LIQUID FUELS PRODUCTION
FROM BIOMASS

Progress Report No. 10
Period Covered - October 1 to December 31, 1979

Contract No. EG-77-C-02-4388-10
Dynatech Project No. DOE-3
Dynatech Report No. 1987

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February 1, 1980

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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 via Kolbe Electrolysis to aliphatic hydrocarbons, which may be used as a diesel fuel.

The specific goals for the current program are:

1. Establish conditions under which substrates other than marine algae may be converted in good yield to organic acids. The primary task in this regard is methane suppression.
2. Modify the current 300 liter fixed packed bed batch fermenter to operate in a continuous mode.
3. Change from membrane extraction of organic acids to liquid-liquid extraction.
4. Optimize the energy balance of the electrolytic oxidation process. The primary task in this regard is to reduce the working potential required for the electrolysis while maintaining an adequate current density.
5. Scale the entire process up to match the output of the 300 liter fermenter.
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 crispus to Hydrilla, a freshwater aquatic weed. A recent Hydrilla fermentation experiment in the 300 liter fermenter using 2-bromoethanesulfonic acid gave less than 2.5% conversion of carbon to methane.

Preliminary experiments have also been completed utilizing corn meal in which 2-bromoethanesulfonic acid and carbon monoxide were both found to be effective methane suppressors. Conversion of over 80% of the corn meal substrate to organic acids has been observed. Work is continuing in the area of methane suppression to identify the best techniques for each biomass substrate.

An analysis of the energy outputs and requirements for the production of liquid hydrocarbon fuel from corn has been performed. Estimates made by R.S. Chambers and his colleagues at the University of Illinois (Science, 1979, Vol. 206, p. 205) were used for the agricultural inputs and by-product credits. A favorable energy balance (output/input) of 1.77/1.00 was obtained.

As a means of expanding the number of potential substrates, pretreatment schemes are being investigated. Additional conversions from residues of Hydrilla fermentations of over 10% have been obtained.

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 similar device of suitable size and material for use with the 300 liter fixed packed bed fermenter has been tested and found satisfactory.

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 fermenter. 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 fermenter.

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 (Sanderson and Wise 1978a). 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 been demonstrated that 2-bromoethanesulfonic acid effectively suppresses the conversion of organic acids to methane, although it is relatively ineffective in preventing the conversion of carbon dioxide and hydrogen to methane.

Removal of the product acids had been accomplished using the membrane separation process described previously (Sanderson and Wise 1978b). 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 fermenter 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:

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 high 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 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.

Section 3

STATIC FERMENTATIONS

3.1 Improvement on Hydrilla Conversions (Pre-treatment)

Conversion of volatile solids contained in Hydrilla to organic acids has typically been between 30 and 40 percent. Higher conversions are desirable and it is recognized that pre-treatment of the weed may be necessary to achieve a significant increase in the formation of acids. Since pre-treatment will tend to solubilize a greater portion of substrate, improved rates may also be realized from a pre-treatment scheme.

A method for testing pre-treatment parameters has been developed as outlined in Figure 3.1. Treatment of residues from fermentations which have ceased to produce acids has been chosen as the best method for optimizing pre-treatment schemes. In this manner, increases in conversion obtained by the various pre-treatments can be readily observed. Residue from a fixed packed bed Hydrilla fermentation was dried to 15 to 16 percent total solids by squeezing. By obtaining a large quantity of residue from a single fermentation a great number of pre-treatment schemes can be tested and compared to each other to determine the effect of varying conditions.

Hydrilla from the initial fixed packed bed fermentation was 31 percent converted. After drying, the residue was found to be comprised of 74 percent volatile solids. The heat of combustion measured in calorimetry studies was 6405 BTU/lb total dry solids. (Fresh Hydrilla has a heating value of 6969 BTU/lb total dry solids.)

Slurries comprised of 5 percent total solids in acid, basic or neutral solutions were subjected to treatment at temperatures up to 120°C for two hours. After cooling to room temperature and neutralization, the

slurries were inoculated with sewage sludge and fermented anaerobically at 37°C. Production of organic acids was measured to monitor conversion. Bromoethanesulfonic acid ($5 \times 10^{-4}M$) was added to all fermentations to inhibit methane formation.

The pre-treatment scheme envisioned involves subjecting an aqueous slurry of substrate to elevated temperatures at acid or alkaline pH. Fermentable sugars are not the necessary end products of heat treatment of polysaccharides. Under mild reaction conditions, the polymers may not be altered significantly, while under extreme conditions the reaction may proceed to products other than sugars. The experiments with Hydrilla residues attempt to identify important parameters by varying reaction conditions of the pre-treatment scheme. The temperature, pH, and reaction time will all be varied independently.

To determine the effect of temperature on pre-treatment, experiments were performed with acid and base treated residue. Acid treated samples were suspended in 1 percent sulfuric acid at a concentration of 5 percent total solids. Each sample was then heated at 20°, 65°, 100°, or 120°C for 2 hours. After cooling to room temperature, the samples were neutralized by addition of base to pH 6-7. Each sample was then inoculated with sewage sludge. Bromoethane sulfonic acid (5×10^{-4}) and $CaCO_3$ (1g/100 ml) were also added to each fermentation flask. Results are plotted in Figure 3.2 as additional conversion vs. fermentation time. (Percent conversion is based on increased conversion above initial fermentation.) A control sample which was not subjected to any acid pre-treatment was also fermented.

