The slug of compressed weed proved to be compacted enough to prevent leakage of liquids and continued cranking resulted in the extrusion of compressed weed through the exit slots. Subsequent tests showed the dewatered weed to be 21% solids. Cranking was kept up until the feed hopper was essentially empty of all solids. At this stage the weed stopped coming out even though there was still a sizeable slug left in the tube. It was apparent that weed would only be expelled from the tube if fresh weed was continually being introduced at the feed end. This has the convenient effect of keeping the tube sealed when the solids in the hopper have been exhausted.

This test provided encouraging evidence that tapered auger devices will be well suited for the desired application. Future efforts will be directed at designing, installing, and optimizing systems, based on this principle, for the continuous operation of the present 300 liter packed bed fermenter. As part of this, auger drive systems will be required. These will be geared so as to balance the feed and removal rates of solids and maintain steady state conditions within the fermenter.

Figure 6.1 Continuous Feed Device

Section 7

FIXED PACKED BED FERMENTATION

In this first large-scale fermentation of fresh-water biomass, the lab-pilot fixed packed bed fermenter was loaded with 43.7 lbs Hydrilla 22.5 l effluent from Expt. 02357 (Chondrus crispus), and 267 liters of water. Because of its apparent value as a methane suppressor (Dynatech Report No. 1889, p.15), 10^{-4} molar bromoethane sulfonic acid ($\text{Br CH}_2\text{CH}_2\text{SO}_3^-$) was added at the start. Previous experiments have shown that Hydrilla fermentations are particularly susceptible to loss of acid products by methane formation 25-50 days after the start, resulting in acid concentrations diminishing to zero. However, reactors containing bromoethanesulfonic acid showed little or no decrease from maximum acid concentrations after 70 or more days.

Results of the Hydrilla fermentation were tabulated after 90 days. The gaseous products are presented in Table 4.1, and it can be seen that only 2.5% of the product is methane (based on carbon conversion). Acid results are found in Table 4.2.

From these data, per cent conversion based on carbon for the experiment may be calculated as follows:

$$\% \text{ Conversion} = \frac{\text{Wt. Carbon in Products}}{\text{Wt. Carbon in Reactants}} = \frac{160 + 1625}{57.00} = 31.30\%$$

An oxidation-reduction balance can be made based on the amounts of reduced products formed during the fermentation. Since carbon dioxide is the only oxidation product produced relative to the hexose starting material (acetic acid is in the same oxidation state as hexose), the quantity of carbon dioxide produced should correlate with the amount of reduced products formed on a reducing equivalent basis. Table 7.3 shows the stoichiometric balance of carbon dioxide production per reduced products observed. The total amount of carbon dioxide expected based on amounts of

reduced products formed is 17.7 gram moles. The amount actually obtained was 36.7 gram moles for a 207% recovery. The maximum amount of the extra carbon dioxide that could have resulted from aerobic fermentation based on the amount of oxygen estimated to be present in the fermenter is around 2.44 gram moles, still resulting in a 182% recovery.

The presence of the excess carbon dioxide can best be explained by the production of cell mass. Work previously done at Dynatech has shown a normal population in biomass fermentations to be 5-6 gms./liter dry cell weight). It is difficult to measure accurate cell concentrations in Hydrilla fermentations because of the tendency of the cells to be adsorbed onto the substrate, however, it is assumed for the present that a 5-6 gm./l. estimate is valid for the current fermentation. Production of cell mass at this concentration would be expected to produce approximately 10 moles of carbon dioxide, which closes the oxidation-reduction balance.

Table 7.1

GASEOUS PRODUCTS - RUN #004432

Fermentor:

<u>Gas</u>	<u>Volume (STP)</u>	<u>g Moles</u>	<u>Wt. Carbon</u>
Carbon Dioxide	805.22 1	35.95	116.47g
Hydrogen	83.62 1	3.73	0.00g
Methane	86.18 1	3.85	34.63g

Extractor:

Carbon Dioxide	15.62 1	0.70	2.26g
Methane	15.69 1	0.70	6.30

Total Carbon in Gaseous Products:

159.66g

Table 7.2

ORGANIC ACID PRODUCTION: RUN #04432

Fermentor:

<u>Acid</u>	<u>Concentration</u>	<u>Moles</u>	<u>Weight Carbon</u>
Acetic	136 meq/l	40.80	980 g
Propionic	30 meq/l	9.00	980 g
Butyric	21 meq/l	6.30	303 g
Valeric	0	0	0 g
Caproic	0	0	0 g
<hr/>			
Total	187 meq/l	56.1 moles	1607 g

