LIQUID FUELS PRODUCTION
FROM BIOMASS

Progress Report No. 8
Period Covered - July 1 to September 30, 1979

Contract No. EG-77-C-02-4388-9
Dynatech Project No. DOE-3
Dynatech Report No. 1956

Submitted to:

Dr. Larry Douglas
Biomass Refining Program
Solar Energy Research Institute
1536 Cole Boulevard
Golden, Colorado 80401

Prepared by:

J.E. Sanderson
D.L. Wise
P.F. Levy
M.S. Molyneaux

October 15, 1979

DYANTECH R/D Company
A Division of Dynatech Corporation
99 Erie Street
Cambridge, Massachusetts 02139

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Section 1

EXECUTIVE SUMMARY

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

The specific goals for the current program are:

1. Establish conditions under which substrates other than marine algae may be converted 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 to date 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 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-Bromoethane-sulfonic 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 nine months.

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

Figure 2.1

Section 3

STATIC FERMENTATIONS

The effort to obtain high conversions of biomass to organic acids has been continued. The loss of organic acids due to methane formation has been prevented (Progress Report No. 7, Dynatech Report No. 1889). This has raised the possibility of producing organic acids from other biomass sources in an effort to obtain the most favorable conversions during fermentation. Treatment of Hydrilla residue has also been pursued further (Progress Report No. 8; Dynatech Report No. 1931) as a means of improving the conversion to acids.

3.1 Acid Production from Corn Meal

The cost of growing terrestrial biomass for conversion to fuels can be predicted with more accuracy than the cost of producing aquatic biomass. Cost estimates for obtaining biomass from cropland have been made. (C. Tinberg and A.D. McElroy in the 2nd Annual Symposium on Fuels from Biomass, 1978; p.859). Characterization of anaerobic fermentation products from corn meal have been begun in our labs so that cost estimates of liquid hydrocarbon production from this grain can be made.

Fermentation mixtures containing 3% corn meal in unstirred flasks were incubated at 37°C to ascertain the organic acids produced, the percent of solids converted, and the reaction order and rate constant of the process. The corn meal slurries were inoculated with 2% sewage sludge or 2% corn meal fermentation effluent. Methane formation was suppressed by addition of $1 \times 10^{-4} \text{ M}$ bromoethanesulfonic acid. CaCO_3 was added at the start of the incubation (1 gm/100 ml) as a buffer. Additional CaCO_3 was added during the course of the incubation as needed to keep the pH between 5.5 and 6.0. Conversion to volatile acids is recorded in Tables 3.1 and 3.2 and plotted in Figure 3.1.

Analysis of the reaction rate data is continuing. The data from fermentation studies thus far do not fit the empirical relationships in first

or second order reactions. Whether this is due to the nature of the corn meal substrate or an experimental artifact is now being investigated. Fermentations with more frequent determinations of acid production and better pH control are now being performed. (The corn meal substrate contains much less carbonate buffer than the aquatic weeds previously fermented. Thus, they require the addition of more buffer as the acids are produced.) It is possible that the fermentation proceeds in two different rate regimes - the first in which the more soluble fermentable sugars are converted and the second, slower region in which less readily dissolved sugars are the substrates. This hypothesis is being investigated.

The effectiveness of bromoethanesulfonic acid in suppressing methane formation in the corn meal fermentations is now being tested. In fermentations with Hydrilla without bromoethanesulfonic acid, methane accumulation became significant 25 days after inoculation. Fermentations with corn meal are now in progress to check for methane formation and stability of the organic acids formed.

The percent conversion of the two corn meal fermentations compare very favorably with those obtained from Chrondrus crispus. Higher conversions are not anticipated, so pre-treatment of the corn meal will only be considered as a means obtaining more favorable reaction kinetics.

Further work is planned to provide better understanding of the reaction kinetics and optimize conditions for the conversion of corn meal to organic acids. The stability of the acids formed and the accumulation of higher molecular weight acids is also to be investigated.