The effect of temperature on base treated residue was tested in a similar manner. After treatment of base in 5 percent total solids slurries with 1 percent (W/V) NaOH at 20°, 65°, 100°, or 120°C for 2 hours, samples were neutralized and fermentations begun. Figure 3.3 shows results of the experiments with base treated Hydrilla residue. An untreated control was also fermented. The conversions of these base treated samples were not as great as the acid treated residue, nor was the effect of temperature on treatment as pronounced.

The acid treated samples gave the greatest increases in conversion with 100°C treatment. Experiments are now in progress varying the acid (or base) concentrations and reaction time to learn the effect of these parameters on pre-treatment. Further analysis of the residues is also planned. Samples will be analyzed for carbon content and reducing sugar levels after hydrolysis. Further analyses to determine hexose and pentose levels as well as lignin content of both fresh substrate and residues from fermentations are also planned. These experiments will lend valuable insights to the technology of fermenting all potential biomass substrates.

3.2 Alternative Biomass Sources

The fermentation process is capable of converting a great variety of biomass sources to organic acids. Efforts at Dynatech have centered on utilization of aquatic biomass. In an effort to expand the process to include more traditional agricultural crops, preliminary experiments have been conducted with a variety of substrates. This will serve to increase the feasibility of the process in the immediate future (before marine farms are operating) and lend the process to more straightforward comparison with other technologies for the production of fuels from biomass. Other forms of marine biomass are also being tested in keeping with the initial goals of the program.

Fermentations of water hyacinth and corn meal have been completed. The heats of combustion of these substrates were measured and are reported in Table 3.1. Fermentations were performed in static flasks under anaerobic conditions using sewage sludge as inoculum. Plots of conversion vs. fermentation time for these substrates appear in Figures 3.4 and 3.5. Conversion percentages are calculated from organic acid concentrations and are based on the total solid content of the fresh substrate. All fermentation slurries contain $5 \times 10^{-4}M$ bromoethane sulfonic acid as a methane suppressor and 1g/100 ml $CaCO_3$ as a buffer. Additional calcium carbonate is added to the fermentations when the pH drops below 5. Total solid concentrations in the flasks were between 3 and 5 percent.

The low conversion to acids of water hyacinth indicates that more investigation is necessary before this substrate can be utilized economically. Appropriate pre-treatment schemes may increase conversions to acceptable levels. Conversions from the corn meal fermentations were much higher and ranged from 65 to 85 percent within 6 days. Significant quantities of butyric, valeric, and caproic acids were also formed in the corn meal experiments, possibly due to maintaining a lower pH than fermentations with other substrates. Data from a typical corn meal fermentation were fit to a first-order rate plot (Figure 3.6). The first-order rate constant is 0.257 per day, and the initial rate is 115 milliequivalents per liter per day.

Experiments are continuing with corn meal in an effort to optimize the formation of higher molecular weight organic acids (particularly caproic). The testing of other terrestrial biomass forms for suitability as fermentation substrates is also planned. Potential terrestrial crop substrates include sugar beet and sorghum.

3.3 Methane Suppression

Previous work at Dynatech has identified 2-bromoethane sulfonic acid as an effective methane suppressor in the fermentation of Hydrilla to organic acids. It is of interest to test other possible methane suppressors which would be less expensive to use and/or shift the conversion to higher molecular weight acids with improved kinetics.

The effects of carbon monoxide on corn meal fermentations was tested (Figure 3.7). The CO is thought to inactivate methane-forming organisms. It can be seen in Figure 3.7 that methane formation begins after one week in the absence of CO. In the flask with CO present in the head space, significant methane levels are not observed after 15 days. The rate and degree of conversion are not affected by the presence of CO.

A variety of reputed methane suppressors were tested in Hydrilla fermentations. Four 5 percent slurries were fermented simultaneously after inoculation with sewage sludge. All contained 1g/100 ml CaCO_3 . One control flask had no methane suppressor added. A second contained $5 \times 10^{-4}\text{M}$ 2-bromoethane sulfonic acid (BES). The third flask was flushed with CO at the beginning of the fermentation and then at weekly intervals. A fourth flask contained Cu^{+2} as CuSO_4 . One hundred milligrams CuSO_4 was added on days 0, 3, and 7, and 200 mg on day 14. Copper sulfate has been reported to reduce methane formation and to shift acid formation to propionic (Slyter and Wolin 1967).

Results of these experiments are shown in Figure 3.8. The control flask began producing methane after 10 days, and the acid level diminished to negligible amounts by 4 weeks. The BES flask reached its highest conversion after 1 week and then plateaued. Low levels of methane were detected in this fermentation. The CO fermentation began producing methane after 2 weeks with decreases in acid levels. Copper sulfate reduced methane formation to approximately one-half the amount seen in the control, but also caused slower conversion to organic acids.

The reason for the apparent success of CO as a methane suppressor in corn meal and failure in Hydrilla fermentations is not obvious. The Hydrilla experiment will be repeated with more frequent CO flushing and at lower pH. (Acidic pH is believed to inhibit methanogens.) The effect of copper sulfate will also be tested at lower levels.

