

**ELECTRO SYNTHESIS OF PROPYLENE OXIDE
IN A BIPOLAR TRICKLE BED REACTOR**

By

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ABSTRACT

The synthesis of propylene oxide by electrolysis of dilute sodium bromide solution with propylene gas was investigated in an electro-chemical bipolar reactor consisting of six parallel fixed beds of graphite particles separated by polypropylene felt diaphragms.

One reactor was operated in single pass and recycle mode with two phase co-current flow of propylene and sodium bromide solution through the beds of graphite particles. The maximum pressure in the system was 2.22 atmospheres absolute.

The effects of superficial current density* ($413 - 2687 \text{ A/m}^2$), electrolyte (sodium bromide solution) concentration (0.2 M and 0.5 M), electrolyte flow rate (100 and $300 \text{ cm}^3/\text{min}$), propylene gas flow rate ($100/1000/1500/2000 \text{ cm}^3/\text{min}$ at STP), reactor outlet temperature (30° and 60°C), bed thickness (six beds - $8.57/4.29/3.07 \text{ cm}$) and different carbon types (Union Carbide and Ultra Carbon) on the space time yield and selectivity for propylene oxide were measured. Depending on the condition for single pass runs, the space-time yield for propylene oxide was between 5.5 kg/hr m^3 and 97.2 kg/hr m^3 , and the selectivity was between 54.5% and 87.3%. The current efficiency and the specific energy consumption varied from 14.0 to 58.2 percent and 5.7 to 59.9 Kwh/kg of propylene oxide. The space-time yield for propylene oxide increased with decreasing bed thickness. For the recycle mode the space-time

*Superficial current density = applied current/electrode area.

yield decreases with time. The highest space time yield obtained after one hour of operation was 127.8 kg/hr m^3 with a selectivity of 95.9%. The current efficiency for hydrogen, oxygen and dibromopropane was also determined.

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CHAPTER 1

INTRODUCTION

Propylene oxide is an organic chemical used as a building block for other chemicals and industrial products. Some of the products manufactured from propylene oxide are:

- a) Propylene glycol which is widely used as an edible solvent for flavours.
- b) Cosmetics, fumigants, paints and surfactants such as alkyl polyoxy propylene.
- c) In recent years large quantities of propylene oxide have been consumed in the production of polyurethanes.

The present list price for propylene oxide reported in the Chemical Marketing Reporter is \$1.05 per kilogram [1].

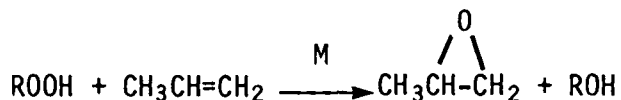
According to K.H. Shimmrock [2] the production capacity of propylene oxide in 1978 was estimated at approximately 1 to 1.1 million metric tons per year each in the United States and in Western Europe, and approximately 0.2 to 0.3 million metric tons per year in the rest of the world excluding the Eastern Block.

Propylene oxide is produced either by the hydroperoxide or the chlorohydrin process. The former process uses an organic hydroperoxide to epoxidize propylene; an organic alcohol is a coproduct. Oxirane, a division of Arco Chemicals, has units at Bayport and Channelview, Texas. The chlorohydrin process involves the reaction of propylene with chlorine and water to produce propylene chlorohydrin, followed by

dehydrochlorination with lime or caustic to give propylene oxide and a salt. Dow Chemicals Company has plants at Freeport, Texas and Plaquemine, Louisiana.

1.1 Hydroperoxide Process

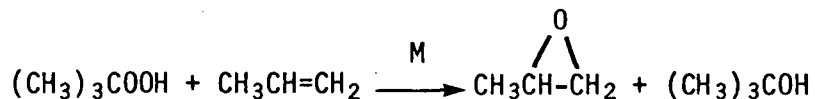
This process is based on the following reactions



At present ethylbenzene and isobutane are being used industrially as the starting materials; thus if isobutane is used, the oxidized product is tert-butyl hydroperoxide:

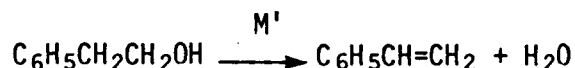


Some tert-butyl alcohol is also formed. The next step is the epoxidation of propylene in the presence of a metal catalyst:



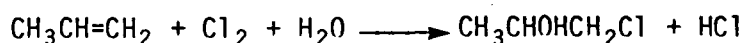
Approximately 3 kgs. of tert-butanol is produced per kilogram of propylene oxide. With ethylbenzene as the starting material, ethyl

benzyl alcohol is the coproduct. The alcohol is then dehydrated in the presence of catalyst to produce styrene. Approximately 2.5 kgs of styrene is produced per kilogram of propylene oxide.

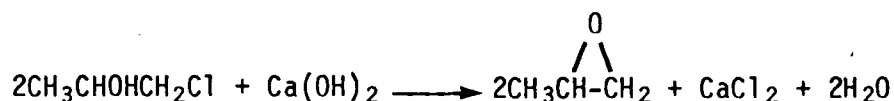


2. The Chlorohydrin Process

The present commercial process is based on mixing propylene and chlorine in equal molar amounts with an excess of water to form a dilute solution of propylene chlorohydrin.



The chlorohydrin is then treated with a slurry of calcium hydroxide to form propylene oxide and an effluent water stream of calcium chloride



Some of the disadvantages of this process are:

- a) the chlorine value is lost as calcium chloride (2.1 tons of calcium chloride is produced which is contained in at least 43 tons of waste water per ton of propylene oxide).

b) calcium chloride has a limited market and therefore causes disposal problems.

c) requires the handling of toxic molecular chlorine.

A variation of the above process would be a combination of a chlor-alkali electrolysis with propylene oxide manufacturing plant. A simplified flow diagram for this process is shown in Figure (1). This process is presently operated by Dow Chemical at Stade (Germany) producing 250,000 tons of propylene oxide per year. In this process chlorine is produced by electrolysis, simultaneously caustic soda is also produced. Therefore, it would be reasonable from a technological point of view to replace the calcium hydroxide used in the dehydro-chlorination stage with caustic soda solution and to re-use the sodium chloride solution produced. This would do away with the burden on waste water, amounting to approximately 43 tons of 5-6 percent calcium chloride solution per ton of propylene oxide. A drawback of this process resides in the fact that brine leaving the saponifier is very dilute. To maintain the water balance, approximately 37 tons of lean brine have to be removed per ton of propylene oxide.

A brief description of other processes for the manufacture of propylene oxide, irrespective of their feasibility on a commercial scale is contained in reference [2]. A detailed account of the properties of propylene oxide is given in reference [3].

In recent years considerable effort has gone into a search for a more economical route to propylene oxide to replace the present conventional processes. The hydroperoxide process produces large amounts of co-product such as tert-butanol that can be manufactured by

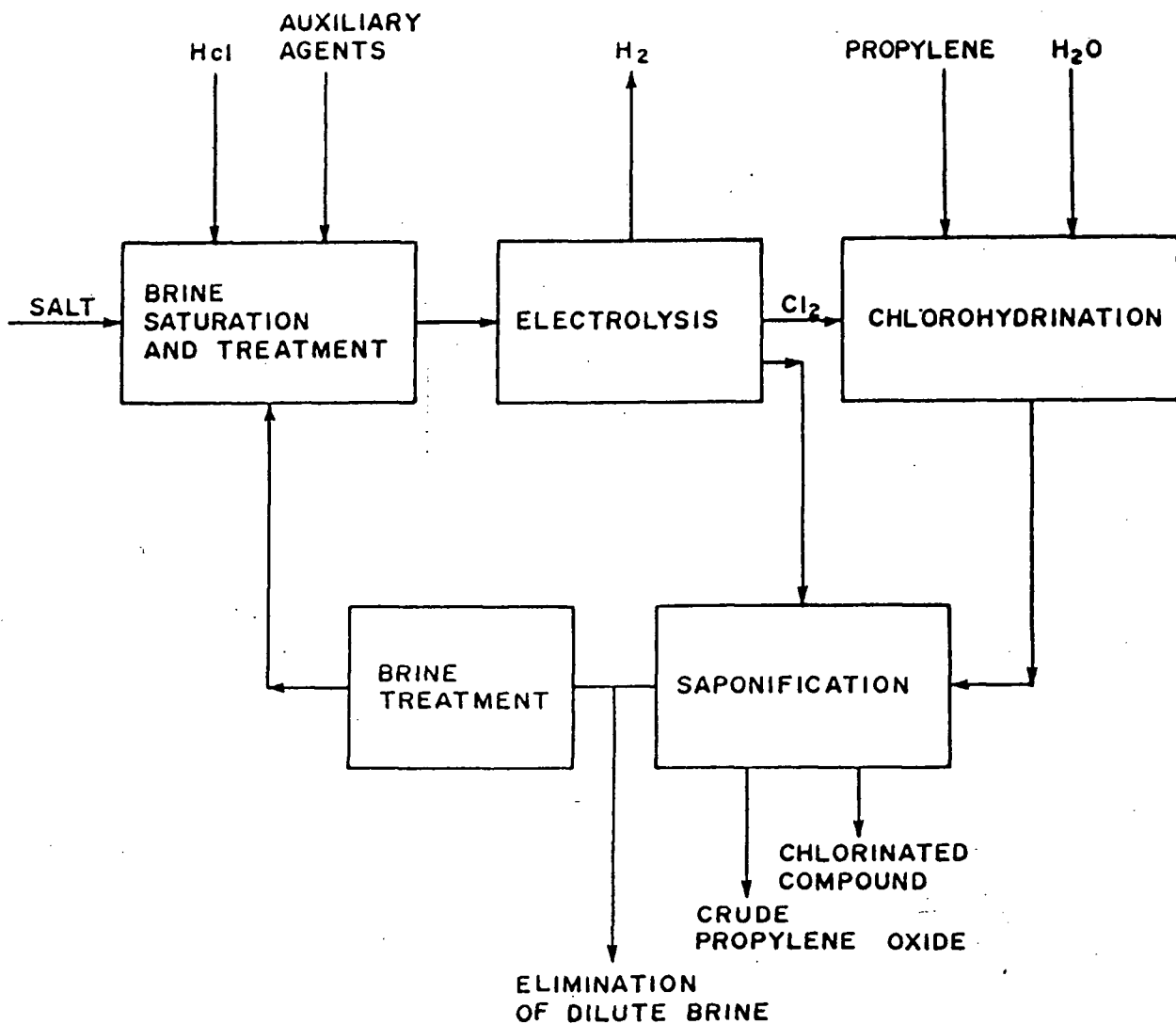
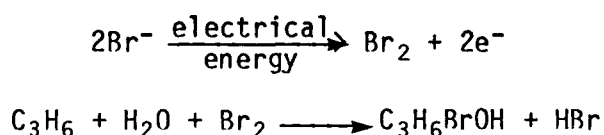


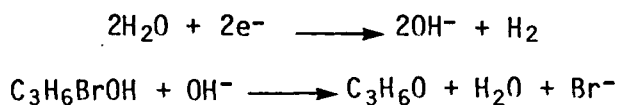
FIGURE 1: COMBINATION OF CHLOR-ALKALI ELECTROLYSIS AND PROPYLENE OXIDE MANUFACTURE

other economical routes and the chlorohydrin process produces large amounts of unwanted by-products such as calcium chloride. One possibility is an electrochemical route in which the propylene is converted to propylene halohydrin by reaction with halogen generated in situ by anodic oxidation of a metal halide solution. The propylene halohydrin is converted to propylene oxide by reaction with the hydroxyl ion generated at the cathode. The general reaction scheme when sodium bromide is used as the electrolyte is [4]:

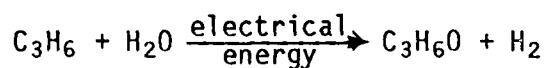
Anode:



Cathode:



Overall:



In principle, only water, propylene and electrical energy are consumed in the formation of propylene oxide and hydrogen. The sodium bromide

solution is continuously oxidized and regenerated within the cell for further use, although losses of bromine may be caused by the formation of hypobromite, bromate, bromite, bromine gas and dibromopropane.

The advantage of this electrochemical route, which obviates the production of waste calcium chloride encountered in the conventional chemical process, has long been recognized but attempts to implement it by various people employing different reactor designs have not proved to be very effective because of low space time yields for propylene oxide, although the selectivity in these reactors for propylene oxide is high.

The object of this thesis is to investigate the feasibility of producing propylene oxide with high space time yield and high selectivity by electrolyzing an aqueous solution of sodium bromide while passing both the propylene gas and the aqueous solution through the electrodes of a bipolar fixed bed reactor.

CHAPTER 2

BACKGROUND

2.1 Previous Work

Numerous experimental studies on the electro-synthesis of organic compounds have been reported in the literature over the past several years. The bulk of this material is summarized in references [5], [6] and [7]. The present discussion is concerned only with previous work directed at the synthesis of propylene oxide by electrolysis of a metal halide solution.

Beck [8] studied the synthesis of propylene oxide in a capillary gap cell with distances between electrodes of up to 0.5 mm. In his experiments, propylene gas dispersed in a dilute sodium bromide electrolyte is supplied through a central hole in a pile of electrode discs and flows radially outwards between the discs. The gap between electrodes was made small to enable low bromide concentrations to be handled with low ohmic losses. A current efficiency of 73 percent for propylene oxide was reported at a current density of 0.1 kA/m^2 with the sodium bromide concentration of 0.5 weight percent and an electrode gap of 0.5 mm. The cell voltage of 3.0 volts corresponded to an energy consumption of 3.8 Kwh/kg of propylene oxide. The maximum space time yield reported based on electrode gap is 162.2 kg/hr m^3 . The electrode thickness varies from 3 to 30 mm.

In 1977 Ghoroghchian et al. [9] employed an electrochemical pump cell, which is similar to the capillary gap cell used by Beck, to

synthesize propylene oxide. As in the capillary gap cell, the sodium bromide solution and the propylene gas are fed through a central hole and flows radially outwards in the gap between the rotating electrodes. The rotational motion increases turbulence and thus helps to re-establish saturation as propylene is consumed. Production rate for propylene oxide of up to 0.661 kg/hr m^3 based on total pump volume was obtained at an electrode rotational speed of 3000 rev/min and the electrolyte temperature of 15°C . The current efficiency was high and reached a maximum (100%) at an electrode gap of 0.25 mm, which corresponds to an energy consumption of 2.69 Kwhr/kg. This cell is not easily scaled up for industrial production of propylene oxide.

A bipolar flow cell was used by King et al. [10] to study the production of propylene oxide. The cell consisted of vertical rows of electrically conductive rods, separated from one another by a small gap. The electrolyte was fed to the top rods, flowed downwards over the vertical rows and was collected from the bottom rods for recirculation. The gaseous reactant, propylene, was passed up the the space between the vertical rows, in continuous contact with the electrolyte film. The cell was operated at atmospheric pressure. The current efficiency for propylene oxide in this cell was between 35-76 percent and the energy consumption was estimated in the range of 3-9 Kwh/kg. The temperature varied from $5\text{-}32^\circ\text{C}$. The general conclusions were that by increasing the temperature and the current at uncontrolled pH the current efficiency for propylene oxide decreases.

Boussoulengas et al. [11] have studied the synthesis of propylene oxide in a bipolar trickle tower. The cell consisted of a tower packed

with several layers of carbon raschig rings each separated by a plastic screen. A mixture of sodium bromide solution and propylene gas trickles down over the packing as a thin film. When a potential is applied across the tower, bipolarity is induced in each element of packing. Current efficiency for propylene oxide of up to 97.5 percent was reported at a conversion of propylene of 74.8 percent with 39 layers of Raschig rings and an electrolyte temperature of below 10°C. This corresponds to a space time yield of 6.48 kg/hr m³ and an energy consumption of 2.92 Kwh/kg. One of the limitations of this process is that the tower is susceptible to flooding and this drastically reduces electrical efficiency.

In the synthesis of propylene oxide, one of the major limitations is the relative low solubility of propylene in the metal halide solution. To overcome this problem, the system can be operated at elevated pressures. Bejerano et al. [12] studied the electrochemical formation of propylene oxide in a cell containing a set of bipolar graphite rods, using an aqueous sodium bromide solution, at pressures of up to 5 atmospheres. Their general conclusions were that by increasing the electrolyte flow and the pressure, the current efficiency for propylene oxide increases, but by increasing the applied voltage and the electrolyte concentration the current efficiency for propylene oxide decreases. At a pressure of 5 atm., with an electrolyte flow rate of 1.3×10^{-4} m³/s and a temperature of 30°C the space time yield was 156.6 kg/hr m³ with a corresponding energy consumption of 9.14 Kwh/kg.

Fleischmann et al. [13] have studied the synthesis of propylene oxide using a bipolar packed bed cell. The cell consisted of a packed

bed made up of a mixture of conducting and non-conducting particles. The conducting particles become bipolar by using dilute electrolyte in the cell and applying sufficient voltage gradient between the contact electrodes so as to overcome the resistance drop in the electrolyte. Glass particles coated with graphite were used as the conducting medium, and the non-coated particles as the non-conducting medium, all particles having a diameter of 0.5 mm. The energy consumption of such a cell was found to be high, in the range of 43-52 Kwh/kg of propylene oxide.

Robertson et al. [14] designed an electrolysis cell consisting of a rolled up electrode and separators known as the Swiss Roll cell and studied the synthesis of propylene oxide in this cell. Specifically, with an anode area of 0.16 m^2 , a current efficiency for propylene oxide of 81 percent was obtained with a power consumption of 2.83 Kwhr/kg.

Recently, Alkire et al. [15] have investigated the feasibility of synthesizing propylene oxide by alternating current electrolysis in a batch monopolar cell. They found that the current efficiency for propylene oxide was independent of sodium bromide concentration but dependent upon the current frequency. Specifically, the current efficiency was 22 percent at a frequency of 1 Hz and a current density of 1750 A/m^2 . The current efficiency decreased to 2 percent at 40 Hz.

None of the above reactor designs have been applied to the commercial production of propylene oxide.

2.2 Electro Synthesis of Propylene Oxide

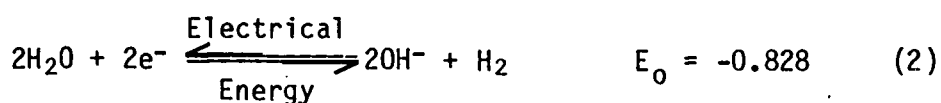
In the electrochemical production of propylene oxide, propylene and a metal halide electrolyte are introduced in the vicinity of the

anode. The electrolyte is oxidized electrochemically at the anode to generate free halogen which reacts with the propylene in the presence of water to form the halohydrin derivative of propylene. Simultaneously, water is reduced at the cathode forming hydroxyl ions and hydrogen gas. The hydroxyl ions produced react with the halohydrin of propylene to form propylene oxide within the cell. The reaction sequence is described in the following review.

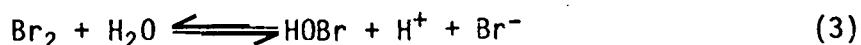
Initially, bromide ions are discharged at the anode. The stoichiometry of this reaction is [16]:



Similarly at the cathode, hydrogen and hydroxyl ions are produced. The stoichiometry is [16]:



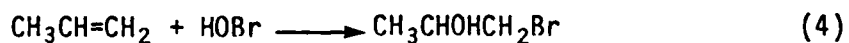
The bromine generated hydrolyzes in the vicinity of the anode forming hypobromous acid as follows:



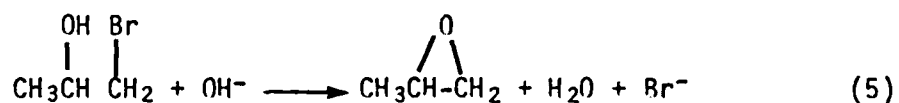
with the equilibrium constant for this reaction [19], $K = 9.6 \times 10^{-9}$
where

$$K = \frac{[\text{HOBr}][\text{H}^+][\text{Br}^-]}{[\text{Br}_2]}$$

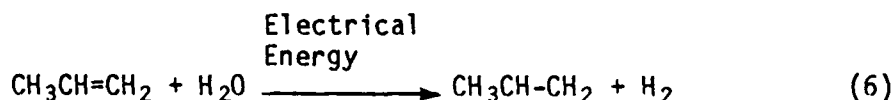
The hypobromite formed in Step (3) from the electrogenerated bromine reacts with propylene to form propylene bromohydrin



The propylene bromohydrin reacts with the hydroxyl ion generated at the cathode to produce the desired propylene oxide



The overall reaction is



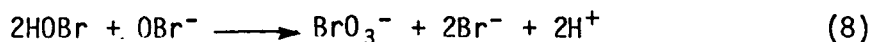
The desired cell reaction utilizes intermediates from both the anode and the cathode. Since the halogen species does not appear in the overall reaction, other halogens can be used, however iodine reaction with

propylene is slower than bromine [17], also the formation of propylene oxide from bromohydrin is more rapid than from chlorohydrin [18].

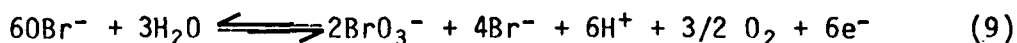
There are a variety of possible loss reactions suggesting that the overall performance of the cell depends on the balance between electrochemical, chemical and transport rate processes. The bromine formed can be hydrolyzed to form hypobromous acid



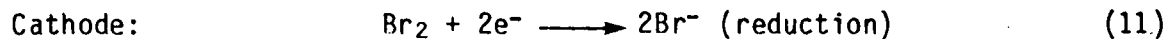
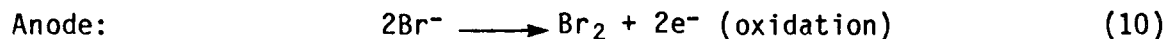
which can further be hydrolyzed to form anions that can disproportionate to form bromate



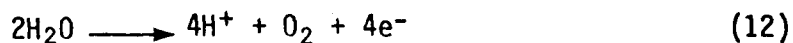
Bromates are also formed by anodic oxidation of the hypobromite



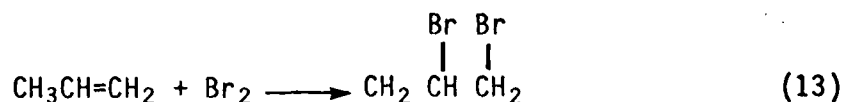
Both reactions 8 and 9 are significant at high concentration of hypobromite. Under good mixing conditions, the transfer of bromine to the cathode where it may be reduced provides another possible loss reaction.



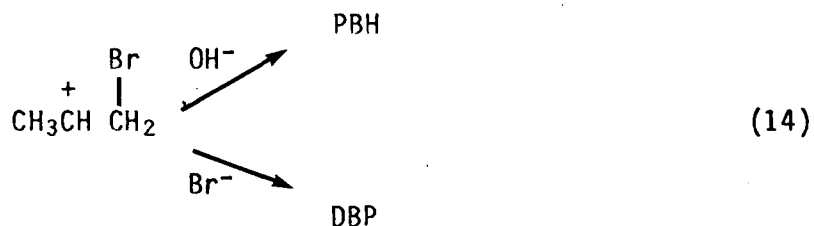
Another undesirable reaction at the anode is the generation of oxygen.



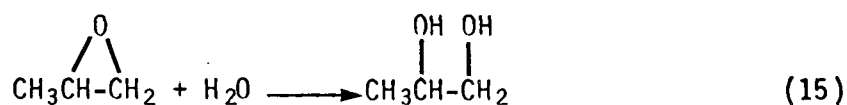
Side reactions involving propylene also occur since the carbonium intermediate is available for nucleophiles other than water. The major by-product is dibromopropane



The formation of propylene bromohydrin (PBH) and dibromopropane (DBP) proceed via the same cationic intermediate



It is obvious from Equation 14, that the achievement of a high selectivity for propylene oxide would require low bromide concentration and high hydroxyl ion concentration. However, the pH value must not exceed an optimum value otherwise the saponification of the propylene oxide to the glycol would become predominant

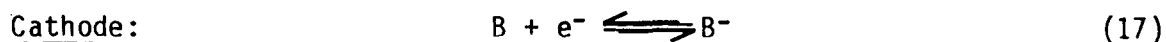


Reactions 8, 9, 11, 12, 13 and 15 are damaging to the current efficiency for propylene oxide.

Extensive work has been done on the hydrolysis of bromine, the analysis and the formation of hypobromite and bromate [19,20]. The reaction of bromohydrin formation has been studied by Goguslavskaya [21], Atkinson and Bell [22] and De La Mare [23].