Table 3.1

Run #06251; 3% Buffered Corn Meal
 with $1 \times 10^{-4} \mu$ Br ETSO_3^- ; Inoculated
 with 2% Sewage Sludge

Incubation Time (Days)	ACID PRODUCTION						A/T	R	%C
	A	P	B	V	C	T			
0	0	0	0	0	0	0	0	0	0
2	68.4	1.23	71.7	0	0	141.3	.48	249.8	50.0
5	111.9	10.5	66.4	1.3	5.3	195.0	.57	321.6	64.3
6	99.0	9.6	94.0	0.9	3.7	207.2	.48	368.4	73.7
7	87.8	10.3	87.8	0	6.2	192.1	.46	350	70.0
26	106.3	9.8	86.9	0	10.5	213.5	.50	382.7	76.5

* Acetic; P: Propionic; B: Butyric; V:Valeric; C: Caproic; T: Total

$R = A + 1.75P + 2.5B + 3.25V + 4.0C$

$\%C = R \times .002$

Table 3.2

Run #06266; 3% Buffered Corn Meal
 with 1×10^{-4} BrETSO₃⁻ - Inoculated with
 2% 06251 Effluent

Incubation Time (Days)	A	P	ACID PRODUCTION				A/T	R	%C
			B	V	C	T			
0	0	0	0	0	0	0	0	0	0
1	23.4	0	41.7	0	0	65.1	.36	127.7	25.5
4	58.2	10.4	52.8	0	8.7	130.1	.45	243.1	48.6
5	50.5	9.5	51.6	0	15.1	126.7	.40	256.4	51.3
6	51.2	8.6	53.7	0	15.8	129.3	.40	263.7	52.7
7	89.8	13.0	78.0	0	17	197.8	.45	375.6	75.1
13	125.8	12.8	97.9	0	7.6	244.1	.52	323.4	64.7

Figure 3.1
Conversion of Corn Meal to Organic Acids

3.2 Improvement on Hydrilla Conversions

Previous work at Dynatech has shown that heating Hydrilla residues to 110°C for one hour at alkaline or acid pH followed by neutralization and reinoculation will produce additional conversion to acids (Progress Report 8, Section 3). Acids produced after treatment of the residue amounted to an extra 12% conversion after the 33-38% accomplished in the initial fermentation.

Heat treatment and refermentation has been attempted on residue from a Hydrilla fermentation in which 50% conversion of the total solids to acids was attained initially. This residue was heated at 110°C for one hour at alkaline pH, then neutralized and reinoculated. To date, additional conversions have not exceeded 1%.

Analysis has shown the residue to contain 48% volatile solids. Most of the non-volatile material is CaCO_3 , added to the initial fermentation as a buffer. Calorimetry studies have shown the heat of combustion of this residue to be 5361 Btu/lb volatile solids. (Fresh Hydrilla was found to have heating values of almost 9000 Btu/lb volatile solids.)

The products of the alkaline heat treatment of the residue have not been identified. Since fermentable sugars are not the necessary end products of heat treatment of cellulosic materials, it is possible that a significant portion of the volatile solids do not represent fermentable substrates. It is also possible that the remaining cellulose in the residue remains inaccessible for fermentation even after alkaline heat treatment.

Further studies are planned in which various treatments of Hydrilla residue will be attempted in an effort to gain better conversions. Optimization will be pursued by changing the pH, temperature and reaction time of residue treatments.

Section 4

KOLBE ELECTROLYSIS

4.1 Reduction of the Applied Electrochemical Potential

The applied electrochemical potential required for electrolytic oxidation of organic acids to alkanes (Kolbe Electrolysis) may be divided into several components:

$$E_T = E_{rev} + IR + E'_A + E'_C + E'_{conc A} + E'_{conc C}$$

where: E_T is the applied voltage

E_{rev} is the reversible potential

IR is the potential required to overcome the internal resistance of the cell

E'_A is the activation overpotential required by steps in the anode reaction slower than electron transfer

E'_C is the activation overpotential at the cathode

$E'_{conc A}$ and $E'_{conc C}$ are the overpotentials created at high current densities due to the depletion of electroactive substances near the electrode surface.