Section 4

KOLBE ELECTROLYSIS

4.1 Introduction

The electrolytic oxidation of monobasic aliphatic organic acids, termed Kolbe electrolysis, is capable of generating paraffins, olefins, esters, alcohols and carbon dioxide at the anode and hydrogen gas at the cathode. The mechanism of the anode reaction is not completely 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, depending on reaction conditions.

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

Oxygen is not produced when aqueous carboxylic acid solutions are electrolyzed. This is noteworthy because the potential at which water electrolysis occurs is less than that at which carboxylic acid electrolysis normally occurs. Presumably, a layer of adsorbed carboxylate covers the electrode surface (Utley 1974 and Allen 1958), inhibiting water electrolysis by preventing the adsorption of water.

Conditions promoting production of a particular Kolbe product can be determined and maintained. Production of the Kolbe dimer,

is thought to be favored by high concentrations of carboxylate, acidic pH (5-6), the absence of foreign anions, high current densities (0.25 amps/cm²), low temperatures, and smooth platinum or iridium anodes. To investigate the effects of some of these variables on the current application, a series of experiments were run using 0.5 molar caproic acid at a pH of 6. The temperature, current density, and electrode configuration were varied and the effect of these variables on the applied potential, paraffin/olefin ration, and power requirements were determined.

4.2 Experimental Apparatus

A diagram of the electrolysis apparatus is presented in Figure 4.2. The main components are the holding vessel, the electrolysis cell, the electrolysis pump, pressure gauge, pH meter, acid flow controller, acid reservoir, acid pump, Wet Test Meter, and magnetic stirring unit. During an electrolysis experiment, the holding vessel initially contains a 400 ml solution of 0.5 N caproic acid. The acid solution is pumped from the holding vessel to the electrolysis cell where the solution flows between two flat plates each having an exposed catalytic surface area of approximately 57.5 cm². Connected to the electrolysis cell is a Sorenson power supply which can deliver 0 - 100 amperes at a voltage range of 0 - 10V. As the acid passes between the two electrodes and is oxidized, hydrocarbon product, carbon dioxide, hydrogen gas, and the remaining non-electrolysed acid solution are expelled from the exit port of the electrolysis cell and are returned to the holding vessel. Between the exit port of the electrolysis cell and the holding vessel is a gauge to observe the internal pressure of the system. If the internal pressure rises above approximately 12 psi there is a danger of rupturing the various tygon tubing connections between components.

Located at the top of the holding vessel is a product gas line which helps to relieve the internal system pressure. This gas line is connected to a Wet Test Meter which measures the total volume of gas produced. Between the Wet Test Meter and the holding vessel is a gas sampling port. Through this port, gas samples can be taken with a syringe and analyzed in a gas partitioner. With the use of a stopwatch, a gas flow rate can be obtained by observing the flow of gas through the Wet Test Meter. The gas partitioner will detect the percentage of each gas in the total gas stream. Under proper experimental conditions, the product gas stream should consist only consist of hydrogen, carbon dioxide, olefin, and possibly a small amount of oxygen from the minor competing reaction of water electrolysis.

Connected slightly downstream from the holding vessel are a pH probe and meter. Under normal operating conditions, the pH is maintained between 6 to 7. Keeping the pH within this range is accomplished by means of a Luft controller. The controller measures differences in the voltage output of the pH meter. Set points on the controller are adjusted to correspond with the pH meter readings. The controller is electronically connected to a pump which pumps acid into the holding chamber. During an acid electrolysis, the pH will rise as the acid concentration decreases. As the pH rises, the change in voltage output from the meter will trigger the controller which will then signal the pump to add more acid to the holding vessel, thus reducing the pH. Another setpoint on the controller shuts the pump off when the pH reaches the lower range value. In this manner, both the pH and the acid concentration can remain fairly constant throughout the course of the run.

4.3 Mass and Energy Balance

Mass Balances -Carbon Balance - The experimental design of the electrolysis system allows for numerous checks on the reaction pathway and final products. Knowing the basic overall reaction and its stoichiometry, all materials both gas and liquid can be accounted for.

The first check on the system is a carbon mole balance. The carbon input consists of the acid initially in the electrolytic solution plus any acid added from the acid reservoir during the course of the experiment. The carbon products are in three forms: (1) carbon dioxide gas and carbon dioxide dissolved in the electrolytic solution, (2) olefin and, (3) paraffin hydrocarbon. The CO_2 in the gas phase and the olefin gas can be measured by taking gas samples and determining the percentage of each gas in the outlet stream with a gas partitioner. The total volume and rate of production of gas is measured with a Wet Test Meter. Thus the volume and rate of production of each component gas can be determined.

The carbon dioxide dissolved in the electrolytic solution can be measured by titrating the remaining electrolytic solution after a completed experiment. The final acid concentration as well as the amount of carbon dioxide dissolved in solution can be determined. A further check on the acid concentration can be made by gas chromatography.

The paraffin hydrocarbon can be measured simply by separating it from the aqueous solution. Since most of the liquid hydrocarbon from a caproic acid run will be decane, one can easily calculate the total number of moles produced. If a mixture of acids were electrolyzed (as with a fermentation sample) one injects the final liquid hydrocarbon product into the gas chromatograph to determine actual content. Injections of the liquid hydrocarbon product from a caproic acid run revealed decane (the Kolbe dimer) as the sole liquid product.