2.3 Electrochemical Cell

Figure 2 represents an idealized electrochemical cell. It consist essentially of two electrically conducting electrodes immersed in a bath of electrically conducting liquid known as the electrolyte. The generalized electrode reaction can be written as follows:



The overall reaction is



The electrodes are connected outside the bath to the terminal of a dc power supply. When an emf of a sufficient magnitude is applied, electron transfer occurs between the electrode and the liquid, resulting in a flow of electricity in the external circuit and chemical reactions at each electrode. By convention, the current flow external to the cell

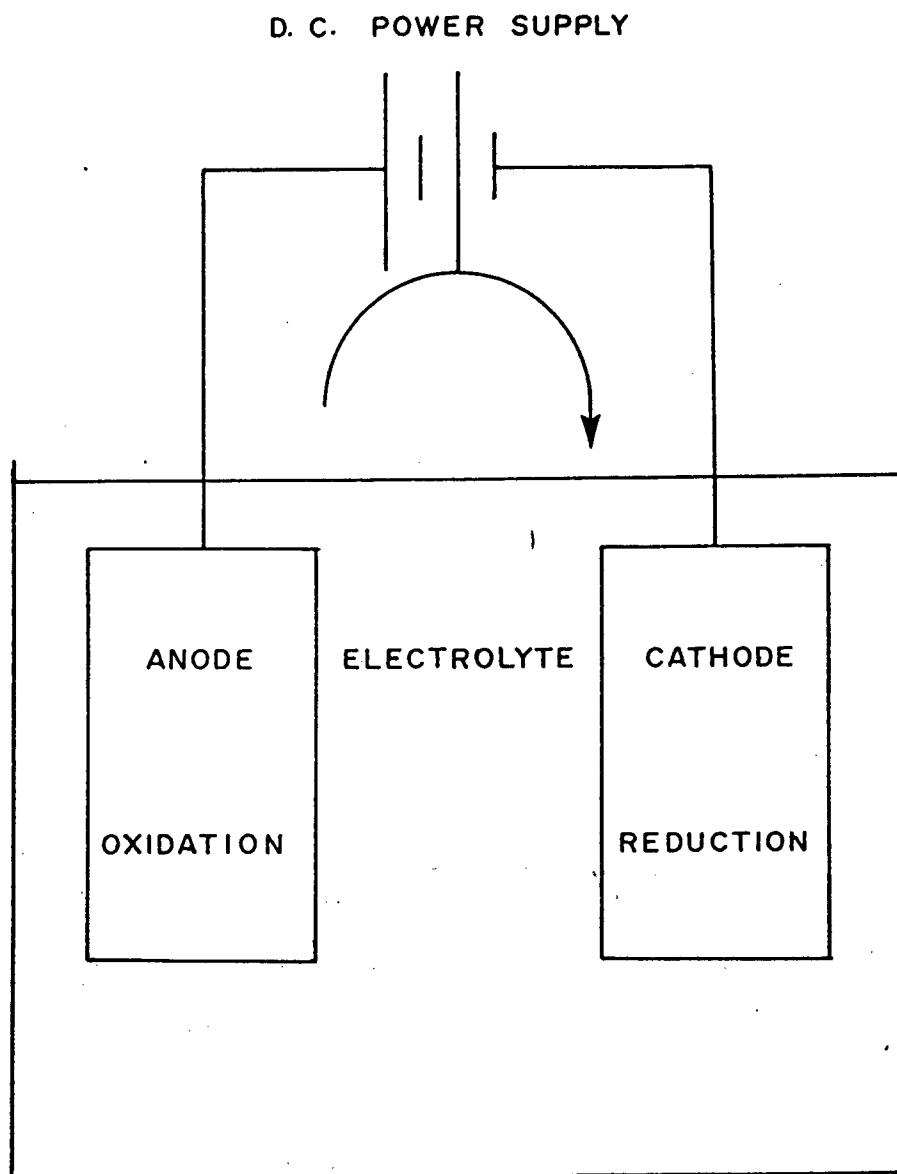


FIGURE 2: A SIMPLE ELECTROCHEMICAL CELL

is from the anode to the cathode. The anodic reaction is called the oxidation reaction, that is, the loss of one or more electron with a corresponding increase in the oxidation state of the species. The cathodic reaction is the opposite - a reduction reaction or a gain of electron with a decrease in the oxidation state of the reactant.

The major characteristic of the cell is the potential difference between the anode and the cathode. Electrode potentials are based on a reference electrodes. The primary reference is the hydrogen electrode with gaseous hydrogen at a pressure of 1 atmosphere. Reactants more readily oxidizable than hydrogen have a negative potential with respect to it; those more readily reduced are positive with respect to hydrogen. The potentials of various electrode reaction with regard to hydrogen are listed in reference [16].

2.4 Bipolar Reactor

Electrochemical reactors employing solid plate bipoles have been used in the industry to produce compounds such as sodium chlorate and adiponitrile. However, for certain electrochemical processes, these solid bipole reactors are inadequate. Such processes include those in which the reactive species are in relatively low concentration or interphase mass transfer is slow and where intimate contact between anode and cathode product is necessary for process efficiency. A particular difficulty with solid plate bipole electrode in such applications is their relatively low specific electrode area, which

allows only low space time yields and gives high capital cost for process plant.

Several authors ([10], [11], and [13]) have utilized different bipolar electrode reactor configurations to overcome the problem mentioned above, but their reactors suffer from limitations such as excessive voltage, high energy consumption, low space time yields and difficulties with scaling up to industrial capacities.

In this work, a bipolar electrochemical reactor consisting of porous carbon matrices and having a cocurrent flow of the electrolyte and a gas was employed. A schematic diagram of a vertical cross section of the electrochemical bipolar reactor used for the synthesis of propylene oxide is shown in Figure 3. The reactor is comprised of six electrically conducting matrix electrode beds of graphite particles sandwiched between two monopole electrodes. The matrix beds adjacent to the monopole electrodes are in electrical contact with them. Each monopole electrode has an inlet and an outlet opening through which the feed enters and the product leaves the reactor. The entire assembly is compressed so that each matrix electrode bed acts as a singular electrically conducting body which has a high surface area and can allow a liquid and a gas to pass through it. Compression of graphite particles in the matrix electrode beds results in higher conductivities than when the particles are loose, as illustrated by Figure 4 and Appendix 1.

The matrix electrode beds are separated from each other by means of an ion conducting diaphragm which was treated with a wetting agent so

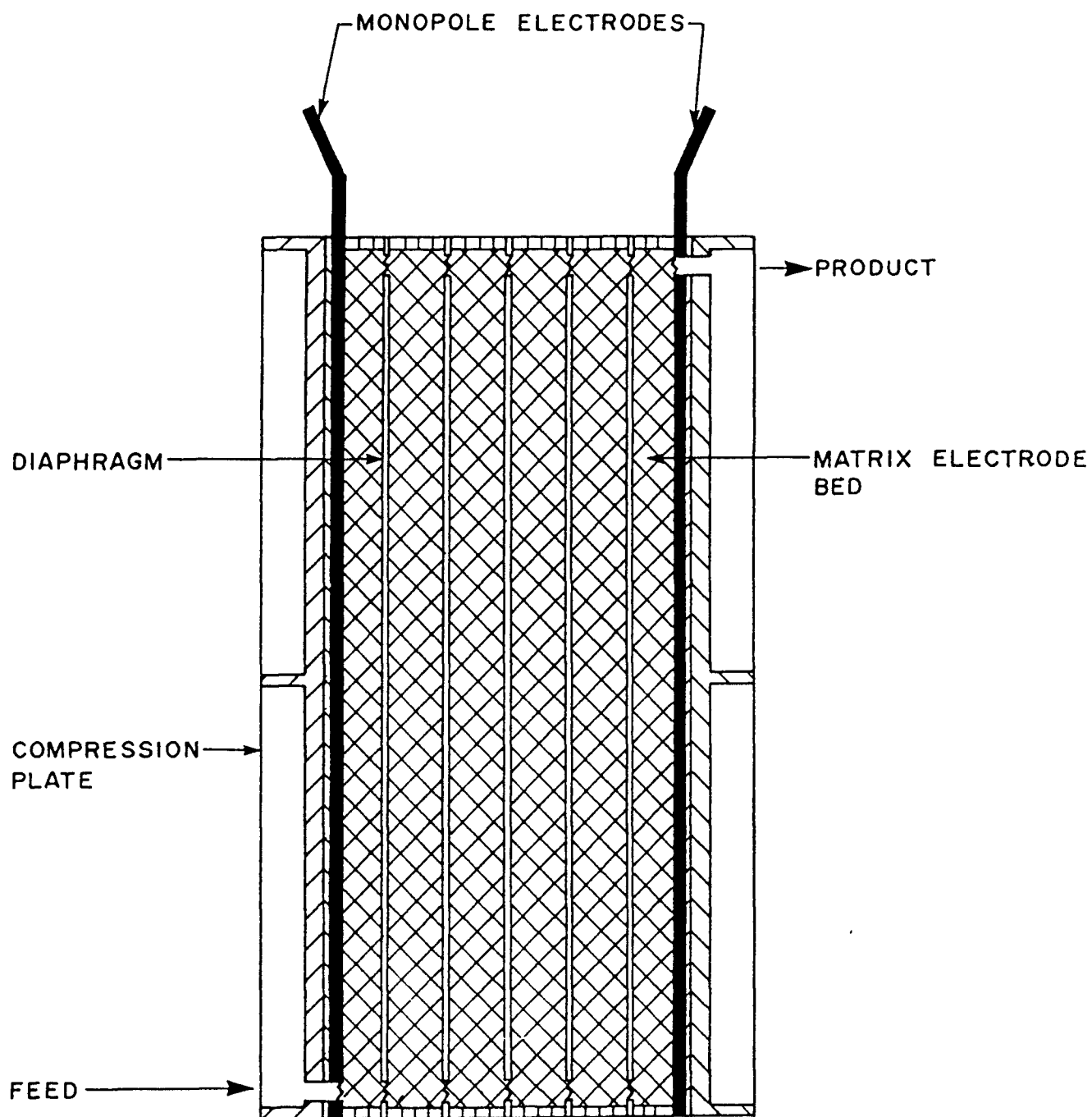


FIGURE 3: VERTICAL CROSS SECTION OF A BIPOLAR REACTOR

THE EFFECT OF THE DEGREE OF BED COMPRESSION
ON THE POTENTIAL DROP AT 10 AMPERES

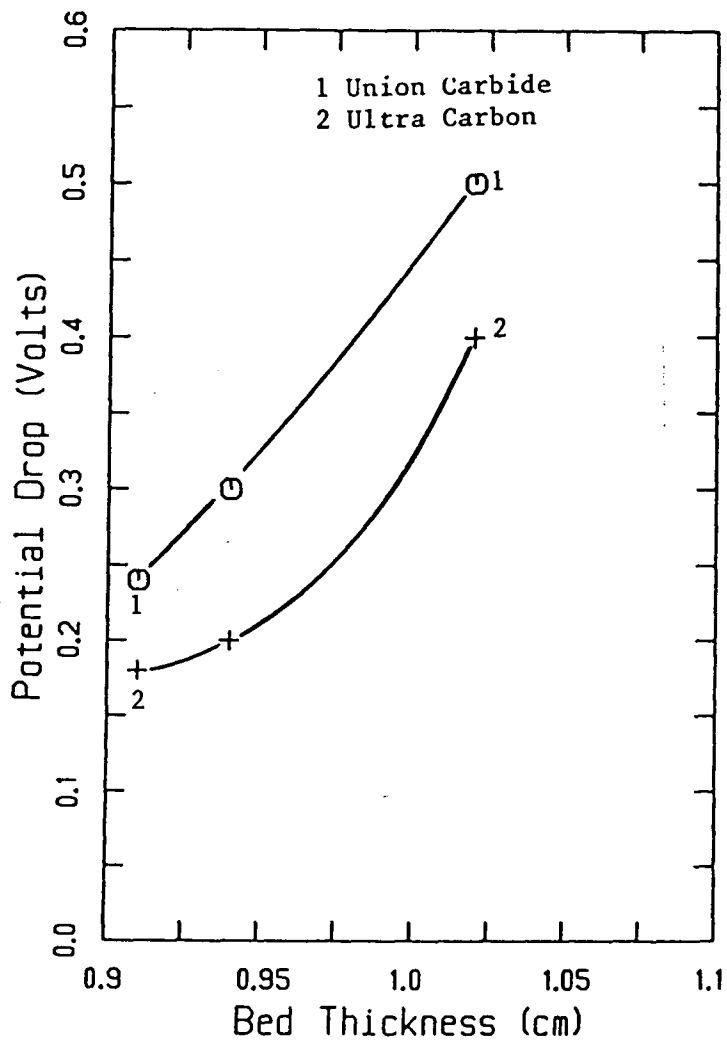


FIGURE 4

Conditions

Graphite Particle Size = 1.168 - 1.68 mm
Cross Section Area = 19.05 x 2.54 cm²

that it will retain electrolyte over gas. The holes are cut in the diaphragm to provide an inlet and an outlet passageway at the bottom and the top ends of each of the matrix electrode beds. The diaphragm was held in place by means of insulating (four Durabla and one neoprene rubber) gaskets which also form the side walls of the reactor (Figure 3). The neoprene rubber provides the resiliency necessary to sufficiently compress the matrix electrode beds to the degree needed for higher matrix electrode bed conductivities.

When a potential is applied across the monopole electrodes and a mixture of appropriate conductivity passed between the monopole electrodes through the matrix electrode beds, each of the matrix electrode beds between the monopoles will act as a bipole electrode.

Figure 5 represents a plot of electrode potential versus distance across the bipole matrix electrode bed. For a given electrochemical reaction, because of the variation of potential over distance, the matrix electrode bed has three distinct areas: the anode region, the cathode region and the unreactive region between the anode and the cathode region. In the unreactive region, the electrode potential is insufficient to drive either the anode or the cathode reaction.

The advantages of this reactor are:

- a) The electrode matrix bed has high specific electrode area which gives high transfer rates for the bromide ion to the anode surface and can sustain high superficial current densities for dilute reactant species.

PLOT OF ELECTRODE POTENTIAL VERSUS
DISTANCE ON A MATRIX ELECTRODE

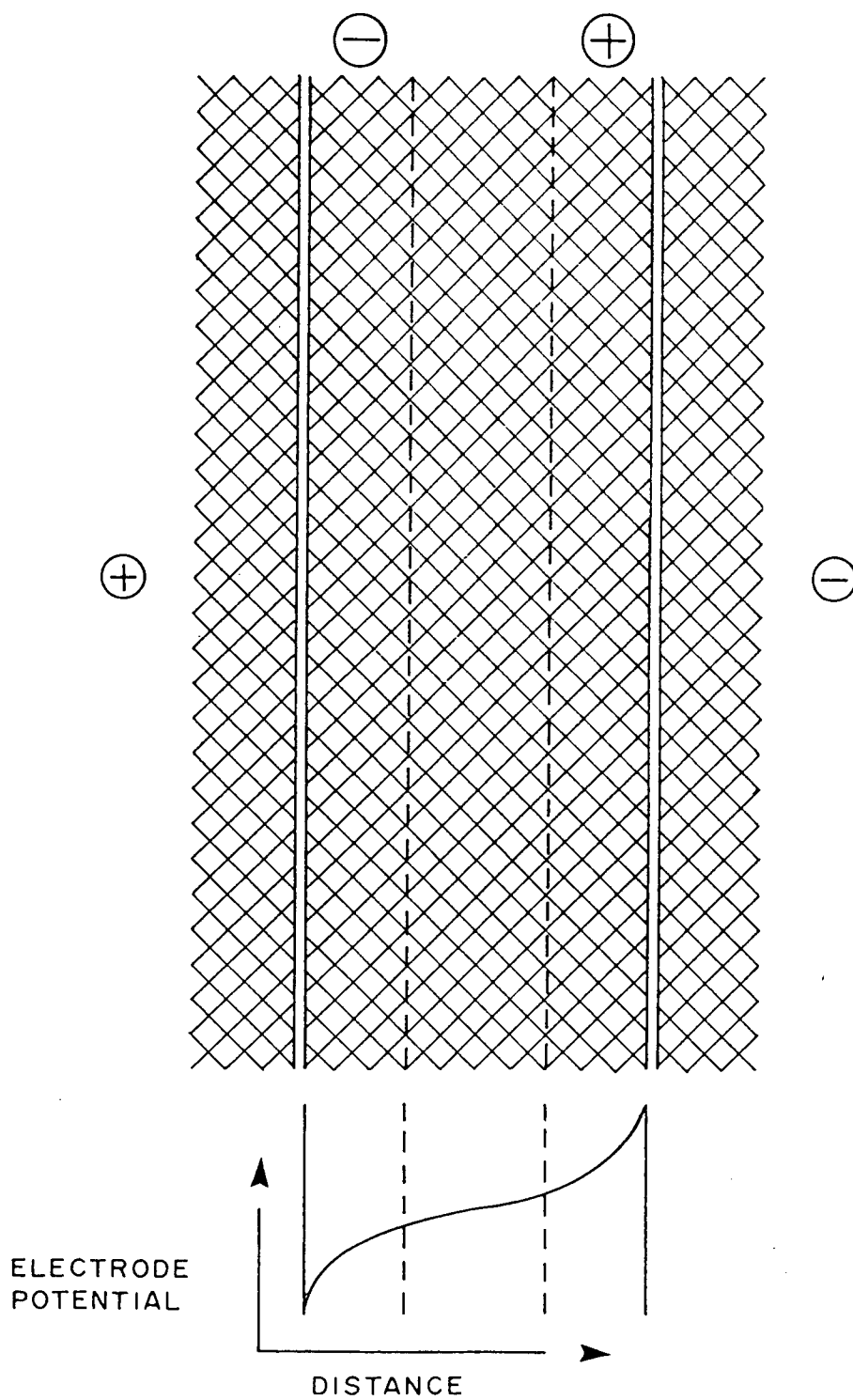


FIGURE 5

- b) It increases the possibility of intimate mixing between the anode and the cathode products within each separate bipole matrix. In the case of the production of propylene oxide this is important because both the anode and the cathode product take part in the reaction.
- c) This reactor gives high gas liquid interfacial area and mass transfer rates for propylene into the electrolyte solution and also decreases the effective electrolyte conductivity which permits the use of thin electrode beds for high space time yields.

CHAPTER 3

OBJECT

The object of this work is to experimentally investigate the possibility of producing propylene oxide with high space time yield and high selectivity in an electrochemical bipolar trickle bed reactor.

The effect of the following variables are to be studied on the space time yield and the selectivity of propylene oxide:

1. Superficial current density
2. Sodium bromide electrolyte concentration
3. Electrolyte flow rate
4. Propylene gas flow rate
5. Reactor outlet temperature
6. Matrix electrode bed thickness
7. Different graphite types (Union Carbide and Ultra Carbon).

The work involves an initial experimental assessment of the effect of the first five variables mentioned above on the space time yield for propylene oxide. Further exploration of the variables that have the greatest positive effect* on the space time yield for propylene oxide were then investigated.

*Positive effect means by increasing the independent variable the dependent variable also increases.

CHAPTER 4

APPARATUS, METHOD AND ACCURACY

4.0

One electrochemical reactor was used in this work. It was a laboratory unit made to operate in a continuous manner with the sodium bromide electrolyte feed rate ranging from 100 to 300 cm³ per minute and the propylene gas feed rate ranging from 100 to 2000 cm³ per minute at standard temperature and pressure. This reactor was built to operate at atmospheric pressure. The reactor along with the ancillary equipment will be described separately.

4.1 Apparatus

Figure 6 represents a line diagram of the equipment used to study the synthesis of propylene oxide in a bipolar fixed bed reactor, and Figure 7 shows photographs of this apparatus. The reactor employs two monopolar electrodes constructed from platinized titanium 1/8 of an inch thick and is charged with graphite particles ranging in size from 1.168 to 1.68 mm. The reactor is fed from the bottom with sodium bromide electrolyte and propylene gas flowing cocurrently through the matrix electrode beds which are separated by polypropylene felt diaphragms. Figure 8 shows the side elevation and top elevation of a bipolar reactor. The electrolyte is pumped from a 40 litre tank. The electrolyte leaving the feed tank divides into two streams; one is recycled back to the feed tank through a constant temperature bath while

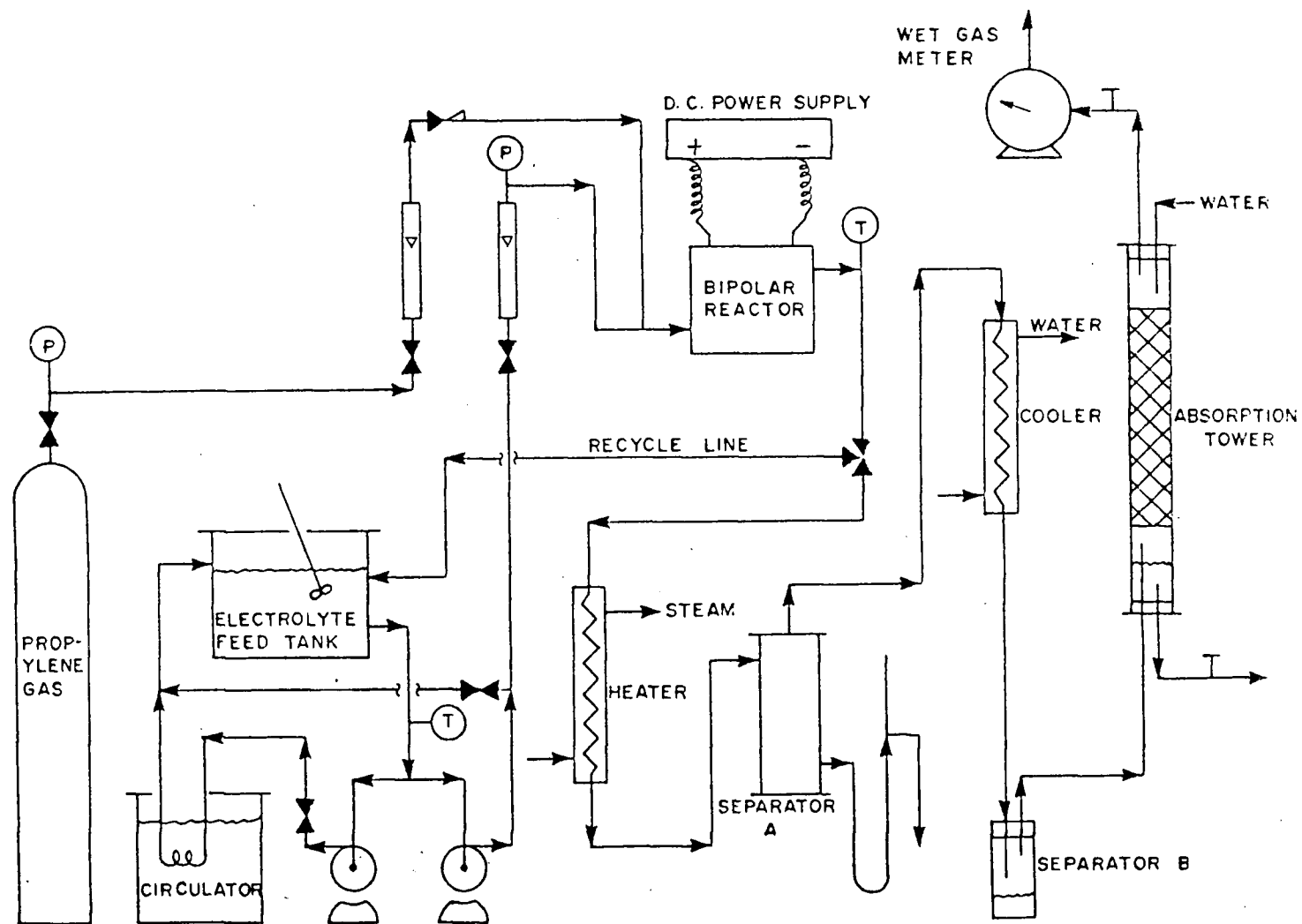


FIGURE 6: APPARATUS FOR THE SYNTHESIS OF PROPYLENE OXIDE

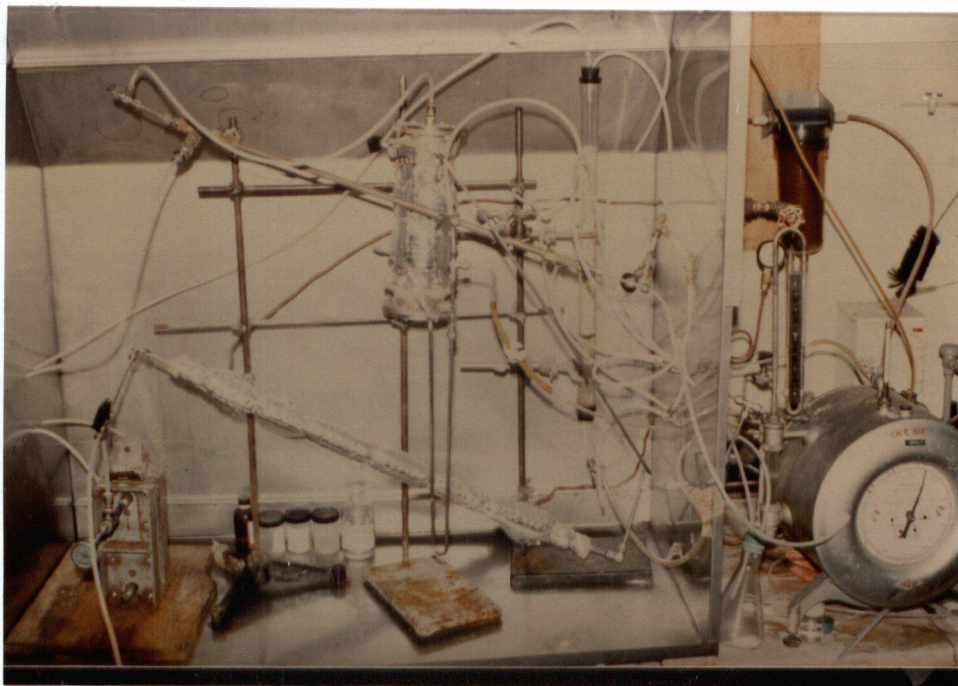
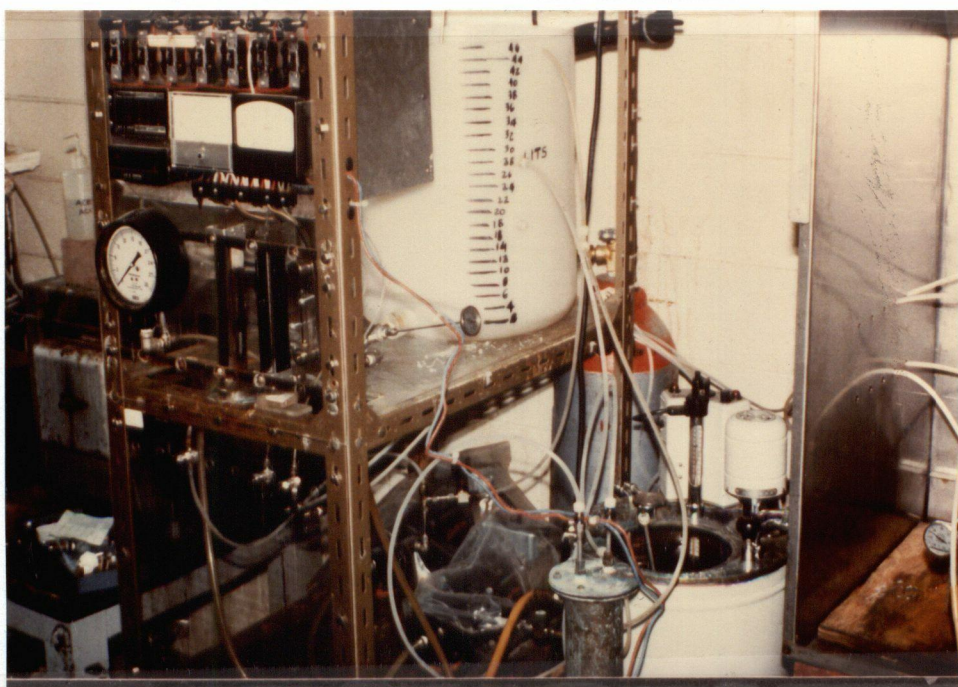


