

**DYNAMIC MODELING AND OPTIMIZATION OF BATCH
ELECTRODIALYSIS PROCESS FOR HYDROCHLORIC ACID
RECOVERY**

FAKHRONY SHOLAHUDIN ROHMAN

UNIVERSITI SAINS MALAYSIA

2009

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ELECTRODIALYSIS PROCESS FOR HYDROCHLORIC ACID
RECOVERY**

by

FAKHRONY SHOLAHUDIN ROHMAN

**Thesis submitted in fulfillment of the
requirements for the degree of
Master of Science**

May 2009

ACKNOWLEDGEMENTS

In the name of Allah, The Most Gracious and the Most Merciful

All praises to Allah for the strengths and His blessing in completing this thesis. Special appreciation goes to my supervisor, Dr Norashid bin Aziz, for his patience, suggestion, supervision and constant support to me in accomplishing this research and writing the thesis. The contribution from Dr. Michael Cizniar, Dr. Miroslav Fikar and Prof. M. A. Latifi, for their Dynamic Optimization Code DYNOPT is greatly appreciated. If they had not put the effort into converting DYNOPT into MATLAB and continually improving it, the dynamic optimization study carried out would have been much harder.

I would like to express my appreciation to the Dean School of Chemical Engineering, Prof Abdul Latif Ahmad for his support and help towards my postgraduate affairs. My acknowledgement also goes to all technicians and office staffs of School of Chemical Engineering for their co-operations. The financial support of Yayasan Felda is gratefully acknowledged.

Sincere thanks to all friends; Nik Izudin, Paidjo, Pak Teguh, Pak Tri, Pak Wahyu, Pak Suhaili, Jibrail, Fadhil, Reza, Dibyo, Syaiful, Guntur, Pak Husein, Pak Sugeng, Bang Fadly and others for their kindness and moral support during my study. Thank for the friendship and memories.

This work is dedicated to my beloved mother, Samini Mintawatie, and my late father, Achyar Effendy, for their endless love, prayer, and encouragements. Also not forgetting my brothers and sisters. Thank for your love and care. To those who indirectly contributed in this research, your kindness means a lot to me. Thank you very much.

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NP	Nernst-Planck
ODE	Ordinary differential equations
PMP	Pontryagin's Minimum Principle
RSM	Respond surface method
SQP	Successive quadratic programming
TPBVP	Two-point boundary value problem
V	Potential drop

LIST OF ABBREVIATIONS

AEM	Anion exchange membrane
ANN	Artificial neural network
ANOVA	Analysis of variance
CCD	Central composite design
CEM	Cation exchange membrane
Conc	Concentrate
$C_6H_{12}O_6$	Glucose
CVI	Control vector iteration
CVP	Control vector parameterization
DAE	Differential algebraic equation
DOE	Design of experiments
DOF	Degree of freedom
Dil	Dilute
ED	Electrodialysis
EM	Empirical model
HCl	Hydrochloric Acid
HJB	Hamilton–Jacobi–Bellman
IDP	Iterative dynamic programming
IT	The irreversible thermodynamics
IVP	Initial value problem
KK	Kedem -Katchalsky
LCD	Limiting current density
LM	Levenberg–Marquardt
MINLP	Mixed-integer non linear programming
MLP	Multilayer perceptron
MS	Maxwell-Stefan
NE	Nernst-Einstein
NLP	Non linear programming

LIST OF SYMBOLS

Symbol	Description	Unit
a	Limiting current density coefficient	$\text{cm}^3 \alpha^{-b-2} \text{s}^b / \text{mol}^\alpha$
a_{ERS}	Electrode surface area	cm^2
a_{me}	Effective membrane surface area per each cell pair	cm^2
A_m	Overall membrane surface area	cm^2
b	Limiting current density coefficient	
C_{BC}	Bulk concentrate concentration	mol/L
C_{BD}	Bulk dilute concentrations	mol/L
$C_{Bf,C}$	Concentration of membrane interface in concentrate compartment	mol/L
$C_{Bf,D}$	Concentration of membrane interface in dilute compartment	mol/L
C_c^0	Initial concentration of hydrochloric acid in the feed stream	mol/L
C_c^t	Final concentration of hydrochloric acid in the feed stream	mol/L
C_{conc}^T	Concentration of hydrochloric acid (HCl) in concentrate tank	mol/L
C_{conc}	Concentration of hydrochloric acid (HCl) in concentrate compartment	mol/L
ΔC_B	Difference of acid concentration in Conc (concentrate) and Dil (dilute) compartments	mol/L
C_{dil}^T	Concentration of hydrochloric acid (HCl) in dilute tank	mol/L
C_{dil}	Concentration of hydrochloric acid (HCl) in dilute compartment	mol/L

D	Concentration diffusion coefficient of acid through membranes	dm^2s^{-1}
D_a	Diffusion coefficient of Cl^- through anion exchange membranes	dm^2s^{-1}
D_c	Diffusion coefficient of H^+ through cation exchange membranes	dm^2s^{-1}
E_D	Donnan potential differences	Volt
E_{el}	Electrode potentials	Volt
E_j	Junction potential differences	Volt
F	Faraday constant	C.mol^{-1}
h	Thickness of the electrolyte solution involved	mm
I	Current	Ampere
j	Current density	A/cm^2
j_{lim}	Limiting current density	A/cm^2
J_i	Overall ion flux	$\text{kmol/m}^2.\text{s}$
J_w	Overall water flux	$\text{kmol/m}^2.\text{s}$
J_{wd}	Flux water based on different concentration	$\text{kmol/m}^2.\text{s}$
k_m	Mass transfer coefficient	dimensionless
k_p	Cost of electrical power in ED stack	RM/kWh
l	Average thickness of membranes	cm
l_a	Thickness of anion exchange membrane	cm
l_c	Thickness of cation exchange membrane	cm
L	Membrane gap	mm
L_w	Membrane constant for water transport by diffusion	cm s^{-1}
N	Number of cell pair	-
p	Vector of time independent parameter	-
Q_{conc}^1	Flowrate of concentrate solutions discharge from the concentrate tank pump	mL/s
Q_{conc}^2	Flowrate of concentrate solutions discharge from the concentrate compartments	mL/s