Employing the above techniques, a total carbon balance can be achieved. An initial mass balance check is the comparison of the number of moles of consumed acid with the number of moles of carbon dioxide produced. One mole of CO_2 should be produced at the anode for each mole of acid which is oxidized. Consequently, the number of moles of consumed acid should equal the number of moles of carbon dioxide produced.

Hydrogen balance - The hydrogen gas flow rate can be determined in the same manner as the CO₂ gas flow rate. For each molecule of acid which is oxidized, one molecule of CO₂ is produced, and one H⁺ ion is discharged. Therefore, the CO₂ flow rate (in mole/min.) should be one to two times that of the H₂ flow rate, depending on the paraffin/olefin ratio.

If oxygen is present in the product gas stream, due to water electrolysis, it is necessary to subtract the appropriate number of moles of O₂ from the total moles of H₂ to account for the hydrogen product from acid electrolysis.

Electricity balance - The total moles of electricity used can be calculated by knowing the number of amperes (coul/sec), the total time of the run (sec), and Faraday's constant of 96,500 coulombs/mole of e⁻. The moles of electricity used should correspond to the moles of product. An electricity balance check can be made with the number of moles of hydrogen produced. H⁺ ions are reduced at the cathode, and it takes two moles of electricity to produce one mole of hydrogen:

Therefore, the moles of electricity should be twice the moles of hydrogen gas.

BTU energy return - A ratio of energy return, specifically from the Kolbe process, gives some idea of the profitability of the process. This ratio can be obtained by calculating the total number of BTU's of electricity applied to the system to produce hydrocarbon product and the heating value in BTU's of both the olefin and paraffin hydrocarbon products. One may also include the heating value of the produced hydrogen since this energy can be either sold or used in a fuel cell which can supply part of the electricity requirements necessary for running the Kolbe electrolysis. A favorable ratio of product energy to supplied electric energy will allow for a positive energy balance within this portion of the total process.

4.4 Experimental Results

4.4.1 Electrode Material

Initial experiments were performed with a smooth, thin sheet of platinum acting as the anode and monel (65% nickel, 35% copper) metal acting as the cathode. After collecting various data with this electrode arrangement, the electrode materials were changed in order to observe the effect of different materials on product distribution, total applied voltage, energy value, and cathode and anode overpotentials. The new electrode material arrangement consisted of a titanium-gold-platinum layered electrode used as the anode and the smooth platinum sheet used as the cathode. It should be noted that a preferable arrangement would have been to keep the smooth platinum sheet at the anode and only switch cathode material between the monel and the tri-plated electrode. This arrangement was not possible, however, because the manufacturer of the tri-plated electrode advised us not to use it as a cathode for fear of removing the platinum coating from the surface.

The experimental results of the different sets of electrodes are listed in Table 4.1. The column headings are abbreviated as: A, nominal current in amperes; CD, the current density in amps/cm²*; V, the voltage measured directly across the electrodes; R-C and R-A, the potential in volts measured from the silver-silver chloride reference solution to the cathode and anode respectively; percent olefin and percent paraffin, the product hydrocarbon percentages.

*Calculated based on an assumed electrode area of 57.5 cm².

From Table 4.1 one can observe the various trends and comparisons between the electrode sets. Except for the 10 ampere data in the first group, two clear trends seem to hold: 1) the percentage of paraffin tends to increase with increased supplied current, and 2) the voltage across the electrodes also increased with supplied current. Each of these trends is directly affected by the electrode material. The platinum sheet cathode and the tri-plated anode yield a lower total applied voltage at a given current density than the monel and platinum electrodes. There is, however, a loss in the percentage of paraffin production, with the two platinum electrodes.

Table 4.2 shows comparative production power figures when both voltage and product distribution are considered. One can see from these figures the comparative tradeoffs of reducing the applied voltage or increasing the paraffin to olefin ratio. From this chart, it would appear that the paraffin to olefin ratio observed at 5 amperes using the monel cathode and platinum sheet anode required the least amount of power for production.

A further comparison between the electrode materials is illustrated in Table 4.3. This chart gives the ratio of the heating value of the hydrocarbon products to the heating value of the electricity needed to perform the electrolysis. Once again, one can see that the monel cathode and platinum anode performed better than did the platinum cathode and tri-plated anode, because of the higher yields of paraffin. The energy gain in reduced voltage due to the two platinum electrodes was not enough to overcome the energy loss due to a reduced paraffin to olefin ratio.

Of further interest is the voltage overpotential of each electrode listed in Table 4.1. When measured from the cathode, the true value of the cathode overpotential is reflected by the reference electrode. A measure of the anode overpotential includes some or all of the IR drop between the electrodes plus the actual anode overpotential. A detailed schematic

of the ECO-Electrorep cell is given in Figure 4.3 with an enlargement of the reference electrode. The opposite situation exists when the reference electrode is located in the anode. The IR drop is then added into the cathode overpotential measurement.