FIGURE 7: PHOTOGRAPHS OF THE APPARATUS FOR THE SYNTHESIS OF PROPYLENE OXIDE

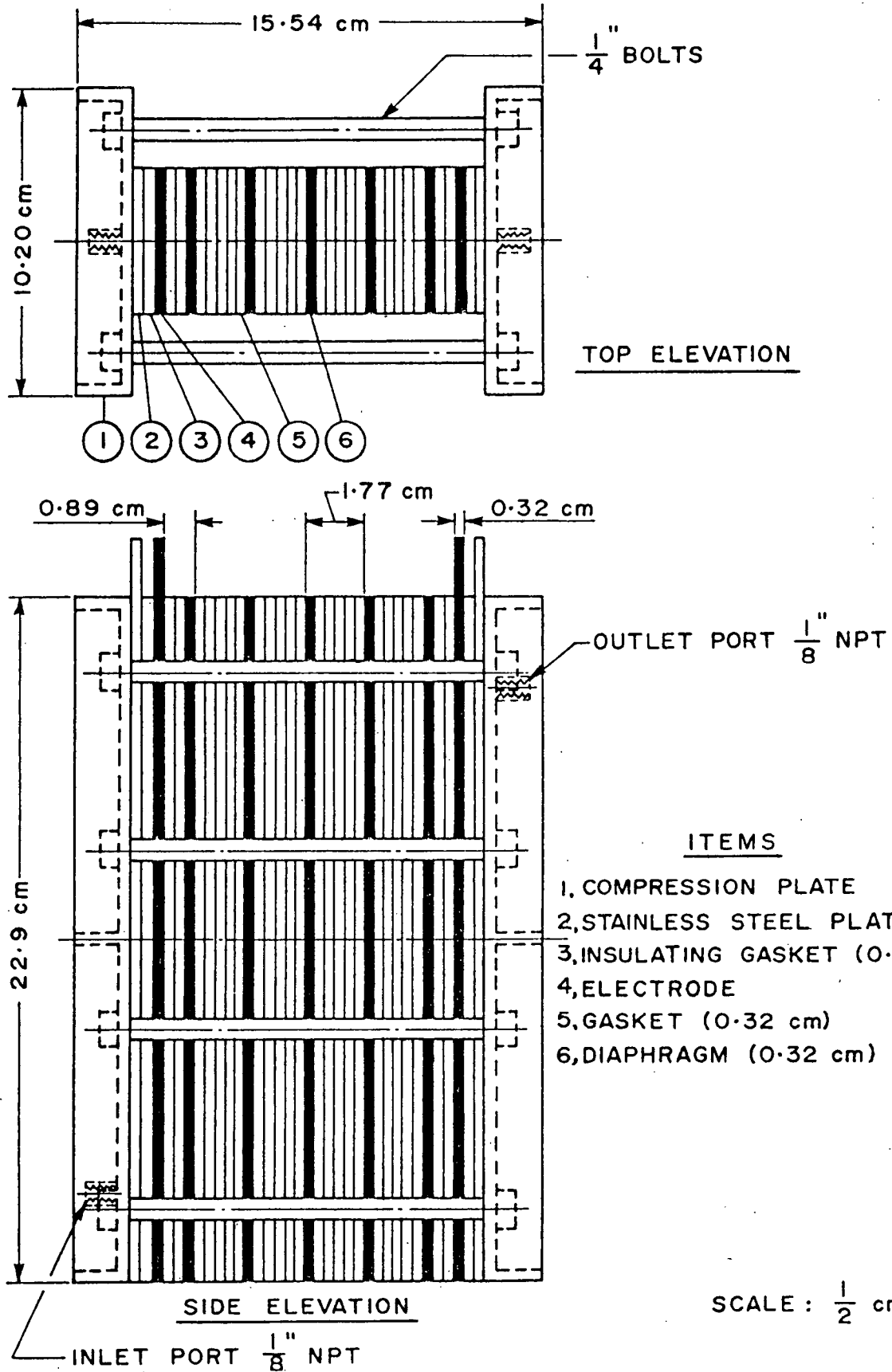


FIGURE 8: SIDE ELEVATION AND TOP ELEVATION OF A BIPOLAR REACTOR

the other is fed to the bipolar reactor. The propylene gas is delivered from a propylene gas cylinder at a line pressure of 22.7 pounds per square inch absolute. The gas mixes with the electrolyte before entering the reactor near the anode. The flows of the sodium bromide electrolyte and the propylene gas to the reactor are measured by rotameters and controlled manually by needle valves. The mixture leaving the reactor can be recycled into the feed tank or passed through a single pass heat exchanger and into the separator. The liquid is disposed of to the drain from the bottom of the separator and the gases which leave from the top are passed through a single pass condenser. The condensate, is collected and analysed. The uncondensed gases enter the absorption tower at the bottom and water is fed from the top of the tower. The liquid leaving the bottom of the tower is sampled before being disposed of to the drain. Flow rate of gases leaving the top of the tower is measured and a sample obtained for analysis.

Power for the reactor is supplied by two direct current power supply connected in series with a maximum power output of 2.25 kW and capable of either current or voltage control up to 30 ampere or 75 volts.

All parts in contact with the electrolyte are made of either stainless steel, nylon, glass, polyethylene or plexiglass. Some corrosion was observed around the stainless steel parts.

The specifications of the parts for this apparatus are given in Appendix 2. Some of the important dimensions of the reactor are given in Table 1 and Figure 9. Photographs of the reactor are shown in Figure 10.

Table 1
Dimensions of an Electrochemical Bipolar Reactor

Compression plates	22.9 cm long x 10.2 cm wide (iron)
Number of cells	5
Monopole electrodes	38 cm long x 5.1 cm wide (platinized titanium)
Particles	Range 1.168 - 1.68 mm (graphite)
Superficial area per cell	48.4 cm ²
Electrode bed thickness	Range 3.1 - 8.6 cm
Diaphragm	22.9 long x 5.1 cm wide (Polypropylene felt)
Type and weight of polypropylene felt	National felt 510 g/m ²

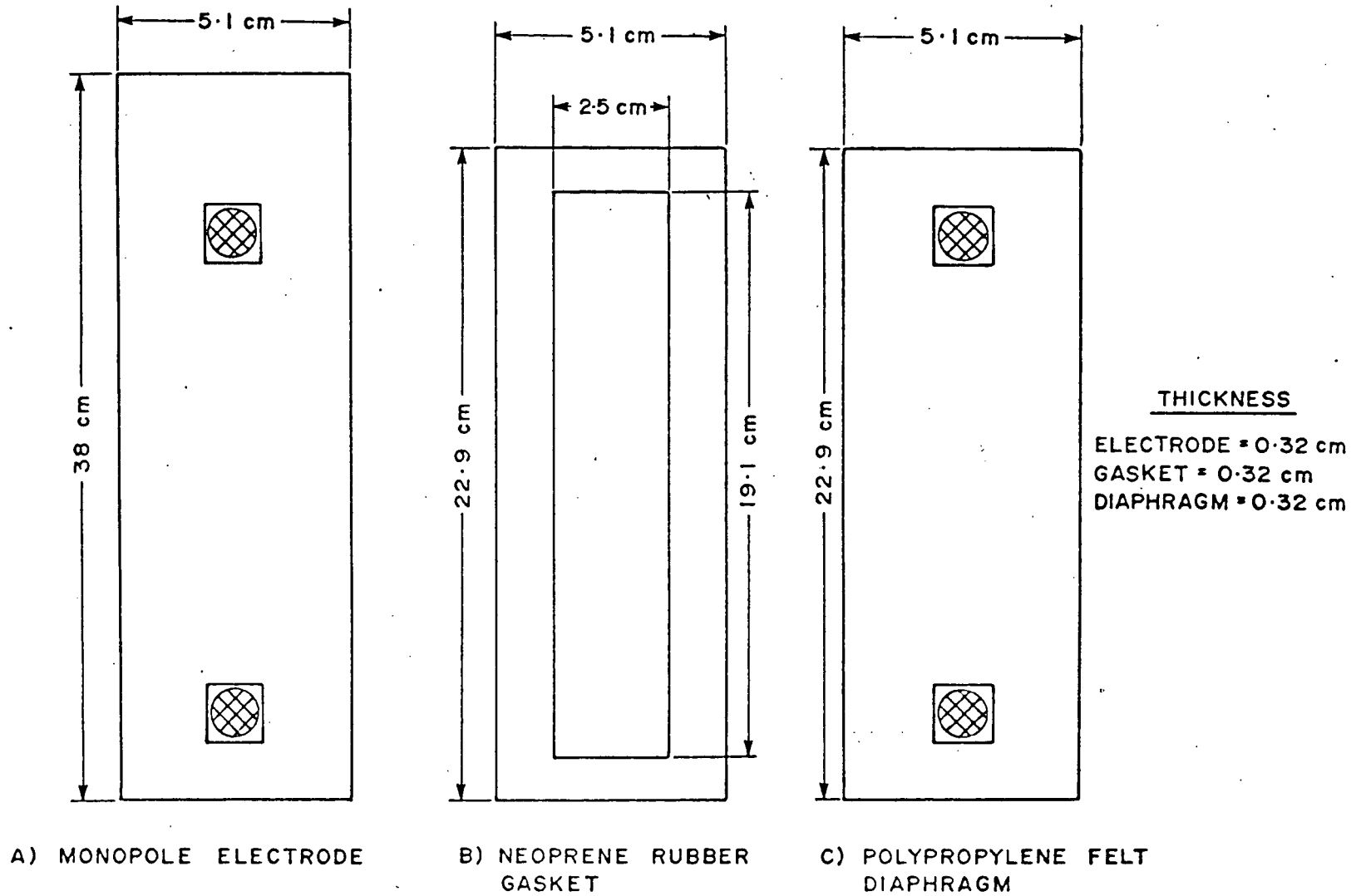
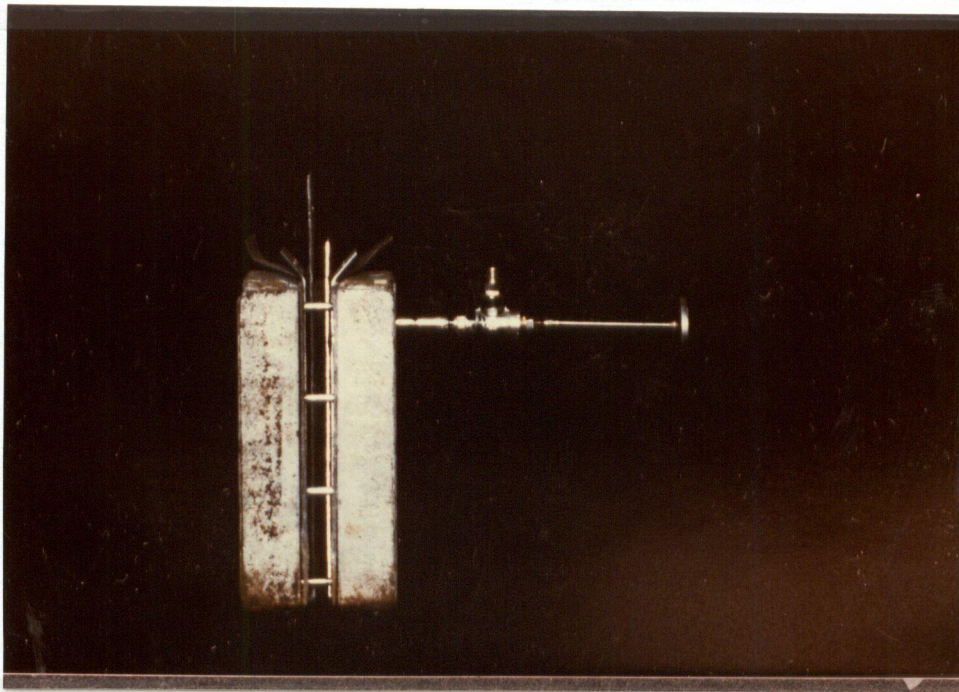


FIGURE 9: DIMENSIONS OF THE ELECTRODE, GASKET AND DIAPHRAGM

SIDE VIEW



FRONT VIEW

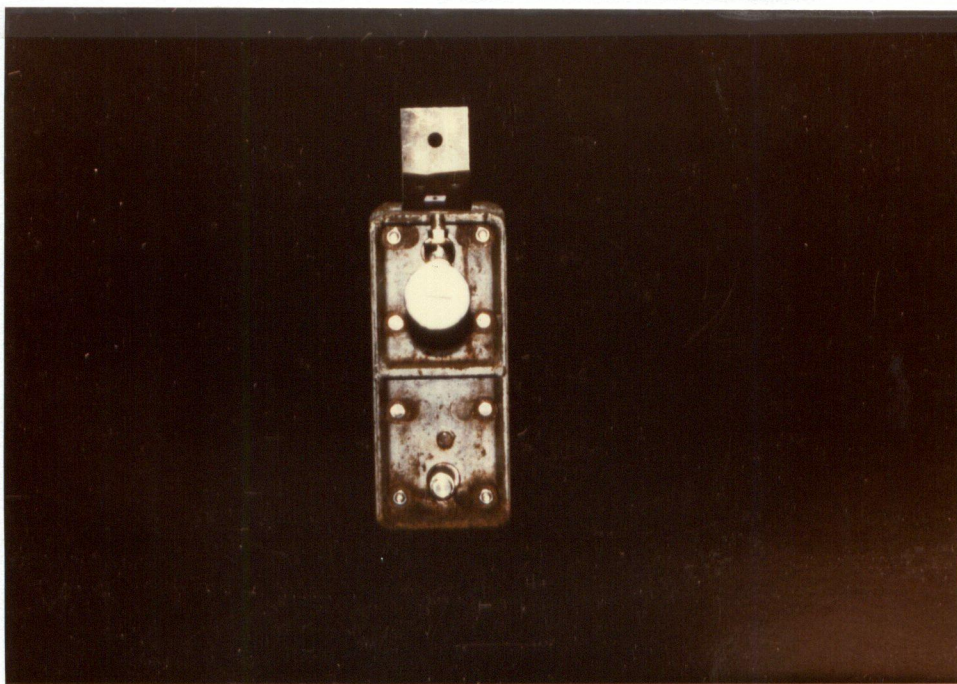


FIGURE 10: ELECTROCHEMICAL REACTOR USED FOR THE SYNTHESIS OF PROPYLENE OXIDE

The graphite used was obtained from two different suppliers, Union Carbide and Ultra Carbon. Particles ranging in size from 1.168 - 1.68mm were obtained by sieving. This material was pretreated by soaking in 1 molar hydrochloric acid overnight, washing in distilled water, soaking in approximately 1 molar sodium hydroxide for 8 hours and then rinsing several times in distilled water.

Scanning electronmicrographs of typical particles, shown in Figure 11 and 12, illustrate that the graphite particles were of irregular shape with a rough, porous, pitted surface.

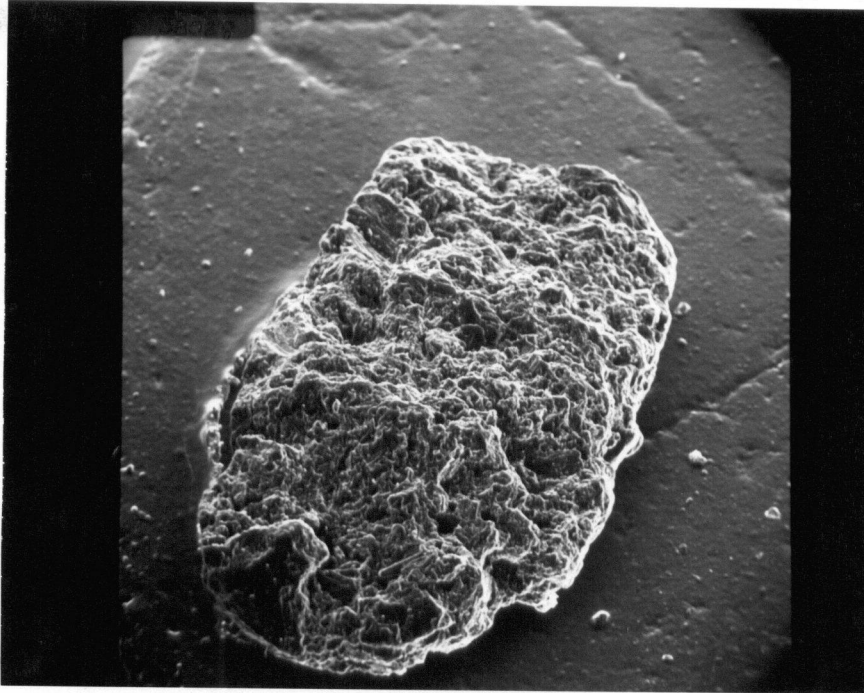
The entire apparatus was installed in a fume hood for safety reasons which included both explosion danger and toxicity of propylene, dibromopropane and propylene oxide.

4.2 Method

First the electrolyte, gas and water rotameters were calibrated. The calibration curves are presented in Appendix 3.

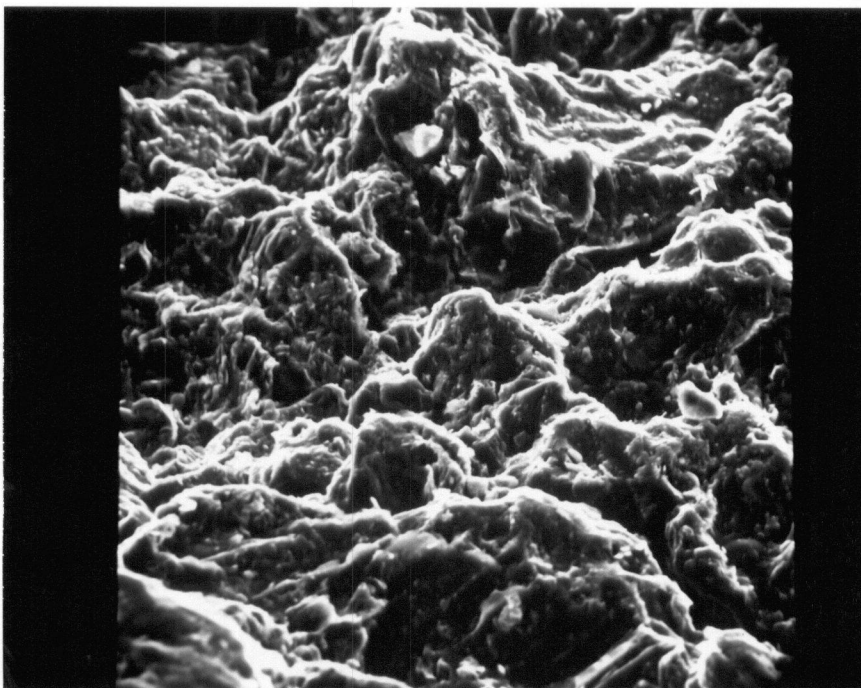
The electrolyte solution was prepared from 99 percent pure sodium bromide (BDH Company) and filtered, deionized water. The water was first filtered in the AMF Cuno filter, model number 1 Mi and then deionized in a Calgon Corporation cartridge deionizer.

Propylene oxide concentration was monitored on a gas-liquid chromatograph (Varian Model 1400) with a flame ionization detector. A 12 ft. column was used. The packing was Carbopak C 80/100 mesh coated with 0.2% CW 1500. The gas phase carrier was helium. A microsyringe was used to inject a ten microliter sample. Analysis of propylene was carried out at 80°C. Calibration samples were prepared by pipetting a



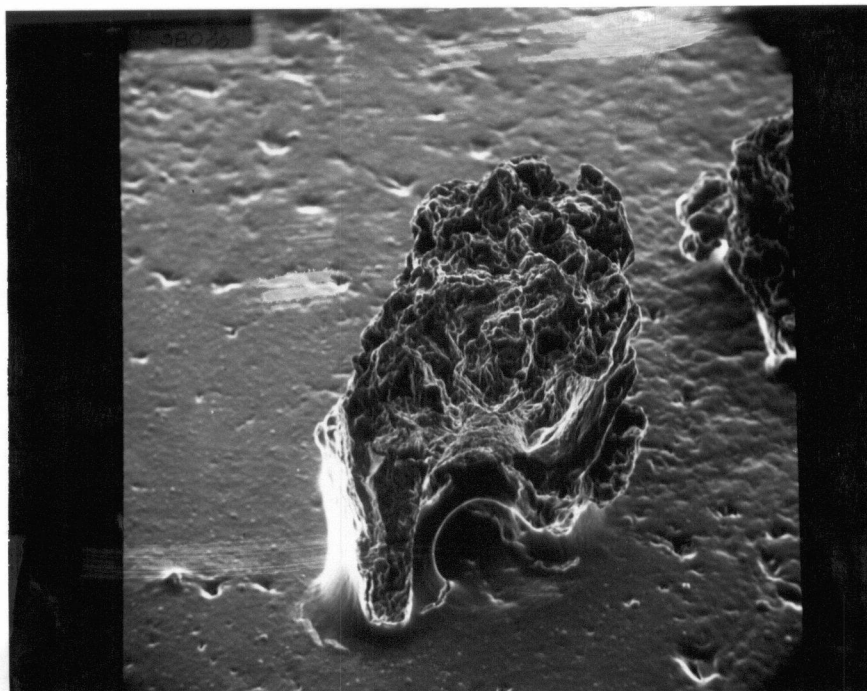
x 26

Particle Size Range 1.168 - 1.68 mm



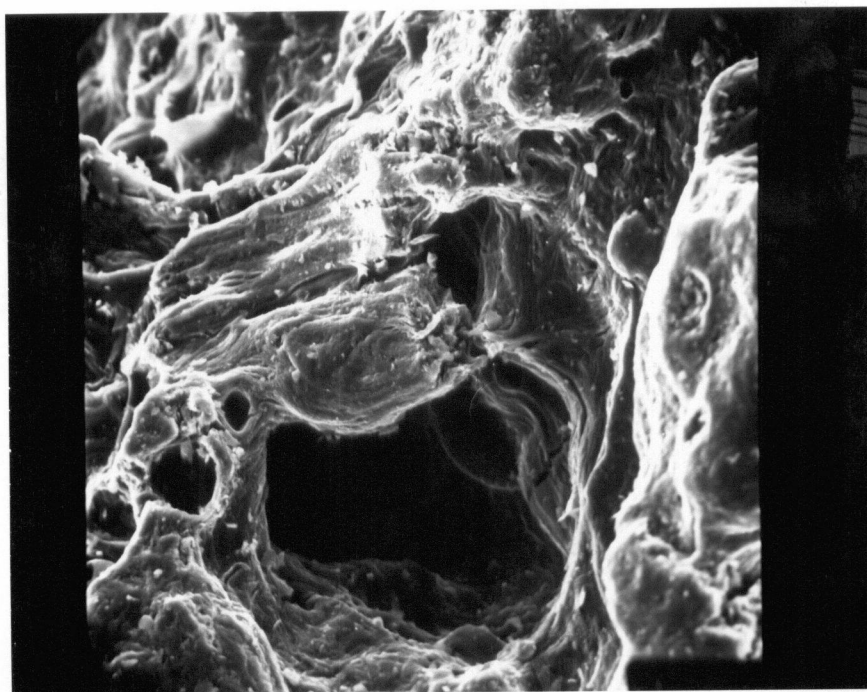
x 300

FIGURE 11: SCANNING ELECTRONMICROGRAPHS OF TYPICAL UNION CARBIDE GRAPHITE PARTICLES



x 26

PARTICLE SIZE RANGE 1.168 - 1.68 mm



x 300

FIGURE 12: SCANNING ELECTRONMICROGRAPHS OF TYPICAL ULTRA CARBON GRAPHITE PARTICLES

known volume of propylene oxide (BDH Company) into a 100 ml volumetric flask containing distilled water. Several samples of varying concentration were prepared. The calibration curve is shown in Figure D of Appendix 3.

Experimentation consisted of a series of runs in which measurements were made on the sodium bromide electrolyte and propylene gas feed rate, the electrolyte temperature entering the reactor, the pH of the electrolyte leaving the bottom of the separator, the electrolyte concentration, the water flow rate to the absorption tower, the reactor outlet temperature, the current to the cell, the voltage drop across the cell, the gas flow rate from the absorption tower, the volume of dibromopropane produced, the total volume and concentration of propylene oxide solution collected and the concentration of propylene oxide solution leaving from the bottom of the absorption tower.

To do the experiments, the electrolyte feed tank was first charged respectively with 0.2 molar and 0.5 molar sodium bromide solution. This solution was circulated through a circulator to control its temperature to the desired level, thereby controlling the reactor outlet temperature. The electrolyte flow rate through the cell was set between 100 and 300 cm³ per minute and the propylene gas flow rate to the cell was also adjusted between 100 and 2000 cm³ per minute (STP). The current through the cell was then set with the power supply in the current control mode.

The analysis for propylene oxide collected in the separator and leaving the bottom of the absorption tower was made on a gas-liquid chromatograph (Varian Model 1400). The hypobromite, bromite and bromate

concentration in the solution leaving the separator bottom were analyzed using the standard idiometric titration with ammonium sulphate (24). The technique is described in section 4.1 of Appendix 4. The dibromopropane forms a separate phase in the propylene oxide solution therefore was easily separated with a microsyringe or pipet. The dissolved dibromopropane in the solution leaving the separator bottom was determined by extracting with ether. This was done at an electrolyte concentration of 0.5 M and the value obtained was presumed to remain constant in contact with undissolved dibromopropane. The gas leaving the absorption tower is sampled through a tee with a Pressure Lok (Precision Sampling Corporation) gas tight syringe and analyzed using a gas chromatograph (Hewlett Packard Model 5710 A Gas Chromatograph) with a thermal conductivity detector. The gas phase carrier was Argon. The gas chromatograph used two columns; one containing molecular sieve which separates hydrogen, oxygen, nitrogen, methane and carbon monoxide and another containing Porapak Q which separates carbon dioxide. Up to five cubic centimetres of gas samples were injected.

A total of 167 runs were performed. The ranges of the operating variables covered in these studies are given in Table 2. Sample calculations are shown in Appendix 4. Table 0 of Appendix 8 shows data replicability.

4.3 Accuracy

Table 3 contain a list of the quantities measured, the method used and an estimate of the accuracy for each method.