Q_{dil}^1	Flowrate of concentrate solutions discharge from the dilute tank pump	mL/s
Q_{dil}^2	Flowrate of concentrate solutions discharge from the dilute compartments	mL/s
R	Electrical resistance	Ω
R_G	Gas-law constant	$\text{mol}^{-1} \text{K}^{-1}$
s_a	Price of acid yielded	RM/mol
t_a^-	Anion transport number in the AEM	-
t^+	Cation transport number in the AEM	-
t_C^+	Cation transport number in the CEM	-
t_C^-	Anion transport number in the CEM	-
t^+	Transport number cation in solution	-
t_f	The final time	s
t_i	Time taking measurements	s
t_w	Water transport number.	dimensionless
T	Absolute temperature	^0K
$u(t)$	Vector of control variables	-
V	Potential drop	Volt
V_{comp}	Volume compartment	mL
V_W	Molar volume of pure water	$\text{dm}^3 \cdot \text{mol}^{-1}$
v	Linear velocity	cm/s
w	Width of membrane	cm
W_{elec}	Electrical energy consumption	Wh
x^{mes}	Measured variable(s) in the afore mentioned time	-
$x(t)$	Vector of states variables	-
y	Actual value	-
\hat{y}	Simulated value	-

\bar{y}	Mean of the y value	-
z	Ion charge	-
<i>Greek</i>		
α	Limiting current density coefficient	-
Γ	Product recovery percentage	%
η	Current efficiency	dimensionless
δ	Boundary layer	mm
Λ_0	Equivalent conductance at infinite dilution	$\text{S dm}^2 \text{mol}^{-1}$
Λ	Molar conductivity in solution	$\text{S dm}^2 \text{mol}^{-1}$
$\theta_1, \theta_2, \theta_3$	Constant value in molar conductivity	$\text{S dm}^{7/2} \text{mol}^{3/2}$
$\zeta(\cdot)$	Objective function (objfun) in Meyer type	-
\wp	Represents the optimization criterion.	-
$\int_{t_0}^{t_f} \Re(\cdot)$	Objective function evaluated over a period of time	
χ	Electrical conductivity	Siemen
$\theta_j(t)$	Lagrange function for the controls variables	-
$\phi_j(t)$	Lagrange function for the states variables	-
<i>Subscript</i>		
conc	Concentrate	
dil	Dilute	
Bf,C	The membrane surfaces in C	
Bf,D	The membrane surfaces in D	
C	Concentrate compartment	
D	Dilute compartments	
D,c	Donnan potential of CEM	
D,a	Donnan potential of AEM	
fa,C	Boundary layers adjacent to the AEM in the C compartment	
fa,D	Boundary layers adjacent to the AEM in the D compartment	

fc,C	Boundary layers adjacent to the CEM in the C compartment
jc.D	Junction potential of CEM in D compartment
ja,C	Junction potential of AEM in C compartment
ja,D	Junction potential of AEM in D compartment
jc,C	Junction potential of CEM in C compartment
fc,D	Boundary layers adjacent to the CEM in the D compartment
ERS	Electrode rinse
jc.D	Junction potential of CEM in D compartment

Superscript

L	Lower bound
U	Upper bound
T	Tank
0	Initial
+	Cation
-	Anion

DYNAMIC MODELING AND OPTIMIZATION OF BATCH ELECTRODIALYSIS PROCESS FOR HYDROCHLORIC ACID RECOVERY

ABSTRACT

Electrodialysis is a feasible method for acid recovery because it has the capability of separating ionic chemicals from non-ionic chemicals in process or waste streams to achieve product purity or eliminate wastes. At the same time, it can also concentrate the separated chemicals involved. Optimum operating conditions are very important for the electrodialysis process to ensure maximum ED performances. To obtain those optimum operating conditions, an optimization technique using mathematical models was implemented. The Nernst-Planck derived relationship was used to build the dynamic process model which contains set of ordinary differential equations (ODE).

A degree of freedom analysis was carried out with 38 unknown parameters were identified. The parameters were determined from the literature and various equations. The developed model was then simulated and the results were compared to Lindheimer *et al.*'s (1993) experimental work. The high accuracy of the developed model was achieved with 99% degree of confidence.

The sensitivity analysis of various ED parameters towards its performances was analyzed. The results showed that process time and energy consumption increased when the higher initial HCl concentration in the dilute and concentrate tanks, higher current

density and lower $V_{\text{conc}}/V_{\text{dil}}$ ratio were applied. However, the effect of flowrate towards process time and energy consumption was not significant.

In order to obtain optimal control trajectory, the dynamic optimization problem was applied using a simultaneous approach i.e. the orthogonal collocation method, where the differential variables were fully discretized. This was implemented within the MATLAB[®] environment by using the *dynopt* code package.

Five objective functions were used in this study: minimize process time (P1), minimize the dilute concentration (P2), minimize energy consumption (P3), maximize degree separation (P4) and maximize operation profit (P5). From the simulation results, it was found that the control trajectories of P5 was chosen to be the most effective control operation in order to achieve the minimum process time for 99% degree of separation. The control trajectory achieved was reliable and practical. Moreover, the process time achieved for P5 was 51.6% faster than the P2, 60.67% faster than P3 and 7.9% faster than P4. The profit and energy consumption of P5 that were achieved were RM 18.54/batch and 780.202 Wh respectively.

The study on the effect of different aspects of optimization towards ED performances was also carried out. Based on the results, it can be concluded that the effective number of interval, number of state collocation and trajectory type for this study was five, three and piecewise continuous linear respectively.