The specific resistance of a 0.5M caproic acid solution has been measured at 1000Hz to be 40 ohm-cm. at 22°C. Knowing the electrode spacing, the current, the surface area of the electrodes, and the specific resistance of the solution, one can calculate the IR voltage drop by the following equation:

$$IR = \frac{Isd}{A}$$

where: $\frac{I}{A}$ = the current density

s = the specific resistance of the solution

d = the distance between the electrodes

The theoretical values for the IR drop of 0.5M caproic acid solutions at room temperature and various current densities were calculated and the values are listed in Table 4.4. One can see from this listing that the use of smooth platinum as the cathode significantly reduces the cathode overpotential when compared to monel. The triplated electrode adds approximately 1.0 to 1.5V in overvoltage (at comparable amperage) to the value obtained with the smooth platinum sheet, when the two are compared at the anode. From the three materials compared, it would seem that the smooth platinum sheet would be the best material to use to reduce the overvoltages on both the anode and cathode.

4.4.2 Current Density Effects

Trends which are functions of the current density are apparent in most of the data listed in Table 4.1. As the current density increases, the percentage of paraffin product also increases. In addition to the paraffin production, one also notes that the applied voltage across the electrodes increases with added current density.

Increased paraffin production with increased current density is explainable according to the proposed radical reaction mechanism (Figure 4.1). Increased current density will increase the concentration of alkyl radicals. An increase in alkyl radicals will result in an increased probability that radicals will react together to form the Kolbe dimer.

The total surface area of each electrode is approximately 57.5 cm². It must be noted, however, that the surface area of the titanium-gold-platinum anode is not completely smooth as is the case with the other electrodes used. Its effective surface area is probably substantially larger than the apparent area of the electrode. The values of the current density for the second data group in Table 4.1 are probably actually less than the given figures. Therefore, comparisons made between the two groups of data may be erroneous.

Various techniques for measuring the surface area of catalysts are available. One such technique which is convenient for a platinum surface is to adsorb a layer of carbon monoxide on to the surface of the catalyst. After flushing an inert gas (such as helium), over the surface, one could then pass oxygen over the surface and measure the total amount of CO₂ produced. By calculating the theoretical projected surface area of a carbon monoxide molecule and measuring the total number of moles of CO₂ produced, a good approximation of the surface area can be attained.

4.4.3 Temperature Effects

Resistance due to the transport of ions across the electrolytic solution (IR) was reduced by increasing the temperature of electrolysis. Heating presumably increases the solution's molecular activity thus facilitating ion transport. Table 4.5 compares the data obtained for high temperature runs (95°C and 70°C) at similar current densities. Since the reference electrode was located at the cathode for each of these runs, one would expect a drop in the R-A reading which contains both the IR voltage and the anode overpotential. In each case there is approximately a 0.6V drop in the R-A reading, indicating a reduction in the IR voltage drop.

Raising the temperature did succeed in lowering the total applied voltage, probably as a result of the IR drop. While the increase in temperature produced a reduction in applied potential, it lowered the paraffin/olefin ratio (Table 4.5) thus subtracting from the overall energy balance.

Mechanistically, one possible explanation of the increased olefin percentage with increased temperature concerns the reaction from the alkyl radical to the alkene. The reaction can be written as (in the case of caproic acid):

If the above reaction is assumed to be reversible between the alkyl radical and the alkene, one can argue that at a higher temperature, the alkene will be more volatile and thus more likely to come out of the liquid solution. Alternatively, at lower temperatures, the alkene is not as likely to leave the solution, thus allowing it the opportunity to react back to the alkyl radical stage where it can combine with another alkyl radical to form a Kolbe dimer. Thus at lower temperatures, one sees a higher percentage of paraffin in the hydrocarbon product.

The relative power requirements needed to produce the various product distributions at different temperatures are listed in Table 4.5. These power requirements are within a fairly close range. Although the power requirements may be similar, the return on energy input reveals the major disadvantage of raising the temperature of the electrolytic solution. The loss of product heating value due to the increased production of olefin outweighs any energy gain netted via a decreased applied voltage due to an IR reduction. Comparing the data at similar current densities, one can see the return on energy value at high temperatures is approximately half the energy return for a lower temperature. Thus the trade off between a larger paraffin to olefin ratio verses a decrease in the applied voltage favors the larger paraffin to olefin ratio when viewed in terms of the return on energy.

Section 5

FIXED PACKED BED FERMENTATION MASS AND ENERGY BALANCES

The first large-scale fermentation of fresh water biomass in the lab-pilot fixed packed bed fermenter has been completed. The fermentation began with 53.7 pounds Hydrilla, 22.5 liters effluent from Expt. 02357 (Chondrus crispus fermentation), and 267 liters of water. To suppress methane formation, 10^{-4} molar bromoethanesulfonic acid ($\text{BrCH}_2\text{CH}_2\text{SO}_3^-$) was also added at the start.

Final results of this Hydrilla fermentation have been tabulated and the residues recovered for future analyses. The gaseous products are listed in Table 5.1. Only 2.5 percent of carbon converted was recovered as methane. Production of organic acids is shown in Table 5.2.