E_{rev} , the reversible potential of the reaction, may be calculated from free energies of formation according to the equation:

$$\Delta G^\circ = -n FE^\circ$$

where:

ΔG° is the free energy

n is the number of electrons transferred, and

F is the faradays constant (96,500 coulombs/mole).

The standard free energies, when all products and reactants are in their standard states, are given in Table 4.1. In order to correct these values for products or reactants not in standard states the Nernst equation is employed:

Table 4.1
 ENTHALPY AND FREE ENERGY (WITH CORRESPONDING OXIDATION POTENTIALS)
 FOR ELECTROLYSIS OF ORGANIC ACIDS

Kolbe Reaction

<u>Acid</u>	<u>ΔH</u>		<u>ΔG</u>	
	<u>kcal/mole</u>	<u>volts</u>	<u>kcal/mole</u>	<u>volts</u>
acetic	0.0	-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

The ΔH 's and ΔG 's presented above were obtained from the enthalpic and free energies of formation of the products and reactants. References 4.1, 4.2, and 4.3 were used as sources of thermodynamic data.

$$E = E_{\theta}^{\circ} + \frac{RT}{nF} \ln A \approx E_{\theta}^{\circ} + 0.06 \ln A \text{ for a 1 electron transfer at room temperature}$$

where:

R is the gas constant

T is the temperature

A is the activity of the product or reactant, and

$\pm$ depends on whether the process is an oxidation or reduction, and whether the activity is of a product or reactant.

In order to decrease contribution of E_{Rev} to E_T it is necessary to increase the activities of reactants and/or decrease the activities of products. The contribution of the IR drop to E_T is due to the resistance of the electrolyte solution. The specific resistance of 0.5 molar caproic acid has been measured at 1000 Hz to be 40 Ωcm at 22°C. With an electrode spacing of 0.05 cm and a current density of 0.25 A/cm² an IR drop of approximately 0.5 volts is calculated for the following equation:

$$IR = \frac{I\rho L}{A}$$

where

$\frac{I}{A}$ is the current density

ρ is the specific resistance, and

L is the electrode spacing

Some factors which may be employed to reduce the IR drop are:

1. Reduce the resistance of the solution:
 - a) by increasing the concentration of electroactive species
 - b) by employing a non-electroactive supporting electrode
 - c) by increasing the temperature
2. Reduce the current density at the anode and/or cathode.
3. Reduce the electrode spacing.

The contributions to E'_T from E'_A and E'_C , the kinetic overpotentials at the anode and cathode, as stated earlier result from reactions in the redox scheme which are slower than electron transfer. These overpotentials as a function of current density are given by the Tafel equation:

$$E' = a + b \ln (I/A)$$

Tafel plots were obtained for a 0.5 N caproic acid solution at pH 7; these are shown in Figure 4.1. From these results:

$$E'_A = 2.32 + 0.090 \ln I$$

and $E'_C = 1.03 + 0.105 \ln I$

where: $E'_A = E'_C = IR + E'_A + E'^{*}_C$

It is apparent, therefore, that these terms E°_A and E°_C are large contributors to the applied potential.

The value of E_C at 0.25 A/cm^2 would be 0.88V. Part of this potential, ~0.42 volts results from operating at pH 7, where the hydrogen ion concentration is low. This potential could be reduced by operating at lower pH. An intriguing possibility, however, is to run the Kolbe oxidation against an entirely different counter electrode from the hydrogen electrode, which operates at a more favorable potential or which produces a valuable by-product.

The rest of E_C , E'_C is about 0.46 V. This is the kinetic overpotential associated with reduction of hydrogen ions at a Monel cathode. A Monel cathode has been used for these measurements because a suitable cathode was available. It is known, however, that reduction of hydrogen ion at a platinum cathode has a negligible kinetic overpotential. More recently measurements have been made using a platinum cathode, which has essentially eliminated this contribution to the cathode overpotential.