PEMODELAN DAN PENGOPTIMUMAN DINAMIK BAGI PROSES ELEKTRODIALISIS KELOMPOK UNTUK PEROLEHAN ASID HDROKLORIK

ABSTRAK

Elektrodialisis merupakan satu kaedah yang sesuai untuk mengitar semula asid disebabkan oleh keupayaannya untuk memisahkan bahan-bahan kimia terion daripada bahan kimia tak terion dalam proses ataupun sisa aliran bagi mencapai ketulenan produk serta menyingkirkan sisa-sisa. Pada masa yang sama, ia juga boleh memekatkan bahan-bahan kimia terpisah tersebut. Keadaan-keadaan operasi optimum adalah amat penting dalam proses elektrodialisis untuk memastikan prestasi ED adalah maksimum. Untuk mendapatkan keadaan-keadaan operasi optimum ini, teknik pengoptimuman menggunakan model matematik telah digunakan. Hubungan berasaskan Nernst-Planck telah digunakan untuk membina model proses dinamik yang mempunyai set persamaan-persamaan kebezaan biasa (ODE).

Analisis darjah kebebasan telah dijalankan dengan 38 pembolehubah-pembolehubah tak diketahui telah dikenalpasti. Pembolehubah-pembolehubah ini dikenalpasti melalui literatur dan pelbagai persamaan. Model yang dibangunkan ini kemudian disimulasi dan keputusan-keputusannya dibandingkan dengan kerja-kerja eksperimen oleh Lindheimer *et al.* (1993). Model yang berketepatan tinggi dengan 99% darjah keyakinan telah diperolehi.

Analisis kepekaan pelbagai pembolehubah ED terhadap prestasi-prestasinya telah dianalisis. Keputusan-keputusan menunjukkan bahawa masa proses dan penggunaan tenaga meningkat apabila kepekatan HCl awal dalam tangki-tangki cair dan pekat yang tinggi, ketumpatan arus yang tinggi dan nisbah $V_{\text{conc}}/V_{\text{dil}}$ yang rendah diaplikasikan. Kesan kadar aliran terhadap masa proses dan penggunaan tenaga adalah tidak bererti.

Untuk memperolehi trajektori kawalan yang optimum, masalah pengoptimuman dinamik telah diaplikasikan menggunakan pendekatan serentak iaitu kaedah penempatan bersama ortogon, di mana parameter-parameter kebezaan telah didiskret dengan sepenuhnya. Ini telah dilaksanakan dalam persekitaran MATLAB[®] dengan menggunakan kod pakej *dynopt*.

Lima fungsi-fungsi objektif telah digunakan dalam kajian ini iaitu; peminimuman masa proses (P1), peminimuman kepekatan cair (P2), peminimuman penggunaan tenaga (P3), pemaksimuman darjah pemisahan (P4) dan pemaksimuman keuntungan operasi (P5). Daripada hasil simulasi, trajektori kawalan P5 telah dipilih sebagai operasi kawalan yang paling berkesan untuk mencapai masa proses minimum bagi 99% darjah pemisahan. Trajektori kawalan yang dicapai adalah boleh diterima dan praktikal. Tambahan lagi, masa proses bagi P5 adalah 51.6% lebih cepat berbanding P2, 60.67% lebih cepat berbanding P3 dan 7.9% lebih cepat berbanding P4. Keuntungan dan penggunaan tenaga yang dicapai bagi P5 masing-masing sebanyak RM18.54/kelompok dan 780.202 Wh.

Kajian mengenai kesan pelbagai aspek pengoptimuman terhadap prestasi ED juga telah dijalankan. Berdasarkan keputusan yang diperolehi, boleh dirumuskan bahawa bilangan sela, bilangan keadaan penempatan bersama dan jenis trajektori yang efektif bagi kajian ini adalah masing-masing lima, tiga dan lurus berterusan sesecebis.

CHAPTER ONE

INTRODUCTION

The percentage of fresh fruit bunch of oil palm which is recovered as palm oil is only 21.6% (by weight), leaving the remaining as by-products, and this includes the palm kernel and solid wastes which comprise of empty fruit bunch (EFB), fiber and shell (Basiron, 2002). From the EFB, sugar can be produced through the hydrolysis process by using hydrochloric acid (HCl) (Asmida, 2005). The acid must be separated from the sugars to yield pure sugar and to reduce the processing costs by recovering and recycling the hydrochloric acid.

There are four main techniques that can be used to recover the acid from the feed solution (Forster *et. al*, 1980; Boeteng, 1991): neutralization-precipitation-discharge, crystallization, solvent extraction and electrodialysis. Among the four, the most frequently employed technique for the disposal of spent acid residues is the neutralization-precipitation-discharge sequence. However, this approach is increasingly being questioned because of the environmental consequences related to the stocking of toxic solid wastes (Boeteng, 1991). In the crystallization technique, the separation is based on the principles of solubility; compounds (solutes) tend to be more soluble in hot liquids (solvents) than they are in cold liquids. If a saturated hot solution is allowed to cool, the solute is no longer soluble in the solvent and forms crystals of pure compound. Impurities are excluded from the growing crystals and the pure solid crystals can be separated from the dissolved impurities by filtration. The disadvantages of the

crystallization method are low yield, high chemical costs and waste production. In solvent extraction, the acid is separated by selective solvent action; that is, some materials are more soluble in one solvent than in another, hence there is a preferential extractive action. However, solvent extraction is handicapped by unfavorable distribution coefficients and environmental problems associated with the hazardous solvents used (Choi *et al.*, 2002).

Electrodialysis (ED) is a well proven technology with a multitude of systems operating worldwide. It is defined as an electrochemical separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. ED can also be used in the separation and concentration of salts, acids, and bases from aqueous solutions, the separation of monovalent ions from multivalent ions, and the separation of ionic compounds from uncharged molecules. ED can be used for either electrolyte reduction in feed streams or the recovery of ions from dilute streams (Farrell *et al.*, 2003).