Table 2
Range of Experimental Variables

Reactor Outlet Temperature	Electrolyte Flow	Gas Flow	Current	Electrolyte Concentration	Electrode Bed Thickness	Inlet Pressure	Particle Size
Degrees Centigrade	cm ³ /min	cm ³ /min STP	Amps	Moles/litre	cm	Atm. Absolute	mm
30-60	100-300	100-2000	2-13	0.2-0.5	3.07-8.57	1.41-2.22	1.168-1.68

The maximum degree of uncertainty in the calculated quantities are as follows:

Space time yield	= \pm 3.5%
Propylene balance	= \pm 8.5%
Dibromopropane balance	= \pm 6.5%
Current efficiency	= \pm 4%
Propylene oxide concentration	= \pm 3%
Rate of propylene oxide production	= \pm 3.5%
Propylene oxide selectivity	= \pm 15%
Propylene conversion	= \pm 6.5%
Propylene oxide yield	= \pm 8.5%
Total moles of hypobromite, bromite and bromate	= \pm 2%

Table 3
Estimates of Experimental Accuracy

Quantity	Range	Method	Accuracy
Current	2-13 Amps	Ammeter	± 3%
Graphite Particle Size	1.168-1.68 mm	Standard sieve	-
Bed Dimensions			
Thickness	3.07-8.57 cm	Vernier gauge	± .01 cm
Height	19.1 cm	Millimeter scale	± .1 cm
Width	2.5 cm	Millimeter scale	± .1 cm
Propylene Gas Flow	100-2000 cm ³ /min	Rotameter	± 5%
Electrolyte Flow	100-300 cm ³ /min	Rotameter	± 2%
Water Flow	190 cm ³ /min	Rotameter	± 2%
Reactor Outlet Temperature	30-60°C	Temperature gauge	± 1°C
Pressure	1.41-2.22 Atm	Marsh pressure gauge	± .1 Atm
pH	7-12	pH meter	± .05 pH
Product Volume	50-775 ml	Graduated cylinder	± 2%
Gas Flow from Tower	100-2000 cm ³ /min	Wet test meter	± 3%
Product Temperature	80-85°C	Mercury thermometer	± .5°C
Dibromopropane Solubility	.014-.016 cm ³ per 150 cm ³ of solution	Extraction with ether	± 5%
Voltage	14-65 volts	Voltmeter	± .5 volt
Iodine and Thiosulphate Titre	1-50 ml	50 ml burette	± .05 ml

CHAPTER 5

RESULTS AND DISCUSSION

5.0 General Considerations

In the electrochemical production of propylene oxide, the effectiveness of the reactor is measured by four figures of merit which are defined as follows:

$$(a) \text{ Space time yield (STY)} = \frac{\text{Propylene oxide production rate}}{\text{Total reactor volume}}$$

$$(b) \text{ Current efficiency (CE)} = \frac{\text{Rate of production of the desired species}}{\text{Rate of production of the desired species in stoichiometric equivalence to the total current in the process}}$$

$$CE = \frac{NZF}{I}$$

$$(c) \text{ Specific energy consumption (SE)} = \text{Energy required to produce a kilogram of the desired product.}$$

$$SE = \frac{ZFV}{CE} \text{ KJ/Kmole}$$

$$SE = \frac{ZFV}{3600 CE MW} \text{ Kwh/kg}$$

$$(d) \text{ Selectivity (SEL)} = \frac{\text{Propylene oxide yield}}{\text{Propylene consumption}}$$

where N = moles of desired product

F = Faraday's number

Z = Stoichiometric number of electrons transferred per mole of product

I = Current

V = Potential drop

MW = Molecular weight of desired product.

The figures of merit listed above are determined by the design and operating conditions of the reactor through their effects on the mass transfer, reaction rates, mixing between anode and cathode, reactor voltage, potential distribution and the extent of current by-pass across the bipole beds.

The major electrode reactions are the bromide ion oxidation to bromine at the anode (reaction 1) and the reduction of water to hydroxyl ion at the cathode (reaction 2). Both these rates increase with current density. The reaction rate is defined as:

$$r = ZFi$$

where r = reaction rate

Z = stoichiometric number of electrons transferred per mole of product

i = current density

The bromine generated reacts with the water present near the anode to generate hypobromous acid (reaction 3) which is then transported to the bulk of the solution. Here it reacts with the dissolved propylene to produce propylene bromohydrin (reaction 4). Improved transverse mixing should raise the space time yield and the current efficiency as it

brings together propylene bromohydrin and hydroxyl ion to form propylene oxide (reaction 5). However, the transfer of bromine to the cathode where it may be reduced is also promoted (reaction 11) but depends on the rate of bromine reaction with propylene. Improved transverse mixing is probably attained by increased gas flow rate and electrolyte flow rate. With higher gas flow rates, the effective conductivity of the mixture in the reactor decreases thereby lowering the ionic current by-pass. Thus, the higher gas flow rates should have a positive effect on the space time yield and current efficiency for propylene oxide. The increased gas flow rate would also reduce the effective bed thickness of the electrode. Active bed thickness under mass transfer control is defined as [27]:

$$\tau = (2K'\Delta V/i^*a)^{0.5}$$

where τ = maximum active thickness of a three dimensional electrode (cm)

K' = effective conductivity of the electrolyte (mho/cm)

ΔV = tolerable potential difference between competing reaction on the electrode (volts)

a = specific surface area (cm^2/cm^3)

i^* = real current density (A/cm^2)

With reduced active bed thickness the potential gradient rises in the active region. Higher potential gradients favour the generation of other by-products such as oxygen and bromates, which reduces the current efficiency for propylene oxide.

Increased electrolyte conductivity, which is related to concentration, would reduce space time yield due to higher ionic by-pass currents. Temperature also affects the electrolyte conductivity. The conductivity increases with increasing temperature. The relative rates of reaction are also affected by temperature. Increasing the temperature should raise the rates of reaction, however the rates of some reaction increase more than others. Thus, the increasing temperature could have either a positive or a negative effect on the space time yield for propylene oxide.

High gas flow rates and electrolyte flow rates would increase mass transfer rates of propylene and the bromide ion. Thus, the increased gas flow rate and electrolyte flow rate raises the space time yield for propylene oxide if the process is limited by the mass transfer of propylene or bromide ion. The process can also be limited by chemical kinetics. At low current densities the process would probably be limited kinetically whereas at high current densities the process is possibly limited by propylene transfer into the solution.

Improved mass transfer and transverse mixing would also prevent the formation of localized pH regions which in turn would increase the space time yield.

Specific energy consumption for propylene oxide is affected by electrolyte conductivity, which determines the cell potential, and the current efficiency of the desired product. The effective electrolyte conductivity is determined by three factors: the gas flow rate, the electrolyte temperature and sodium bromide concentration. With higher

gas flow rates the cell potential required to drive the current is larger, thereby increasing the specific energy consumption for propylene oxide. High temperature would yield a lower cell voltage and may give a reduced specific energy consumption for propylene oxide. Increased sodium bromide concentration should yield a higher specific energy consumption for propylene oxide due to higher ionic by-pass current, which reduces the current efficiency for propylene oxide, and increases the possibility of dibromopropane production rate via reaction 14.

Finally, the relative reaction rates and mass transfer rates of propylene and bromide ion affect the selectivity for propylene oxide. The relative reaction rates are determined by temperature, concentration of various reactants and the kinetic parameters. With increased gas and electrolyte flow rates, which effects the mass transfer rates, the selectivity for propylene oxide would vary depending on other factors such as current. At high current, the selectivity would probably decrease.

The above discussion indicates current, temperature, electrolyte flow rate, gas flow rate and electrolyte concentration would be expected to affect the figures of merit.

5.1 Preliminary Experiments

Prior to the main investigation of the electrosynthesis of propylene oxide using a bipolar reactor, preliminary studies were undertaken to determine the limitations of the equipment.

Early experiments were done to determine the minimum reactor outlet temperature which could be attained at a propylene gas flow* of 100

cm³/min and an electrolyte flow rate of 100 cm³/min. This value was determined to be 30°C.

The maximum flow capacity of the reactor was 2000 cm³ per minute* of propylene with 300 cm³ per minute of electrolyte. At these flow rates, the pressure drop in the system was 1.22 atmospheres. Raising the gas flow above 2000 cm³ per minute or the electrolyte flow over 300 cm³ per minute raises the pressure drop in the system to the extent that the flows could not be controlled at the desired rate. Increasing the propylene flow beyond 2000 cm³ per minute flooded the absorption tower.

Initially, a stainless steel electrode was employed as the cathode but it was found to be unsuitable as it corroded and pitted. The stainless steel cathode was replaced with a platinized titanium cathode.

5.2 Factorial Experiments

The list of independent variables and dependent variables is illustrated by Table 4. Results obtained from a factorial experiment performed at two levels are presented in Tables 5, 6 and 7.

In determining which of the five independent variables mentioned in Table 4 had the largest positive effect on the space time yield for propylene oxide, the technique of analysis of variance was utilized (25). The source table resulting from this analysis is illustrated in Table N of Appendix 7 and summarized in Table 8. The principal features of these results are discussed below.

*All gas flows given at STP.

Table 4
List of Independent and Dependent Variables

<u>Independent Variables</u>	<u>Levels</u>
Reactor outlet temperature (°C)	30 and 60
Current (Amps)	2 and 5
Electrolyte concentration (M)	0.2 and 0.5
Electrolyte flow rate (cm ³ /min)	100 and 300
Propylene gas flow rate (cm ³ /min) STP	100 and 1000
<u>Dependent Variable</u>	
Space time yield for propylene oxide	
Selectivity for propylene oxide	
Current efficiency for propylene oxide	
Current efficiency for dibromopropane	
Current efficiency for hydrogen and oxygen	
Current efficiency for bromates, bromite and hypobromite	
Specific energy consumption for propylene oxide	

Table 5
Factorial Experiment Results

				Reactor Outlet Temperature °C									
				30				60					
				Current (Amps)				Current (Amps)					
				2		5		2		5			
				Concentration (M)*		Concentration (M)		Concentration (M)		Concentration (M)			
				0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5		
				Electrolyte Flow (cm ³ /min)	300	Gas Flow (cm ³ /min)	1000	STY kg/h m ³ =12.4 A SEL % = 72.2 Current efficiency PO % = 47.3 DBP % = 18.3 Hydrogen % = 59.8 Oxygen % = 4.9	14.8 H 70.1	30.5 I 85.8	32.5 P 83.4	5.9 Q 54.5	11.8 X 66.6
100	7.4 B 77.5 28.2 9.1 40.2 3.7	11.1 G 78.0 42.6 12.0 47.7 2.9	16.2 J 85.2 24.7 4.3 63.2 5.3				21.9 O 87.3 33.8 4.9 30.8 3.1	4.8 R 65.9 18.2 9.4 38.1 3.7	5.3 W 59.8 20.5 13.8 25.2 2.2	14.6 Z 71.3 22.3 8.9 37.0 3.3	22.9 E 85.8 35.1 5.9 39.8 1.9		
100	Gas Flow (cm ³ /min)	1000	11.5 C 72.3 44.0 16.8 58.5 4.8				12.3 F 73.5 47.3 23.2 53.5 0.0	21.2 K 81.8 32.4 7.2 52.9 4.9	30.3 N 86.1 46.3 7.5 47.8 2.2	5.4 S 58.5 20.8 14.9 39.8 9.5	8.5 V 61.8 32.7 20.0 37.7 0.0	18.8 A1 80.0 28.8 7.2 51.8 5.6	26.3 D1 83.2 40.3 8.2 45.0 2.1
		100	5.5 D 67.1 20.9 10.3 35.0 4.3				11.3 E 81.7 43.3 9.7 41.0 3.4	13.4 L 81.7 20.5 4.6 33.5 4.8	18.7 M 85.3 28.7 4.9 35.4 7.5	4.0 T 63.9 15.5 8.7 29.9 3.4	6.3 U 68.7 24.0 10.9 34.6 3.3	12.8 B1 80.8 19.7 4.7 51.5 8.5	13.6 C1 82.3 20.8 4.5 28.6 2.0

*Sodium bromide concentration.

Table 6
Factorial Experiment Results

Reactor Outlet Temperature °C									
30					60				
Current (Amps)					Current (Amps)				
2					2				
Concentration (M)					Concentration (M)				
0.2					0.2				
0.5					0.5				
11.30					11.20				
11.45					11.35				
11.02					10.83				
11.40					11.20				
10.83					10.65				
11.60					11.60				
7.4					7.4				
11.5					11.6				
10.0					10.0				
15.5					15.5				
5.9					5.9				
11.58					11.58				
11.23					11.23				
7.4					7.4				
29.2					29.2				
15.8					15.8				
11.35					11.35				
10.96					10.96				
11.01					11.01				
11.45					11.45				
10.55					10.55				
9.2					9.2				
11.45					11.45				
7.3					7.3				
36.1					36.1				
11.13					11.13				
10.6					10.6				
25.0					25.0				
10.8					10.8				
11.35					11.35				
9.70					9.70				
11.43					11.43				
17.7					17.7				
10.3					10.3				
11.45					11.45				
10.25					10.25				
29.8					29.8				
12.6					12.6				
11.40					11.40				
10.86					10.86				
19.3					19.3				
18.2					18.2				
7.9					7.9				
10.63					10.63				
11.40					11.40				
10.15					10.15				
11.60					11.60				
9.2					9.2				
22.8					22.8				
6.6					6.6				
11.45					11.45				
10.55					10.55				
9.2					9.2				
11.01					11.01				
7.3					7.3				
36.1					36.1				
11.13					11.13				
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Table 7
Factorial Experiment Results

Electrolyte Flow cm ³ /min				Reactor Outlet Temperature °C							
				30				60			
				Current (Amps)				Current (Amps)			
				2		5		2		5	
				Concentration (M)		Concentration (M)		Concentration (M)		Concentration (M)	
				0.2	0.5	0.2	0.5	0.2	0.5	0.2	0.5
300	Gas Flow cm ³ /min	1000	A	Current efficiency	H	I	P	Q	X	Y	FI
				BrO ⁻ = 4.4	8.2	4.4	2.5	3.6	6.2	5.9	1.8
				BrO ₂ ⁻ = 2.3	0.0	2.2	0.1	2.3	0.0	3.8	.2
				BrO ₃ ⁻ = 6.2	11.5	25.7	1.7	5.3	3.0	27.2	.8
				Total = 12.9	19.7	32.3	4.3	11.2	9.2	36.9	2.8
	Gas Flow cm ³ /min	100	B	4.0	14.9	6.0	13.8	4.5	6.2	11.0	7.5
				10.4	.7	2.9	2.9	0.0	3.9	7.7	4.1
				31.2	14.3	45.6	24.5	7.5	5.2	46.4	9.3
				45.6	29.9	54.5	41.2	12.0	15.3	65.1	20.9
100	Gas Flow cm ³ /min	1000	C	2.1	3.2	3.5	4.0	1.5	2.7	3.0	4.5
				2.4	2.4	1.6	1.3	.8	0.0	0.6	1.8
				8.5	4.5	21.9	12.4	1.3	4.4	15.5	4.2
				13.0	10.1	27.0	17.7	3.6	7.1	19.1	10.5
	Gas Flow cm ³ /min	100	D	6.0	3.4	4.2	4.9	3.0	3.0	3.8	3.9
				2.4	0.8	3.5	1.0	4.0	.2	2.2	1.8
				16.9	5.1	48.2	27.5	4.5	2.6	29.8	16.1
				25.3	9.3	55.9	33.4	11.5	5.8	35.8	21.8

Table 8

The Significance of the Effect of Operating Variables on Space Time Yield,
Current Efficiency, Selectivity and Specific Energy Consumption

Independent Variable	Dependent Variable									
	Propylene Oxide				Current Efficiency					
	Space Time Yield	Selectivity	Current Efficiency	Specific Energy Conspt.	Dibromo-propane	Hydrogen	Oxygen	Hypobromite	Bromite	Bromate
Temperature (T)	* (-)	* (-)	* (-)							* (-)
Current (A)	* (+)	* (+)		* (+)	* (-)					* (+)
Electrolyte Conc. (C)	* (+)		* (+)	* (-)	* (+)		* (-)		* (-)	* (-)
Electrolyte Flow Rate (L)	* (+)		* (+)	* (-)				* (+)		
Gas Flow Rate (G)	* (+)		* (+)	* (-)	* (+)	* (+)		* (-)	* (-)	* (-)
A x L	*									
A x G	*				*					*
A x C					*					*
T x A			*	*						

*Statistical significance level = 0.05 or lower, (+) or (-) indicate that increasing the independent variable (increase) (decrease) the dependent variable.

5.2.1 Reactor Outlet Temperature

The results in Tables 5 to 8 and Table N of Appendix 7 indicate the following features:

- a. Temperature has a negative effect* on the space time yield, selectivity and current efficiency for propylene oxide.
- b. Temperature also has a negative effect on the current efficiency for bromates.

The first effect can be explained in part by reduced solubility of propylene in the electrolyte solution with increasing temperature. A graphical illustration of the relation between temperature and solubility of propylene in water is contained in Figure F of Appendix 4. As the solubility of propylene decreases, the formation of propylene oxide becomes limited by it, thereby reducing the space time yield for propylene oxide. This negative effect of temperature was also found by King et al. [10]. The variation in the limiting current density, which is defined as

$$i_L = \frac{ZFKC_b}{1 \pm t}$$

where K = mass transfer coefficient

C_b = bulk concentration

*Negative effect means by increasing the independent variable the dependent variable decreases.

t = transport number

i_L = real limiting current density

with concentration of propylene is illustrated in Table 9. The mass transfer coefficient was calculated from the model presented in reference [27].

The limiting current density for propylene can be increased by operation of the reactor at elevated pressure. Bejarano et al. [12] operated their reactor at pressures of up to 5 atmospheres and determined the space time yield for propylene oxide to be 156.6 kg/hr m^3 .

The conductivity of the electrolyte solution rises with higher temperature resulting in a lower current efficiency and higher specific energy consumption for propylene oxide. This increased specific energy consumption occurs even though the voltage requirement to drive current through the reactor is lower at a higher temperature. Table 10 illustrates this. The above suggests that the reduced current efficiency and higher specific energy consumption for propylene oxide is due to increased bypass current associated with increased solution conductivity. This is also supported by the fact that temperature does not have a very large effect on the current efficiency for dibromopropane, hypobromite, bromite and bromates.

Increasing temperature also affects the relative rates of the chemical and electrochemical reactions.

Table 9

Effect of Propylene Concentration on the
Real Limiting Current Density for Propylene

Temperature °C	Solubility wt %	Concentration M	Limiting Current Density (A/m ²)
30	2.4×10^{-2}	5.7×10^{-3}	50.7
60	$8. \times 10^{-3}$	1.9×10^{-3}	16.9

Conditions

Electrolyte flow = 300 cm³/min
Propylene flow = 1000 cm³/min (STP)
Mass transfer coefficient = 4.61×10^{-5} m/sec

Table 10

The Effect of Temperature on Voltage Requirement
and Specific Energy Consumption for Propylene Oxide

Illustration for boxes G and W of Tables 5

	Temperature °C	
	30	60
Voltage requirement	17 V	14V
Specific energy consumption	7.4 Kwhr/kg	12.6 Kwhr/kg
Current efficiency for propylene oxide	42.6%	20.5%

5.2.2 Current

The findings in Table 5 to 8 and Table N of Appendix 7 illustrate the following features:

- a. Superficial current density has a positive effect* on the space time yield, selectivity and specific energy consumption for propylene oxide.
- b. The bromate current efficiency increases with higher currents.
- c. Superficial current density has a negative effect on the current efficiency for dibromopropane.

Higher superficial current densities result in increased bromine generation rates (reaction 1) which can match the propylene gas absorption process to form propylene bromohydrin by reaction 4. Box A and I of Tables 5 and 6 indicate that the current efficiency for propylene oxide decreases together with the current efficiency for dibromopropane. However, the current that went into the formation of dibromopropane for both cases remains approximately the same (75.6 A/m^2 and 79.5 A/m^2). The above suggests that although the current efficiency for propylene oxide decreases, the extra current does go into producing propylene oxide and the bromates as indicated by Table 11. Table 7 shows a steep rise in the total bromate formation with an increase in the superficial current density indicating that the formation takes place through the electrochemical rather than chemical route (reaction 9).

Table 11

Current that Goes into Producing Propylene Oxide,
Dibromopropane and Total Bromates

Superficial current density (A/m ²)	Dibromopropane (A/m ²)	Total bromates (A/m ²)	Propylene oxide (A/m ²)
413 A/m ²	75.6	53.3	195.3
1033 A/m ²	79.5	333.7	481.4

From the data of Appendix 6 it would be expected that, by increasing the superficial current density, the oxygen current efficiency would decrease. However, analysis (Table 8) indicates that current had no effect.

5.2.3 Sodium Bromide Concentration

The data of Tables 5 to 8 and Table N of Appendix 7 show the following effects:

- a. Concentration has a positive effect on the space time yield and current efficiency for propylene oxide.
- b. The current efficiency of dibromopropane increases with increasing concentration.
- c. Concentration has a negative effect on the current efficiency for oxygen, bromite and bromate.
- d. Propylene oxide specific energy consumption decreases with increasing concentration.

Although, it would be expected that the current efficiency for propylene oxide would decrease with increasing electrolyte concentration due to higher current by-pass this was not observed. The higher current efficiency for propylene oxide can be attributed to lower total bromate and oxygen current efficiency with increasing electrolyte concentration. The current that previously went into generating the bromates and oxygen now goes into the generation of propylene oxide and dibromopropane thereby increasing their current efficiency. This

contradicts the results of Bejarano et al. [12]. They showed that the current efficiency for propylene oxide followed the expected trend, that is, a decrease with increasing electrolyte concentration. However, their results indicated that increased electrolyte concentration had a negative effect on the bromate formation which is in agreement with the results in Table 7.

The lower specific energy consumption for propylene oxide can be ascribed in part to the lower voltage required to drive the current through the reactor as the electrolyte concentration and hence the higher conductivity increases. The conductivity of 0.2 M sodium bromide solution is 0.0183 mho/cm and that of 0.5 M solution is 0.0423 mho/cm.

5.2.4 Electrolyte Flow Rate

Tables 5 to 8 and Table N of Appendix 7 illustrate the following features:

- a. The electrolyte flow rate has a positive effect on the space time yield and current efficiency for propylene oxide.
- b. The specific energy consumption decreases with increased electrolyte flow rate.
- c. Hypobromite current efficiency increases with increased electrolyte flow rate.

Table 12 shows that with increased electrolyte flow rate the mass transfer coefficient [27] for the bromide ion and propylene increases suggesting improved mass transfer rates. With increased electrolyte

Table 12

The Effect of Electrolyte Flow Rate and Concentration on the Mass Transfer Coefficient and the Real Limiting Current Density for the Bromide Ion.

	Electrolyte Flow Rate (cm ³ /min)															
	100								300							
	Gas Flow Rate (cm ³ /min)								Gas Flow Rate (cm ³ /min)							
	100		1000		1500		2000		100		1000		1500		2000	
	Conc. (M)		Conc. (M)		Conc. (M)		Conc. (M)		Conc. (M)		Conc. (M)		Conc. (M)		Conc. (M)	
	.2	.5	.2	.5	.2	.5	.2	.5	.2	.5	.2	.5	.2	.5	.2	.5
K (m/s)	6.92 x 10 ⁻⁵		7.83 x 10 ⁻⁵		8.17 x 10 ⁻⁵		8.54 x 10 ⁻⁵		9.58 x 10 ⁻⁵		1.07 x 10 ⁻⁴		1.11 x 10 ⁻⁴		1.15 x 10 ⁻⁴	
i _L (A/m ²)	2671	6678	3022	7556	3153	7884	3296	8241	3698	9245	4130	10326	4285	10712	4439	11098
i _{LS} (A/m ²)	4910	12277	5556	13891	5796	14494	6059	15150	6798	16996	7593	18983	7878	19693	8161	20403

i_L = real limiting current density

i_{LS} = limiting superficial current density

flow rate the mixing condition within the reactor possibly improves. The effective conductivity of the mixture also increases due to higher electrolyte hold up. Improved mass transfer rates of propylene and bromide ion, and mixing conditions could possibly account for the increased space time yield and current efficiency for propylene oxide.

The specific energy consumption decreases due to higher current efficiency for propylene oxide and due to increased electrolyte solution temperature entering the reactor with increased electrolyte flow rate to control the reactor outlet temperature.

5.2.5 Propylene Gas Flow Rate

The following features were observed in Tables 5 to 8 and Table N of Appendix 7:

- a. Propylene gas flow has a positive effect on the space time yield and current efficiency for propylene oxide.
- b. The gas flow rate has a negative effect on the specific energy consumption for propylene oxide.
- c. Dibromopropane and hydrogen current efficiency increase with increasing gas flow rate.
- d. Propylene gas flow has a negative effect on the hypobromite, bromite and bromate current efficiency.

Increasing propylene gas flow rate possibly increases the transverse mixing of reactants within the reactor producing high space time yield, and current efficiency for propylene oxide. This could also explain the increased current efficiency for dibromopropane. Increased

gas flow rate also improves the overall mass transfer coefficients for propylene as demonstrated in Table 13. The improved mass transfer coefficient suggests higher mass transfer rates producing larger space time yields for propylene oxide. With increasing gas flow rate the effective mixture conductivity decreases. High space time yield and current efficiency for propylene oxide can also be attributed to this fact due to reduced current by-pass associated with a lower effective mixture conductivity.

The reduced total bromate current efficiency can possibly be explained in part by the improved mixing conditions in the reactor. These conditions decrease the high local concentrations of hypobromite, which in turn reduce the bromate formation by reactions 8 and 9.

The lower specific energy consumption for propylene oxide is probably due to high current efficiency for propylene oxide.

Increased hydrogen current efficiency can be explained in terms of less by-pass current with high gas flow rates. Improved mass transfer for propylene which suppresses the concentration of hypobromous acid can also explain the higher current efficiency for hydrogen.

5.3 pH Effects

Although the effect of pH was not studied separately some mention of it should be made as it is a very important variable.

The formation of propylene oxide is dependent on the saponification of propylene bromohydrin, which is favoured by basic conditions (reaction 14). Therefore, the current efficiency of propylene oxide is

Table 13

The Effect of Propylene Gas Flow Rate on the Overall Mass Transfer Coefficient for Propylene at Varying Electrolyte Flow Rate

	Electrolyte Flow Rate (cm ³ /min)							
	100				300			
	Gas Flow Rate (cm ³ /min)*				Gas Flow Rate (cm ³ /min)*			
	100	1000	1500	2000	100	1000	1500	2000
K_o (m/sec)	1.54×10^{-5}	1.94×10^{-5}	2.10×10^{-5}	2.24×10^{-5}	3.96×10^{-5}	4.61×10^{-4}	4.83×10^{-4}	5.01×10^{-4}
i_{LS} (A/m ²)	31.1	39.2	42.5	45.3	80.1	93.2	97.7	101.3

i_{LS} = Limiting superficial current density

Temperature = 30°C

Concentration = 5.7×10^{-3} M

*All gas flows given at STP

a function of the pH of the electrolyte. If the pH is too high, the propylene oxide can be hydrolyzed to propylene glycol, and at low pH the formation of dibromopropane is favoured (reaction 14). This suggests that there is an optimum pH for the formation of propylene oxide.