Extractor:

Acetic	10 meq/l	.06	1.44 g
Propionic	3 meq/l	.028	.65 g
Butyric	21.5 meq/l	.13	6.20 g
Valeric	8.5 meq/l	.05	3.06 g
Caproic	17 meq/l	.10	7.35 g
<hr/>			
Total	60 meq/l	.36 moles	18.7 g

Total Weight Carbon converted to acids:	1606.24
	+ 18.7
	<hr/> 1625. g

Table 7.3

CARBON DIOXIDE PRODUCTION - RUN #04432

Source	Quantity	Stoichiometry		Rate	Moles CO ₂
Hydrogen	3.73 moles	$C_6H_{12}O_6$	$2CH_3COOH + 2CO_2 + 4H_2O$	1:2	1.9
Propionic	9.02 moles	$7CH_3COOH$	$4CH_3COOH + 2CO_2 + 2H_2O$	1:2	4.5
Butyric	6.43 moles	$5CH_3COOH$	$2CH_3(CH_2)_2COOH + 2CO_2 + 2H_2O$	1:1	6.4
Valeric	0.05 moles	$13CH_3COOH$	$4CH(CH_2)_3COOH + 6CO_2 + 6H_2O$	3:2	0.1
Caproic	0.10 moles	$4CH_3COOH$	$CH_3(CH_2)_4COOH + 2CO_2 + 2H_2O$	2:1	0.2
Methane	4.55 moles	$C_6H_{12}O_6$	$3CO_2 + 3CH_4$	1:1	4.55
					17.7 moles

Section 8

CALORIMETRY

In order to assess the efficiency of a process for converting a biomass species to liquid fuel it is preferable to look at the conversion on an energy basis. The first step is to evaluate the energy content of the biomass substrate. Table 8.1 lists the heat of combustion of a number of biomass materials of interest to the current program both on a dry solids and a volatile solids basis. The measurements were performed using a Parr Model 1341 oxygen bomb calorimeter at 30 atm pressure.

Although little consistency is observed among the heat content on a total solids basis, more correlation exists for the values on a volatile solids basis among species in each of the three groups. The freshwater weeds were found to have heating values of 9000 Btu/lb volatile solids, whereas two of the marine algae species are right at 7200 Btu/lb v.s. (Chondrus crispus gave a somewhat higher value of 8000) and the agricultural residues gave around 8300 Btu/lb v.s. The last two entries are the heat contents of the Hydrilla residues described in Section 3. The first residue 04593, is the residue after conventional fermentation. The second residue, 04593D, is the residue after hot alkaline treatment as described followed by a second fermentation. The heating values when compared with unfermented Hydrilla shown no particular trend. A trend in heating values vs. degree of fermentation, either up or down, would indicate that one fraction of the volatile solids has been converted in preference to another fraction. For example, an increase in heating value based on volatile solids might indicate conversion of cellulose in preference to lignin. A lack of a definite trend is largely inconclusive, but this type of analysis is planned for future experiments.

Table 8.1

Heats of Combustion of Biomass Species

Substrate	%Vol. Solids <u>vol wt</u> T.S. wt	Btu/10 Total Solids	Btu/lb Volatile Solids
1) <u>Freshwater weeds</u>			
Duckweed	74.09	6763	9128
<u>Hydrilla</u>	77.87	6969	8950
2) <u>Marine algae</u>			
<u>Ulva lochica</u>	55.59	4027	7244
<u>Gracilaria</u>	69.16	4985	7209
<u>Chondrus crispus</u>	65.75	5258	7997
3) <u>Agricultural Residues</u>			
Rice straw	82.6	6800	8232
Wheat straw	91.7	7817	8525
Barley straw	91.4	7540	8250
4) <u>Fermentation Residues</u>			
Residue 04593 <u>Hydrilla</u>	80	6326	7908
Residue 04593-D <u>Hydrilla</u>	39	3314	8497

Appendix

LIQUID FUEL PRODUCTION FROM BIOMASS

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ABSTRACT

As an extension of our previous work on the production of methane via nonsterile anaerobic fermentation, we have modified the process to produce longer chain aliphatic hydrocarbons instead of methane. This product may be used without further modification as a fuel for Diesel engines or as a substitute feedstock for the production of gasoline. The work to date uses marine algae as the primary substrate, but work is currently in progress to adapt the process for use with other aquatic and terrestrial forms of biomass.

