

ANALYSIS OF EXPERIMENTAL VARIABLES FOR THE KOLBE  
ELECTROLYSIS OF ORGANIC ACIDS TO HYDROCARBONS

by

MARK RAYMOND NABER

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Department of Chemical Engineering  
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Thesis Supervisor

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Chairman, Department

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Submitted to the Department of Chemical Engineering  
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ABSTRACT

Kolbe electrolysis involves the electrochemical conversion of organic acids to hydrocarbon. Various factors such as temperature, current density, electrode material and electrolytic solution flowrate have been analyzed to observe their effect on hydrocarbon product distribution, supplied power and energy return. The results of the study indicate that low temperature and low current density with the monel cathode and the platinum sheet anode electrodes yield the highest percentage of products at the lowest supplied power and with the largest return on energy. Changing the flowrate had no effect on the product distribution or the energy return.

Thesis Supervisor:

Costas G. Vayenas  
DuPont Assistant Professor  
of Chemical Engineering

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## Chapter 1: INTRODUCTION AND BACKGROUND

Although the electrolysis of acids to produce hydrocarbon product has been studied for almost two hundred years, there are still many unanswered questions as to the exact reaction mechanism or the optimum operating conditions. With the increasing costs of crude oil, research in the area of synthetic fuels has grown rapidly. The electrolysis of acids, a major step in the production of hydrocarbons from biomass, has thus become an important factor in the search for alternative energy sources.

The general concern of this thesis is to find general relationships among the applied electrolysis voltage, the hydrocarbon product distribution, the return on energy and various experimental parameters such as electrode material, current density, temperature and flowrate past the electrodes. Chapter 2 analyses the energy requirements of electrolysis while Chapter 3 gives a detailed discussion of the effects of the experimental variables. Chapter 4 provides suggestions for further study.

### 1.1 Early Studies of Kolbe Electrolysis

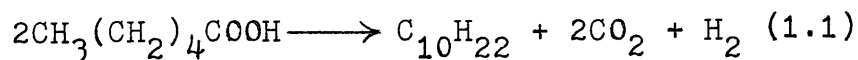
Preliminary studies of electrolysis and other electrochemical processes date back to the early nineteenth

century when researchers were first becoming acquainted with these phenomena. Rheinold and Erman were the first investigators who used electricity as a potential oxidizing or reducing agent in the electrolysis of dilute aqueous solutions of alcohol. In 1830, Ludersdorff undertook the first detailed studies of electrolysis product formation using various electrode materials. Faraday's extensive research led him to the realization that the electrolysis process could be used to synthesize or decompose a compound. As early as 1834, he observed that the electrolysis of an acetate solution yielded hydrocarbon product.<sup>11</sup>

The principles of electrolytic oxidation and reduction were not established however until the middle nineteenth century when Kolbe made his important discoveries. In 1845, Kolbe completely replaced the chlorine in trichloromethylsulphonic acid with hydrogen via electrolytic means. He noted that the trichloromethylsulphonic acid was completely decomposed in an aqueous solution at a platinum electrode. Concerning the experiment Kolbe stated "This acid, which is stable to the strongest oxidizing media breaks down with little difficulty at a platinum anode."<sup>1</sup> Kolbe also studied the anodic oxidation of organic substances which resulted in the synthesis of hydrocarbons from the electrolysis of the salts of monobasic aliphatic acids. The Kolbe reaction involves the removal of carbon dioxide from the acid anion

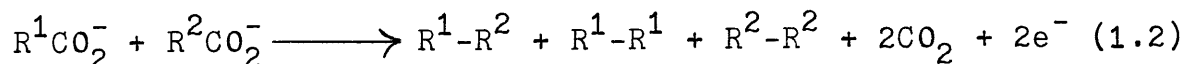


with subsequent dimerization of the remaining alkyl radical. For example, caproic acid will form decane according to the following process: <sup>1</sup>



The most important competing reaction to the above process is the formation of olefin (pentene and some decene in the case of caproic acid).

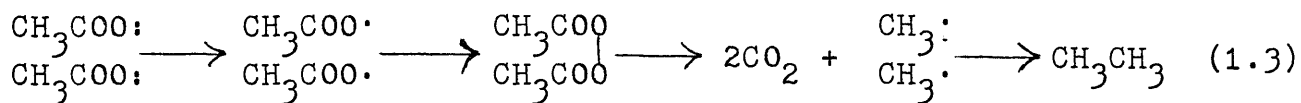
In the event that a mixture of carboxylic acids is electrolysed, 'cross coupling' can occur via the Kolbe reaction: <sup>11</sup>



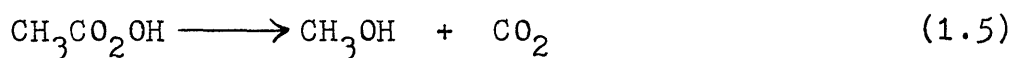
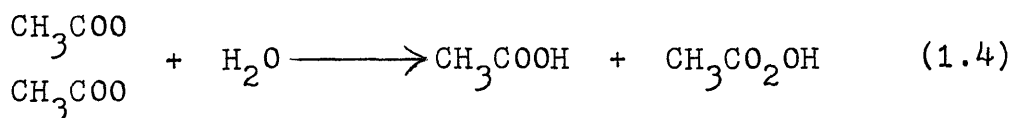
## 1.2 Reaction Mechanisms

The major observed products of electrolytic oxidation of aliphatic acids are paraffins, olefins, alcohols, esters and carbon dioxide, all produced at the anode. Hydrogen gas is the lone product observed at the cathode. Although the exact mechanism of the anode reaction is not well understood, several theories have been developed to account for these various electrolysis products. One of the proposed mechanisms developed by Schall and Fichter is known as the peroxide theory.<sup>9</sup> This theory provides a mechanism whereby acetyl radicals formed at the anode, react to form diacetyl peroxide, decompose to form alkyl radicals and thence hydrocarbon product. The mechanism could be shown

as follows:<sup>1</sup>

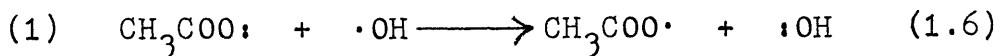


The production of alcohol is explained by the decomposition of peroxide to yield a per-acid. In an alkaline solution, the per-acid could hydrolyze to yield alcohol.<sup>1</sup>

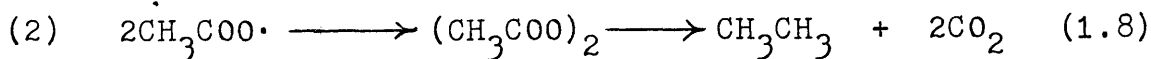
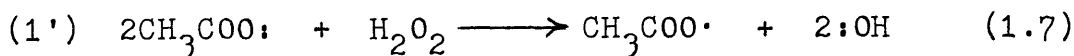


In an acidic medium, the formation of olefins and esters can be explained by the dehydrogenation of alcohol and the reaction of alcohol with acid.

A modified version of the above stated theory proposed by Glasstone and Hickling is known as the 'Hydrogen Peroxide Theory'.<sup>4</sup> This theory suggests that hydrogen peroxide which is first formed at the anode from hydroxyl radicals, or hydroxyl radicals themselves react with acetate ions and form acetate radicals. The acetate radicals then combine to yield ethane and carbon dioxide. The mechanism can be outlined as follows:<sup>4</sup>

