MODELING OF AN ELECTROCHEMICAL PROCESS FLOWSHEET USING ASPEN

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ABSTRACT

A methodology is described for the computer-aided design and modeling of electrochemical process flowsheets. In this study, the design, costing, and economic analysis of the electrochemical production of methyl ethyl ketone was used as an example. The process steps include rigorous distillations, absorbers, an electrochemical cell model, pumps, flashes, and heat exchangers involving electrolyte systems.

The public version of ASPEN (Advanced System for Process Engineering) was modified for use in the study. ASPEN was chosen because of its electrolyte capability and adaptable programming structure. Within the ASPEN framework, enhancements made during the course of this work are portable to the electrolytic industry.

While not in the scope of this work, process flowsheet optimization is the ultimate goal for computer-aided process simulation. This work will lay the foundation on which a flowsheeting package capable of electrochemical process optimization can be built.

INTRODUCTION

Recent technological advances coupled with rising energy costs and environmental awareness have created many options for the electrolytic industry. Improved cell and electrode materials can reduce capital and energy costs for existing processes while opening avenues for new ones. New reactor designs have been developed to increase further the possibilities. New electrolytic routes have been identified for products ranging from existing organic commodities to new specialty chemicals (such as agricultural and pharmaceutical chemicals).

With so many options available, electrolytic process development can no longer be done cost effectively by experimentally verifying each and every option. Computer-aided simulation and design techniques provide a mechanism to screen options while identifying sensitive control variables and gaps in knowledge where more basic research is needed. Design alternatives for electrochemical process flowsheets can be explored efficiently while providing feedback for further developmental research. The best design can be chosen based on the entire process rather than just the electrolytic cell.

While computer-aided simulation and design (flowsheeting) techniques have been available for the last two decades, their use has generally been restricted to process flowsheets with nonelectrolytes. The major restriction was lack of adequate modeling of electrolyte thermodynamics. Recent developments in electrolyte thermodynamics along with advances in electrochemical reactor modeling have made electrochemical flowsheeting possible.

This work describes a methodology for the computer-aided modeling and design of electrochemical process flowsheets, and uses a modification of the public version of ASPEN (Advanced System for Process Engineering). In this study, the design, costing, and economic analysis of the electrochemical production of methyl ethyl ketone (MEK) is used as an example. While not in the scope of this study, process flowsheet optimization is the ultimate goal behind the framework developed here.

LITERATURE SURVEY

Process Flowsheeting.-- The computer-aided simulation and design (flowsheeting) of petrochemical process flowsheets is well-established. Several reviews of the state of chemical process flowsheeting systems are available [1-4]. Westerberg et al. [5] have written an excellent introductory monograph on the subject. Many systems, such as CHESS, PROCESS, and FLOWTRAN, have been commercially available for years.

A process flowsheeting system solves the set of nonlinear equations that describe a process flowsheet. This set may contain thousands to tens of thousands of equations for a chemical process. The structure of almost all existing process flowsheeting systems is sequential modular. A sequential modular system divides the nonlinear equations into module-level and flowsheet-level equations. A unit module consists of a set of module-level equations describing a particular unit operation (distillation, electrolytic cell, absorber, etc.). Given streams and equipment parameters, the module will calculate output streams from the unit. The units of a flowsheet are connected by stream connection equations. Design contraints on an overall process, such as a product purity requirement, are handled by design specification equations. A design constraint is met by adjusting a designated variable (which may be a stream flow rate, equipment parameter, etc.) called a free variable. Stream connection and design specification equations comprise the flowsheet-level set.

Modeling of Electrolyte Systems.-- There has been little use of flowsheeting techniques for electrochemical processes until very recently. Advances in this area are being spurred on by intense research in the modeling of electrolyte thermodynamics. Work by Criss and Cobble [6], Meissner and Tester [7], Pitzer [8], and Bromley [9] laid the foundation. From these earlier works, many electrolyte activity coefficient models have been developed with the range of applicability from dilute solutions to fused salts [10-15]. Several articles show the extension of these models to mixed solvents, vapor-liquid-liquid systems, and vapor-liquid-solid systems [16-19]. Mauer gives a survey of thermodynamic models proposed for electrolyte systems [20].

While general-purpose flowsheeting programs have been available for about twenty years, these programs were in general limited to petrochemical flowsheets. Though Zemaitis [21] had developed a stand-alone program for certain separation operations involving electrolytes, no general-purpose flowsheeting program was available commercially for electrochemical flowsheets. The ASPEN project [22,23] conducted at the Massachusetts Institute of Technology under a Department of Energy contract became the first attempt at such a system. This public version of ASPEN (not to be confused with Aspen Technology's private system, ASPEN PLUS) included electrolyte and solids handling capabilities [24,25].