In the anaerobic fermentation of biomass to methane, organic acids are produced. In the modified fermentation, the approach has been to suppress methane formation and to extract the organic acids from the fermentation broth for electrolytic oxidation (Kolbe electrolysis) to aliphatic hydrocarbons.

Preliminary economic analysis based on a 1000 ton/day plant design and assumed biomass costs indicates that this process is capable of producing liquid fuels at a cost competitive with the most optimistic forecasts for alternative processes.

This work was carried out on Department of Energy Contract No. EG-77-C-02-4388, under the direction of Dr. Roscoe Ward.

INTRODUCTION

As an extension of the work on anaerobic fermentation of biomass to organic acids conducted previously under Department of Energy sponsorship, a program for the production of liquid hydrocarbon fuels from biomass was initiated. The process, as presented in Figure 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. Figure 2 is a plot of total reducing equivalents of acid versus time, where the asymptotic value of 0.34 reducing equivalent per liter represents 90% of the total carbon in the substrate.

However, in the course of this work, it was found that when other substrates were used, methane formation was a serious competitive process. Current program work 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. 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) that onion and garlic residues can be successfully converted into acids by the microbial population present in dairy manure. An interesting feature of this substrate is that no methane is formed as part of the products. Since this substrate is known to contain some antibacterial components [Ref.1], it is apparent that only methanogenic bacteria are affected by their presence. As Figure 3 indicates, addition of onion-garlic residues to Hydrilla fermentation is a potential preventive measure of methane formation. This peculiar property

LIQUID HYDROCARBONS FROM BIOMASS ---
PROCESS FLOWSHEET

Figure 1

Organic Acids Concentration Vs. Time

Figure 2

5% Chondrus crispus

Figure 3

may be exploited by using onion-garlic residues along with other substrates in order to prevent methane formation.

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

A number of approaches to methane suppression have been evaluated including fermentation at low pH (pH 5), addition of methane analogues (CHCl_3), and inclusion of materials that have been reported as effective suppressors of methane formation in cattle rumen (Salinomycin, Pfizer). But the best results to date have been obtained with 2-bromoethane-sulfonic acid.

The results from a set of static Hydrilla fermentation experiments illustrating the efficacy of this compound in suppressing methane formation are illustrated in Figure 4. The conversions achieved were significantly higher when the methane inhibitor was added--35%-40%--versus 25%-29% in the control. In addition, at 60 days fermentation in flasks containing the inhibitor, 100% of the acids produced still remained in solution.

Figure 4 Effect of the Addition of Bromoethane Sulfonic Acid (Coenzyme M Analogue) on the Conversion of Hydrilla into Acids.

ENERGETICS OF THE PROCESS

In the course of developing a process for converting biomass to liquid fuels, one of the primary considerations is the energy balance of the process which may be defined either of two ways:

$$E_B = \frac{E_O}{E_S + E_P}$$

where E_O is the energy output, E_S is the energy content of the substrate and E_P is the energy consumed in the process.

In the case where the energy of the substrate is essentially unreclaimable by other means:

$$E_B = \frac{E_O}{E_P}$$

Table 1 presents a comparison of the estimated energy yield of a woody, low moisture biomass with a high moisture form. As can be seen from this example, the energy content of the high moisture material is essentially unusable in thermal processes. However, energy balances discussed herein are defined in the former manner.

As with other fermentation processes to produce liquid fuels from biomass, this process is anaerobic. Table 2 presents estimates of energy output from an aerobic cellulose fermentation versus an anaerobic one. The aerobic process is highly exothermic, the remaining heating value being primarily in the cell mass produced. The anaerobic process, on the other hand, is only mildly exothermic. This is an important distinction since the object of the process is to produce fuels, not low quality heat.

Table 2

Aerobic vs Anaerobic Fermentation of Cellulose

Aerobic [~10% Cell Mass Production]

Anaerobic [~1% Cell Mass Production]

Biomass Energy Yield from Fermentation Vs. Combustion

Table 1

SUBSTRATE	COMPOSITION %				BTU/LB (DAF)	
	CELLULOSE	LIGNIN	H ₂ O	ASH	FERMENTATION	COMBUSTION
WOODY BIOMASS	50	25	20	5	$\frac{3750 + 0 + 0}{.75} = 5000$	$\frac{3750 + 3175 - 260}{.75} = 8900$
HIGH MOISTURE BIOMASS (SHORT ROTATION PLANTS, AQUATIC BIOMASS, SOME AGRICULTURAL RESIDUES.)	12	0	85	3	$\frac{900 + 0 + 0}{.12} = 7500$	$\frac{900 + 0 - 1100}{.12} = -1700$

Unlike other fermentation processes, however, this process is conducted in a nonsterile manner. The heat required to sterilize the substrate before fermentation can be considerable. Table 3 presents estimates of the energy required to autoclave high and low moisture biomass. Particularly in the case of the high moisture biomass, the energy required for sterilization is a serious burden to the process. Fermentation of biomass to liquid fuels via organic acids has other advantages over competitive processes (e.g. ethanol fermentation) besides being suitable for nonsterile operation.