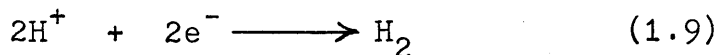


or



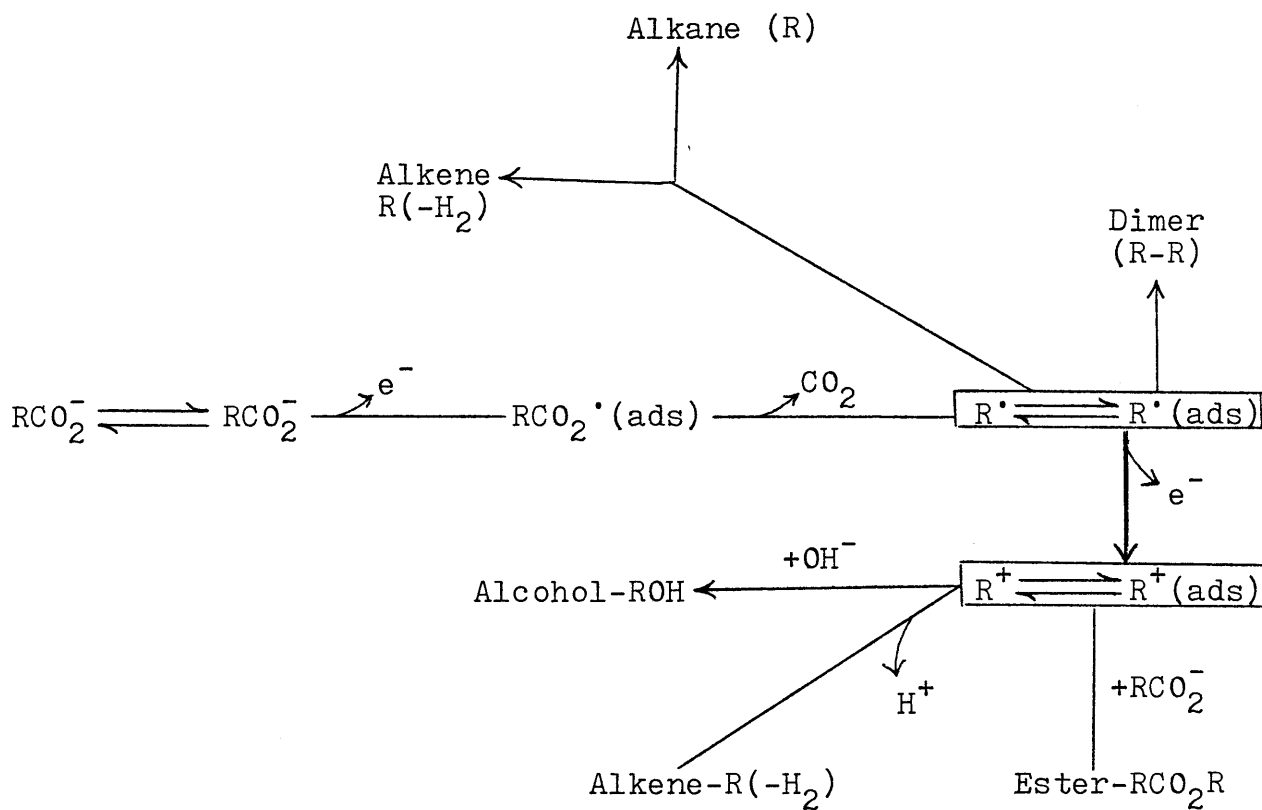
A likely mechanism of the anodic oxidation of carboxylates is given in figure 1.1. This reaction sequence is known as the free radical mechanism.<sup>11</sup> The carboxylate ion is first adsorbed to the anode surface, oxidized to form the carboxylate radical which then decarboxylates to yield an alkyl radical. The alkyl radical can react with another alkyl radical and form the Kolbe dimer or disproportionate to form alkenes and alkanes which contain half the carbon atoms of the Kolbe dimer. Alternatively, the alkyl radical can be further oxidized thus forming a carbonium ion which can react (usually in the presence of base) to form alcohols, alkenes or esters.

The cathode reaction involves the reduction of hydrogen ions in the formation of hydrogen gas.<sup>2</sup>



Oxygen production is minimal when aqueous carboxylic acid solutions are electrolyzed. This is an important observation because the potential at which water is electrolyzed (1.5 V) is lower than the normal voltage for Kolbe electrolysis (2.0 V). It is thought that the acid molecules adsorb on the catalyst faster than or preferentially to the water molecules. A layer of adsorbed carboxylate would then cover the electrode surface thus inhibiting water electrolysis by preventing the adsorption of water.

Figure 1.1  
 ANODIC OXIDATION OF CARBOXYLATES  
 REACTION MECHANISM



### 1.3 Synthetic Fuels from Biomass via Kolbe Electrolysis

Kolbe electrolysis is the major end step in the production of hydrocarbons from biomass. The total process, presented in figure 1.2, consists of the non-steril anaerobic fermentation of biomass to various organic acids, an extraction process which separates the higher molecular weight acids (primarily butyric, valeric and caproic), and finally the electrolytic oxidation of these acids to aliphatic hydrocarbons, primarily hexane, heptane, octane, nonane and decane. The cathode product in the electrolytic oxidation is hydrogen. The hydrogen gas is a valuable co-product in itself or can be used in a fuel cell to generate part of the electricity required for electrolysis. Olefin, another gaseous by-product of electrolysis has a significant heating value and can be marketed.<sup>9,10,11</sup>

The acid extraction system is divided into two segments. The first extraction is accomplished via a continuous contacting mass transfer in which the acidic fermentation broth is brought in contact with a solvent whose partition behavior is such that the higher acids are selectively extracted and whose solubility in the aqueous solution is minimal in order to minimize solvent losses. Most hydrocarbons meet the above characteristics as an acid extraction solvent.

The second extractor separates the product acids from the hydrocarbon stream. This process is a counter current