As a selective transport technique, ED uses an ion-selective membrane as a physical barrier through which ions are transported away from a feed solution. An energy intensive phase change is unnecessary which is in contrast to the common separation techniques of distillation and freezing. From the environmental protection and economical viewpoints, ED is the most suitable technique to separate acid from feed solution. It not only eliminates wastes but it can also recover valuable materials (Blackburn, 1999; Radzi, 2006). ED has the capability of separating ionic chemicals

from non-ionic chemicals in process or waste streams in order to achieve product purity or to eliminate wastes. The product could be concentrated up to a certain amount with the separation process (Blackburn, 1999; Thang *et al.*, 2005).

1.1 Electrodialysis

Electrodialysis (ED) is an electrochemical process for the separation of ions across charged membranes from one solution to another under the influence of electrical potential difference which is used as the driving force. It is used to remove ionized substances from liquids through selectivity ion permeable membranes. In the process, the ions are selectively transported through the appropriate membrane while non-ionic and macromolecular species are rejected (Huang and Juang, 1986).

To achieve separation by electrodialysis, cation and anion membranes are alternated with plastic spacers in a stack configuration with a positive electrode (anode) at one end and a negative electrode (cathode) at the other. Both of these membranes are mono polar; this means that they are permeable to only one type of ions. When a DC voltage is applied across the electrodes, the electrical potential created causes anions to move in the direction of the cathode. The ion-selective membranes form barriers to the ions of the opposite charge. The result is that anions attempting to migrate to the anode will pass through the anion membrane but are stopped by the cation membrane. In a similar manner, cations trying to migrate to the cathode pass through the cation membrane but are stopped by the anion membrane. Hence, the membranes form alternative compartments of ion-diluting cells and ion-concentrating cells which

compose of a single ED cell pair. Then, the ED stack is arranged to from a number of ED cell pairs (Costa *et al.*, 2002).

There are two popular modes of operation of the ED stack, i.e., batch and continuous operations. As a membrane-based process, the performance of an ED unit over extended period may be susceptible to deterioration owing to the fouling and plugging of anion and cation-exchange membranes. Batch operations are attractive in this regard since membrane cleaning and the replacement of severely fouled membranes and electrodes by new ones, where required, can be carried out between consecutive batch operations (Parulekar, 1998). Batch-mode laboratory and commercial scale ED can be operated at constant low pressure (about 1.5 atmospheres) and constant low voltage (about 0.5 volts per membrane) where the process is simply continued until the desired electrolyte level is obtained (Mc Rae, 1986).

1.2 The requirements of ED optimization

The high performance of ED can be achieved if optimum operating conditions or parameters that reflect the process can be observed. There are three main process parameters that affect the electrodialysis performance: concentration of feed solution, current applied and feed flowrate (Montiel, *et al.*, 2005).

One of the electrodialysis stack performance indicators which is usually being used by many researchers is product recovery percentage. Product recovery percentage gives a picture of how much the product in the feed stream can be transferred into a desired product stream. In this case, the product recovery percentage also means the

separation percentage. It refers to the difference in the initial and final concentration of the electrolyte solution.

On the other hand, the practical utilization of ED as an effective separation process performance also depends on economic considerations. The operating costs for an ED stack consist of energy-related costs and maintenance costs (the cost of fouled and plugged membranes replacement and the cost of electrodes and cleaning chemicals). The energy consumption required in an ED process is the sum of the electrical energy to transfer ionic species through the ion-selective membranes and the energy required to pump various solutions through the ED stack. This cost is strongly dependent on the operating parameters of the ED stack such as current density, potential drop across the ED stack and operating time (Parulekar, 1998; Lee *et al.*, 2002).

ED optimization is usually performed experimentally or by simulating the mathematical model of the process. The mathematical models for the determination of the optimal condition of an ED can provide a tool to assist decision-makers to evaluate and examine many alternatives with minimal effort. The construction of a mathematical model of the ED process is the crucial step in this optimization. Such a model is normally termed as a simulation model. Its purpose is to predict the values taken on by the constrained parameters of a system corresponding to any particular policy (or set of values of the decision variables). The benefits of using mathematical modeling are easy to identify thoroughly the characteristics of the ED process and subsequently to reduce operating costs for experimental trials and to improve efficiency (Panagiotis and Papageorgiou, 2005). As computers have become more powerful, the size and

complexity of the problems which can be solved by the optimization techniques have correspondingly expanded (Edgar and Himmelblau, 1988).

To obtain optimum operating conditions, researchers such as Belfort and Daily (1970), Choi, *et al.* (2002), Lee *et al.* (2002), Turek (2002) and Panagiotis and Lazaros (2004) have implemented a static optimization technique such as iterative, successive quadratic programming (SQP) and mixed-integer non linear programming (MINLP). However, they assumed that the process considered was in steady state conditions which led to algebraic type equations.

In the ED batch operations, all the reactants are initially charged in a stack and processed according to a predetermined course of action during which no materials are added or removed. The process variables undergo significant changes during the duration of the batch. There is no steady state and thus no constant setpoint around which the process can be regulated. Hence, the major objective in batch operations is not to keep the system at an optimal constant setpoint but to optimize objective functions that express the system performance. In addition to the dynamic system equations which act as constraints, there are bounds on the inputs as well as state-dependent constraints. Flowrate is an example of an input constraint which must have a non-negative value. State-dependent constraints typically result from operability considerations such as limits on current density and terminal constraints normally arise from ED performance considerations.

The solution for such optimization problems is not very straightforward since the constraints on the process involve a combination of differential and algebraic

equations. Thus, ED batch optimization problems involve both dynamic and static constraints and fall under the class of dynamic optimization problems (Vemuri, 2004).

Only one study involving the dynamic optimization technique in the ED process has been reported. Parulekar (1998) worked on the dynamic optimization of salt recovery from sodium chloride-water feed solution in order to obtain optimal current / voltage trajectory. The objective function considered was minimizing energy consumption which was solved by using the classical method which is Pontryagin's Minimum Principle.