1. Prehydrolysis of the substrate to soluble components is not required. Yeast fermentations to ethanol have either acid or enzymatic hydrolysis of the substrate as a prerequisite step; that is to say, these organisms do not produce extracellular cellulolytic enzymes.
2. Pentose fractions as well as hexose fractions are converted to organic acids. Yeast fermentations convert only hexose sugars to ethanol. Since most forms of biomass contain cellulose as well as hemicellulose, this limits the potential yield of the process, and yield is an important consideration in the economics and energy balance of a process. Table 4 shows a cost breakdown of this process by components. From this table it is seen that at a biomass cost of \$30/ton and a 50% conversion, the contribution to the biomass is approximately 50%. At lower yields, the contribution would be proportionately greater.
3. Organic acids, particularly the longer chain acids, may be removed from the fermentation by solvent extraction using solvents which are nontoxic to the microorganisms responsible for acid production. Ethanol is generally removed from fermentation broths by distillation, the most energy-intensive part of the process. Solvent extraction is a much less energy intensive process but we are unaware of any suitable extraction system for ethanol that is biocompatible.

Table 3

Energy Requirements for Sterilization

Autoclave 50% Fermentables

Heat Requirement = 240 BTU/lb Fermentables

Autoclave 10% Fermentables

Heat Requirement = 1200 BTU/lb Fermentables

Table 4

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
ELECTRICAL POWER AND ROYALTY	.63
TAXES AND OTHER OPERATING COSTS	.37
TOTAL COST, \$/MMBTU	<u>6.42 @ \$30/TON BIOMASS</u>

The primary negative factor in the process under discussion is its requirement for electricity. Although the formation of hydrocarbons from organic acids is thermodynamically spontaneous, in practice, it has been observed that activation energy is required to produce the desired product. Table 5 presents the free energies and enthalpies of formation of hydrocarbons from organic acids. It is one of the primary goals of this research to reduce the voltage required as much as possible.

Table 5

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

KOLBE REACTION

<u>ACID</u>	<u>H</u>		<u>H</u>	
	<u>KCALS/MOLE</u>	<u>VOLTS</u>	<u>KCALS/MOLE</u>	<u>VOLTS</u>
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

PROCESS DESIGN

Fermentation

In the process as described, the fermentation step is envisioned as occurring in a fixed packed bed fermenter. The mass transfer ordinarily accomplished by stirring in conventional digesters can be equally well fulfilled by a stream of liquid of the proper composition moving at the required rate through the fermenter. This same liquid stream may be used to control the temperature, add nutrients, control pH, and to remove reaction inhibiting products and toxic components. In addition, the piping arrangement involved may be employed to dewater the undigested material when the digestion stage is completed.

Figure 5 shows one possible arrangement for the fixed packed bed fermenter. In this case it may be used as a batch reactor for organic acid production. The fermenter, A, is filled with solid substrate. An aqueous medium containing nutrients and microorganisms is added in sufficient amounts to saturate the substrate and to fill the digester head space and circulation loop as shown. The pump, B, is used to circulate the liquid through the loop and through the packed mass of comminuted solid substrate containing fermentation microorganisms. As fermentation proceeds, required buffers and additional nutrients may be added through the inlet port, C; the acid is removed in sub-system D, which may be an ion exchange column, liquid-liquid extractor, or membrane device. Toxic compounds may also be removed from the aqueous phase by passing it through a cleaner, E, which may contain, for example, activated charcoal. When fermentation is economically completed, the undigested material is partially dewatered by opening valve F and pumping liquid out by means of pump G. The partially dewatered material is then removed, fresh substrate added, and the cycle above repeated.

Figure 5

Application of the fixed packed bed concept to a continuous plug flow system is presented in Figure 5. Here solid substrate is fed into the bottom of the fermenter and removed from the top of the fermenter. As with the batch-type packed bed system, fermenter liquid is circulated through the bed and organic acids are recovered in an external sub-system.