LIQUID HYDROCARBONS FROM BIOMASS ---  
PROCESS FLOWSHEET

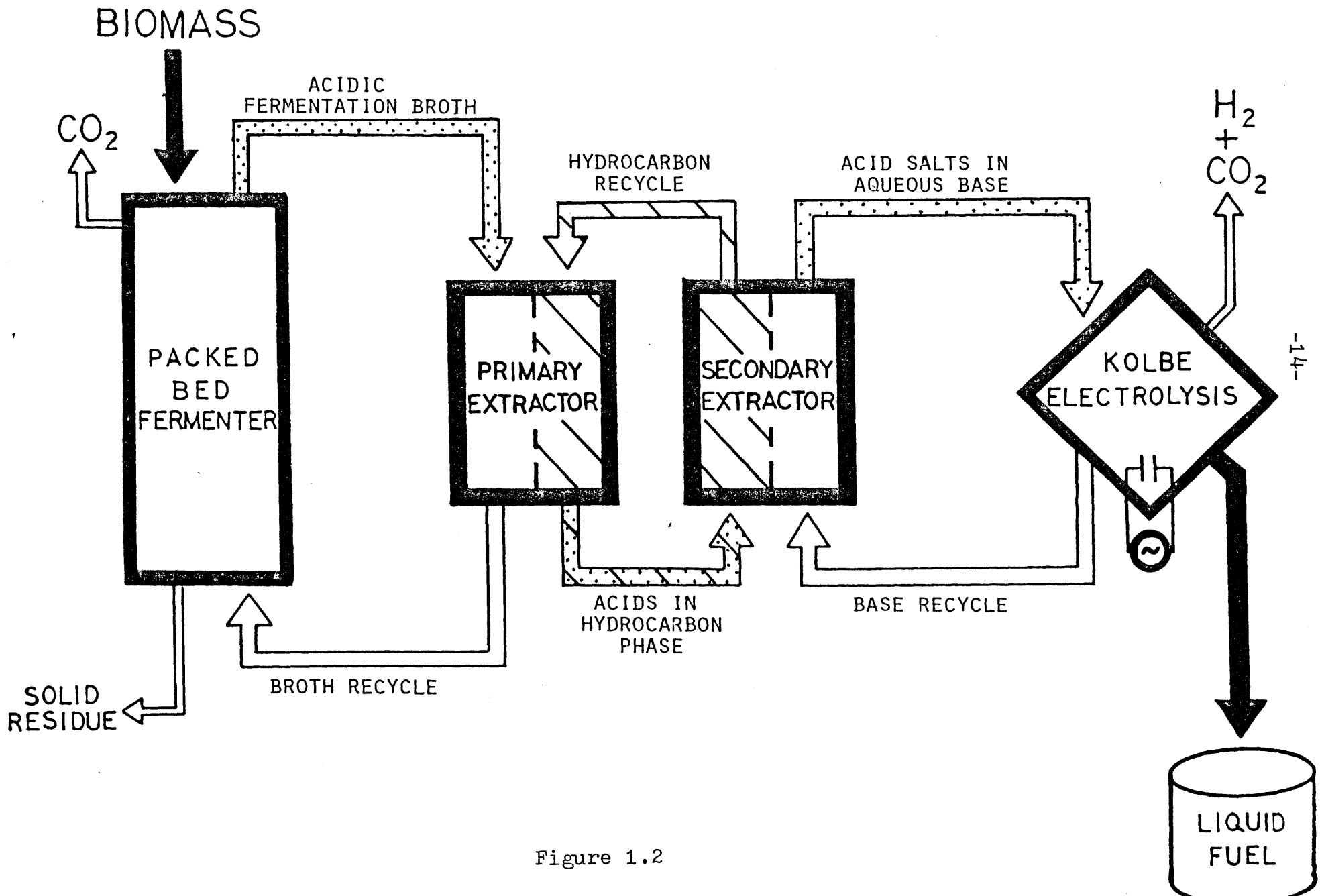


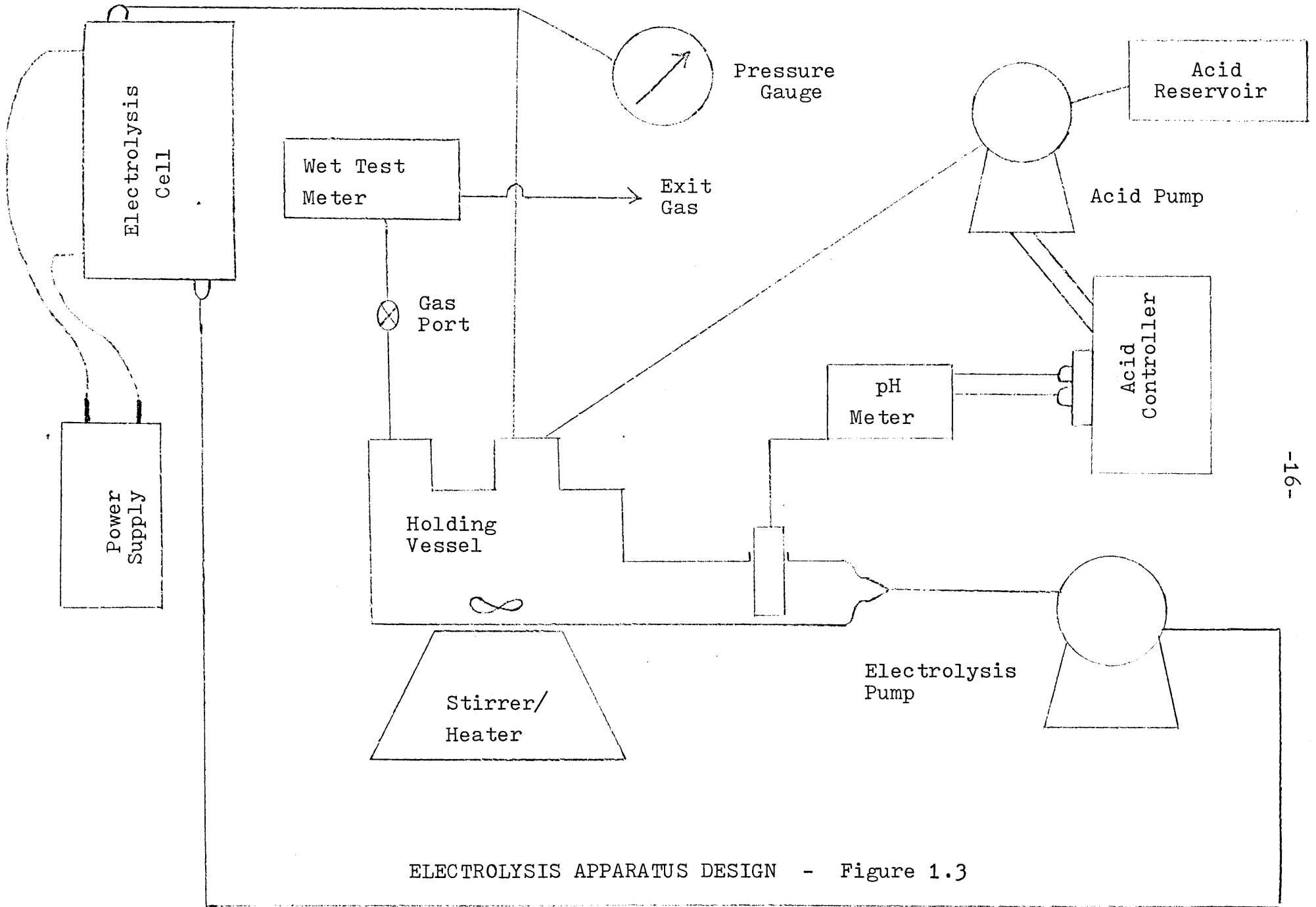
Figure 1.2

extraction with aqueous base (pH = 7.5 - 9.0). The base removes the acids from the hydrocarbon stream and can then be drawn from the extractor to the electrolysis unit. Acid anions are removed from the base solution via Kolbe electrolysis and the base is then returned to the extractor.

To maximize the efficiency of the process, one needs to look at the ways to increase high carbon acid production from the fermentation and to minimize the electric power requirements. The major electric power requirement is in the operation of the Kolbe electrolysis unit.

#### 1.4 Electrolysis Experimental Apparatus

A diagram of the electrolysis apparatus is presented in figure 1.3. The main components are the holding vessel, the electrolysis cell, the electrolysis pump, the 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  $57.5 \text{ cm}^2$ . Connected to the electrolysis cell is a power supply which can deliver 0 - 100 amperes at a voltage range of 0 - 10 volts. As the acid passes between the two electrodes and is oxidized, hydrocarbon product,



ELECTROLYSIS APPARATUS DESIGN - Figure 1.3



carbon dioxide, hydrogen gas and the remaining non-electrolyzed 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 the produced gas. 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 flowrate 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 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 is a pH probe (with temperature detector) and meter. Under normal operating conditions, the pH is maintained between

6 - 7. Maintaining the pH within this range is accomplished with an acid flow 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 delivers acid to the holding vessel. During an acid electrolysis, the pH will rise as the acid concentration decreases. As the pH rises, the change in the 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.

The magnetic stirrer within the holding vessel maintains complete mixing of the aqueous acid solution and any entering acid. Built into the stirring unit is a heating plate. With the use of a propylene glycol bath around the holding vessel, the temperature of the acid solution can be raised.

Voltage readings can be taken across the electrodes with a voltage meter. In addition, the individual electrode potentials can be measured against a silver-silver chloride reference electrode, (located next to one of the electrodes).

A description of the reference electrode and its function is presented in section 3.1.

## Chapter 2: ELECTROLYSIS ENERGY REQUIREMENTS

### 2.1 Reaction Thermodynamics

At a constant temperature and pressure, the Gibbs free energy of reaction,  $\Delta G$ , is equivalent to electrical energy by the expression: <sup>11</sup>

$$\Delta G = -nFE \quad (2.1)$$

where  $n$  = the number of electrons transferred per molecule,  $F$  is the Faraday constant (96,520 coulombs/mole) and  $E$  is the potential difference in volts.  $\Delta G$  is expressed in joules/mole ( $2.39 \cdot 10^{-4}$  kcal = 1 joule).

From the laws of thermodynamics, one can obtain the relationship between the enthalpy of reaction,  $\Delta H$  and the free energy of reaction. This relationship is expressed as: <sup>8</sup>

$$\Delta H = \Delta G + T\Delta S \quad (2.2)$$

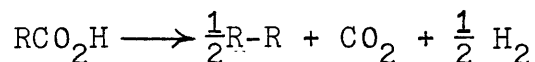
where  $\Delta S$  is the change in entropy. The entropy change is not convertible to electricity. A negative entropy change is liberated as heat and a positive entropy change is supplied as heat or electricity. Only the Gibbs free energy must be supplied as electricity. <sup>11</sup>

Enthalpies and free energies of reaction are presented in Table 2.1. <sup>3,6</sup> Products with five or fewer carbon atoms are considered to be in the gaseous state. Products with more than five carbon atoms are considered to be liquid. Solution

Table 2.1

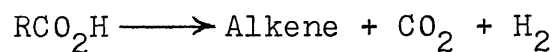
ENTHALPY AND FREE ENERGY (WITH CORRESPONDING  
OXIDATION POTENTIALS) FOR ELECTROLYSIS OF ORGANIC ACIDS

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	9.0	-0.39	-4.4	0.19
Propionic	10.8	-0.47	-4.6	0.20
Butyric	4.8	-0.21	-5.1	0.22
Valeric	3.9	-0.17	-5.8	0.25
Caproic	8.3	-0.36	-6.5	0.28

Elimination Reaction



<u>ACID</u>	<u>ΔH</u>		<u>ΔG</u>	
	<u>kcal/mole</u>	<u>volts</u>	<u>kcal/mole</u>	<u>volts</u>
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

Note: The ΔH's and the ΔG's presented above were obtained from the enthalpic and free energies of formation of the products and reactants. References 3 and 6 were used as sources of thermodynamic data.

effects have not been considered however if the solution thermodynamics for an acid - water mixture (0.5 N acid) are assumed,  $\Delta H$  does not change significantly while  $\Delta G$  changes by +4 kcal/mole for both paraffin and olefin production.