1.3 Problem statement

More than 70% (by weight) of the processed fresh fruit bunch in the oil palm mills was left over as oil palm wastes. The oil palm waste which is in the form of empty fruit bunch (EFB) can produce sugar by using the hydrolysis process. To obtain pure sugar and to recover the acid, an appropriate separation technique is needed. Electrodialysis is a feasible technique to recover hydrochloric acid from feed solution because separation and concentration can be carried out simultaneously. However, operating the electrodialysis process at the optimum operating conditions is a must to ensure minimum process time, maximum degree separation, minimum energy consumption and maximum profit will be achieved.

A model based optimization is a powerful technique to obtain optimal operation since it can reduce operating costs for experimental trials. In this optimization technique, the construction of a mathematical model which can represent the ED process

is a must. However, it is difficult to develop such a model that corresponds to complete the ED process characteristic. The developed model should neither be too simple, which cannot represent the detailed behavior of the ED, nor too accurate, which will provoke the complex computations.

At present, many researchers have implemented a static optimization technique to solve this problem. They assumed the process considered is in steady state conditions which lead to algebraic type equations. In contrast, the ED batch process is a dynamic system which is presented as a set of ordinary differential equation (ODE) or differential algebraic equation (DAE). As a result, the static optimization technique can deteriorate the results achieved. Due to such limitations, a dynamic optimization technique is the best solution because it can deal with ordinary differential equations (ODE) and differential algebraic equations (DAE).

In the past, the ED dynamic optimization was carried out by using the classical method i.e. Pontryagin's Minimum Principle. However, this method is computationally expensive and has slow convergence. The discretization technique, such as orthogonal collocation techniques, is found to be an efficient solution method. This approach avoids the requirement of analytical differentiation to derive the necessary optimal conditions. The original optimal control problem is transformed into a finite dimensional optimization problem, typically a NLP. Then, the optimal control solution is given by applying a standard NLP solver to directly solve the optimization problem. However, the need for discretization on both state and control variables in this method leads to a large scale optimization problem, which remains the challenge of this technique.

The various issues highlighted above have led to this research which focused on the development of an adequate dynamic model of ED and the determination of its optimal operating conditions using the effective dynamic optimization technique. In this study, HCl recovery using ED was chosen as a case study. There are two main parts of this study: the development of the first principle model of the ED process for hydrochloric acid recovery and dynamic optimization studies using the orthogonal collocation method.

In the first part, the model of the ED for hydrochloric acid recovery was developed and simulated in the MATLAB[®] environment. The simulation results achieved were then compared with the actual data provided in the literature. Sensitivity analysis was also conducted in order to see the relation of various ED parameters to its performance.

The next stage of the research is to determine the optimal control trajectories which minimize/maximize various objective functions. The objective functions considered are minimize process time, minimize energy consumption, maximize degree of separation, minimize dilute concentration and maximize process profit. Finally, the effect of different aspects of optimization i.e. the number of intervals and the number of state collocations and types of control trajectory towards ED performances were evaluated.

1.4 Objectives of the research

The goals of this work are:

- a. To develop a computer code for the first principle model of the electro dialysis process for HCl-sugar separation.
- b. To compare the simulation results of the first principle model for hydrochloric acid recovery using ED with those experimental data available in the literature.
- c. To study the effect of various process variables such as applied current, feed flowrate, and initial feed/product concentration and volume tank to the electro dialysis performance.
- d. To obtain the optimum conditions of the electro dialysis process that lead to maximum profit, maximum degree of separation, minimum process time, minimum HCl concentration in dilute tank and minimum energy consumption using the dynamic optimization technique.
- e. To study the effect of different aspects of optimization towards ED performance.

1.5. Organization of Thesis

This thesis is divided into five chapters.

Chapter 1 describes the importance of electro dialysis and its optimum condition requirements for hydrochloric acid recovery. In addition, this chapter also outlines the problem statement and the objectives of the study.

Chapter 2 provides an overview of the electro dialysis process and its application in sugar-acid recovery. Principle and component, transport phenomena, electrochemical system, the parameters and the performances of ED are also given in detail. At the same time, a review of the mathematical models and the optimization approaches for the ED process are provided. Finally, a discussion on the dynamic optimization technique and the description of the orthogonal collocation method is presented.

Chapter 3 describes the methodology of this research. The development of computer codes for the first principle model is outlined. The assumptions and the mathematical expressions of mass balances and the electrochemical system in ED process are highlighted in this section. The degree of freedom analysis (DOF) procedure and its results are also presented. This chapter also explains the approach to estimate the required parameters that are not available in the literature. Then, the performance indicator chosen for the comparison study between the simulation results and the literature is explained. The list of important parameters chosen for the sensitivity study is also mentioned in this chapter. Finally, the dynamic optimization study procedure is explained.

Chapter 4 presents the results and discussion of the research. The unknown parameters of the proposed model obtained are presented. The results of the model comparison is also presented. The sensitivity analysis study which demonstrates the effect in varying the initial dilute and concentrated concentration of hydrochloric acid, initial ratio volume tanks and current density towards process time and energy consumption for 99% degree

of the separation is discussed. The results of the dynamic optimization study of five different objective functions are evaluated and compared. Finally, the effect of the different aspects of optimization towards ED performances is discussed.

Chapter 5 summarizes the results obtained in the present study. The conclusions and the recommendations for future study are also highlighted.

CHAPTER TWO

LITERATURE REVIEW

This chapter presents a review of the principles of the electro dialysis (ED) process and the electrochemical system. The ED parameters and its index performances are explained. The mathematical model reviewed, which described the transport phenomena in the ED process, is also explained systematically. Finally, the ED optimization techniques are presented at the end of this chapter.

2.1 Electro dialysis applications for acid-sugar separation

A few researchers have studied the separation of acid and sugar using electro dialysis. Huang and Juang (1986) reported that more than 40% of current efficiencies in sulfuric acid-glucose-xylose mixture from dilute sulfuric acid hydrolysis can be obtained by the batch electro dialysis process. The effects of concentration, flowrate and temperature on the limiting current density were investigated experimentally. Finally, they proposed a Nusselt correlation based on the Nernst-Planck equation which relates the mass-transfer rate to the limiting current density. The ion exchange membranes used in this study were Selemion CMV and Selemion AMV manufactured by Asahi Glass Co. of Japan.