From these data, conversion percentages can be calculated based on the carbon contents of products and reactants:

$$\% \text{ Conversion} = \frac{\text{Wt Carbon in Products}}{\text{Wt Carbon in Reactants}} = \frac{160 + 1625}{5700} = 31.5\%$$

An oxidation-reduction balance based on the amounts of reduced products formed has been presented in a previous report (Sanderson et al 1979). In this balance, the quantity of carbon dioxide (the only oxidation product formed relative to the hexose starting material) produced should correlate with the reduced products formed on a reducing equivalent basis. CO_2 is also produced by acidification of carbonate and in the production of cell mass. The recovery of CO_2 was 97 percent, closing the oxidation-reduction balance.

Mass and energy balances can also be obtained from the products detected and by finding the weight of total solids and energy content of the residue in the 300-liter fermenter. The weights and energy content of products appear in Table 5.3. The fresh Hydrilla has been found to contain 0.4 millimole carbonate per gram weed, or 7.8 moles total in the fresh substrate. This carbonate is assumed to be present in the fresh weed as CaCO_3 , accounting for 905 grams of ash as indicated in Table 5.4. Upon acidification, the CaCO_3 decomposes to CO_2 and Ca(OH)_2 which remains dissolved in the fermenter broth and was not recovered with the residue. Inclusion of the CaCO_3 as part of the ash recovered in the residue, will account for 97 percent of the ash content of fresh Hydrilla (Table 5.4). The CO_2 produced from acidification of the carbonate is not included in the total weight of fermentation products since its weight has already been included as CaCO_3 . In the material balance presented in Table 5.4, 97 percent of the weight of substrate is accounted for in residue and products.

Calorimetry measurements on the residue have established its heat of combustion as 6405 BTU/lb. Fresh Hydrilla has an energy content of 6969 BTU/lb total solids as measured by calorimetry. In the energy balance which appears in Table 5.6, 81.3 percent of the substrate energy is recovered in residue and products.

Further analysis of the residue will allow a carbon balance to be performed on this 300-liter fermentation experiment.

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 allow it 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 inch rubber, in a step-wise fashion. Shaft diameter ranges from 1 inch at the narrow end to 2 1/2 inches 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 percent 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 percent 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 be expelled from the tube only 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.

A device similar in operation to the one tested is built by the James Division of Beloit Corporation. A drawing of their smallest model, Pressmaster 3, is shown in Figure 6.2. Recently a trial was run in Beloit's laboratory using this device to dewater Hydrilla residue. The results of this trial, presented in Table 6.1, indicate that the device is capable of removing in excess of 8 pounds of Hydrilla residue per hour from a continuous fermenter at 30 percent solids.

Section 7

MASS, ENERGY AND CARBON BALANCE

7.1 Fate of Biomass Input

It is of interest to consider the yield of mass, energy and carbon from the proposed process. Figures 7.1 through 7.3 present bar charts indicating the fate of one pound of hypothetical biomass containing 75 percent cellulose and equivalent fermentables, 10 percent liquid and other organic nonfermentables, and 15 percent ash. Percentages of the final components are indicated along the abscissa. Such a hypothetical biomass would contain 6500 BTU's and 38 percent carbon. Of this amount, 0.44 pounds containing 0.13 pounds carbon and 2850 BTU would form a solid residue; an additional 0.05 pounds 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 an 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 pounds of organic acids.

In the electrolysis the organic acids are converted to alkanes (0.17 pounds) along with carbon dioxide (0.12 pounds) and hydrogen (.01 pound). The alkane product contains 50 percent of the energy and 39 percent of the carbon of the biomass. The remainder of the carbon is present primarily as residue (34 percent) or CO_2 (27 percent). Energy not incorporated into the hydrocarbon product may be further utilized. Hydrogen produced can be used to run a molten fuel cell producing one-third of the electrical requirement of the Kolbe Electrolysis. Low-grade heat produced in the fermentation to acids can be used to maintain the fermenter at the desired temperature. A portion of the energy contained in the residue may also be salvable.

7.2 Overall Energy Balance

There has been a continuing debate concerning the energy balance for production of "gasohol." A comprehensive analysis of the energy requirements and by-product credits for gasohol production from corn is presented by R. S. Chambers, et al. 1979). This analysis is summarized in Figure 7.4 for the production of fuel-grade ethanol from corn by traditional fermentation, distillation, and purification processes. Values used are based on production and processing of one bushel (56 pounds) of corn. The corn grain is assumed to be 70 percent converted to products. Half the energy remaining in the residue is taken as a feed by-product credit. The final product (14.5 pounds) represents 2.5 gallons of ethanol. The energy requirement exceeds the output, resulting in an unfavorable energy balance (output/input) of 0.72.

Production of liquid fuels from corn can be subjected to an analogous analysis. This scenario is presented in Figure 7.5. Values for agricultural requirements and side-product credits are the same as those suggested by Chambers in his ethanol analysis. Conversion of 70 percent of the corn grain to liquid fuel is assumed. (Higher conversions have already been achieved in static fermentations with corn meal. See Section 3.2.) The major process energy requirement is for electricity in the electrolysis step. A conversion efficiency of 30 percent is assumed for the production of electricity from other fuels. The energy balance (output/input) for the production of liquid hydrocarbon fuels from corn is 1.77.