For the Kolbe reaction,  $\Delta G$  is slightly negative and  $\Delta H$  is positive. The thermodynamics states that the reaction is theoretically spontaneous, requiring heat but not electricity. The electrical input to the Kolbe reaction is necessary however for kinetic reasons. This suggests that if the correct catalyst were chosen, the energy requirements would be greatly reduced.

From the listing in Table 2.1, one can see that the olefin reaction is not spontaneous. The thermodynamic requirements are however, much lower than the potentials at which the reaction is currently run.

## 2.2 Applied Electrochemical Potential

In order for electrolytic oxidation and reduction to occur, one must supply an electrochemical potential to the electrolysis cell and solution. This electrochemical potential may be divided into several components according to the following equation:<sup>11</sup>

$$E_T = E_{rev} + IR + E'_A + E'_C + E'_{conc A} + E'_{conc C} \quad (2.3)$$

where:  $E_T$  is the total applied voltage.

$E_{rev}$  is the reversible potential of reaction.

IR is the potential required to overcome the internal resistance of the cell (i.e. the resistance of the electrolytic medium).

$E'_A$  is the activation overpotential required by steps in the anode reaction which are slower than the electron transfer step.

$E'_C$  is the activation overpotential required by steps in the cathode reaction which are slower than the electron transfer step.

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

The reversible potential of reaction,  $E_{\text{rev}}$ , can be calculated according to the thermodynamic equation presented in section 2.1, namely:

$$\Delta G = -nFE \quad (2.1)$$

$\Delta G$  may be calculated by summing the free energies of formation of the Kolbe reaction products and reactants.

The IR term in equation 2.3 is due mainly to the resistance of the electrolytic solution to ion transport. The specific resistance of a 0.5 N caproic acid solution has been measured at 1000 Hz to be 40 ohm - cm. at 22<sup>o</sup> C.<sup>11</sup> 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:<sup>1</sup>

$$IR = \frac{Isd}{A} \quad (2.4)$$

where:  $I/A$  = the current density.

$s$  = the specific resistance of the solution

$d$  = the distance between the electrodes.

According to equation 2.4, reducing the IR voltage drop can be accomplished by reducing the electrode spacing, reducing the current density, or reducing the specific resistance of the solution by either raising the temperature or increasing the number of ions in solution.

The kinetic overpotentials ( $E'_A$  and  $E'_C$ ) are believed to be caused by the reaction steps at the anode and cathode which are slower than the electron transfer steps. Each overpotential can be expressed as a linear plot of the log of the current density. This expression is known as the Tafel equation and is written as:<sup>12</sup>

$$E' = a + (b)\ln(I/A) \quad (2.5)$$

Both the slope and the y-intercept of the above equation are functions of the electrode materials and the specific electrode reaction.

The remaining contributions to  $E'_T$  are the terms  $E'_{conc A}$  and  $E'_{conc C}$ . These terms become significant when there are mass transfer limitations of the ions in the electrolytic solution. Mass transfer limitations will occur when there



is no stirring of the solution or no flow of solution near the electrodes. With no stirring of flow, the maximum current density obtainable by diffusion is given by the expression: <sup>1</sup>

$$I/A = 0.0223DCn$$

where: D = the diffusion coefficient in cm<sup>2</sup>/day.  
C = the concentration of electroactive species in moles/liter.  
n = the number of electrons transferred.

The value obtained from the above equation is approximately 0.01 A/cm<sup>2</sup>. Current densities needed to attain the desired products are however, in the range of 0.1 - 1.0 A/cm<sup>2</sup>. To minimize the concentration overpotentials, experiments have been performed with the electrolytic solution flowing through the cell.

### 2.3 Mass and Energy Balances

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

Carbon Balance The first check on the system is a carbon mass balance. The carbon input is from 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 carbon dioxide in the gas phase and the olefin gas can both 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 also be measured.

The carbon dioxide dissolved in the aqueous solution can be measured by titrating the remaining acid solution after a completed experiment. The titration is performed with equal volumes of 1 N HCl and the acid solution, to which is added incremental volumes of 0.1 N NaOH. With this technique, the final acid concentration as well as the amount of carbon dioxide dissolved in solution can both be determined. A further check on the acid concentration can be made by injecting a solution sample into the gas chromatograph.

The paraffin hydrocarbon can be measured simply by separating it from the acid solution. This is easily done since the hydrocarbon will not readily dissolve in an aqueous solution. Most of the liquid hydrocarbon from a caproic acid run will be decane. Thus, one can easily calculate the total number of moles of liquid hydrocarbon

produced. If a mixture of acids were electrolyzed, (as is the case with a fermentation sample), one could inject the final liquid hydrocarbon product into the gas chromatograph to determine the actual paraffin content. Injections of the liquid hydrocarbon product from caproic acid runs 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 to compare the number of moles of consumed acid with the number of moles of carbon dioxide produced. According to the assumed reaction equation, one mole of carbon dioxide is produced at the anode for each mole of acid which is oxidized. Consequentially, the number of moles of consumed acid should equal the number of moles of carbon dioxide produced. If the two figures do not agree, one should assume a gas leak in the system.

Hydrogen Balance      The hydrogen gas flowrate can be determined in the same manner as the carbon dioxide gas flowrate. For each mole of paraffin produced, the ratio of the moles of carbon dioxide to hydrogen gas produced is two to one. For each mole of olefin produced, the ratio of the moles of carbon dioxide gas to the moles of hydrogen gas produced is one to one. If oxygen is present in the gas product stream, it is necessary to subtract the appropriate

number of moles of hydrogen from the total number of moles of hydrogen to account for the hydrogen produced solely from acid electrolysis.

Electricity Balance      The total moles of electricity used can be calculated by knowing the number of amperes (coulombs/sec.), the total time of the experiment (sec.), and Faraday's constant (96,500 coulombs/mole of electricity). An electricity balance check can be made with the number of moles of hydrogen produced.  $H^+$  ions are reduced at the cathode. According to equation 1.9, it takes two moles of electricity to produce one mole of hydrogen gas. Thus, the moles of electricity should be two times the moles of hydrogen gas product. Often times the calculated value of the moles of electricity used and the electricity used on the basis of the hydrogen flowrate do not correspond. This discrepancy can be accounted for on two accounts, (1) the ampere meter on the voltage supply is not reading properly or (2) there is a short between the two electrodes due to some foreign material buildup thus allowing electricity to pass through the system without oxidizing acid. In order to insure a correct value of the amperage, the hydrogen flowrate is used as the basis for measuring the amount of current used for acid electrolysis. If the electricity calculated from the hydrogen flowrate is less than that calculated from the power supply ampere meter, the system is assumed to have

an electrical short. If the electricity calculated from the hydrogen flowrate is larger, it is assumed that there is an error on the part of the ampere meter reading. Using the hydrogen flowrate as a basis, 'real current' values were obtained for use in data analysis.

B.T.U. Energy Return      A ratio of the 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 B.T.U.s of electricity applied to the system to produce hydrocarbon product and the heating value (in B.T.U.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 to make a fuel cell which can supply part of the electric needs for the operation of the electrolysis. A favorable ratio of product energy to supplied energy is of course desirable

## Chapter 3: EXPERIMENTAL RESULTS

### 3.1 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 change the 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 two different sets of electrodes are listed in Table 3.1. The column headings are abbreviated as, RCD, real current density; R-Amp, real amperes; A, the number of amperes read from power supply meter;  $V_{ps}$ , the voltage observed on the power supply's voltage meter;  $V_e$ , the voltage measured directly across the electrodes



with a voltage meter; R-C and R-A, the potentials measured from the silver-silver chloride reference solution to the cathode and anode respectively; %olefin and %paraffin, the product hydrocarbon percentages. The voltage reading on the power supply included the resistances of the electrical connections to the electrolysis cell. With better connections and wiring, it is assumed that the operating voltage will approach the voltage measured directly across the electrodes.