Hongo *et al.* (1986) separated lactic acid from fermentation broth which contained glucose using continuous electro dialysis. They claimed the amount of lactic acid obtained was 82.2 g/liter, which was 5 times greater than using the conventional

technique. The purity of glucose in all the experiment trials was about 91%. The experiment was conducted by using two anodes and concentration compartments, with one cathode compartment. The ion exchange membranes applied were Neosepta ACH-45T and Neosepta CH-45T which were manufactured by Tokuyama Soda Co., Ltd. of Japan.

In their study, Weier *et al.* (1992) recovered propionic and acetic acid from sugar in a fermentation broth. Current efficiencies, water transport, and product concentrations were determined experimentally for replicated solutions of the acids and for the fermentation broths. The maximum degree of recovery for the propionic and acetic acid obtained was 89.5% and 83.2% respectively. The highest efficiency of 97.1% (based on acid transferred) was achieved at high total acid concentrations and with the absence of competing ions. The experiment was carried out by using a laboratory-scale electrodialysis unit which consisted of two cell pairs. The ED batch stack applied consisted of alternating cation- and anion-exchange membranes (Ionics CR61- CZL386 and AR103QZL386 respectively).

Goldstein (1993) recovered acid from acid-sugar hydrolyzate. The acid considered were hydrochloric acid (HCl) and sulfuric acid (H₂SO₄). The sugars were retained in the hydrolyzate at concentrations of up to 60%. The maximum percentage of sugar which remained in the product tank at the final ED process was 6% for H₂SO₄ and 5% for HCl respectively. The HCl and H₂SO₄ concentration which remained was about 2.2%. The ion exchange membranes used in this experiment were Selemion CMV and Selemion AMV manufactured by Asahi Glass Co. of Japan.

Andres *et al* (1997) applied ED to concentrated tartaric acid from glucose in the grape juice industry waste. A mathematical model which expressed a simple algebraic equation was used to predict the final tartaric acid concentration and the electro-osmotic effects. The tartaric acid yield was approximately 60%. The current efficiency and energy consumption obtained were about 65% and 5×10^3 kJ kg⁻¹ tartaric acid respectively. However, the influence of glucose in the tartaric acid electrodialysis was not explained fully. This study was conducted by using a complete ED batch unit which consisted of 10 cell pairs sandwiched between two electrodes made of non-corrosive materials.

Chukwu and Cheryan (1999) have separated acetic acid from unreacted glucose and other nutrients from fermentation broths. A material balance around all the stages indicated that an acetate recovery of more than 90% in the concentrate (product) stream in each stage was achieved. The effect of the current applied on acetate flux, water flux and energy consumption was studied experimentally. The results showed that a higher current caused higher acetate flux, water flux, and energy consumption. The separation was conducted using a bench-top ED batch unit which contained 20 cation-exchange membranes (CR61 CZL-386, Ionic Inc) and 20 anion-exchange membranes (AR103 QZL-386, Ionics Inc).

Jetoo (2000) used an ED batch for the deacidification of sugar in synthetic cane juice. There was 35% acid removal from the juice. The effect of the voltage under constant flowrate and temperature towards pH acid was studied experimentally. It was

found that a higher amount of voltage applied decreased the pH acid. The ED batch laboratory used comprised of 5 sets cells.

Madzingaidzo *et al* (2002) separated lactic acid from glucose-acid solution using batch circulation and feed-bleed electro dialysis. It was found that the lactate concentration in the product stream could be increased to a maximum of 15%. The effect of current density towards energy consumption, current efficiency and water transport was studied experimentally. It was shown that high current density decreased energy consumption and water transport but at the same time increased current efficiency. The maximum current efficiency achieved was 96%. The electro dialysis stack which was used consisted of eight cell pairs of thermostable cation (CMX) and anion exchange (AMX) Neosepta membranes manufactured by Tokuyama Soda, Japan.

Sairi (2005) recovered citric acid from sugar in pineapple juice solution using five compartments of the ED batch system. The deacidification value was 27.53% which was indicated by maximum reduction of the conductivity and total acidity in the diluted stream. The effect of the initial feed concentration and the electrical current on water and ion transport were studied experimentally. The results showed that water and ion transport in the electro dialysis process were strongly dependent on the electrical current applied to the system rather than feed concentration. The researcher also found the optimum current applied using experimental based-optimization i.e. one-variable-at a time.

Radzi (2006) recovered hydrochloric acid from synthetic glucose- hydrochloric acid mixture. The characteristic study gauged the performance of the ED system based on time duration to complete the separation, recovery percentage, average flux, current efficiency and energy consumption. The researcher conducted the ED experiment using anion and cation-exchange membranes (PC Acid 60 and PC-SK) in batch mode. The optimization study was also done by using the design of experiment (DOE) where a central composite design (CCD) and response surface methodology (RSM) were combined to obtain the optimum values of the selected parameters. The best results for energy consumption, recovery percentage and average flux achieved were 37.93 KWh, 97.4% and 5.3 Km²/m².s respectively.

It can be concluded that many of studies in the separation of acid-sugar using ED were conducted experimentally. A few studies used models to predict the behavior of the ED but they were too simple and were unable to represent the real ED process. Due to the limitations of the models that were developed, there is a great need to develop a first principle model. Moreover, a reliable optimization technique such as dynamic optimization should be implemented to determine the optimum operating conditions for acid-sugar separation in the ED process.

From the optimization point of view, only experimental based-optimization was implemented on this ED system. In fact, no study which has implemented dynamic optimization in the ED system for acid recovery has been reported.