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LIQUID HYDROCARBONS FROM BIOMASS ---
PROCESS FLOWSHEET

Figure 2.1

Figure 3.1

Pre-treatment Procedure for the Residue From
Fixed Packed Bed Hydrilla Fermentation

FIGURE 3.2

HYDRILLA RESIDUE - ACID TREATED

FIGURE 3.3

HYDRILLA RESIDUE - BASE TREATED

Figure 3.4

A 5% WATER HYACINTH FERMENTATION

Figure 3.5

CONVERSION OF 5% CORNMEAL
TO ORGANIC ACIDS
(06287-C)

Figure 3.6

3% CORNMEAL FERMENTATION

RUN # 06287-B

Figure 3.7 Effect of CO on the Anaerobic Digestion of Cornmeal to organic acids and methane.

FIGURE 3.8

METHANE SUPPRESSION IN HYDRILLA FERMENTATIONS

Figure 4.1

Anodic Oxidation of Carboxylates Reaction Mechanism

Figure 4.2
EXPERIMENTAL APPARATUS DESIGN

Figure 4.3
ECO Electroprep Cell

Reference Electrode - Enlarged View

Figure 6.2

Pressmaster-3
Screw Press

Figure 7.1

LIQUID FUELS FROM BIOMASS
MASS BALANCE

Figure 7.2

LIQUID FUELS FROM BIOMASS CARBON BALANCE

Figure 7.3

LIQUID FUELS FROM BIOMASS
ENERGY BALANCE (1 LB. BIOMASS BASIS)

Figure 7.4

Figure 7.5

TABLE 3.1
HEATS OF COMBUSTION OF BIOMASS SPECIES

	BTU/lb Total Solids	BTU/lb Volatile Solids
Cornmeal	8088.8	8096.9
Water Hyacinth	6527.0	7153.7
Hydrilla	6969.0	8950.0
Hydrilla Residue	6404.8	8684.4

Table 4.1

APPLIED POTENTIAL AND PRODUCT DISTRIBUTION AS A FUNCTION
OF ELECTRODE MATERIALS AND CURRENT DENSITY

Electrode Materials: Cathode (Monel) Anode (Platinum Sheet)

(CATHODE REFERENCE)

<u>A</u>	<u>CD</u>	<u>V_e</u>	<u>R-A</u>	<u>R-C</u>	<u>% Olefin</u>	<u>% Paraffin</u>
5	0.113	(4.0)	2.00	1.30	31.91	68.09
10	0.195	(4.25)	1.55	1.20	45.38	54.62
15	0.276	(4.80)	1.85	1.90	26.15	73.85

Electrode Materials: Cathode (Platinum Sheet) Anode (Titanium-gold-platinum)

(ANODE REFERENCE)

<u>A</u>	<u>CD</u>	<u>V_e</u>	<u>R-A</u>	<u>R-C</u>	<u>% Olefin</u>	<u>% Paraffin</u>
10	0.122	4.0	2.60	1.00	53.67	46.33
15	0.261	4.2	2.80	1.10	51.18	48.82
20	0.307	4.6	2.90	1.30	46.62	53.38

Table 4.2

RELATIVE POWER REQUIREMENTS

Monel Cathode - Platinum Sheet Anode

$$@ 10 \text{ amperes } (0.4633 + (2)(0.5367))(4.0V) = 6.1468$$

$$@ 15 \text{ amperes } (0.4882 + (2)(0.5118))(4.2V) = 6.3496$$

$$@ 20 \text{ amperes } (0.5338 + (2)(0.4662))(4.6V) = 6.7445$$

Platinum Sheet Cathode - Titanium-Gold-Platinum Anode

$$@ 5 \text{ amperes } (0.6809 + (2)(0.3191))(4.0V) = 5.2764$$

$$@ 10 \text{ amperes } (0.5462 + (2)(0.4538))(4.25V) = 6.1780$$

$$@ 15 \text{ amperes } (0.7385 + (2)(0.2615))(4.8V) = 6.0552$$

Table 4.3

ELECTROLYSIS RETURN OF ENERGY

Electrodes

- Cathode (Monel)
- Anode (Platinum Sheet)

" 5 ampere"	Return	=	10.42/1
"10 ampere"	Return	=	8.23/1
"15 ampere"	Return	=	9.73/1

Electrodes

- Cathode (Platinum Sheet)
- Anode (Titanium-Gold-Platinum)

"10 ampere"	Return	=	7.74/1
"15 ampere"	Return	=	6.93/1
"20 ampere"	Return	=	5.67/1

NOTE: Returns are calculated as a ratio of the number of BTU's of electricity which produced hydrocarbon to the heating value (in BTU's) of the olefin and paraffin product.

Table 4.4

IR VOLTAGE AND ELECTRODE OVERPOTENTIALS

Electrode Materials

- Monel Cathode
- Platinum Sheet Anode

(CATHODE REFERENCE)

<u>R-amperes</u>	<u>IR</u>	<u>Cathode Voltage</u>	<u>Anode Voltage (adjusted value)</u>
6.49	0.236	1.3	1.77
11.24	0.390	1.2	1.16
15.85	0.550	1.9	1.30

Electrode Materials

- Platinum Sheet Cathode
- Titanium-Gold-Platinum Anode

(ANODE REFERENCE)

<u>R-amperes</u>	<u>IR</u>	<u>Cathode Voltage (adjusted value)</u>	<u>Anode Voltage</u>
7.00	0.240	0.76	2.60
15.00	0.520	0.580	2.80
17.63	0.610	0.690	2.90

NOTE: Calculated IR voltage plus the adjusted voltage value yields the experimentally observed voltage readings listed in Table 4.1.