In the present study, during the course of the electrolysis, there was a rapid rise in the pH value within the reactor. The reactor outlet pH for all the experimental runs ranged from 9.70 to 11.58.

5.4 Further Investigation

Data in Table N of Appendix 7 show that superficial current density and propylene gas flow rate have the major effect on the space time yield, selectivity and current efficiency for propylene oxide. Further experiments were carried out to see how far their effect could be extended.

5.4.1 Effect of Current and Propylene Gas Flow Rate

Typical results obtained from these experimental runs are presented in Table J of Appendix 4 and illustrated in the graph of Figure 13. As seen from the graph, the space time yield for propylene oxide increased with current applied to the reactor, went through a maximum, then decreased as the current was increased further. Increasing propylene gas flow had the same effect as raising the current; the space time yield for propylene oxide increases, reaches a maximum, and then falls. These results indicate there is a maximum superficial current density for a given condition beyond which the space time yield decreases. This is due to increased rate of bromine generation, which leads to the

EFFECT OF CURRENT AND GAS FLOW RATE ON SPACE TIME YIELD

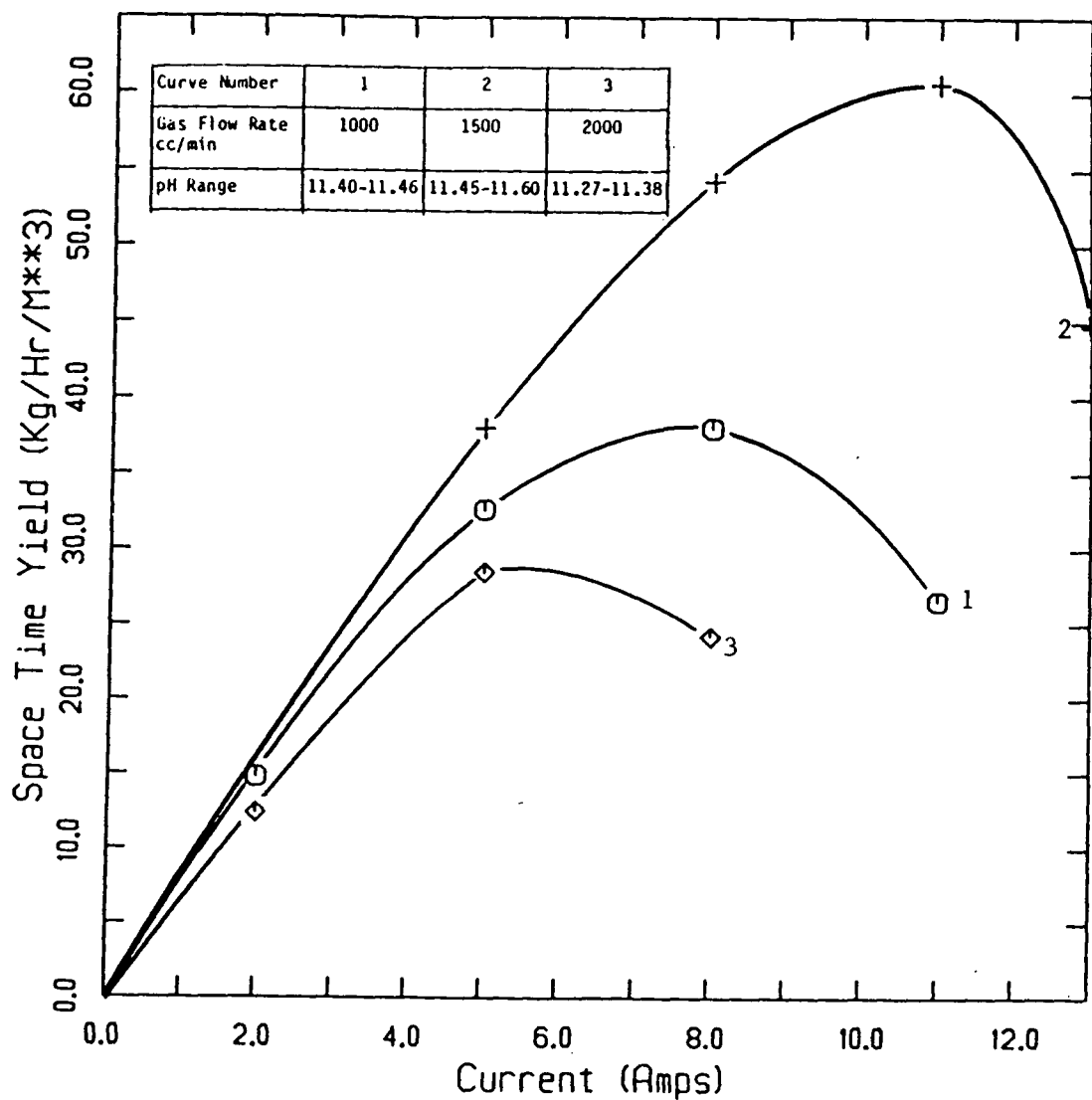


FIGURE 13

Conditions

Graphite Particle Size = 1.168 - 1.68 mm
 Graphite Type = Union Carbide
 Temperature = 28-35°C
 Concentration = 0.5 M
 Liquid Flow = 300 cc/min
 Pressure = 1.4 - 2.2 atm
 Bed Thickness = 8.57 cm
 Area = $4.84 \times 10^{-3} \text{ m}^2$

depletion of dissolved propylene in the solution. The excess bromine generated is then free to participate in various loss reactions reducing the space time yield for propylene oxide. Increasing propylene gas flow had the same effect as increasing superficial current density.

Initially the space time yield for propylene oxide increases probably due to improved mixing and mass transfer in the reactor. However, a further increase in the gas flow rate results in a lower residence time for the mixture in the reactor which could account for low space time yields for propylene oxide. Increased gas flow rate could also reduce transverse mixing in the reactor producing low space time yields for propylene oxide.

Figure 13, 14 and Table J of Appendix 4 show that the specific energy consumption increases together with the space time yield for propylene oxide. This occurs until the space time yield reaches a maximum. Beyond this point there is a trade off between space time yield and specific energy consumption. The specific energy consumption increases although the space time yield for propylene oxide decreases.

The effect of superficial current density on the current efficiency for propylene oxide at a propylene gas flow rate of 1500 cm³/min is presented in the graph of Figure 15. This figure also illustrates the effect of superficial current density on the dibromopropane and oxygen current efficiency. One of the features observed from this graph is the decreasing current efficiency for propylene oxide and dibromopropane with increasing superficial current density. The amount of oxygen formed, however, increases. Decreasing current efficiency for propylene

EFFECT OF CURRENT AND GAS FLOW RATE ON SPECIFIC ENERGY CONSUMPTION

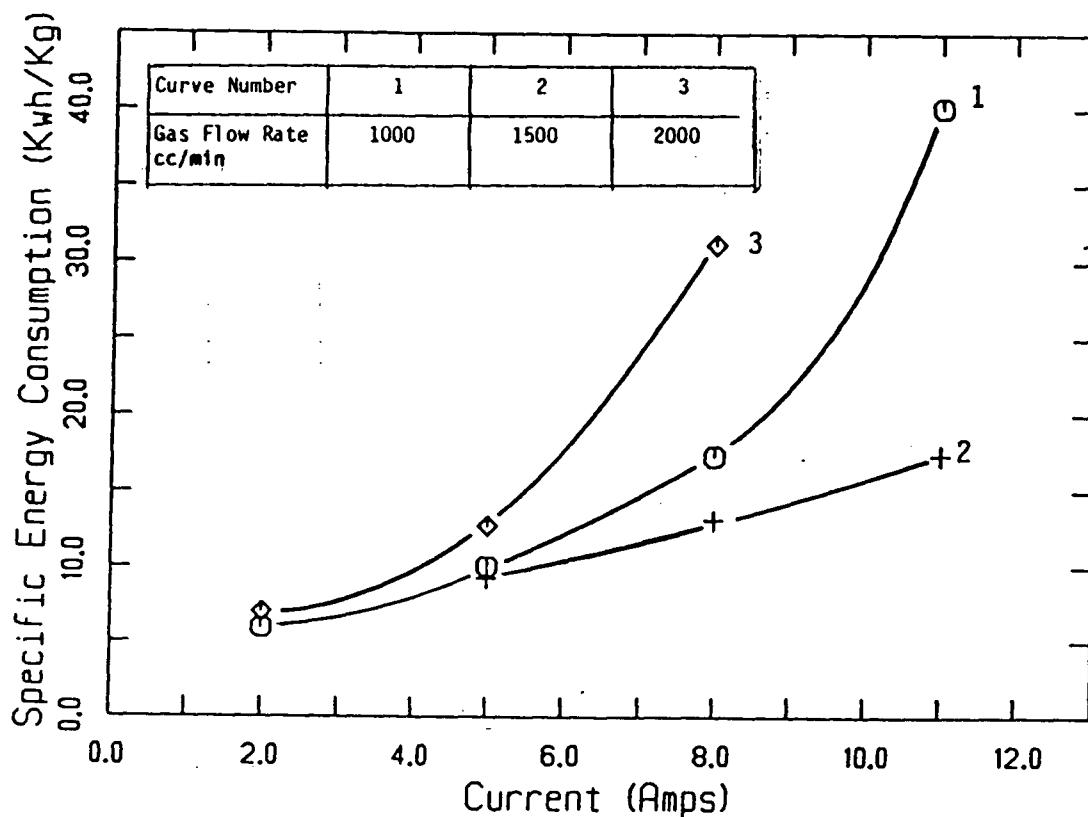


FIGURE 14.

Conditions

Graphite Particle Size = 1.168 - 1.68 mm
 Graphite Type = Union Carbide
 Temperature = 28-35°C
 Concentration = 0.5 M
 Liquid Flow = 300 cc/min
 Pressure = 1.4 - 2.2 atm
 Bed Thickness = 8.57 cm
 Area = $4.84 \times 10^{-3} \text{ m}^2$

SELECTIVITY AND CURRENT EFFICIENCY AS A FUNCTION OF APPLIED CURRENT

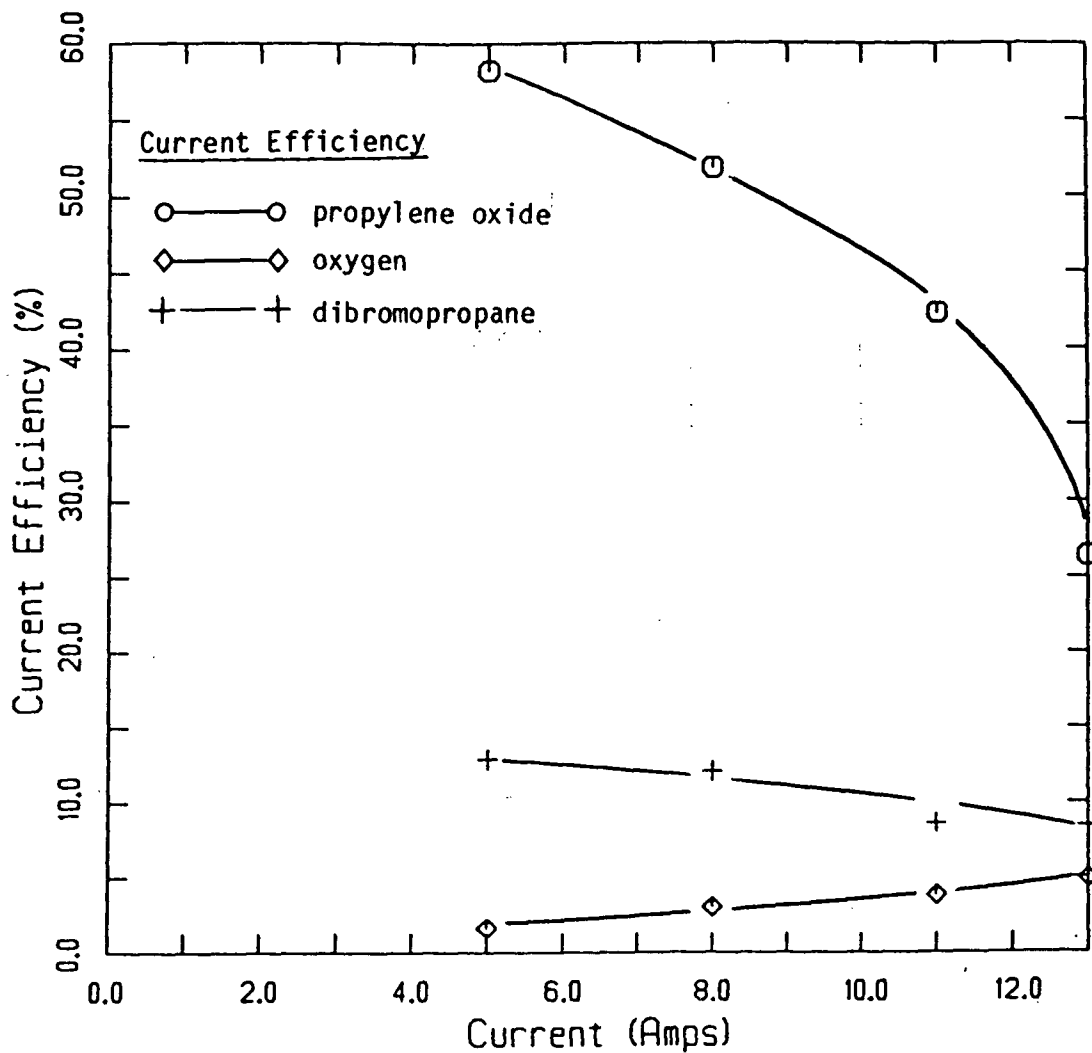


FIGURE 15

Conditions

Graphite Particle Size = 1.168 - 1.68 mm
 Graphite Type = Union Carbide
 Temperature = 28-35°C
 Concentration = 0.5 M
 Liquid Flow = 300 cc/min
 Pressure = 1.4 - 2.2 atm
 Bed Thickness = 8.57 cm
 Area = $4.84 \times 10^{-3} \text{ m}^2$

oxide and increasing current efficiency for oxygen is the reason for higher energy consumption. Similar effects are observed at propylene gas flow rates of 1000 and 2000 cm³/min.

5.4.2 Effect of Bed Thickness

Having investigated the effect of superficial current density and propylene gas flow rate, the effect of bed thickness on the space time yield for propylene oxide was then explored.

Results are presented in Table K of Appendix 4 and shown in graphical form in Figure 16. This figure shows how the space time yield for propylene oxide is affected by the reactor bed thickness. It clearly shows that the space time yield for propylene oxide increases with decreasing reactor bed thickness. Table K indicates that the propylene oxide production rate, current efficiency and selectivity decrease initially, then remain approximately constant. From these results, it appears that the by-pass current increases as the reactor bed thickness is lowered.

In order to maximize the space time yield for propylene oxide experimental runs were done at a smaller reactor bed thickness with increasing current and propylene gas flow rate. Findings from these experiments are illustrated in the graph of Figure 17 and Table L of Appendix 4. Figure 17 shows how the increasing superficial current density and propylene gas flow rate at smaller reactor bed thickness affect the space time yield for propylene oxide. One feature is clearly seen in this figure: the space time yield for propylene oxide increases

EFFECT OF BED THICKNESS ON SPACE TIME YIELD

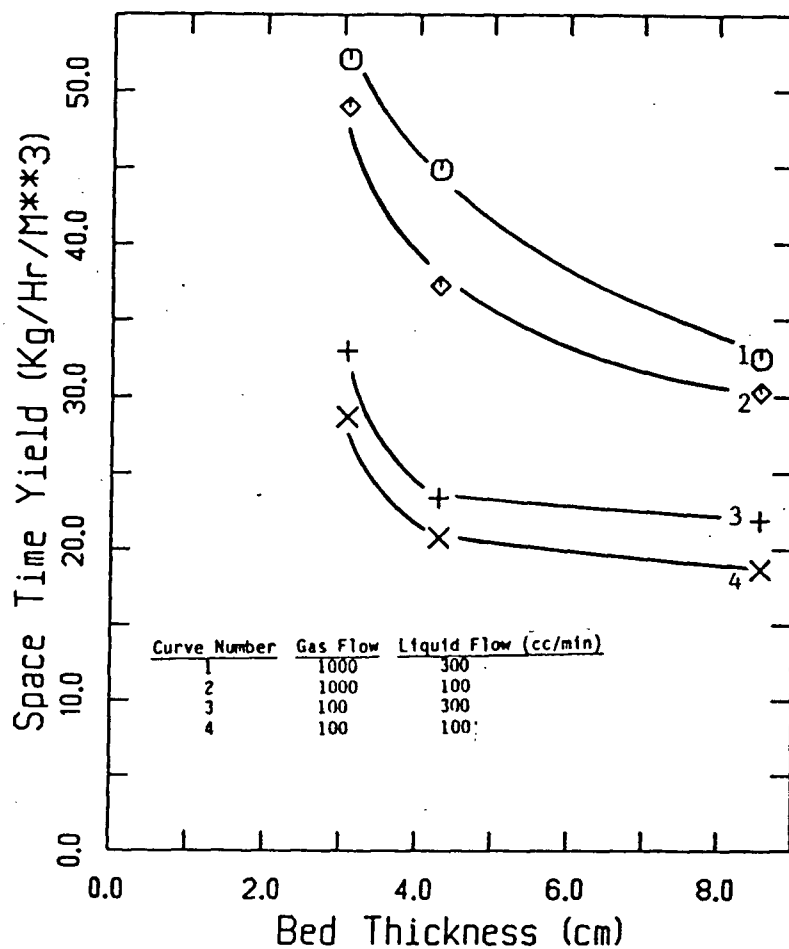


FIGURE 16

Conditions

Graphite Particle Size = 1.168 - 1.68 mm
 Graphite Type = Porous
 Temperature = 29-32°C
 Concentration = 0.5 M
 Current = 5 amps
 Pressure = 1.4 - 2.2 atm
 Bed Thickness = Thickness of 5 beds including diaphragms

EFFECT OF BED THICKNESS, CURRENT AND PROPYLENE GAS FLOW RATE
ON THE SPACE TIME YIELD FOR PROPYLENE OXIDE

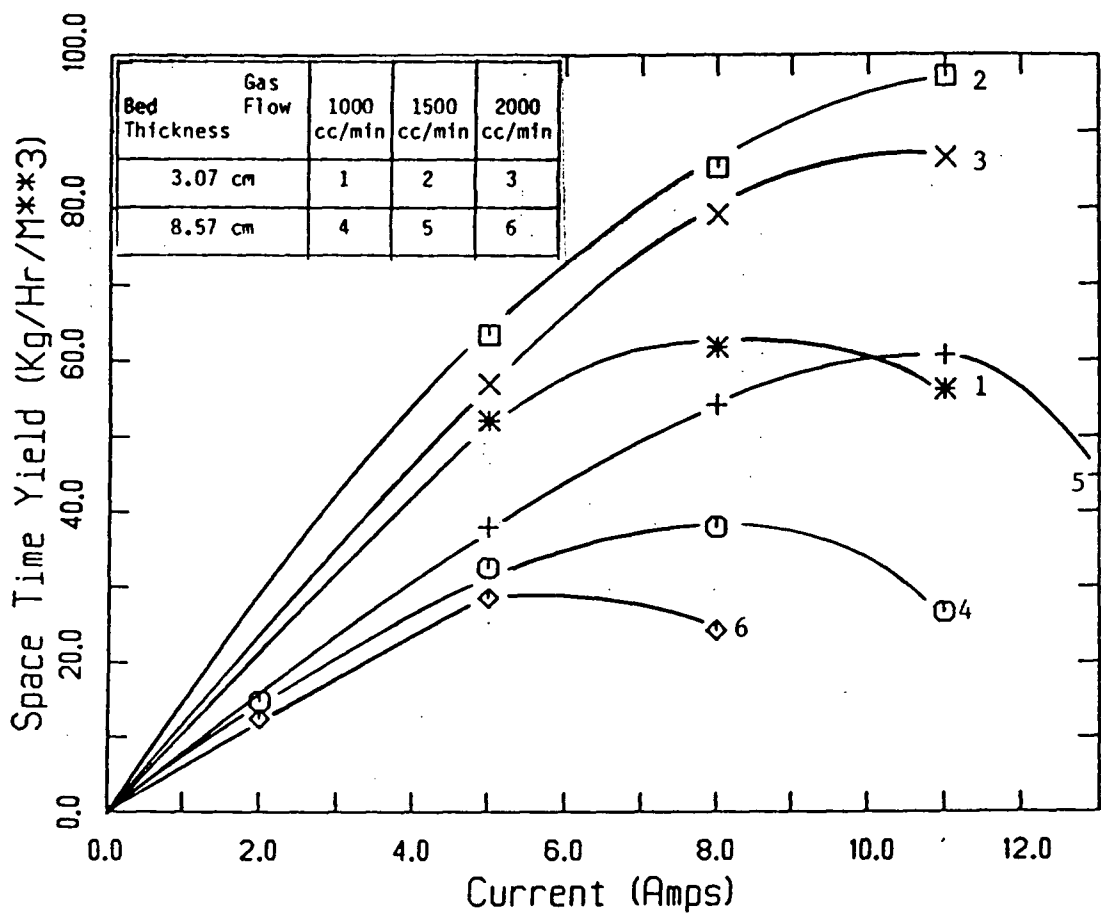


FIGURE 17

Conditions

Graphite Particle Size = 1.168 - 1.68 mm
 Graphite Type = Union Carbide
 Temperature = 28-35°C
 Concentration = 0.5 M
 Liquid Flow = 300 cc/min
 Pressure = 1.4 - 2.2 atm
 Area = $4.84 \times 10^{-3} \text{ m}^2$

with decreasing bed thickness. The higher space time yield for propylene oxide with smaller reactor bed thickness can be ascribed to the unequal drop in the ratio of reactor volume and propylene oxide production rate.

5.4.3 Effect of Different Graphite Types

Findings from experiments done with different graphite samples are presented in Table 14. Changing the graphite sample from Union Carbide to Ultra Carbon yields lower space time yield, current efficiency, selectivity and production rate for propylene oxide. These results are probably due to higher porosity of the Ultra Carbon graphite as illustrated by Figure 11. The highly porous surface creates dead space where localised low pH regions caused by poor mass transfer characteristics can develop, allowing the undesirable reactions to take place thereby reducing the selectivity and space time yield for propylene oxide. The lower space time yield for propylene oxide is also supported by the fact that the current efficiency for dibromopropane increases.

5.4.4 Electrolyte Recycle

Finally, recycle runs were done. The calculations are presented in Appendix 4. The results are illustrated in Figures 18 and Tables G, H and I of Appendix 4. The interesting feature of Figure 18 is that the space time yield for propylene oxide falls with time. The decrease in space time yield for propylene oxide could be due to the rising pH of the recycling electrolyte solution, as seen in Tables G, H and I

Table 14

The Effect of Different Carbon Type on the Space Time Yield
for Propylene Oxide

					Carbon Type	
					Union Carbide	Ultra Carbon
Liquid Flow cm ³ /min	300	Gas Flow cm ³ /min	1000	STY kg/hr m ³	32.5	25.6
				PO Produced cm ³ /hr	16.2	12.8
				C.E. (PO) %	49.9	39.4
				C.E. (DBP) %	9.9	10.2
				Selectivity %	83.5	79.5
	100	Gas Flow cm ³ /min	100	STY kg/hr m ³	21.9	18.6
				PO Produced cm ³ /hr	11.0	9.3
				C.E. (PO) %	33.8	28.6
				C.E. (DBP) %	4.9	6.2
				Selectivity %	87.3	82.3
	100	Gas Flow cm ³ /min	1000	STY kg/hr m ³	30.3	18.9
				PO Produced cm ³ /hr	15.1	9.5
				C.E. (PO) %	46.3	29.1
				C.E. (DBP) %	7.5	8.7
				Selectivity %	86.1	77.0
		Gas Flow cm ³ /min	100	STY kg/hr m ³	18.7	11.1
				PO Produced cm ³ /hr	9.4	5.5
				C.E. (PO) %	28.7	17.0
				C.E. (DBP) %	4.9	6.0
				Selectivity %	85.4	73.8

Conditions:

Concentration = 0.5 M
 Current = 5A
 Temperature = 28 - 34°C
 Bed Thickness = 8.57 cm
 Pressure = 1.4 - 2.2 atm.

PROPYLENE OXIDE SPACE TIME YIELD VARIATION DURING RECYCLE CONDITION

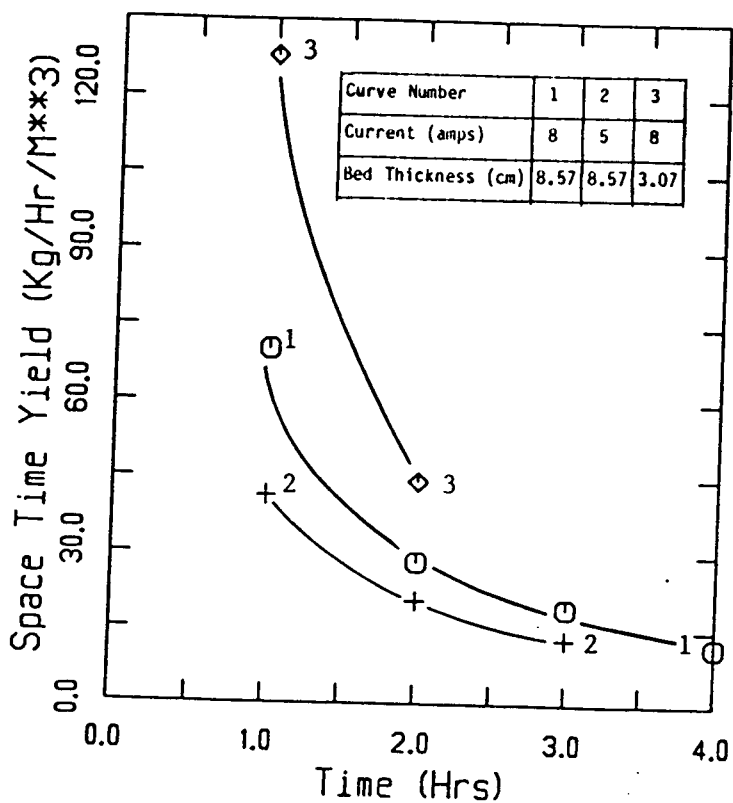


FIGURE 18

Conditions

Graphite Particle Size = 1.168 - 1.68 mm
Graphite Type = Union Carbide
Temperature = 29-36°C
Pressure = 1.4 - 2.2 atm
Electrolyte Conc. = 0.5 M
Propylene Gas Flow Rate = 1500 cm²/min

of Appendix 4. The rising pH of the electrolyte solution could result in the propylene oxide being converted to propylene glycol by reaction 15 or the molecular bromine being converted to hypobromite which is then oxidized to bromate by reactions 8 and 9. The formation of hypobromite, bromite and bromates are damaging to the current efficiency for propylene oxide. These results also indicate that maybe the optimum pH in these experiments is less than or equal to 10.45. The second possible reason for the decrease in the space time yield for propylene oxide could be attributed to the rising electrolyte temperature. Propylene solubility in water decreases with increasing temperature (Figure E, Appendix 4). The fall in the performance of propylene oxide formation could also be due to carry over of the corrosion products from the equipment and impurities present in the electrolyte which can catalyze the homogenous production of the bromide ion from the hypobromite ion by reaction 19.