2.2 ED principle

Figure 2.1 shows a schematic diagram of a typical ED cell arrangement consisting of a series of anion- and cation- exchange membranes (AEM and CEM). The membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. A cell consists of a volume with two adjacent membranes. If an ionic solution such as an aqueous salt solution is pumped through these cells and an electrical potential is established between the anode and cathode, the positive charged cations migrate towards the cathode and the negative charged anions migrate towards the anode. The cations pass easily through the negative charged cation-exchange membrane but are retained by the positive charged anion-exchange membrane. Likewise, the negative charged anions pass through the AEM and are retained by the CEM. The overall result is an increase in the ion concentration in the compartments while simultaneously, in the other compartments, it becomes depleted. The depleted solution is generally referred to as dilute and the concentrated solution as brine or concentrate. The driving force for the ion transport in the ED process is the applied electrical potential between the anode and the cathode. The total spaces occupied by the dilute and the concentrate solutions between two contiguous membranes and the two contiguous anion and cation-exchange membranes make up a cell pair. A device composed of individual cells in alternating series with electrodes on both ends is referred to as an ED stack (Strathman, 2004).

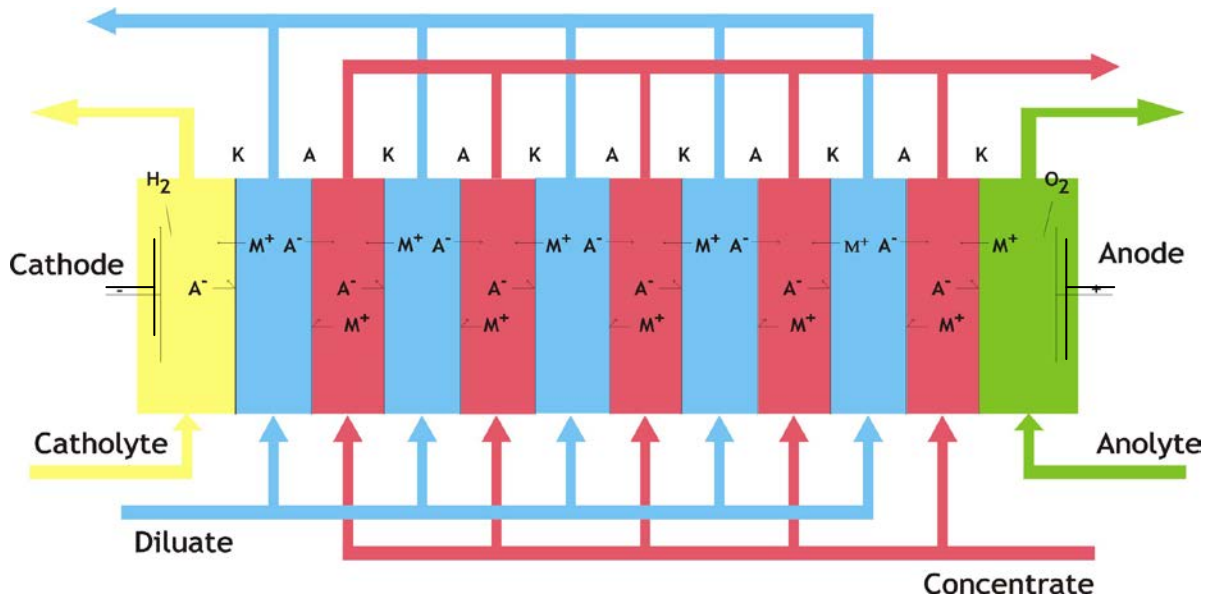


Figure 2.1: Electrodesialysis process with series of cation and anion exchange membranes (PC Cell, 2006)

2.3 ED stack component

There are at least five main components of ED applications which can be seen in the ED stack as shown in Figure. 2.2. They are DC supply, electrodes, ion -exchange membranes, solvents and electrolytes and spacers.

2.3.1 Direct current supply

It provides an effective means to reinforce ion transport, i.e., cations and anions migrate towards the cathode and anode respectively. Furthermore, the migration rate of ions can be controlled by adjusting the current density (Huang, *et al.*, 2007)

2.3.2 Electrodes

The oxidation/reduction reactions on the cathode and the anode rely on the transformation from ionic conduction to electron conduction and thus provide the original driving force for ion migration. In general, the electrode applied in the ED is inert and plate-shaped. Naturally, gas bubbles are formed on the interface of the solvent and electrode. Metal deposition is likely to occur on the surface of the cathodes due to redox reaction (Huang, *et al.*, 2007). However, at the same time, residue must not be formed inside the electrode chambers while the chamber itself must be thin enough to avoid too much resistance to the electrical current (Nunes and Peinemann, 2001).

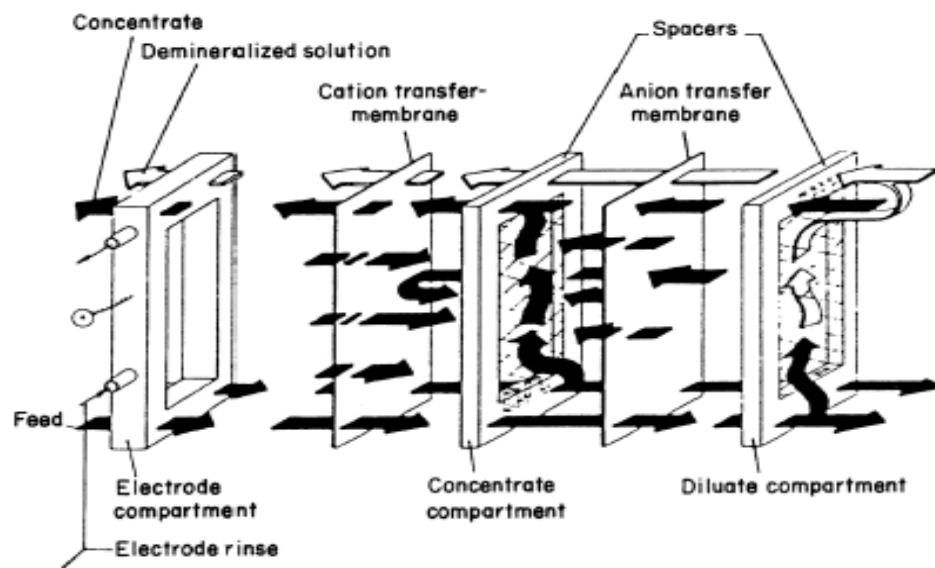


Figure 2.2: Geometry of ED stack (Perry and Green, 1998)

2.3.3 Ion-exchange membranes

There are two types of ion-exchange membranes which can be applied in the ED: cation and anion selective membranes. They are well known membranes for hindering the passage of co-ions (anions and cations respectively) due to the Donnan repulsion (Huang, *et al.*, 2007).