Currently in operation is a 300 liter fixed packed bed fermenter. It is constructed of 12-inch diameter glass tubing and is 15 feet in height. It is supported by a triangular frameowrk of 1 1/4-inch pipe and is enclosed with plywood and plexiglass. The temperature is controlled at 100°F by circulating warm air inside the enclosure. A flow rate of 3 gallons per hour is sufficient to fluidize the substrate, initially at 10% solids, in the reactor to reduce the operating pressure at the pump (approximately 7 feet below the top of the column) to 3 PSIG.

Figure 6 is a schematic diagram of the type of device designed to add substrate and reserve solid residue in a continuous manner. The primary element is an auger with a tapered shaft that will separate liquid and solid fractions by squeezing. A bench-model feeding device has recently been constructed. It consists of a 4-inch earth auger built up to the proper taper with 1/8-inch rubber strips encased in a plexiglass structure. Testing of this device is in progress prior to converting the 300 liter fermenter to continuous operation.

As was stated earlier, the overall product cost is very sensitive to conversion yield. This fact is illustrated more fully in Figure 7, which is a plot of product cost versus retention time and indicates that the added cost due to a larger fermenter volume is outweighed by the reduction in conversion yield only after about a 60 day retention time, which corresponds to 83% of the fermentable material converted.

LIQUID HYDROCARBONS FROM BIOMASS
CONTINUOUS FEED SYSTEM

Cost of Liquid Fuel Produced as a Function of Retention Time

Figure 7

Extraction

Removal of product acids is accomplished by liquid-liquid extraction using preferably a hydrocarbon or alternatively a fluorocarbon solvent. Figure 8 shows the extractor set-up for a large-scale operation. The primary extractors, which remove the higher acids from the fermenter effluent and transfer them to the aqueous stream which is then fed to the electrolysis cell. Since these extractors are designed to remove a small portion of the acids from a large volume of fermentor effluent, they are cocurrent units. The secondary extractors, which are designed to remove most of the acids from that portion of the fermentor effluent which is returned to the growth system as it is displaced by the water introduced with the fresh biomass, are countercurrent devices. Furthermore, the hydrocarbon or fluorocarbon phase must be augmented with or replaced by a substance with a higher partition coefficient for the lower molecular weight acids such as trioctylphosphine oxide [Ref. 2].

Electrolysis

Although the mechanism of Kolbe electrolysis has been a source of disagreement for many years, one suggested reaction scheme, presented in Figure 9 [Ref. 3], is suitable for current purposes. Basically the organic acid anions are oxidized to the corresponding radicals. These radicals decarboxylate to form alkyl radicals which may either dimerize to form the Kolbe product, disproportionate to form an alkene-alkane mixture, or may be oxidized further to form alkene, alcohol, or ester. Recent experiments involving the electrolytic oxidation of mixed organic acids produced by the anaerobic fermentation of Chondrus crispus gave the product spectrum shown in Figures 10 and 11. Figure 10 gives the gas chromatogram of the liquid products, and Figure 11 shows the gaseous products. The gaseous products are labeled as alkenes but the corresponding alkanes would not be resolvable under the analysis conditions. This particular experiment was run at pH 6, an applied voltage of 4.65V and an anodic current density of 0.8 amps/cm².

Figure 8

Anodic Oxidation of Carboxylates Reaction Mechanism

Figure 9

Figure 10

Liquid Electrolysis Products

Figure 11

Gaseous Electrolysis Products

The electrolysis was performed in the flowthrough cell shown in Figure 12. A flowthrough cell configuration is used to minimize polarization effects at both the anode and cathode. It consists of a platinum wire anode inside a platinum tube. The electrode spacing is 300 μm . An additional platinum wire electrode is used to measure the open circuit operating voltage while the electrolysis is taking place. The difference between the operating voltage and the open circuit voltage is a measure of the IR drop in the cell and other current density dependent overpotentials.

These current density-dependent potentials give rise to an optimum current density. Figure 13 shows a plot of product cost versus current density with a minimum at approximately 0.3 amps/cm^2 . Lower current densities have higher prorated capital costs whereas higher current densities give rise to excessive electrical requirements.

Energetics are critically dependent on the efficiency of the electrolysis process. Figure 14 presents the cost of liquid fuel produced as a function of applied voltage. A voltage of greater than 4V may be used before a cost of \$7.00/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.

Electrolysis Cell

Figure 12

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

Figure 13

Cost of Liquid Fuel Produced as a Function of Electrolysis Voltage

Figure 15

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