From Table 3.1, 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 current, and (2) the voltage across the electrodes increases with 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 3.2 shows comparative production power figures when both voltage and product distribution are considered. The 'current' value takes into account the fact that it takes two electrons to produce olefin and one electron to produce paraffin. One can see from these values, the comparative tradeoffs of reducing the applied voltage or



Table 3.2

RELATIVE POWER REQUIREMENTS

Monel Cathode - Platinum Sheet Anode

@ 5 amperes	$(0.6809 + (2)(0.3191))(4.0V)$	=	5.3
@ 10 amperes	$(0.5462 + (2)(0.4538))(4.2V)$	=	6.2
@ 15 amperes	$(0.7385 + (2)(0.2615))(4.8V)$	=	6.0

Platinum Sheet Cathode - Tri-plated Anode

@ 10 amperes	$(0.4633 + (2)(0.5367))(4.0V)$	=	6.1
@ 15 amperes	$(0.4882 + (2)(0.5118))(4.2V)$	=	6.3
@ 20 amperes	$(0.5338 + (2)(0.4662))(4.6V)$	=	6.7

Note: Ampere values are the readings taken from the power supply ampere meter.

increasing the paraffin to olefin ratio. From this chart, it would appear that the paraffin to olefin ratio observed at 6.5 'real amperes' using the monel cathode and platinum sheet anode required the least amount of power to produce.

A further comparison between the electrode materials is illustrated in Table 3.3. This chart gives the ratio of the heating value (in B.T.U.s) of the hydrocarbon products to the heating value of the electricity needed to oxidize the acid. Once again one can see that the monel cathode and platinum anode outperformed 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 effects of material changes on the overpotentials of each electrode listed in Table 3.1. These overpotentials are measured with a silver-silver chloride reference electrode which can be located at either the anode or the cathode. Its design is simply a saturated silver-silver chloride solution separated from either the anode or cathode by a thin fritted glass disc. A silver probe is inserted into the solution and is connected to a voltmeter with a piece of wire. When the reference electrode is located at the cathode, it reflects the true value of the cathodic overpotential. A measure of the anode

Table 3.3

ELECTROLYSIS RETURN ON ENERGY

Electrodes

- Cathode (Monel)		
- Anode (Platinum Sheet)		
5 ampere	Return =	10.4/1
10 ampere	Return =	8.2/1
15 ampere	Return =	9.7/1

Electrodes

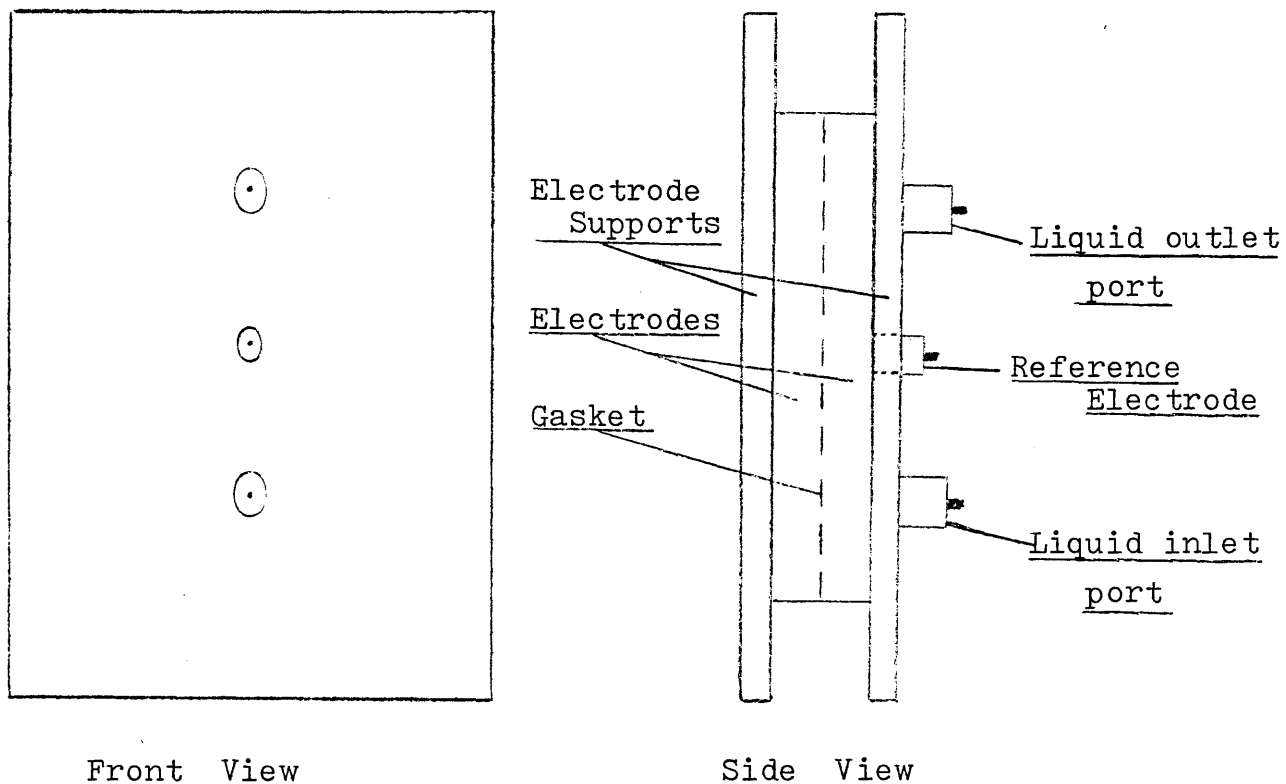
- Cathode (Platinum Sheet)		
- Anode (Tri-plated)		
10 ampere	Return =	7.7/1
15 ampere	Return =	6.9/1
20 ampere	Return =	5.7/1

Note: Returns are calculated as a ratio of the heating value (in B.T.U.s) of the olefin and paraffin hydrocarbon products to the number of B.T.U.s of electricity used to produce the products.

overpotential would include some or all of the IR voltage drop between the electrodes plus the actual anode overpotential. A detailed picture of the electrolysis cell is given in Figure 3.1 with an enlargement of the reference electrode. The opposite situation exists when the reference electrode is located at the anode. The IR voltage drop is then added to the cathode overpotential measurement. The potential of the silver-silver chloride electrode is + 0.197 V. versus the normal hydrogen electrode.

The theoretical values for the IR voltage drop of a 0.5 N caproic acid solution at room temperature, an electrode spacing of approximately 0.05 cm., and at various current densities are listed in Table 3.4. The values were obtained according to equation 2.4. 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 tri-plated electrode adds approximately 1.0 - 1.5 V. in overvoltage (at comparable amperage densities) to the value obtained with the smooth platinum sheet, when the two are compared at the anode. From the comparison of the three metals, it would seem that the smooth platinum sheet would be the best material to reduce the overvoltages on both the anode and the cathode.