M can be cobalt, nickel or chromium.

This reaction is parasitic as it reduces the availability of the OBr^- ion which reacts with propylene to produce propylene bromohydrin by reaction 4. The concentration of bromates increase with time as seen in Table I of Appendix 4.

The results of this experiment indicate the possibility for raising the space time yield for propylene oxide by determining the optimum pH

of the electrolyte solution, by controlling the temperature and by using equipment constructed of non-corroding material such as titanium and Teflon.

5.5 Commercial Potential

A very simple costing exercise was undertaken to determine the commercial potential for a 10,000 short tons per year production plant for propylene oxide. A line diagram for the proposed plant is illustrated in Figure 19. Using the best results from the experiments done (Table 15) and assuming that the reactor scales up linearly, it was calculated that 36 reactors having an electrode area of 1 m^2 with 40 cells will be required. The calculations are presented in Appendix 5. The fixed capital investment cost is shown in Table 16 and the operating cost in Table 17. From Table 17 it can be seen that the cost of propylene oxide is calculated at \$3.97 per kilogram making the process economically unjustifiable as the present price of propylene oxide is \$1.05 per kilogram.

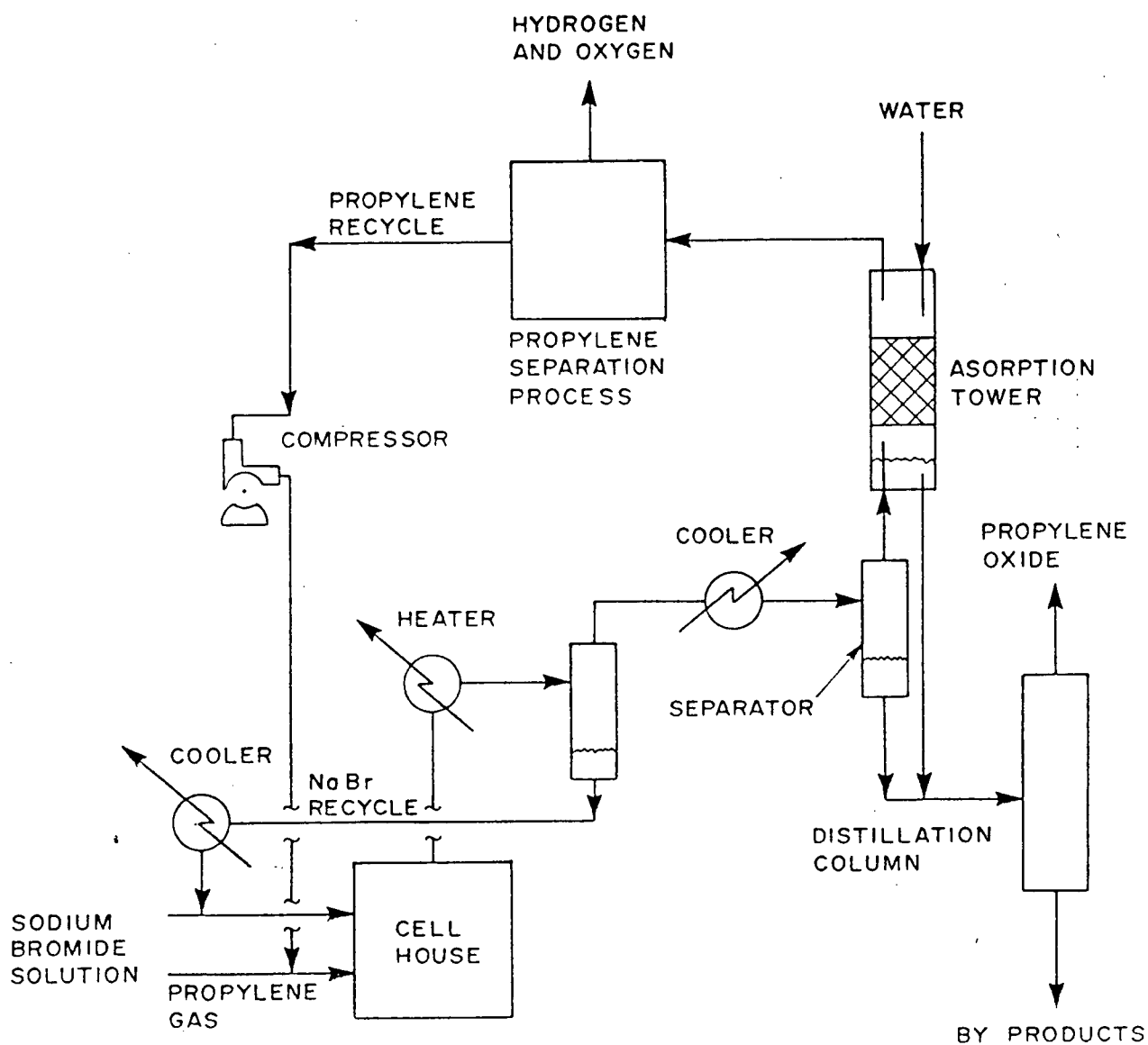


FIGURE 19: PROPOSED PROCESS FOR THE MANUFACTURE OF PROPYLENE OXIDE

Table 15
Experimental Conditions Used for the Scale Up of
Propylene Oxide Reactor

Bed thickness*	= 3.07×10^{-2} m
Propylene gas flow rate	= 1.5×10^{-3} m ³ /min
Electrolyte flow rate	= 3.0×10^{-4} m ³ /min
Current (superficial Current density)	= 8A (1650A/m ²)
Electrolyte concentration	= 0.5 M
Reactor outlet temperature	= 30°C
Voltage per cell	= 6V
Space time yield	= 127.8 kg/m ³ hr
Current efficiency for propylene oxide	= 56.5%
Selectivity for propylene oxide	= 95%
Specific energy consumption	= 9.8 Kwhr/kg

*Bed thickness = thickness for five beds including diaphragms.

Table 16

Fixed Capital Investment Cost for Propylene Oxide Plant having a
Capacity of 10,000 Short Tons Per Year

Cell House Costing (36 reactors, 40 cells/reactor, 1 m²/cell)

<u>Item</u>	<u>Cost \$ M</u>
Compression plates	\$ 270.0
Electrodes	72.0
Gaskets	360.0
Graphite	22.8
Diaphragms	28.8
Reactor assembly	<u>156.0</u>
Total reactor cost	<u>909.6</u>
Rectifier	<u>1,740.0</u>
Total cell house cost (4 time reactor cost + rectifier cost)	<u><u>\$5,378.4</u></u>

The total plant cost is estimated at \$22.0 M

Table 17
Operating Cost

<u>Item</u>	<u>Cost</u>	
	<u>\$ M/day</u>	<u>\$/kg</u>
Power (\$0.04/Kwh)	15.4	0.56
Raw material - propylene (\$0.44/kg)	12.0	0.44
- sodium bromide (\$1.0/kg)	73.5	2.66
Labour	2.0	0.07
Total operating cost	102.9	3.73
Capital cost*	6.5	0.24
Total propylene oxide cost	109.4	3.97

*Plant depreciated over 10 years (straight line depreciation technique).

CHAPTER 6

CONCLUSIONS

Propylene oxide was synthesized in a bipolar electrochemical reactor consisting of two monopole electrodes constructed from platinized titanium and four bipole beds of graphite particles separated by polypropylene diaphragms.

In the operation of the bipolar reactor in a single pass mode, the following variables had a major effect on the space time yield for propylene oxide.

- a. Propylene gas flow rate (increasing the flow rate raises the space time yield for propylene oxide).
- b. Superficial current density (increasing the current density also raises the space time yield for propylene oxide).
- c. Electrode bed thickness (decreasing the bed thickness raises the space time yield for propylene oxide).

The electrolyte concentration and flow rate had a very small positive effect on the space time yield for propylene oxide. Increased temperature had a negative effect on the space time yield for propylene oxide.

The smaller reactor bed thickness, consisting of Union Carbide graphite and propylene gas flow rate of $1500 \text{ cm}^3/\text{min}$ (STP) at a superficial current density of 2282 A/m^2 gave the best results for a

single pass operation. At these conditions the space time yield for propylene oxide was determined to be 97.2 kg/hr m^3 with a current efficiency of 24.3% and a selectivity of 72.0%.

For the recycle mode the best space time yield for propylene oxide was obtained after one hour of operation. This value was calculated to be 127.8 kg/hr m^3 . The corresponding current efficiency and selectivity were 56.5% and 95.9%.

As it stands, the process is not economically justifiable as the cost of propylene oxide was determined to be approximately \$4.0 per kilogram. This suggests that further work is required which should be directed at increasing the space time yield and selectivity for propylene oxide while maintaining a reasonable current efficiency. Work should also be directed at reducing the bromide losses which impose a major cost factor.

In conclusion, this work shows that it is possible to produce propylene oxide with a fairly high space time yield and selectivity in an electrochemical bipolar trickle-bed reactor.

CHAPTER 7

RECOMMENDATIONS

The following recommendations are suggested for future work in the synthesis of propylene oxide:

- a. The process should be investigated at a controlled electrolyte pH.
- b. To increase propylene solubility in the electrolyte, operation of the reactor at elevated pressures should be considered.
- c. Smaller graphite particles should be tested.
- d. Different diaphragm and membrane materials should be tested.
- e. The effect of electrolyte concentrations higher than 0.5 M and lower than 0.2 M should be tested.
- f. Experiments at a reactor outlet temperature below 30°C should be considered.

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APPENDIX 1

**POTENTIAL DROP THROUGH A BED OF GRAPHITE
AT VARIOUS CURRENTS**

Table A

The Effect of Degree of Bed Compression on the Potential Drop

Union Carbide				Ultra Carbon			
Degree of Compression	Bed Thickness (cm)	Current (Amps)	Potential Drop (volts)	Degree of Compression	Bed Thickness (cm)	Current (Amps)	Potential Drop (volts)
Loose	1.02	1.0	.06	Loose	1.02	1.0	.05
		5.0	.25			5.0	.20
		10.0	.50			10.0	.40
Medium	0.94	1.0	.02	Medium	0.94	1.0	.02
		5.0	.15			5.0	.10
		10.0	.30			10.0	.20
Tight	0.91	1.0	.02	Tight	0.91	1.0	.02
		5.0	.11			5.0	.10
		10.0	.24			10.0	.18

Particle Size = 1.168 - 1.68 mm.
 Cross Sectional Area = 48.4 cm².

APPENDIX 2

ANCILLARY EQUIPMENT

1. Ammeter
Triplet, Model number 420, D.C. amperes.
2. Absorption Tower
One tower 24 inches long and 1 inch in diameter filled with 1/4 inch berl saddle rings.
3. Circulator
Colora temperature bath, Model number 34375.
4. Condenser
2 ft of 1/4 inch stainless steel tube enclosed by 1/2 inch copper tube.
5. Feed Tank
50 litres of Nalgene polyethylene tank.
6. Fittings
Swagelok 316 S.S. and nylon.
7. Heat Exchanger
2 ft of 1/4 inch stainless steel tube enclosed by 1/2 inch copper tube.
8. Mixer
Talboys Engineering Corp. Model Number 104.
9. pH Meter
Cole Parmer Instruments Co., Model Number 5986-00 Combined electrode.
10. Power Supply
Sorensen, S.R.L. 20-25
Sorensen, D.C.R. 40-25B
11. Pressure Gauge
Marsh mastergauge type 100-3SS 316 S.S.
12. Pumps
Eastern D-11 centrifugal pump 316 S.S. 1/8 H.P. motor.

13. Reagents

Propylene - Canadian Liquid Air Ltd., C.P. grade 99.0% propylene.

Sodium Bromide - BDH Ltd., 99.0% pure.

Water - filtered and deionized.

14. Rotameters

Electrolyte - Brooks, tube size R-6-15-A
Float S.S.

Gas - Brooks, tube size R-2-15-D
Float S.S. and glass

Water - Brooks, tube size 4-65
Float S.S.

15. Separator

1 ft. long and 3.5 inches in diameter (S.S.) with S.S. flange on both ends.

16. Thermometers

Fisher Scientific Co., U.S.A., Range -10 to 110°C.

17. Tubing

Poly-flow-1/4 inch and stainless steel 1/4 inch tube.

18. Valves

Whitey and Nupro 1/4 inch S.S.

19. Wet Test Meter

Precision wet test meter, MFD by Precision Scientific Co., Chicago, U.S.A.

APPENDIX 3

CALIBRATION CURVES

Table B

Calibration of the Electrolyte Rotameter

Float Elevation	Flow - cm^3/min
1	29
4	135
7	237
10	338
13	438
15	499

Table C

Calibration of the Propylene Gas Rotameter

Float Elevation	Flow - cm^3/min Delivery Pressure = 8 psig
1	101
3	291
5	505
7	700
9	883
11	1,081
13	1,299
15	1,495

Table D

Calibration of the Water Rotameter

Float Elevation	Flow - cm^3/min
0.5	32
1.0	63
2.0	126
3.0	190
4.0	252

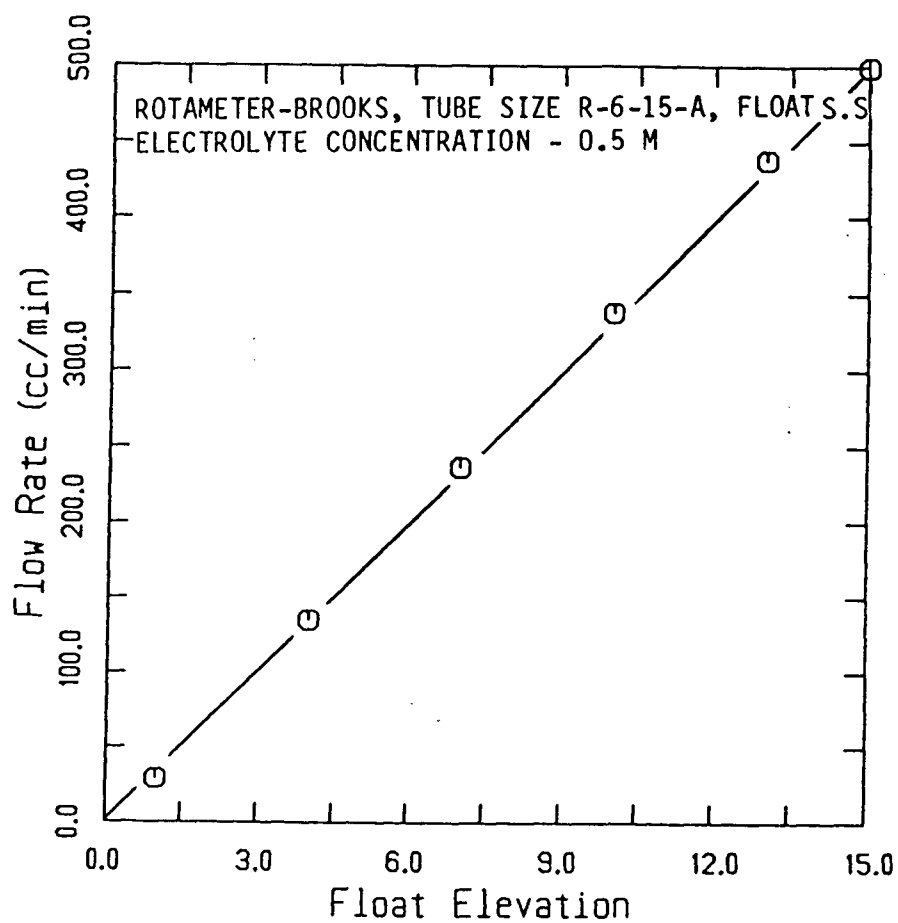


FIGURE A: CALIBRATION CURVE FOR THE ELECTROLYTE FLOW

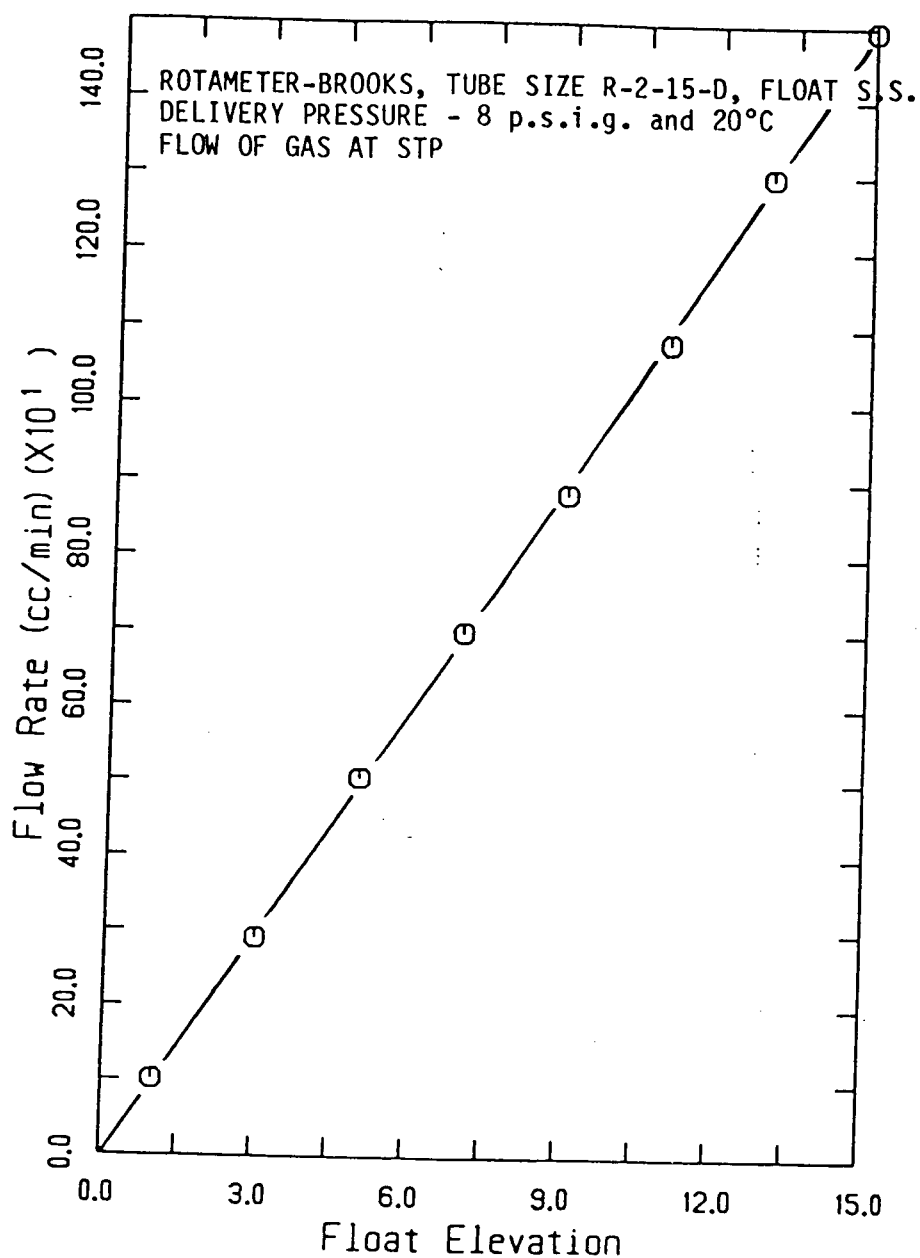


FIGURE B: CALIBRATION CURVE FOR THE PROPYLENE GAS FLOW

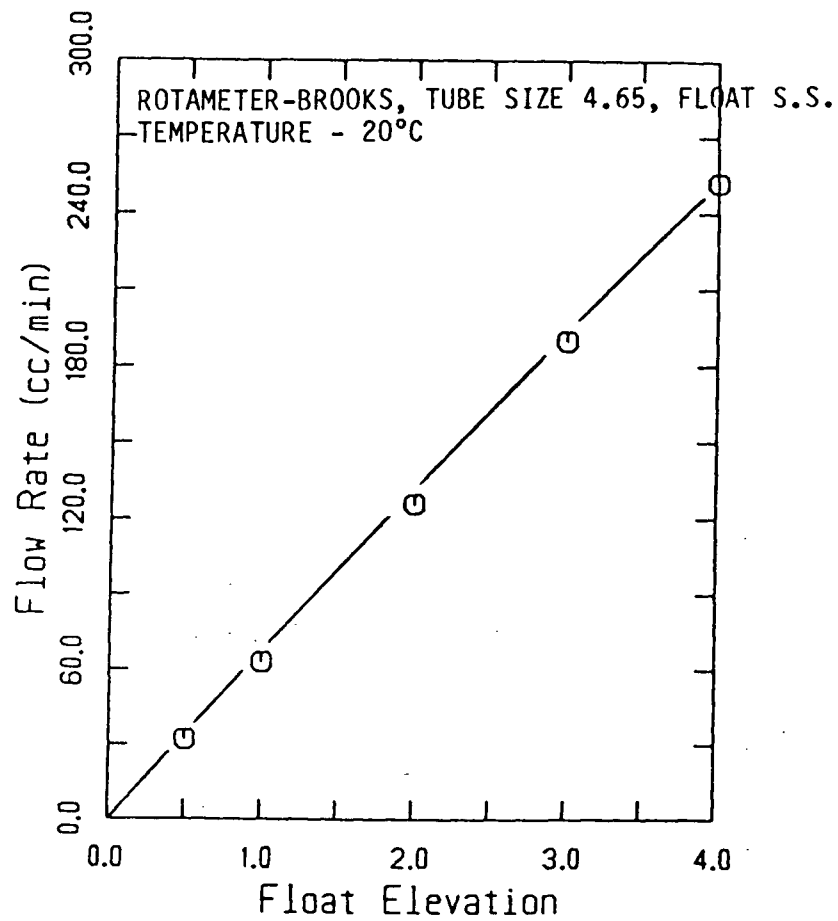


FIGURE C: CALIBRATION CURVE FOR THE WATER FLOW

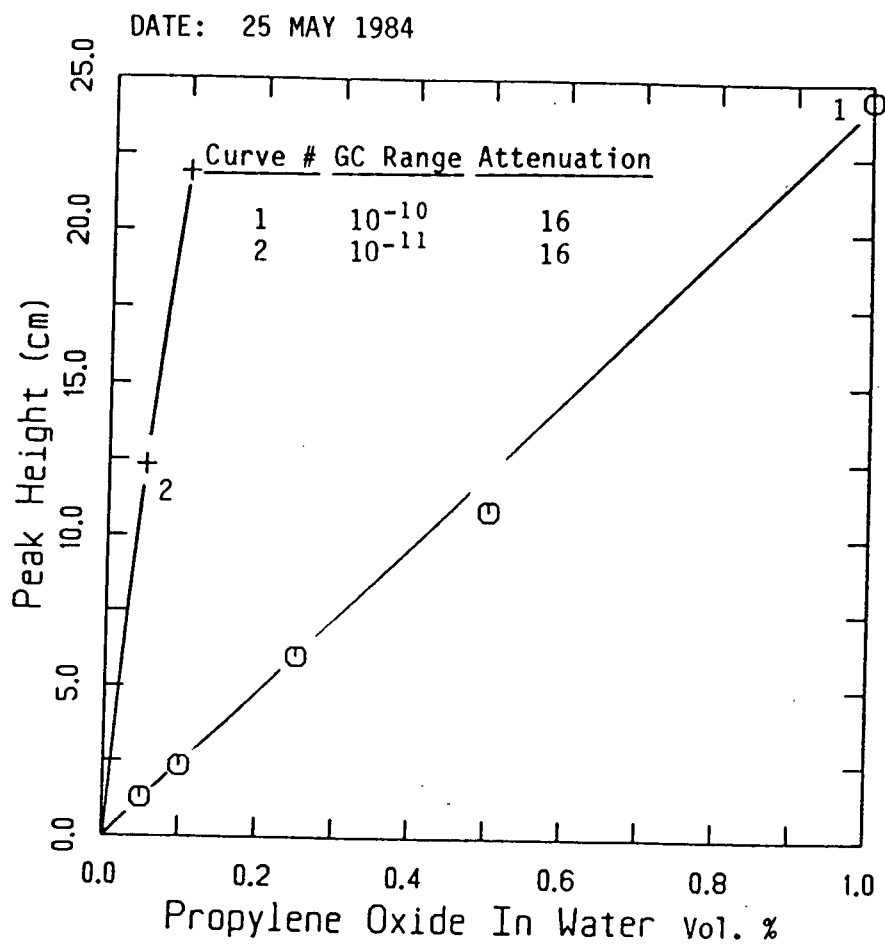


FIGURE D: CALIBRATION CURVE FOR PROPYLENE OXIDE

APPENDIX 4

TABULATED EXPERIMENTAL RESULTS, ANALYTICAL TECHNIQUE AND SAMPLE CALCULATIONS

4.0 Propylene Oxide

Upon leaving the condenser the product mixture was delivered to a 500 ml. beaker where the propylene oxide solution was separated from the gas. The gas flows to the absorption tower where some propylene and all the propylene oxide is absorbed in the water flowing counter current to the gas flow. The gas leaving the top of the tower is sampled through a tee before being passed through the wet test meter.