The ion permeable membranes used in electrodialysis are sheets of ion-exchange resins. They usually contain polymers to improve their mechanical strength and flexibility. The resin component of a cation-exchange membrane would have negative charged groups chemically attached to the polymer chains. Ions with a charge opposite to the fixed charge (counter ions) are freely exchanged at these sites. The concentration of counter ions (e.g., H^+) is relatively high therefore, counter ions carry most of the electric current through the membrane. The fixed charges attached to the polymer chains repel ions of the same charge (co-ions); in this case, the anions. Since their concentration in the membrane is relatively low, anions carry only a small fraction of the electric current through a cation permeable membrane. The attachment of positive fixed charges to the polymer chains forms anion permeable membranes which repel positive ions. The basic parameters for a good ion exchange membrane are high permselectivity, high electrical conductivity, moderate degree of swelling, low electrical resistance, and excellent chemical, thermal and mechanical stability (Mulder, 1996).

2.3.4 Solvents and electrolytes

Solvents provide a continuum for ion transport by filling the space between the electrodes and the required membranes while electrolytes are the current carriers between the cathode and the anode. The solubility of salts or electrolytes in solvents is critical to the electrical resistance and thus affects the energy consumption of ED stacks; it also affects operation stability (Huang, *et al.*, 2007). The electrolyte can remove gases produced as a result of unavoidable electrode reactions (Rautenbach and Albrecht, 1989).

2.3.5 Spacers

In the ED stacks, spacers have several functions; as supporting nets and as turbulence promoters to increase mass transfer rates, reducing the polarization concentration and reducing fouling layers. The spacers net prevent the membranes from touching each other, creating compartments. The stacked spacers form, with their holes, tubes which are arranged in a way to build two different channel systems (Kuroda, *et al.*, 1983). In this way, the concentrate and dilute circuit is built to connect the appropriate fluid channels with the appropriate compartment in the cell. Spacers play an important role in membrane systems as they are related to problems of mass transfer, homogenizing and mixing behavior (Chiapello and Bernard, 1993). Careful design spacers may increase the mixing of solutions near the membrane surface and may lead to cost saving in terms of membrane surface area installed, electrical energy needed for pumping and current supplied through the membrane stacks. The spacer is usually made of a non-conducting and hydrophobic material, elastic enough to form a seal with the membrane and yet rigid enough to not be pushed out from the stack at the time of stack tightening (Nunes and Peinemann, 2001). Ion-conducting spacers are used to receive extremely diluted solutions (Shahi, *et al.*, 2001).

2.4 Transport phenomena in ED

To separate ions in the ED system, they must be transported from one solution through a cation-exchange membrane or an anion-exchange membrane into another solution. At the same time, water that accompanies the ions is also transported through ion exchange membranes.

2.4.1 Ion transport in ED process

In general, ionic mass transport takes place by diffusion, migration, and convection. If there are differences in the electrostatic potential at various points in the electrolyte, the resulting electric field produces a flow of charge in the direction of the field. This is termed as migration or conduction. If there is a difference in the concentration of ions in different regions of the electrolyte, the resulting concentration gradient produces a flow of ions. This phenomenon is termed as diffusion. Convection is the mechanical transport of ions or molecules through a solution as a result of stirring, vibration or the temperature gradients (Bockris and Reddy, 1970).

2.4.1(a) Ionic drift under an electrical field: Migration or conduction

When a potential gradient, i.e., electric field, exists in an electrolyte solution, the ions feel the electric field. The positive ions drift/flux towards the negative electrode; the negative ions, in the opposite direction. Through time, the ions are under the influence of an applied-force field which produces current density (Bockris and Reddy, 1970). Although all ions feel the externally applied electric field to extend their charges, some respond by migrating more than others. Even if there are equal numbers of the various ions, those which have higher mobility contribute more to the communal task of transporting the current through the electrolytic solution than the ions handicapped by lower mobility. It is logical, under these circumstances, to seek a quantitative measure of the extent to which each ionic species is taxed with the job of carrying the current. This quantitative measure, known as the transport number, is defined by the fraction of the total current carried by the particular ionic species. The transport number considered is

distinguished in the solution and in the ion selective membrane. This definition requires that the sum of the transport number of all the ionic species be unity (Denaro, 1965).

2.4.1(b) Ionic drift under a chemical-potential gradient: Diffusion

Diffusion is the movement of molecular components due to a local gradient in the chemical potential. A non uniformity of chemical potential implies that the free energy is not the same everywhere and therefore, the system is not at equilibrium. The system attains equilibrium by equalizing the chemical potential, i.e., by transferring the species from the high-concentration regions to the low-concentration regions. Thus, the negative gradient of chemical potential behaves like a driving force which produces a net flow, or flux, of the species (Rautenbach and Albert, 1989). When the driving force is small, it may be taken to be linearly related to the flux. On this basis, an equation can be derived for the rate of steady-state diffusion which is identical to the empirical first law of Fick (Bockris, 1980).

2.4.1(c) Convection

The transport of ions by convection is largely determined by pressure gradient and wetted area. Convection does not carry an electrical current. It is a perpendicular component of an ascending flow produced by the decrease in the solution density near the membrane surface in the boundary layer (Tanaka, 2004). Convection is generally negligible in dilute solutions (Cussler, 1997; Tanaka, 2003).