ELECTROLYSIS CELL - Figure 3.1



Reference Electrode - Enlarged View

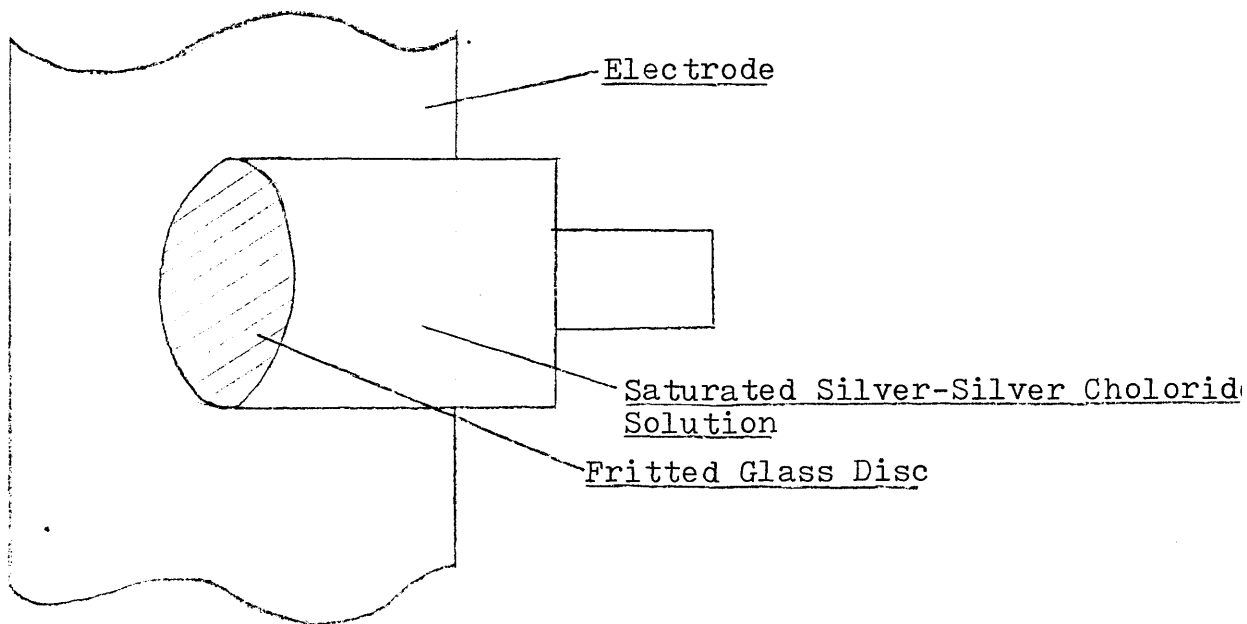


Table 3.4

IR VOLTAGE AND ELECTRODE OVERPOTENTIALS

Electrode Materials

- Monel Cathode
- Platinum Sheet Anode

(CATHODE REFERENCE ELECTRODE)

R-Amps	IR	Cathode Voltage	Anode Voltage (adjusted value)
6.5	0.24	1.3	1.76
11.2	0.39	1.2	1.21
15.8	0.55	1.9	1.35

Electrode Materials

- Platinum Sheet Cathode
- Tri-plated Anode

(ANODE REFERENCE ELECTRODE)

R-Amps	IR	Cathode Voltage (adjusted value)	Anode Voltage
7.0	0.24	0.76	2.6
15.0	0.52	0.58	2.8
17.6	0.61	0.69	2.9

Note: Calculated IR voltage plus the adjusted voltage value yields the experimentally observed voltage readings listed in Table 3.1.

### 3.2 Current Density

To compare the effects of different current densities, the hydrogen gas flowrate will be the basis for the calculation of the amount of electricity used to produce hydrocarbon product. Trends which are functions of the current density are illustrated in the data listed in Table 3.1. As the current density increases, the percentage of paraffin product also increases. In addition to the paraffin production increase, one also notes that the applied voltage across the electrodes also increases with added current density.

Increased paraffin production production with increased current density is explainable according to the proposed radical reaction mechanism given in Figure 1.1. Increasing the current density will increase the concentration of alkyl radicals. An increase in alkyl radicals will result in an increased probability that two radicals will react together to form the Kolbe dimer.

The total surface area of each electrode is approximately 57.5 cm<sup>2</sup>. It must be noted however that the surface area of the tri-plated titanium-gold-platinum anode is not completely smooth as is the case with the other electrodes. Because of a slight ruffed surface, its surface area is somewhat larger than the areas of the other electrodes. This means that the values of the current densities for the second group listed in Table 3.1 are probably somewhat less

than the given figures. For the purpose of this thesis however, the superficial surface area of  $57.5 \text{ cm}^2$  will be used in comparing data.

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 carbon dioxide produced. By calculating the theoretical projected surface area of a carbon monoxide molecule and measuring the total number of moles of carbon dioxide produced, a good approximation of the surface area can be attained.

Plotting the  $\ln$  of the 'real current density' versus the anode and the cathode overpotentials yields the Tafel plots given in Figures 3.2 and 3.3. From the graphs, the line equations are:

Platinum Sheet Anode - Monel Cathode

$$E_A' = 2.03 + 0.08 \ln(i)$$

$$E_C' = 2.15 + 0.4 \ln(i)$$

Platinum Sheet Cathode - Platinum Tri-plated Anode

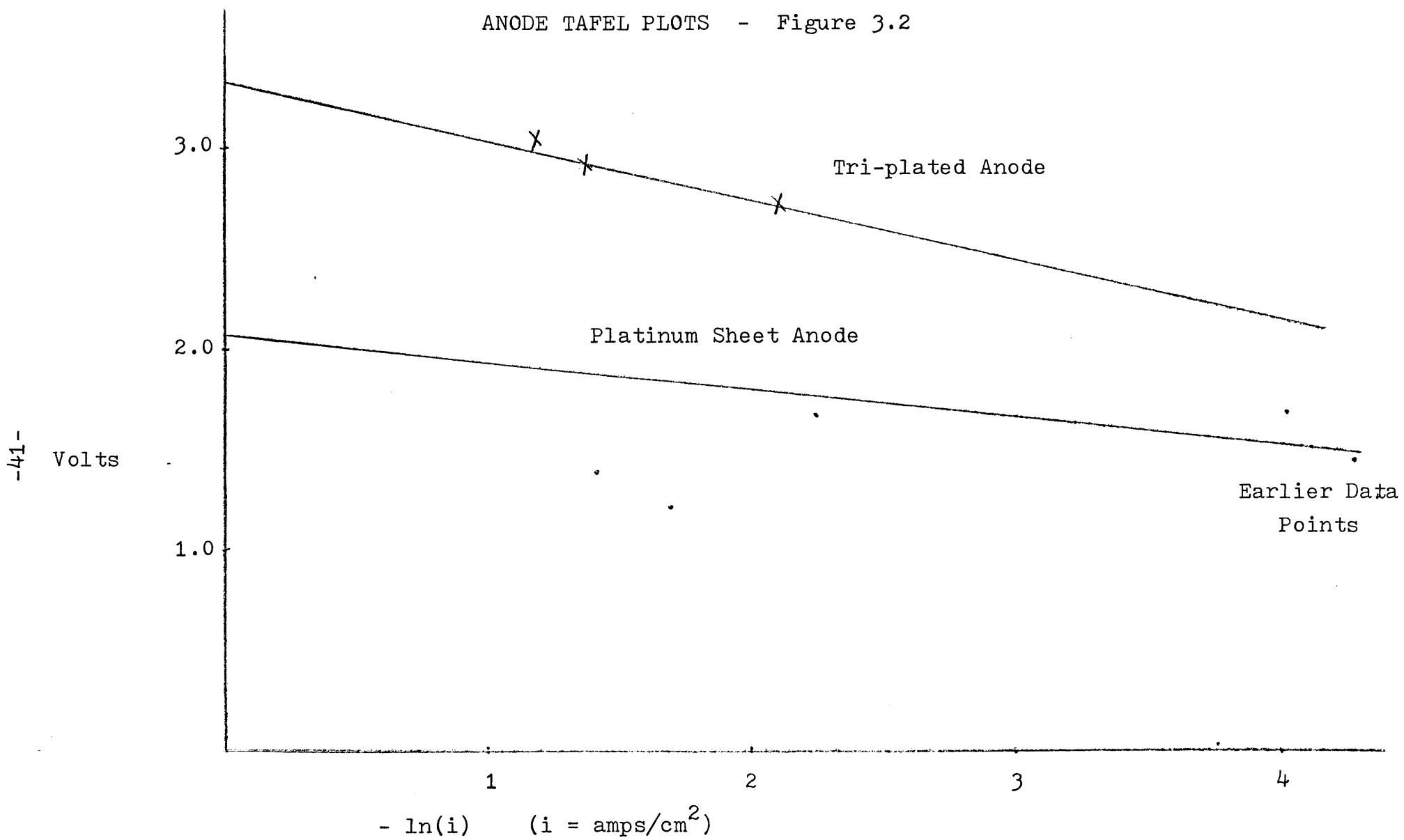
$$E_A' = 3.25 + 0.25 \ln(i)$$

$$E_C' = 1.60 + 0.25 \ln(i)$$

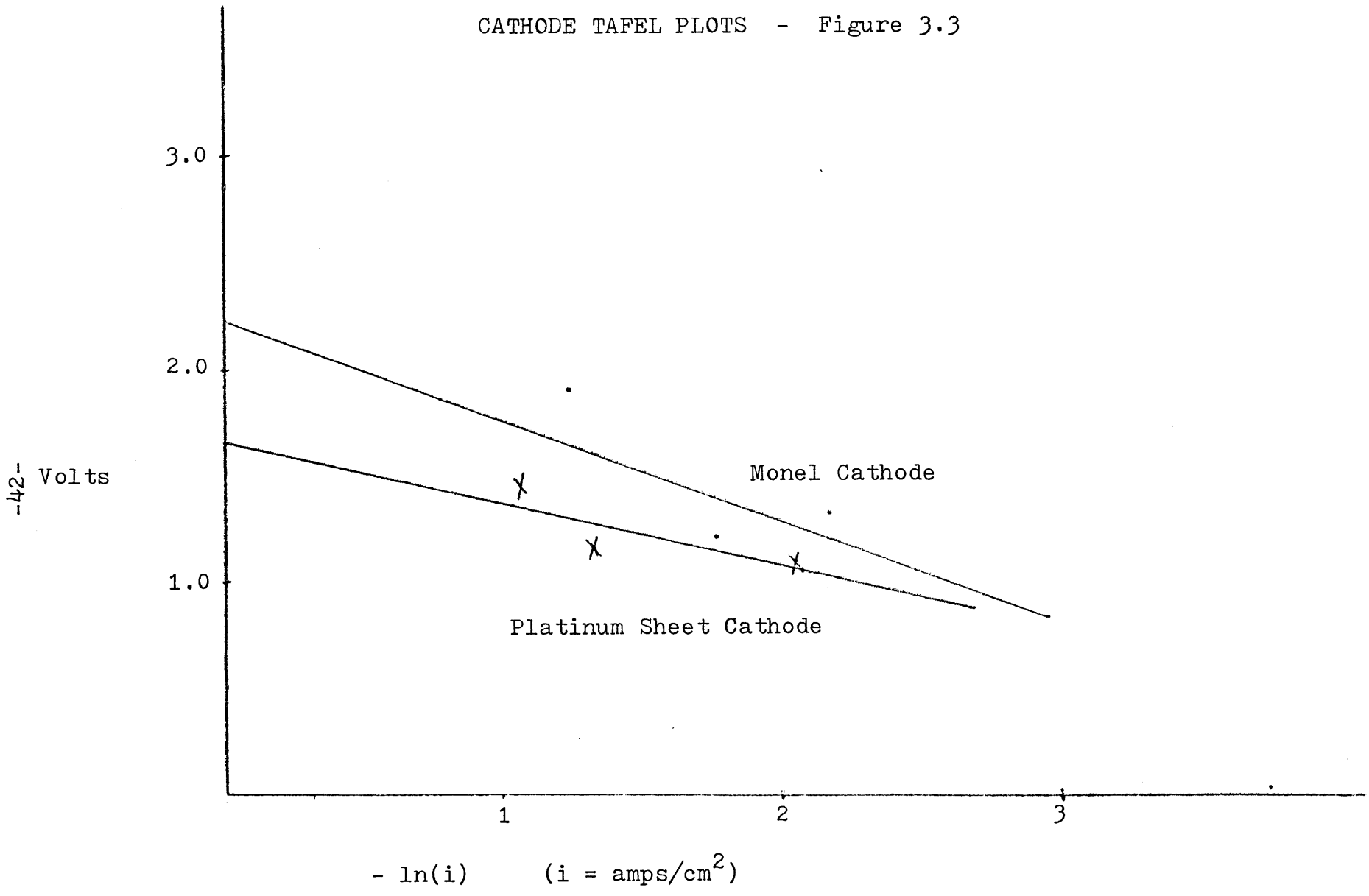
where:  $i$  is in  $\text{amps/cm}^2$



ANODE TAFEL PLOTS - Figure 3.2



CATHODE TAFEL PLOTS - Figure 3.3



Both the slope and the y-intercept are a function of electrode material and electrode reaction. Each equation for  $E'_A$  and  $E'_C$  can be plugged into equation 2.3 to determine the theoretical total applied voltage necessary, at a given current density.

Comparing the two anode plots, one can see that the platinum tri-plated electrode does not function in the same catalytic manner as the smooth platinum electrode. The differences in line slope and intercept would indicate that the two electrodes are not the same metal. It is possible that the platinum surface of the tri-plated electrode is porous to the acid molecules and that some of the anodic oxidation is taking place on the gold or platinum underlayers. This would account for the higher overpotentials on the tri-plated electrode.

### 3.3 Temperature

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 3.5 compares the data obtained for the high temperature runs (70°C and 95°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

HIGH TEMPERATURE ELECTROLYSIS DATA - Table 3.5

Comparisons on Current Density Basis  
(ANODE REFERENCE ELECTRODE)

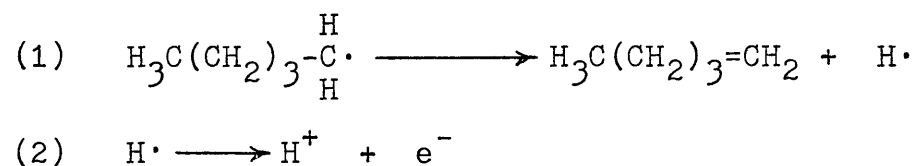
<u>RCD</u>	<u>R-Amps</u>	<u>A</u>	<u>V<sub>ps</sub></u>	<u>V<sub>e</sub></u>	<u>R-A</u>	<u>R-C</u>	<u>%Olefin</u>	<u>%Paraffin</u>	<u>Temp.</u>
0.18	10.1	20	4.2	3.6	2.0	1.1	78.37	21.63	95° C
0.12	7.0	10	4.4	4.0	2.6	1.0	53.67	46.33	40° C
0.25	14.1	15	4.1	3.7	2.2	1.1	65.33	34.67	70 C
0.26	15.0	15	5.0	4.2	2.8	1.1	51.18	48.82	50 C

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

and the anode overpotential. In each case, there is approximately a 0.6 V 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 voltage drop. While the lowering of the voltage produced a gain in the electrolysis energy balance, raising the temperature also lowered the paraffin/olefin ratio (Table 3.5) 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 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 the Kolbe dimer. Thus at lower temperatures, one sees a higher percentage of paraffin in the

hydrocarbon product.

The relative power requirements to produce the various product distributions at different temperatures are listed in Table 3.6. These power requirements are within a fairly close range. Although the power requirements may be similar, the return on energy figures reveal 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. Comparing the data at similar current densities, one can see that the return on energy value at high temperatures is approximately half the energy return for lower temperatures. Thus the trade-off between a larger paraffin to olefin ratio verses a decrease in the applied voltage favors the paraffin to olefin ratio when viewed in terms of return on energy.

#### 3.4 Flowrate Past Electrodes

Experiments were performed to observe the effect of changing the flowrate of the electrolytic solution past the electrodes. Two possible situations were hypothesized, (1) a gas head space may be forming inside the electrolysis cell if the solution flowrate were not fast enough, thus reducing the catalytic surface contact area to the solution and (2) a faster flowrate may reduce the concentration boundary layer over the electrodes. The experiments were

HIGH TEMPERATURE EXPERIMENTS - Table 3.6

Relative Power Requirements

T = 40 C	(0.4633 + (2)(0.5367))(4.0V)	= 6.1
T = 95 C	(0.2163 + (2)(0.7837))(3.6V)	= 6.4
T = 50 C	(0.4882 + (2)(0.5118))(4.2V)	= 6.3
T = 70 C	(0.3467 + (2)(0.6533))(3.7V)	= 6.2

Return on Energy

	<u>B.T.U. Ratio</u>	<u>Current Density</u>
T = 40 C	7.7/1	0.18
T = 95 C	3.4/1	0.12
T = 50 C	6.9/1	0.26
T = 70 C	3.9/1	0.25

run with an initial flowrate of 92 ml./min. This value was increased to 195ml./min. and then to 267 ml./min. while observing the product gases at each setting.