* The current method of measuring E°_A may include part of the IR drop.

The measured kinetic overpotential at the platinum anode, although it may include part of the IR drop, is substantial, amounting to ~ 1.8 volts even at 10^{-3} A/cm². The reduction of this overpotential will require the selection of an anode material which has a lower overpotential for organic acid oxidation than platinum. The approach will be to measure the absorption of organic acids as a function of voltage and to identify electrode materials which have maximum absorption at lower voltages than platinum. Experimentally what is involved is making capacitance measurements using the test electrode material as one plate using a standard material such as platinum as the other plate and the organic acid solution as the dielectric.

Most of the noble metals have already been thoroughly investigated for use in Kolbe electrolysis. Therefore, the study will concentrate on active metals, which may be suitable if the applied potential can be reduced significantly or if the metal surfaces can be sufficiently passivated, and "Petrovskite Lattice", type materials, consisting of oxides of transition metals such as LaCrO₃, LaVO₃, or NaWO₃.

One successful approach to the elimination of the anode overpotential which is receiving much attention currently is the use of photoactive n-type semiconductor anodes. It has been shown that anodes of appropriate formulations of titanium dioxide (Ref. 4.4) and strontium titanate (Ref. 4.5) under stimulation of visible light give Kolbe products with negligible anodic overpotentials. Although current densities tend to be low and there have been some problems with electrode stability (Ref. 4.6) this approach shows a lot of promise.

The contribution to E_T from $E'_{\text{conc A}}$ and $E'_{\text{conc C}}$ become evident when the electrolysis rate is limited by diffusion. In an unstirred cell the maximum current density obtainable by diffusion is given by (Ref. 4.7):

$$\frac{I}{A} = 0.0223 D C_n$$

where: D is the diffusion coefficient in cm² day⁻¹
 C is the concentration of electroactive species in moles/liter,
 n is the number of electrons transferred

This equation gives a current density of $\sim 0.01 \text{ A/cm}^2$. Since current densities of $0.1 - 1.0 \text{ A/cm}^2$ are ordinarily required to give the desired product, the contribution of the anode concentration overpotential would be expected to be considerable. For this reason most of the experiments in this work have been performed in a variety of flow through cells, either of flat plate (ECO 100) or annular construction to minimize the effect of the concentration of overpotentials. It has been demonstrated that anode and cathode potentials quoted herein were measured in a flow regime where these potentials are independent of the flow rate. Whereas flow rate independence does not prove that concentration overpotentials are negligible, it is suggestive of this conclusion. Experimentation at different concentrations of electroactive species will shed more light on the presence of concentration overpotentials, assuming the effect an electrolyte resistance can be factored out successfully.

In the preceding discussion an explanation has been given for the applied potential currently required to electrolytically oxidize organic acids to liquid hydrocarbon fuels. Also given are the experimental parameters which must be optimized to reduce the applied potential. Among these are:

1. Temperature
2. pH
3. Concentration of electroactive species
4. Use of supporting electrolyte
5. Current density
6. Cell geometry
7. Anode material
8. Cathode material

It should be noted, however, that another important dependent variable, one which will be affected by many of these experimental parameters is the olefin/paraffin ratio. This factor must be monitored as well as applied potential in order to determine the conditions required to give the lowest possible applied potential consistent with a favorable olefin/paraffin ratio.

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Section 5

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 at 267 liters of water. Because of its apparent values as a methane suppressor (Dynatech Report No. 1889, p.15), 10^{-4} molar bromoethanesulfonic acid ($\text{Br CH}_2 \text{CH}_3 \text{SO}_3^-$) 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 5.1, and it can be seen that only 2.5% of the product is methane (based on carbon conversion). Acid results are found in Table 5.2.

From these data, percent 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 5.3 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.

A potential source of CO₂ production is carbonate present in Hydrilla which decomposes to CO₂ under the slightly acidic conditions of the fermentation.