Sample Calculation

Electrolyte flow	= 300 cm ³ /min
Gas flow	= 1000 cm ³ /min (STP)
Reactor outlet temperature	= 30°C
Run time	= 10 min
Current	= 8 amps
Voltage	= 34 volts
Bed thickness (5 beds + diaphragms)	= 8.57 x 10 ⁻² m
Carbon type	= Union Carbide
Electrolyte concentration	= 0.5 M
Electrode area	= 4.84 x 10 ⁻² m ²
Water flow to the absorption tower	= 190 cm ³ /min
Gas flow rate leaving the tower	= 1091 cm ³ /min

a. Space Time Yield

$$STY = \frac{\text{Production rate}}{\text{Reactor volume}}$$

$$\text{Reactor volume} = 4.15 \times 10^{-4} \text{ m}^3$$

Sampling flask

$$\text{Volume} = 242 \text{ ml.}$$

$$\% \text{ propylene oxide} = 0.82$$

Absorbition tower

$$\text{Water flow rate} = 190 \text{ cm}^3/\text{min}$$

$$\% \text{ propylene oxide} = .063$$

$$\begin{aligned} \text{Production rate} &= \frac{(242 \text{ cm}^3)(60 \text{ min/hr})(.82/100)}{(10 \text{ min})} \\ &+ (.063/100)(190 \text{ cm}^3/\text{min})(60 \text{ min/hr}) \end{aligned}$$

$$= 19.1 \text{ cm}^3 \text{ of propylene oxide/hr}$$

$$STY = \frac{(19.1 \text{ cm}^3/\text{hr})(1 \text{ m}^3/1 \times 10^6 \text{ cm}^3)(831 \text{ kg/m}^3)}{(4.15 \times 10^{-4} \text{ m}^3)}$$

$$\underline{STY = 38.2 \text{ kg/hr m}^3}$$

b. Dibromopropane balance (Figure E)

Leaving Separator B (Stream 4)

Vapour pressure of dibromopropane at room temperature = 5 mm Hg

Stream 4

$$\begin{aligned} \text{Dibromopropane in stream 4} &= \left(\frac{5 \text{ mm Hg}}{760 \text{ mm Hg}} \right) (10 \text{ min})(1091 \text{ cm}^3/\text{min}) \\ &= 71.8 \text{ cm}^3 \text{ of gas} \end{aligned}$$

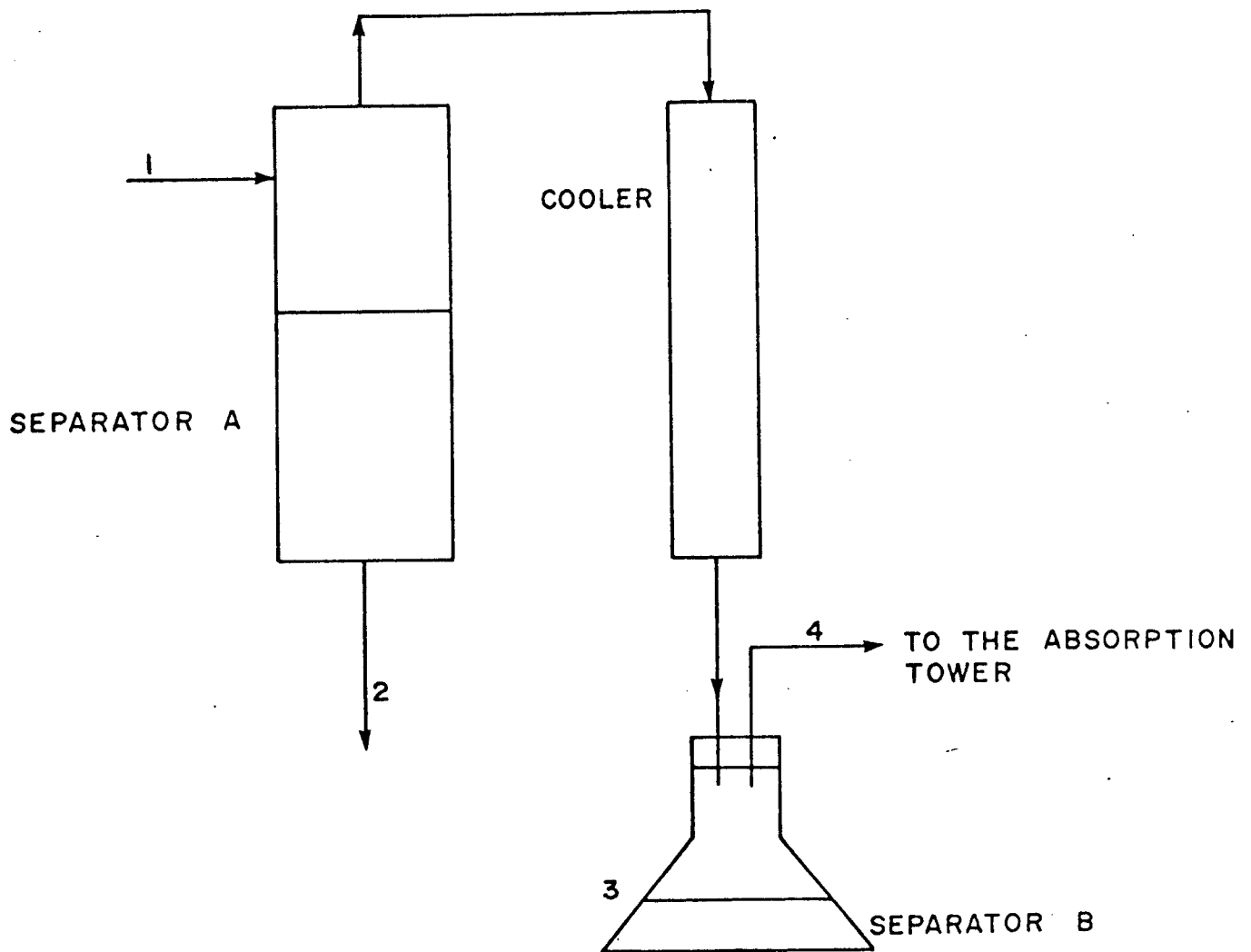


FIGURE E

1 mole of gas at room temperature occupies 24,400 cm³.

molecular weight of dibromopropane = 201.9 g/mole

density of dibromopropane = 1.9 g/cm³

$$\frac{(71.8 \text{ cm}^3 \text{ of gas})(201.9 \text{ g/mole})}{(24,400 \text{ cm}^3 \text{ of gas/mole})(1.9 \text{ g/cm}^3)} \\ = \underline{0.31 \text{ cm}^3 \text{ of liquid dibromopropane in stream 4}}$$

Stream 3

Volume of dibromopropane as a separate phase = 0.20 cm³

Amount of dissolved in the propylene oxide solution

$$= \frac{(0.25 \text{ g DBP})}{100 \text{ g H}_2\text{O}} (92 \text{ cm}^3) \left(\frac{1 \text{ g H}_2\text{O}}{\text{cm}^3 \text{ H}_2\text{O}} \right) \left(\frac{1 \text{ cm}^3 \text{ DBP}}{1.9 \text{ g DBP}} \right) \\ = 0.12 \text{ cm}^3$$

$$\underline{\text{Total dibromopropane in steam 3} = 0.32 \text{ cm}^3}$$

Stream 2

$$\text{Total dibromopropane in steam 2} = \frac{(.015 \text{ cm}^3 \text{ DBP})}{150 \text{ cm}^3} \left(\frac{300 \text{ cm}^3}{\text{min}} \right) (10 \text{ min}) \\ = \underline{0.30 \text{ cm}^3}$$

Stream 1

$$\text{Steam 1} = \text{Steam 2} + \text{Steam 3} + \text{Steam 4}$$

$$\underline{\text{Total dibromopropane produced} = 0.93 \text{ cm}^3}$$

c. Propylene Balance

(i) Moles of propylene entering (gas flow at STP)

$$= \frac{(1000 \text{ cm}^3/\text{min})(10 \text{ min})}{(24,400 \text{ cm}^3/\text{mole})} = 0.416 \text{ mole}$$

(ii) propylene consumed to produce dibromopropane and propylene oxide

$$\begin{aligned} &= \frac{(0.93 \text{ cm}^3 \text{ of DBP})(1.9 \text{ g/cm}^3)}{(201.9 \text{ g/mole})} \\ &+ \frac{(19.1 \text{ cm}^3/\text{hr})(1\text{hr}/60 \text{ min})(10 \text{ min})(.83 \text{ g/cm}^3)}{(58.0 \text{ g/mole})} \\ &= \underline{.054 \text{ moles}} \end{aligned}$$

(iii) propylene dissolved in separator A underflow (Figure E)

The solubility of propylene at 83°C = .0032 g/100g of water

propylene dissolved in the electrolyte

$$\begin{aligned} &= (300 \text{ cm}^3/\text{min})(10 \text{ min}) \left(\frac{.0032 \text{ g P}}{100 \text{ g H}_2\text{O}} \right) \left(\frac{1 \text{ g H}_2\text{O}}{\text{cm}^3 \text{ H}_2\text{O}} \right) \left(\frac{1 \text{ mole P}}{42 \text{ g P}} \right) \\ &= \underline{.0023 \text{ moles}} \end{aligned}$$

(iv) propylene dissolved in separator B.

$$\begin{aligned} &= (92 \text{ cm}^3) \left(\frac{.044 \text{ g P}}{100 \text{ g H}_2\text{O}} \right) \left(\frac{1 \text{ g H}_2\text{O}}{\text{cm}^3 \text{ H}_2\text{O}} \right) \left(\frac{1 \text{ mole P}}{42 \text{ g P}} \right) \\ &= \underline{.0010 \text{ moles}} \end{aligned}$$

(v) propylene dissolved in the tower underflow

$$\begin{aligned} &= (190 \frac{\text{cm}^3}{\text{min}})(10 \text{ min}) \left(\frac{.044 \text{ g P}}{100 \text{ g H}_2\text{O}} \right) \left(\frac{1 \text{ g H}_2\text{O}}{\text{cc H}_2\text{O}} \right) \left(\frac{1 \text{ mole P}}{42 \text{ g P}} \right) \\ &= \underline{.0198 \text{ moles}} \end{aligned}$$

SOLUBILITY OF PROPYLENE IN WATER

AT 1 ATM. ABSOLUTE

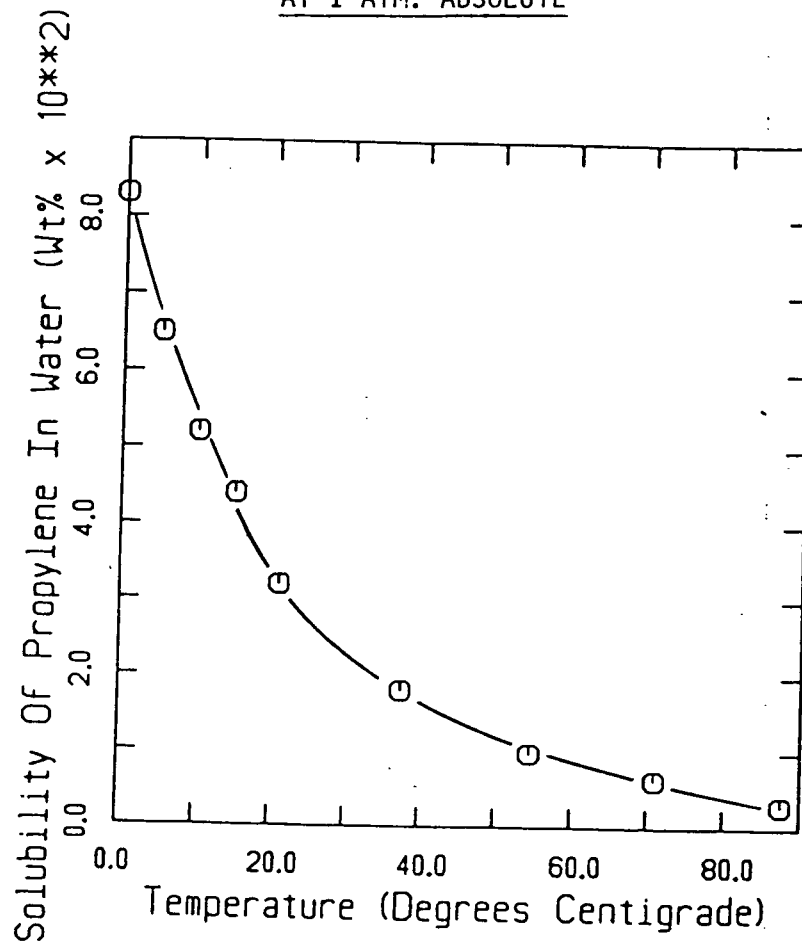


FIGURE F

(vi) Propylene leaving in the gas. Since the GC only detects N_2 , H_2 , O_2 , CH_4 , CO , and CO_2 the following technique was used. First 1 ml of nitrogen gas is injected into the gas chromatograph to determine its purity. Next 4 ml of gas sample is injected. Finally 1 ml of nitrogen gas and 4 ml of the gas sample are combined and analyzed.

Nitrogen (1 ml)

1 ml of gas analyzed has 99.6% nitrogen and .4% oxygen.

Gas Sample (4 ml)

4 ml of gas sample contained 93.578% hydrogen, 3.634% oxygen and 2.788% nitrogen.

Combined Sample (5 ml)

5 ml of the combined gas sample contained 37.694% hydrogen, 2.109% oxygen and 60.197% nitrogen.

Let P = propylene, H = hydrogen, O = oxygen, N = nitrogen

All units are in ml

For the gas sample

x = ml. of gas sample detected

$$H/x = .93578, \quad O/x = 0.0364, \quad N/x = .02788 \quad (1)$$

$$4.0 - x = P$$

For nitrogen gas sample injected = 1 ml.

$$N = 0.996 \text{ ml}$$

$$O = 0.004 \text{ ml}$$

For the combined sample let $Z = \text{ml of sample detected.}$

$$N \text{ balance: } 0.60197 Z = .996 \text{ ml} + N \text{ in gas sample} \quad (3)$$

$$O \text{ balance: } 0.02109 Z = .004 \text{ ml} + O \text{ in gas sample} \quad (4)$$

$$H \text{ balance: } 0.37694 Z = H \text{ in gas sample} \quad (5)$$

$Z = 1 \text{ ml of nitrogen gas sample} + x \text{ ml of gas sample}$

$$\text{From Eq. (3) } .60197 (1 + x) = .996 + N \quad (6)$$

$$\text{From Eq. (1) } N/x = .02788 \quad (7)$$

Substitute Eq. (7) into Eq. (6)

$$.60197 (1 + x) = .996 + .02788 x \quad (8)$$

Solving Eq. (8) gives

$$x = (.996 - .60197)/(.60197 - .02788)$$

$$\underline{x = 0.686 \text{ ml}}$$

amount of propylene leaving in the gas

$$= 4.0 - 0.686 = \underline{3.314 \text{ ml}}$$

$$= (3.314/4.0)(100) = \underline{82.85\%}$$

moles of propylene leaving in gas =

$$\frac{(1091 \text{ cm}^3/\text{min})(10 \text{ min})(.8285)}{(24400 \text{ cm}^3/\text{mole})} = 0.370 \text{ moles}$$

Total moles in = 0.416 moles

Total moles out = 0.447 moles

% difference = 7.45%

d. Propylene oxide yield = $\frac{\text{propylene oxide produced}}{\text{propylene feed}}$

$$\begin{aligned} \text{propylene oxide yield} &= \frac{(19.1 \text{ cm}^3/\text{hr})(1 \text{ hr}/60 \text{ min})(10 \text{ min})(.83 \text{ g}/\text{cm}^3)}{(58 \text{ g}/\text{mole})(0.416 \text{ moles})} \\ &= .1095 \text{ or } 10.95\% \end{aligned}$$

e. Propylene conversion = $\frac{\text{propylene consumed in the production of propylene oxide and dibromopropane}}{\text{propylene feed}}$

$$\begin{aligned} \text{propylene conversion} &= \frac{.054 \text{ moles}}{0.416 \text{ moles}} \\ &= \underline{0.1298 \text{ or } 12.98\%} \end{aligned}$$

f. Propylene oxide selectivity = $\frac{\text{propylene oxide yield}}{\text{propylene conversion}}$

$$= .1095/.1298$$

$$= \underline{.8436 \text{ or } 84.36\%}$$

g. Current efficiency and specific energy consumption

current efficiency of propylene oxide

$$= \frac{(.0456 \text{ moles})(2)(96500 \text{ coul/eq.})}{(10 \text{ min})(60 \text{ sec/min})(8 \text{ Amps/cell})(5 \text{ cells})}$$
$$= \underline{0.3667 \text{ or } 36.67\%}$$

Specific energy consumption of propylene oxide

$$SE = \frac{(26.8)(Z)(V)}{(MW)(CE)}$$

MW = molecular weight

CE = current efficiency

V = voltage drop/cell

Z = number of electrons

$$SE = \frac{(26.8)(2)(34 \text{ V/5})}{(58 \text{ g/mole})(.3667)}$$

$$\underline{SE = 17.1 \text{ kwhr/kg}}$$

Similarly the current efficiency and the specific energy consumption for hydrogen, nitrogen, oxygen and dibromopropane were determined.

Table E

Compound	Current Efficiency %	Specific Energy Consumption kwhr/kg
Oxygen	3.6	3150.6
Hydrogen	58.7	1553.7
Propylene oxide	36.7	85.7
Dibromopropane	7.1	127.1

4.1 Hypobromite, Bromite and Bromate

On leaving the reactor the liquid was collected in a 150 ml beaker and analyzed for hypobromite, bromite and bromate as follows:

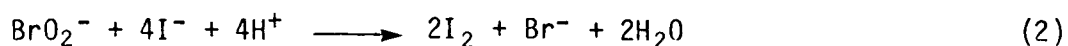
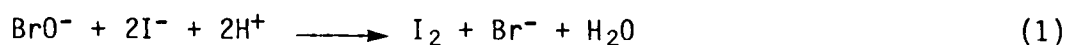
- First a 0.1 N arsenious oxide solution was prepared (26) and titrated with a standard 0.1 N solution of iodine to determine the exact normality. 0.01 N sodium thiosulphate solution was also prepared.
- To a 5 ml of mixture containing the hypobromite, bromite and bromate, was added 3 to 4 grams of solid potassium iodide, followed by 10 ml of 4 N sulphuric acid. The solution was diluted to twice its volume, and the liberated iodine was titrated with thiosulphate using starch as the indicator.
- 5 ml of the mixture was added to a flask containing an excess of ammonium sulphate and about 1 gram of sodium bicarbonate. After 10 minutes, 3 to 4 grams of solid potassium iodide and 10 ml of 4 N sulphuric acid was added. The solution was let stand for 5 minutes before it was diluted to twice its volume and titrated with thiosulphate.

d. To 5 ml of mixture, a known excess of arsenious oxide was added (4 ml). After 5 minutes, 4 to 5 grams of sodium bicarbonate was added. The solution was titrated with iodine using starch as the indicator.

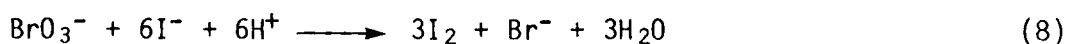
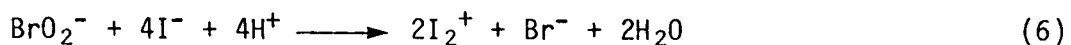
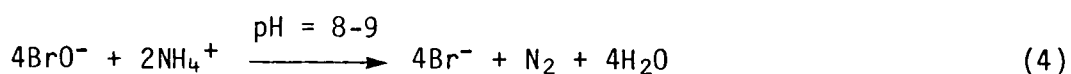
e. 5 ml of mixture was added to a flask containing an excess of ammonium sulphate and about 1 gram of sodium bicarbonate. After 10 minutes a known excess of arsenious oxide was added (4 ml) and the solution was let stand for 5 minutes before titrating with iodine.

The equations for the reactions are:

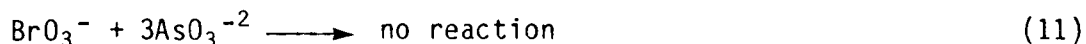
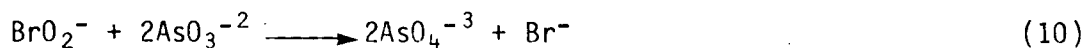
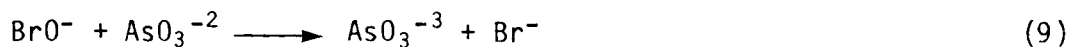
For (b)



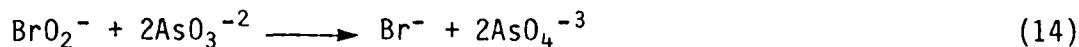
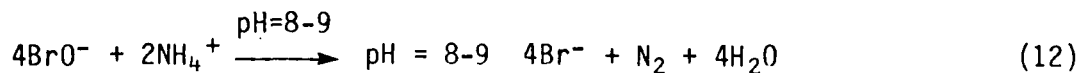
For (c)



For (d)



For (e)

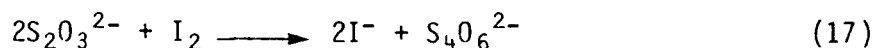


Sample Calculation (Box T, Table 7)

(i) Total hypobromite, bromite, bromate present is calculated from procedure (b) and Eq. (1), (2), and (3).

Average volume of thiosulphate used = 3.25 ml

$$\begin{aligned} \text{moles of } \text{S}_2\text{O}_3^{2-} \text{ used} &= (.01 \text{ moles/L})(3.25 \text{ L}/1000)(10^6 \text{ } \mu\text{moles/mole}) \\ &= 32.5 \text{ } \mu\text{moles} \end{aligned}$$



moles of $\text{I}_2 = 32.5 \text{ } \mu\text{moles}/2 = 16.25 \text{ } \mu\text{moles}$.

From Equations (1), (2) and (3)

the ratio of $\text{I}_2:\text{BrO}^-, \text{BrO}_2^-, \text{BrO}_3^- = 2:1$.

moles of $\text{BrO}^-, \text{BrO}_2^-, \text{BrO}_3^- = 8.13 \text{ } \mu\text{moles}$

(ii) Total bromite and bromate is calculated from procedure (c) and Equations (4) to (8).

Average volume of thiosulphate used = 1.75 ml

moles of $S_2SO_3^{2-}$ used = 17.5 μ moles

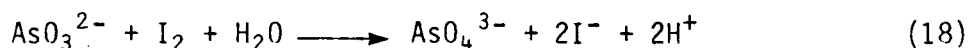
moles of I_2 = 8.75 μ moles

Ratio of $I_2:BrO_2^-$, BrO_3^- = 5:2

moles of BrO_2^- , BrO_3^- = 3.50 μ moles

(iii) Total hypobromite and bromite is calculated from procedure (d) and Equation (9) to (11).

Average volume of iodine used = 3.7 ml



moles of AsO_3^{2-} present initially

$$= (0.1012 \text{ N})(1M/4N)(4.0 \text{ L}/1000)(10^6 \text{ } \mu\text{moles/mole})$$

$$= 101.2 \text{ } \mu\text{moles}$$

moles of I_2 used =

$$= (3.7 \text{ L}/1000)(.1 \text{ N})(1M/2N)(10^6 \text{ } \mu\text{moles/mole})$$

$$= 185.0 \text{ } \mu\text{moles}$$

moles of AsO_3^{2-} unreacted from Equation (18)

$$= 185.0 \text{ } \mu\text{moles}/2 = 92.5 \text{ } \mu\text{moles}$$

moles of AsO_3^{2-} reacted = 101.2 - 92.5 = 8.7 μ moles

Ratio of $AsO_3^{2-}:BrO^-$, BrO_2^- from Equations (9) and (10) = 3:2

moles of BrO^- , BrO_2^- = 5.8 μ moles

(iv) Moles of bromite is determined from procedure (e) and Equations (12) to (16).

Average volume of iodine used = 3.8 ml

moles of AsO_3^{2-} initially present = 101.2 μmoles

moles of I_2 used = 190 μmoles

moles of AsO_3^{2-} unreacted = 95 μmoles

moles of AsO_3^{2-} reacted = 6.2 μmoles

Ratio of $\text{AsO}_3^{2-}:\text{BrO}_2^-$ = 2:1

moles of BrO_2^- = 3.1 μmoles .

Moles of hypobromite = i - ii = 8.13 - 3.50 = 4.63 μmoles

moles of bromate = i - iii = 8.13 - 5.8 = 2.33 μmoles

moles of bromite = 3.10 μmoles

Current efficiency for bromite

$$\frac{(3.10 \times 10^{-6} \text{ moles/5 ml})(100 \text{ ml/min})(4)(96500 \text{ coul/mole})}{(60 \text{ sec/min})(10 \text{ amps})}$$

$$= \underline{0.04 \text{ or } 4.0\%}$$

Similarly the current efficiency for hypobromite and bromate was determined.

Table F

Compound	μmoles	Current Efficiency %
Hypobromite	4.63	3.0
Bromite	3.10	4.0
Bromate	2.33	4.5

4.2 Recycle

For the recycle mode the mixture leaving the reactor was circulated back to the feed tank. The gas leaving the feed tank was analyzed for propylene oxide and the amount was determined to be negligible. After one hour of operation the mixture was passed through the system (heat exchanger, separator and condenser) at the same flow rate as the recycle flow. The technique described in Section 4.0 was employed to determine the space time yield. The same procedure was used to determine the space time yield after 2, 3 and 4 hours of operation.

First Hour

Reactor bed thickness	= 8.57 cm
Electrolyte flow rate	= 300 cm ³ /min
Initial volume	= 26 L
Current	= 8 A
Temperature	= 30 - 36°C
Electrolyte Concentration	= 0.5 M
Propylene gas flow rate	= 1500 cm ³ /min (STP)

$$\begin{aligned}\text{Total volume recycled} &= (300 \text{ cm}^3/\text{min})(60 \text{ min/hr})(1 \text{ L}/1000 \text{ cm}^3)(1 \text{ hr}) \\ &= \underline{18 \text{ L}}\end{aligned}$$

Assume all the propylene oxide was produced during the recycle.

Using the same analytical technique described in 4.0 the propylene oxide produced was determined to be 24.3 cm³/hr.

Volume of propylene oxide in feed tank

$$\begin{aligned} &= (24.3 \text{ cm}^3/\text{hr})(26 \text{ L}/18 \text{ L})(1 \text{ hr}) \\ &= 35.1 \text{ cm}^3 \end{aligned}$$

Space time yield in the first hour

$$\begin{aligned} &= \frac{(35.1 \text{ cm}^3/\text{hr})(.831 \text{ g}/\text{cm}^3)(1 \text{ kg}/1000 \text{ g})}{(4.15 \times 10^{-4} \text{ m}^3)} \\ &= \underline{70.3 \text{ kg}/\text{hr m}^3} \end{aligned}$$

Second Hour

Total produced in 2 hours = amount produced in the 1st hour + amount produced in the 2nd hour

a Again using the techniques of 4.1 the total propylene oxide produced was determined to be = $37.0 \text{ cm}^3/\text{hr}$.