Table 4.5

HIGH TEMPERATURE ELECTROLYSIS DATA

Comparisons on Current Density Basis

(ANODE REFERENCE ELECTRODE)

<u>Temp.</u>	<u>CD</u>	<u>Relative Power Required</u>	<u>A</u>	<u>V</u>	<u>R-A</u>	<u>R-C</u>	<u>% Olefin</u>	<u>% Paraffin</u>	<u>Product/Process Energy/Energy</u>
95°C	0.18	6.4	20	3.6	2.0	1.1	78.37	21.63	3.4/1
40°C	0.12	6.1	10	4.0	2.6	1.0	53.67	46.33	7.7/1
70°C	0.25	6.2	15	3.7	2.2	1.1	65.33	34.67	3.9/1
50°C	0.26	6.3	15	4.2	2.8	1.1	51.18	48.82	6.9/1

NOTE: The electrodes used for the above experiments were the Platinum Sheet Cathode and the Titanium-Gold-Platinum Anode.

Table 5.1

GASEOUS PRODCUTS - 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	116.47 g
Hydrogen	83.62 1	3.73	0.00 g
Methane	86.18 1	3.85	34.63 g

Extractor:

Carbon Dioxide	15.62 1	0.70	2.26 g
Methane	<u>15.69 1</u>	<u>0.70</u>	<u>6.30 g</u>

Total Carbon in Gaseous Products:

160 g

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	<u>0</u>	<u>0</u>	<u>0</u>
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	<u>17 meq/l</u>	<u>.10</u>	<u>7.35 g</u>
Total:	60 meq/l	.36 moles	18.7 g

Total Weight Carbon Converted to Acids:

$$1606.24 + 18.7 = 1625.0 \text{ g}$$

Table 5.3

MASS AND ENERGY CONTENT OF PRODUCTS RUN 04432

<u>Product</u>	<u>Moles Formed</u>	<u>Weight</u>	<u>Energy Content</u>
CO ₂	36.65	1612.6 grams	0 BTU
H ₂	0.016	7.5	832
CH ₄	4.55	72.8	3440
Acetic	40.86	2415.6	32,233
Propionic	9.03	668.2	12401
Butyric	6.43	565.8	13,405
Valeric	0.05	5.1	132
Caproic	<u>0.10</u>	<u>11.6</u>	<u>335</u>
Total:	97.67	5395.2 grams	62,778 BTU

Table 5.4

MATERIAL BALANCE: RUN 04432

Initial:

Total Dry Solids	17,675 grams
Ash (including CaCO_3)	3,889
Volatile Solids	13,786

Final:

Total Dry Solids	10,971 grams
Ash	2,852
Unrecovered CaCO_3	905
Volatile Solids	8,119

Weight of Products:

Total Formed	5,395.2 grams
CO_2 from Carbonate	<u>343.2</u>
Remaining	5,052.0
H_2O Produced	<u>166.0</u>
	5,218.0 grams

$$\text{Recovery} = \frac{\text{Final Total Solids} + \text{Product} + \text{CaCO}_3}{\text{Initial Total Solids}} = \frac{10971 + 5218 + 905}{17675} = 97 \%$$

Table 5.5

HEAT RELEASED IN FORMATION OF PRODUCT
ACIDS FROM GLUCOSE

<u>Acid</u>	<u>Pound-Moles Formed</u>	<u>BTU's Released</u>
Acetic	5.4	475.2
Propionic	1.74	1664.8
Butyric	1.25	929.9
Valeric	0.011	9.0
Caproic	<u>0.026</u>	<u>28.2</u>
Total		3107.1

Table 5.6

ENERGY BALANCE: RUN 004432

Initial: (Fresh Hydrilla)

$$38.97 \text{ lbs} \times 6969 \text{ BTU/lb} = 271,582 \text{ BTU}$$

Final:

$$24.19 \text{ lbs} \times 6405 \text{ BTU/lb} = 154,937 \text{ BTU}$$

Products:

$$\text{Total} \quad 62,778 \text{ BTU}$$

Heat Produced:

$$\text{Total} \quad 3,107 \text{ BTU}$$

$$\text{Recovery} = \frac{\text{Energy in Residue} + \text{Products}}{\text{Energy in Fresh Substrate}} = \frac{154937 + 62558 + 3107}{271582} = 81.3\%$$

Table 6.1

3" Horizontal Pilot Press
 Test No. BT-284
 Dynatech R/D Company
 Fermentation Residue

Sample		1	2	3	6
Spindle Compaction		1:1			2.8
Spindle Speed	RPM	10	20	30	20
Cone Location	Inches	3.75	3.75	3.75	3.75
Temperature	°F	86	86	86	88
Inlet Consistency	%	11.4	11.4	11.4	10.8
Cake Consistency	%	31.5	28.7	26.7	31.4
Effluent Solids Suspended	gm/liter	11.11	14.70	16.87	13.26
Cake Discharge Rate	BD#/hr	8.2	15.2	14.3	10.7
Effluent Discharge Rate	gal/hr	7.8	16.2	14.7	13.0