Carbonate present in the weed as CaCO₃ is also decomposed under acidic conditions, producing CO₂.

The maximum production of CO₂ from the decomposition of carbonate was determined. A known quantity of Hydrilla was suspended in aqueous 0.05 to 0.1 N HCl. The gas evolved from the suspension was collected in an inverted buret immersed in a saturated salt solution. The volume of gas evolved was recorded and its composition was determined by gas partition chromatography.

The CO₂ released following this acid treatment is 0.0004 moles/gram Hydrilla. In the lab-pilot fixed packed bed fermenter loaded with 43 lbs. Hydrilla, this can account for 7.8 gram/moles CO₂. Combined with the carbon dioxide expected from reduced products and from aerobic fermentation due to oxygen present in the fermenter, the 36.7 gram moles actually obtained represent a 131% 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 grams/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 CO_2 , which results in a 97% recovery and closes the oxidation - reduction balance.

Table 5.1

GASEOUS PRODUCTS - RUN #004432

Fermenter:

<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

160g

Total Carbon in Gaseous Products:

Table 5.2

ORGANIC ACID PRODUCTION: RUN #04432

Fermenter:

<u>Acid</u>	<u>Concentration</u>	<u>Moles</u>	<u>Wt. 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
Caproic	0	0	0
<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
 1625. g

Table 5.3

CARBON DIOXIDE PRODUCTION - RUN # 04432

Source	Quantity	Stoichiometry	Rate	Moles CO ₂
Hydrogen	3.73 moles	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$	1:2	1.9
Propionic	9.02 moles	$7CH_3COOH \rightarrow 4CH_3CH_2COOH + 2CO_2 + 2H_2O$	1:2	4.5
Butyric	6.43 moles	$5CH_3COOH \rightarrow 2CH_3(CH_2)COOH + 2CO_2 + 2H_2O$	1:1	6.4
Valeric	0.05 moles	$13CH_3COOH \rightarrow 4CH(CH_2)_2COOH + 2CO_2 + 2H_2O$	3:2	0.1
Caproic	0.10 moles	$4CH_3COOH \rightarrow CH_3(CH_2)_4COOH + 2CO_2 + 2H_2O$	2:1	0.2
Methane	4.55 moles	$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$	1:1	4.55
				17.7 moles

Section 6

MASS, ENERGY AND CARBON BALANCE

It is of interest to consider the yield of mass, energy and carbon from the proposed process. Figure 6.1 presents a flow sheet indicating the fate of one pound of hypothetical biomass containing 75% cellulose and equivalent fermentables, 10% liquid and other organic nonfermentables, and 15% ash. Such a hypothetical biomass would contain 6500 Btu's and 38% carbon. Of this amount 0.44 lbs containing 0.13 lbs carbon and 2850 Btu would form a solid residue, an additional 0.05 lbs carbon would be lost as carbon dioxide. The remainder of the material is converted by anaerobic fermentation to mixed organic acids. These acids are extracted into a nonaqueous phase and then re-extracted into aqueous base for use in the Kolbe electrolysis step. The fermenter effluent is recycled except for a small amount which is discarded to allow for the water added to the fermenter with the biomass. This water would contain 0.03 lbs of organic acids.

In the electrolysis the organic acids are converted to alkanes (0.17 lbs) along with carbon dioxide (0.12 lbs) and hydrogen (.01 lb). The alkane product contains 50% of the energy and 38% of the carbon of the biomass.

LIQUID HYDROCARBON FUELS FROM BIOMASS
MASS, ENERGY, & CARBON FLOW SHEET

YIELDS:

Based on Mass	18%
Based on Energy	60%
Based on Carbon	38%

ACKNOWLEDGEMENTS

We would like to thank Dr. John Ryther of the Woods Hole Oceanographic Institute for supplying samples of some of the aquatic plants used in this study. We also would like to thank Professor G.S. Zeikus of the University of Wisconsin and Professor C. Cooney of the Massachusetts Institute of Technology for helpful advice and discussion.