Total volume after 1 hour = 20 lit.

Total propylene oxide produced in the second hour
 $= (37.0 - 24.3) \text{ cm}^3/\text{hr} = 12.7 \text{ cm}^3/\text{hr}$

Concentration of propylene oxide in feed tank
 $= (12.7 \text{ cm}^3/\text{hr})(20 \text{ L}/18 \text{ L})(1 \text{ hr})$
 $= 14.1 \text{ cm}^3$

Space time yield = $\underline{28.3 \text{ kg}/\text{hr m}^3}$

Third Hour

Total propylene oxide produced = $49.3 \text{ cm}^3/\text{hr}$

Total volume after 2 hours = 14 L

Space time yield = $\underline{19.2 \text{ kg}/\text{hr m}^3}$

Fourth Hour

Total propylene oxide produced = $62.5 \text{ cm}^3/\text{hr}$

Total volume after 3 hours = 8 L

Space time yield = 11.8 kg/hr m^3

Table G

Time (hours)	Space Time Yield kg/hr m^3	pH
1	70.3	10.58
2	28.3	10.65
3	19.2	10.70
4	11.8	10.99

Table H

Time (hours)	Space Time Yield kg/hr m^3	pH
1	41.4	10.45
2	20.6	10.55
3	13.1	10.63

Condition for Table H: Bed Thickness = 8.57 cm
 Electrolyte flow rate = $300 \text{ cm}^3/\text{min}$
 Initial volume = 14 L
 Current = 5A
 Temperature = $29 - 32^\circ\text{C}$
 Electrolyte Concentration = 0.5 M
 Propylene gas flow rate = $1500 \text{ cm}^3/\text{min}$ (STP)

Table I

Time (hours)	Space Time Yield kg/hr m ³	pH	Total Bromates in μmoles
1	127.8	10.52	53.4
2	44.3	10.96	70.5

Condition for Table I: Bed Thickness = 3.07 cm
Electrolyte flow rate = 300 cm³/min
Initial volume = 14 L
Current = 8A
Temperature = 30 - 32°C
Electrolyte Concentration = 0.5 M
Propylene gas flow rate = 1500 cm³/min (STP)

Table J

The Effect of Current and Propylene Gas Flow on the Space Time Yield and,
Energy Consumption for Propylene Oxide and Current Efficiencies

Current Amps	pH	Gas Flow cm ³ /min (STP)	Space Time Yield kg/hr m ³	Energy Consumption Kwhr/kg	Current Efficiency - %				Selectivity Percent
					Propylene Oxide	Dibromopropane	Oxygen	Hydrogen	
2	11.45	1000	14.8	5.9	56.5	24.1	0.0	62.6	70.1
5	11.42	1000	32.6	10.0	49.9	9.9	1.1	62.4	83.5
8	11.40	1000	38.0	17.3	36.4	7.0	3.6	56.9	83.9
11	11.46	1000	26.6	40.1	18.6	7.0	4.5	58.3	72.5
5	11.50	1500	38.0	9.2	58.2	12.9	1.6	59.4	81.8
8	11.53	1500	54.2	13.1	51.9	12.1	3.0	62.1	81.1
11	11.60	1500	60.7	17.4	42.3	8.6	3.8	58.0	83.1
13	11.45	1500	44.8	31.2	26.4	8.4	4.9	56.9	76.0
2	11.35	2000	12.4	7.0	47.6	29.6	-	-	61.8
5	11.27	2000	28.5	12.7	43.6	13.9	2.9	56.3	75.8
8	11.38	2000	24.2	31.1	23.2	7.7	5.5	60.9	75.2

Conditions: Graphite Particle Size = 1.168 - 1.68 mm
 Graphite Type = Union Carbide
 Temperature = 28 - 35°C
 Concentration = 0.5 M

Liquid Flow Rate = 300 cc/min
 Pressure = 1.4 - 2.2 atm
 Bed Thickness = 8.57 cm

Table K

Effect of Bed Thickness on Space Time Yield for Propylene Oxide

Electrolyte Flow cm ³ /min											
100				300							
Gas Flow cm ³ /min				Gas Flow cm ³ /min							
100		1000		100		1000					
				STY PO Produced Current eff. PO Current eff. DBP pH Selectivity				Bed Thickness Volume (m ³)			
= 18.7 kg/hr/m ³ = 9.4 cm ³ /hr = 28.7% = 4.9% = 11.01 = 85.3%				= 30.3 kg/hr/m ³ = 15.1 cm ³ /hr = 46.3% = 7.5% = 10.55 = 86.1%				= 4.29 cm = 2.07 x 10 ⁻⁴			
= 20.8 kg/hr/m ³ = 5.2 cm ³ /hr = 16.0% = 7.9% = 9.83 = 67.0%				= 37.3 kg/hr/m ³ = 9.3 cm ³ /hr = 28.7% = 10.8% = 9.93 = 72.6%				= 52.1 kg/hr/m ³ = 9.3 cm ³ /hr = 28.7% = 10.8% = 10.03 = 72.6%			
= 23.4 kg/hr/m ³ = 5.8 cm ³ /hr = 17.9% = 6.6% = 9.78 = 73.0%				= 44.9 kg/hr/m ³ = 1.2 cm ³ /hr = 34.4% = 10.6% = 9.82 = 76.5%				= 3.07 cm = 1.49 x 10 ⁻⁴			
= 33.0 kg/hr/m ³ = 5.9 cm ³ /hr = 18.1% = 6.8% = 10.06 = 72.7%				= 21.9 kg/hr/m ³ = 11.0 cm ³ /hr = 33.8% = 4.9% = 11.23 = 87.3%							

Conditions:

Temp. = 30°C
 Conc. = 0.5 M
 Current = 5A
 Carbon Type = Union Carbide
 Graphite Particle Size = 1.168 - 1.68 mm
 Pressure = 1.4 - 2.2 atm

*PO = Propylene Oxide
 DBP = Dibromopropane
 STY = Space Time Yield

Table L

Effect of Bed Thickness, Superficial Current Density and Propylene Gas Flow Rate
on the Space Time Yield for Propylene Oxide

		Bed Thickness - cm							
		3.07 (volume = 1.49×10^{-4})			8.57 (volume = $4.15 \times 10^{-4} \text{ m}^3$)				
		Current Amps			Current Amps				
		5	8	11	2	5	8	11	13
Gas Flow - cm^3/min	2000	Space time yield (kg/hr m^3) = 56.9	79.1	86.5	12.4	28.5	24.2	-	-
		pH = 10.73	10.98	11.03	11.35	11.27	11.38	-	-
		Selectivity % = 69.5	74.4	75.5	61.8	75.8	75.2	-	-
		<u>Current Efficiency</u>							
		Propylene oxide = 31.3	27.2	21.6	47.6	43.6	23.2	-	-
	1500	Dibromopropane = 13.8	9.3	7.1	29.6	13.9	7.7	-	-
		PO Prod. rate = 10.2	14.2	15.5	5.6	14.3	12.3	-	-
		63.4	85.2	97.2	-	38.0	54.2	60.7	44.8
		10.98	10.92	10.83	-	11.50	11.60	11.60	11.45
		73.5	71.2	72.0	-	81.8	81.1	83.1	76.0
		34.9	29.3	24.3	-	58.2	51.9	42.3	26.4
		12.6	11.8	9.5	-	12.9	12.1	8.6	8.4
		11.35	15.3	17.4	-	19.0	27.0	30.3	22.3
	1000	52.1	61.7	56.2	14.8	32.6	38.0	26.6	-
		10.03	10.87	10.76	11.45	11.40	11.40	11.46	-
		72.6	67.1	57.8	70.1	83.5	83.9	72.5	-
		28.7	21.2	14.0	56.5	49.9	36.4	18.6	-
		10.8	10.4	10.2	24.1	9.9	7.0	7.0	-
		9.3	11.0	10.1	7.4	16.2	19.0	13.3	-

Conditions: Graphite partial Size = 1.168 - 1.68 mm
 Graphite type = Union Carbide
 Temperature = 28-35°C
 Concentration = 0.5 M

Liquid Flow = 300 cc/min
 Pressure = 1.4 - 2.2 atm.
 Area = 48.4 cm^2

APPENDIX 5

COSTING EXERCISE

Stream factor	= 0.9
Space time yield	= 127.8 kg/hr/m ³ (reactor vol)
Monopole electrode area	= 4.84×10^{-3} m ²
Reactor volume	= 1.5×10^{-4} m ³
Bed thickness	= 3.07×10^{-2} m
Graphite density	= 1.92×10^3 kg/m ³
Porosity	= 0.4
Specific surface area of carbon	= 2400 m ² /m ³
Graphite particle size	= 1.168 - 1.68 mm
Temperature	= 30°C
Weight of graphite in the reactor	= 0.172 kg
Applied current	= 8A
Applied voltage	= 30V
Current density	= 1650 A/m ³
Voltage/cell	= 6V
Electrolyte Conc.	= 0.5 m
Electrolyte flow rate	= 3.0×10^{-4} m ³ /min
Gas flow rate	= 1.5×10^{-3} m ³ /min (8 psig and 20°C)
G/L Ratio	= 5
CE propylene oxide	= 56.5%
Production rate	= (STY) (Reactor Vol) = (127.8 kg/hr m ³) (1.5×10^{-4} m ³) = 1.92×10^{-2} kg/hr

Capacity = 10,000 short tons/yr

$$= \frac{2.0 \times 10^7 \text{ lbs/yr}}{(2.2 \text{ lbs/kg})(365.25 \text{ day/yr})(24 \text{ hrs/day})(0.9)}$$
$$= 1.15 \times 10^3 \text{ kg/hr}$$

Reactor Vol = $1.5 \times 10^{-4} \text{ m}^3$

Production rate = $1.92 \times 10^{-2} \text{ kg/hr}$

Reactor Vol = x

Production rate = $1.15 \times 10^3 \text{ kg/hr}$

$$x \approx 9.0 \text{ m}^3$$

Similarly the gas flow was determined.

Reactor Dimensions

Electrode length = 1 m

Electrode width = 1 m

Electrode area = 1 m^2 per cell

bed thickness = $3.07 \times 10^{-2} \text{ m}$

Therefore 40 bipolar cells bed thickness = 0.25 m

$$\text{Reactor Vol} = (1 \text{ m}^2)(.25 \text{ m}) = 0.25 \text{ m}^3$$

No. of reactors required = $9 \text{ m}^3 / 0.25 \text{ m}^3$

$$= \underline{36 \text{ reactors each consisting 40 cells}}$$

Cost of a Single Reactor

Compression plates (constructed from iron) including bolts and plumbing cost $\approx \$2,500/\text{m}^2$. Approximately 3 m^2 is required.

$$\text{Cost}_{\text{CP}} = (3 \text{ m}^2)(\$2,500/\text{m}^2) = \$7,500$$

Monopole electrodes constructed from platinized titanium cost \approx \$1,000/m².

$$\text{Cost}_{\text{E}} = (2 \text{ m}^2)(\$1,000/\text{m}^2) = \$2,000$$

$$\text{Diaphragm cost} = (40)(1 \text{ m}^2)(\$20/\text{m}^2) = \$800.$$

$$\text{Wt. of graphite required} = (1.92 \times 10^3 \text{ kg/m}^3)(0.6)(0.25 \text{ m}^3) = 288 \text{ kg}.$$

$$\text{Graphite cost} = (288 \text{ kg})(\$2.20/\text{kg}) = \$634.$$

$$\text{Neoprene gasket cost} = (\$100/\text{m}^2)(100 \text{ m}^2) = \$10,000.$$

$$\text{Single reactor material cost} = \underline{\$20,934}.$$

$$\text{No. of reactors required} = 36$$

$$\text{Total reactor material cost} = \underline{\$753,624}.$$

Parameters for a large scale reactor

$$\text{Electrode area} = 1 \text{ m}^2$$

$$\text{Current density} = 1650 \text{ A/m}^2$$

$$\text{Electrolyte conc.} = 0.5 \text{ m}$$

$$\text{Current} = 1650 \text{ A}$$

$$\text{Voltage/cell} = 6\text{V}$$

$$\text{Reactor vol.} = 0.25 \text{ m}^3$$

$$\text{Porosity} = 0.4$$

No. of cells/reactor = 40

Bed thickness for 40 cells = 0.25 m

G/L ratio = 5

Applied voltage = 240 V

Propylene gas flow rate = 2.5 m³/min

Electrolyte flow rate = 0.5 m³/min

$$\begin{aligned}\text{CE of propylene oxide} &= (29.4 \text{ cm}^3/\text{hr})(1 \text{ hr})(.831 \text{ g/cm}^3)(1 \text{ m}/58 \text{ g}) \\ &= \frac{(0.4212 \text{ moles})(2)(96500 \text{ coul/eq.})}{(3600 \text{ sec})(40 \text{ V})} \\ &= \underline{56.5\%}\end{aligned}$$

$$\begin{aligned}\text{CE of dibromopropane} &= (1.93 \text{ cm}^3/\text{hr})(1 \text{ hr})(1.9 \text{ g/cm}^3)(1 \text{ m}/201.9 \text{ g}) \\ &= \frac{(.0182 \text{ moles})(2)(96500 \text{ coul/eq.})}{(3600 \text{ sec})(40 \text{ V})} \\ &= \underline{2.44\%}\end{aligned}$$

$$\underline{\text{Selectivity} = 95.9\%}$$

$$\begin{aligned}\text{Consumption of propylene} &= \frac{(1500 \text{ cm}^3/\text{min})(60 \text{ min/hr})(1 \text{ hr})}{24030 \text{ cm}^3/\text{mole}} \\ &= \underline{3.75 \text{ moles}}\end{aligned}$$

$$\begin{aligned}\text{Consumption} &= (.4212 + .0182)/3.75 \\ &= \underline{11.73\%}\end{aligned}$$

$$\text{Propylene oxide yield} = \underline{11.23\%}$$

Rectifier Cost

$$\begin{aligned}\text{Rectifier cost} &= \left(100 + \frac{10000}{480}\right) 1.44 \times 10^4 \text{ KW} \\ &= \underline{\$1.74 \times 10^6}\end{aligned}$$

This cost includes transformers, voltage regulators, controls, switch gears and rectifiers.

Operation Cost

$$\text{Power Cost} = \$.04/\text{Kwhr}$$

$$\begin{aligned}\text{Power requirement for 24 hrs} &= \frac{(480 \text{ V})(30,000 \text{ A})(24 \text{ hrs})}{1000 \text{ watts/kw}} \\ &= 3.46 \times 10^5 \text{ Kwhr} \\ &= 3.84 \times 10^5 \text{ Kwhr}\end{aligned}$$

$$\eta = 0.9$$

Cost = \$15,400/day

Raw Materials Cost

$$\text{Propylene} = \$0.20/\text{lb}$$

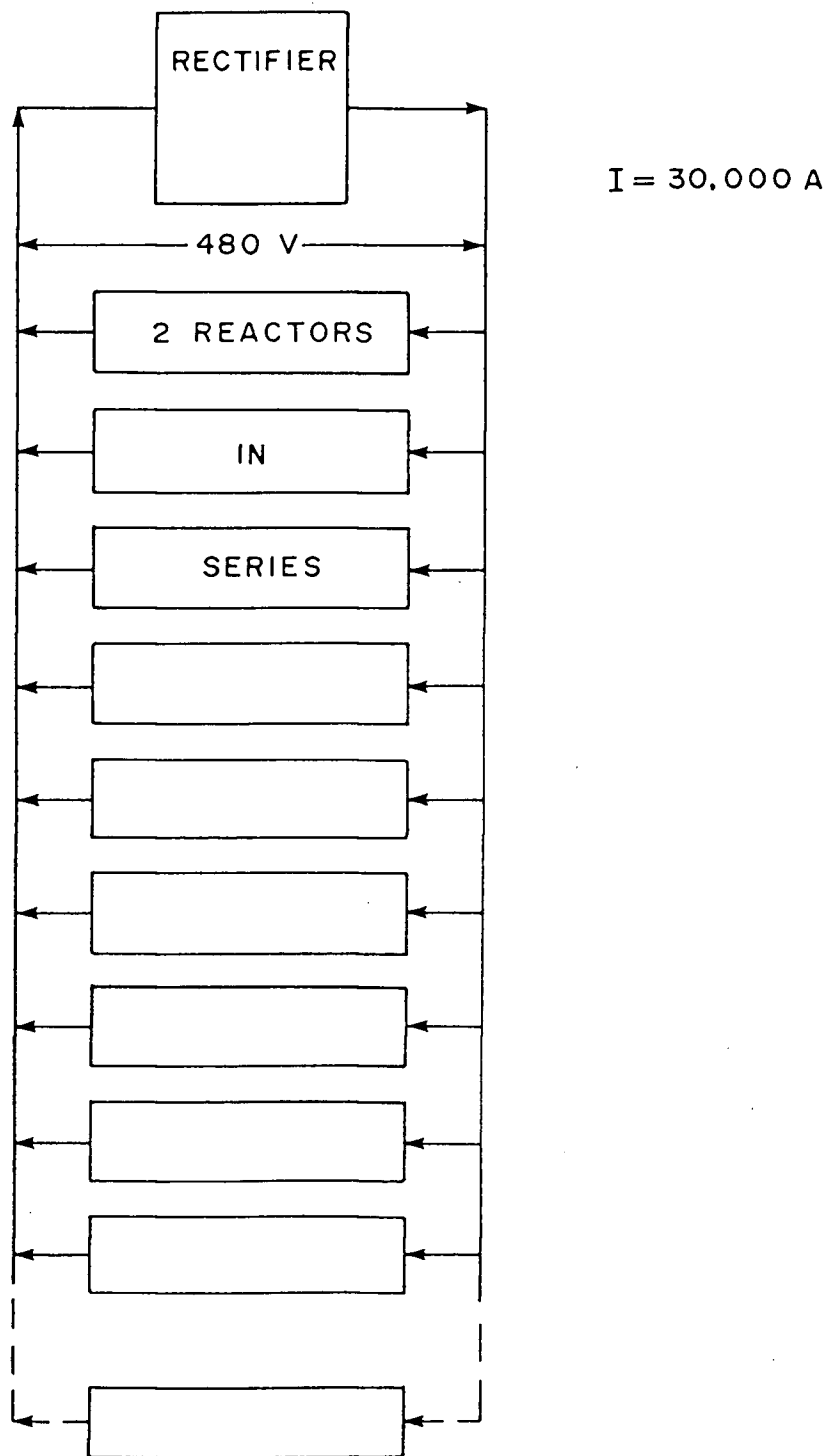
$$\text{NaBr} = \$1.00/\text{lb}$$

$$\begin{aligned}\text{Propylene required} &= (2.5 \text{ m}^3/\text{min})(36)(60 \text{ min/hr})(24 \text{ hr/day}) \\ &= 1.30 \times 10^5 \text{ m}^3/\text{day} = 1.30 \times 10^8 \text{ lit/day}\end{aligned}$$

$$\begin{aligned}\text{PV} &= nRT \quad (1 \text{ atm})(1.30 \times 10^8 \text{ lit/day}) = (n)\left(.082 \frac{\text{L atm}}{\text{mole K}}\right)(293 \text{ K}) \\ n &= 5.4 \times 10^6 \text{ moles/day}\end{aligned}$$

$$\text{Consumption} + \text{losses} = 12\%, \text{ recycle} = 88\%.$$

$$\begin{aligned}\text{Make up/day} &= (.12)(5.4 \times 10^6 \text{ moles/day}) \\ &= 6.47 \times 10^5 \text{ moles/day}\end{aligned}$$



PROPOSED LAY OUT FOR THE REACTORS

FIGURE G

$$\begin{aligned}\text{lbs required} &= (6.47 \times 10^5 \text{ moles/day})(42 \text{ g/moles})(1 \text{ lb}/454 \text{ g}) \\ &= 6.0 \times 10^4 \text{ lbs/day}\end{aligned}$$

$$\text{Cost propylene} = (\$0.20/\text{lb})(6 \times 10^4 \text{ lbs/day})$$

$$\boxed{= \$1.20 \times 10^4/\text{day}}$$

Total Br^- lost as hypobromite, bromite and bromate in the 1st hour.

$$(18 \text{ L}) \frac{(53.4 \times 10^{-6} \text{ moles})}{(5 \text{ cm}^3)} (100 \text{ cm}^3/\text{lit}) = 0.192 \text{ moles}$$

Total Br^- lost as dibromopropane

$$\left(\frac{0.15 \text{ cm}^3 \text{ DBP}}{150 \text{ cm}^3}\right) \left(\frac{18,000 \text{ cm}^3}{(201.9 \text{ g/mole})}\right) (1.9 \text{ g/cm}^3) = .017 \text{ moles of DBP}$$

Ratio Br^- :DBP = 2:1

Moles of Br^- lost as DBP = .034 moles

Total Br^- lost per hour = 0.226 moles or 5.42 moles/day.

Moles entering the reactor/day

$$\begin{aligned}&= (300 \text{ cm}^3/\text{min})(60 \text{ min/hr})(24 \text{ hr/day})(0.5 \text{ moles/L})(1 \text{ L}/1000 \text{ cm}^3) \\ &= 216 \text{ moles/day}\end{aligned}$$

$$\text{Make up stream} = (5.42/216)(100) = 2.5\%$$

gram moles entering cell house per day

$$= (0.5 \text{ moles/L})(500 \text{ L/min})(36 \text{ reactors})(60 \text{ min/hr})(24 \text{ hr/day})$$

$$= 1.3 \times 10^7 \text{ moles/day}$$

$$\text{Make up stream} = (.025)(1.3 \times 10^7 \text{ moles/day}) = 3.24 \times 10^5 \text{ moles/day}$$

$$\text{Cost of NaBr per day} = (3.24 \times 10^5 \text{ moles/day})(102.9 \text{ g/mole})$$

$$(1 \text{ lb}/453.6 \text{ g})(\$1.00/\text{lb}) = \$7.35 \times 10^4/\text{day}$$

Labour

3 shifts at 4 people/shift @ \$15/hr

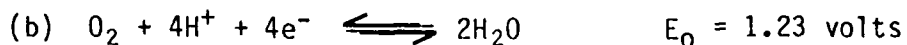
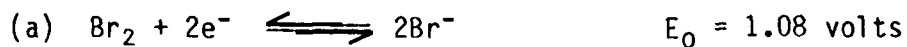
$$\text{Cost/day} = (3)(4)(8)(\$15/\text{hr}) = \$1,440/\text{day}$$

$$\approx \underline{\$2,000/\text{day}}$$

APPENDIX 6

OVERPOTENTIAL FOR OXYGEN AND BROMINE OVER GRAPHITE

The two competing reactions at the anode are:



Using Nernst equation the reversible potential for reaction (a) at a concentration of 0.5 M was determined. Similarly the reversible potential for reaction (b) at an average pH (pH = 10.64) obtained in the experiments was determined.

The Nernst equation for reaction a and b at 25°C are:

$$E_a = 1.08 - .03 \log \frac{[\text{Br}^-]^2}{[\text{Br}_2]}$$

$$E_b = 1.23 - .015 \log [\text{H}^+]^{-4}$$

The overpotential for oxygen at 25°C over graphite was calculated using the Tafel Equation given in reference [28]

$$\text{overpotential} = .4 + .17 \log i$$

where i is in A/m^2

The bromine overpotential over graphite was obtained from reference [29]

Table M

Overpotential of Oxygen and Bromine Over Graphite

Oxygen: $E_o = 1.23$ volts $E_a = 0.59$ volts $\Delta Gr = 113.9$ KJ/mole

Current Density (A/m ²)	Overpotential (V)	Total potential (V)
10	0.57	1.16
100	0.74	1.33
1,000	0.91	1.50
5,000	1.03	1.62
10,000	1.08	1.67

Bromine: $E_o = 1.08$ volts $E_b = 1.10$ volts $\Delta Gr = 212.3$ KJ/mole

Current Density (A/m ²)	Overpotential (V)	Total potential (V)
100	0.002	1.102
1,000	0.027	1.127
5,000	0.160	1.260
10,000	1.33	1.430

APPENDIX 7

SOURCE TABLE RESULTING FROM FIVE FACTOR ANALYSIS

Table N
Source Table Resulting from Five Factor Analysis of Variance

Independent Variable	Dependent Variable									
	Propylene Oxide				Current Efficiency					
	Space Time Yield	Selectivity	Current Efficiency	Specific Energy Conspt.	Dibromo-propane	Hydrogen	Oxygen	Hypobromite	Bromite	Bromate
T	0.26 (-)	427.8 (-)	685.4 (-)							381.1 (-)
A	5.86 (+)	1758.3 (+)		336.7 (+)	562.0 (-)					1436.1 (+)
C	0.49 (+)		744.0 (+)	875.7 (-)	37.2 (+)		60.5 (-)		26.7 (-)	1303.7 (-)
L	0.39 (+)		350.5 (+)	89.1 (-)				72.9 (+)		
G	1.65 (+)		1804.5 (+)	379.5 (-)	300.8 (+)	1815.0 (+)		46.5 (-)	22.2 (-)	896.9 (-)
A x L	0.19									
A x G	0.47				83.4					222.0
A x C					20.6					636.6
T x A			399.8	99.4						
Residual (D.F.)	0.40 (24)	647.3 (29)	551.8 (26)	302.1 (26)	65.9 (26)	2249.3 (30)	111.5 (30)	119.4 (29)	108.4 (29)	848.0 (25)
Total	9.71	2833.4	4536.0	2082.5	1069.9	4064.3	172.0	304.5	157.3	5724.4

T = temperature

A = current

C = concentration

L = electrolyte flow rate

G = propylene gas flow rate

A x L = First order interaction. It measures the extent to which the effect of one factor, in this case current, depends upon the value of the other factor, electrolyte flow rate.

D.F. = degrees of freedom

The numbers reported above are the sums of squares.

APPENDIX 8

DATA REPLICATION

Table 0
Data Replication

Current	Space Time Yield for Propylene Oxide kg/hr m ³	
5	38.49 A	37.53 B
8	55.81	52.59
11	63.67	57.73
13	43.40	46.20

Conditions:

Graphite particle size = 1.168 - 1.68 mm

Graphite type = Union Carbide

Temperature = 28-35°C

Concentration = 0.5 M

Liquid flow rate = 300 cm³/min

Gas flow rate = 1500 cm³/min at STP

Pressure = 1.4 - 2.2 atm

Bed thickness = 8.57 cm