The gas product ratio of carbon dioxide to hydrogen was steady at each setting. This would seem to indicate that there was either no or minimal gas head space between the electrodes at all three settings and that the mass transfer limitations of the ions in solution, were minimized across the electrode concentration boundary layer. A mathematical treatment of the mass transfer across a boundary layer and suggestions for minimized friction flow over electrodes are treated in the appendix chapter.



#### Chapter 4: CONCLUSIONS AND RECOMMENDATIONS

The results of this study suggest that the more favorable operating conditions for Kolbe electrolysis are at a lower temperature, at low current densities and with the monel cathode and smooth platinum anode electrodes. These conditions gave the best return on energy at relatively low power requirements.

A close look at the data however reveals that the above found results could likely be improved upon. A look at the individual electrode overpotentials shows that the smooth platinum electrode had the lowest overvoltage readings for both the anode and the cathode. The smooth platinum electrode also had the best paraffin to olefin ratio when acting as the anode. Perhaps a combined effect of low overvoltages and high paraffin to olefin ratios could be attained if both the electrodes were smooth platinum.

The use of high temperature to reduce the IR voltage drop may prove to be worthwhile if the system could be pressurized at the same time. High pressure may prevent the formation of alkenes by keeping them in solution and thus increasing the probability that they will react as alkyl radicals thus producing Kolbe dimer. The use of high pressure would of course mean a redesign of the experimental apparatus to withstand the added stress. Temperature increases could be

maintained simply by supplying insulation around each component of the apparatus.

To improve data collection, one might consider using reference electrodes at both the anode and the cathode. In this way, one could keep a more accurate account of each electrode overpotential with no added IR effect. This is the next experimental step which Dynatech plans to pursue.

Finally, one other area of improvement would be to maintain a more constant pH. This could be done by using a more accurate controller and pH unit. Controlling the pH will maintain a consistency in the amount of dissolved carbon dioxide thus maintaining a steadier product gas flowrate.

In addition to the above suggestions, other experimental variables need to be analyzed. These variables include such things as electrolytic concentration, supporting electrolytes, pH, and cell geometry.

APPENDIX A  
MATHEMATICAL ANALYSIS OF LAMINAR  
FLOW OVER A FLAT PLATE

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

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

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  $\Delta x$  and  $\Delta y$  approach zero.

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

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:

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

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

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

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

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

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

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

$v_y = 0$  at  $y = 0$

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

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

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

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

This equation is satisfied by a stream function,  $\psi$ ,

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

Redefinition variables

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

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

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

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

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

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

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

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

$$\frac{d\rho(\xi)}{d\xi} = 2$$
 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  $\frac{d\rho(\xi)}{d\xi} \Big|_{\xi=0} = 0.664 \sqrt{\frac{v}{D_{AB}}} \quad (A.8)$

Mass transfer to wall is:

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

$$= D_{AB} W (C_{A_o} - C_{A_s}) \int_{\xi=0}^{\xi=L} \frac{1}{2} \sqrt{\frac{V_o}{v}} \frac{d\rho(\xi)}{d\xi} dx$$

$$= D_{AB} W (C_{A_s} - C_{A_o}) \int_{\xi=0}^{\xi=L} \frac{1}{2} \sqrt{\frac{V_o}{v}} \frac{d\rho(\xi)}{d\xi} dx$$

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

Using equation (A.8):

$$N_A = -D_{AB} W C_{A_0} \sqrt{\frac{v L}{\nu}} \quad 0.664 \sqrt{\frac{\nu}{D_{AB}}}$$

$$N_A = -0.664 D_{AB} W C_{A_0} \sqrt{\frac{v L}{\nu}} \quad \sqrt{\frac{\nu}{D_{AB}}}$$

APPENDIX B  
ELECTROLYSIS CELL SCALE-UP AND  
IMPROVED CELL DESIGN



The electrolysis cell will be of the filter press design. A series arrangement of the electrodes will allow for the use of high voltages while minimizing resistance losses. 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  $18,2000 \text{ cm}^2$ , 17 - 18 such units will be required.

To generate  $0.27 \text{ amp/cm}^2$  of current,  $2.2 \cdot 10^{-6}$  moles/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,

$$N_A = -(0.664D_{AB}C_{AO}/L)(V_0L/v)^{1/2}(v/D_{AB})^{1/3} \quad (B.1)$$

where:  $N_A$  = the mass flux of A (acid) in moles/cm<sup>2</sup>-sec =  $-2.2 \cdot 10^{-6}$

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

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

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

$V_0$  = the fluid velocity far from the plate =  $150 \text{ cm/sec}$

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

Equation B.1 is derived in Appendix A. This equation is valid for laminar flow. With an electrode spacing of 0.33 cm, the Reynolds number = 1150, which is in the laminar flow region.

To satisfy equation B.1,  $L = 2.7 \text{ cm}$ . This means that the

desired flux cannot be achieved for electrodes of length greater than 2.7 cm and suggests the use of a short electrode which covers 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 re-establish the bulk acid concentration close to the anode. Because acid will be consumed, the bulk acid concentration will not remain at  $5 \cdot 10^{-4}$  moles/cm<sup>3</sup>. About 21% of the acid will be consumed during a pass through the electrolysis cell so the average bulk acid concentration will be  $4.5 \cdot 10^{-4}$  moles/cm<sup>3</sup>. If this value of  $C_{A0}$  is placed in equation B.1, L then equals 2.4 cm. This means that the grooves should be spaced no more than 2.4 cm. apart.

APPENDIX C  
RETURN ON ENERGY CALCULATIONS

Heating Value of Electricity:

$$(\text{number of amperes})(\text{number of volts}) = \text{number of watts}$$

$$(\text{number of watts})(\text{time of run}) = \text{watt-hrs.}$$

$$3.14(\text{watt-hrs}) = \text{number of B.T.U.s}$$

Heating Value of Hydrocarbon Product

$$\begin{aligned} \text{Paraffin: } & 6389.68 \text{ B.T.U./mole times (number of moles)} \\ & = \text{number of B.T.U.s} \end{aligned}$$

$$\begin{aligned} \text{Olefin: } & 3326.58 \text{ B.T.U./mole times (number of moles)} \\ & = \text{number of B.T.U.s} \end{aligned}$$

LITERATURE CITATIONS

1. Allen, Milton J. Organic Electrode Processes, Reinhold Publishing Corporation, New York, 1958.
2. Casper, M.S. Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Unusual Techniques, Noyes Data Corporation, Park Ridge, N.J., 1978
3. CRC Handbook of Chemistry and Physics, Weast, Robert C. ed., 56th edition, CRC Press, Cleveland, Ohio, 1975.
4. Glasstone and Hickling, "Studies in Electrolytic Oxidation. Part VI. The Anodic Oxidation of Acetates: The Mechanism of the Kolbe and the Hofer-Moest Reaction in Aqueous Solution", Journal of the Chemical Society, 1934, pp. 1878 - 1888.
5. Gurney, Ronald W. Ionic Processes in Solution, McGraw-Hill Book Company, Inc., New York, 1953.
6. Janz, G.J. Thermodynamic Properties of Organic Compounds, Academic Press, New York, 1967.
7. Milazzo, Giulio Electrochemistry: Theoretical Principles and Practical Applications, Elsevier Publishing Company, New York, 1963.
8. Modell, M. and Reid, R.C. Thermodynamics and Its Applications, Prentice-Hall, Englewood Cliffs, NJ., 1974.
9. Sanderson, J.E. and Wise, D.L. "Acetic Acid Production from Marine Algae", Dynatech R/D Company Report No. C-02-4388-3, 1978.
10. Sanderson J.E. and Wise, D.L. "Acetic Acid Production from Marine Algae", Dynatech R/D Company Report No. C-02-4388-4, 1978.
11. Sanderson, J.E. et all, "Liquid Fuels Production from Biomass", Dynatech R/D Company Report No. C-02-4388-8, 1979.

12. Utley, J.H.P. "Anodic Reactions of Carboxylates", Techniques of Chemistry, 5, pt.1. Wiley Publishing Company, New York, 1974.
13. Weedon, B.C.L. "Anodic Syntheses with Carboxylic Acids", Quarterly Reviews, pp. 380 - 398.