ASPEN was written to include Chen's local composition model for electrolyte systems. Chen's electrolyte model [11] is designed to model the excess Gibbs energy of electrolyte systems from dilute solutions to fused salts. This approach predicts long-range forces between ions by a Debye-Huckel term. Short-range forces between all other species are modeled by the local composition approach similar to those used in several nonelectrolyte models (NRTL, UNIQUAC, UNIFAC). The model requires two binary parameters for each solvent-ion or solvent-solvent component pair. Ion-ion binary parameters are only needed when two electrolytes are present with a common ion. In the absence of electrolytes, Chen's model reduces to the NRTL model [26].

This initial version was capable of performing single stage equilibrium of streams containing electrolytes. The electrolyte capability was restricted to process units that didn't involve multistage operations such as distillations and absorbers. This work has resulted in a modified version of ASPEN capable of electrolyte multistage simulation. Enhancements were made to the rigorous distillation module, RADFRC, and the equilibrium reactor, REQUIL. The electrolyte implementation was corrected to default to the NRTL model when no electrolyte was present. This correction became essential in the rigorous distillation where electrolytes would not be present above the feed tray.

Another serious drawback of ASPEN was the lack of an operational data regression system for electrolyte data. Electrolyte models, such as Chen's, involve binary parameters that must be regressed from vapor-liquid equilibrium (VLE) and heat of mixing data in the range of interest. There is presently no method to select these parameters in the absence of experimental data. For this reason, a data regression system is essential for accurate representation. In this study, the ASPEN Data Regression System (DRS) was modified to allow electrolyte model parameter estimation from VLE and heat of mixing data. This modification also corrected ASPEN's inability to regress data to estimate other binary parameters such as Henry's coefficients.

Electrolytic Cell and Process Design.-- Electrochemical science and technology research in recent years has produced advances in electrolytic cell modeling. Design models based on scientific principles have been developed for common electrochemical reactor designs. Pickett [27] compiled much of this work in an electrochemical reactor design monograph.

The most common industrial configurations are the parallel plate reactor and the porous (or three-dimensional) electrode reactor. Savinell [28] and Oloman [29] recently outlined general aspects of electrochemical reactor design. Several models have been developed for parallel plate reactors [30-33] which account for ohmic, kinetic, and concentration effects. Representation of gas evolving electrodes has been formulated [34,35]. Models for porous electrode reactors [36,37] have arisen out of a need to increase surface area for low current density reactions such as many electroorganic syntheses [38]. Porous electrode technology has been reviewed in recent publications [39,40].

Research has broadened to consider optimal design of electrolytic cells. Cera [41] explored optimization of a chlor-alkali cell using the GRG algorithm. Soon [42] and Yung [43] have utilized successive quadratic programming for cell optimization. The scope of optimization will eventually expand to entire electrochemical process flowsheets [44] since interactions between the cell and recovery operations must be considered [45,46]. Engineering costing methods for electrochemical installations [47,48] are being established to allow analysis on an economic basis.

DEVELOPMENT OF AN EXAMPLE PROCESS FLOWSHEET

Process Selection.-- Electroorganic processes were considered to have two distinct advantages as example processes. First, many of the new electrolytic processes in development stages are electroorganic. Beck et al. [49,50] have reviewed several preliminary designs for large-scale electroorganic processes. Jansson [51] recently outlined electroorganic syntheses from bench-scale to production units. Secondly, organic petrochemical simulation experience can be translated to electroorganic process simulation.

Electrochemical production of methyl ethyl ketone (MEK) from n-butenes was chosen as an example. Beck considered the electrochemical route to be less energy intensive than the conventional petrochemical route. Energy costs rising faster than capital costs would give advantage to the electrochemical process. Worsham [52-54] and Griffin et al. [55] outlined the details involved in MEK electrochemical production. The MEK process had several attributes that made it an appropriate choice to illustrate computer-aided electrochemical process design.

1. Alternative product recovery schemes could be developed and compared.
2. The process was closely related to the conventional route which made capital and utility cost comparison straightforward.
3. Electrolytic cell operation data were readily available in the literature.
4. Vapor-liquid equilibrium and heat of mixing data needed for physical property modeling were available.
5. The product recovery required multistage separations involving electrolytes.

This study was based on Worsham's electrochemical process for MEK [53,55]. A simple electrolytic cell model was written to closely represent Worsham's results. Two different product recovery schemes were developed during the course of this work.

Methodology Outline.-- The major goal of this study was to develop a methodology for the computer-aided design, costing, and economic analysis of an electrochemical flowsheet. The subsequent sections give details involved in applying the methodology to the example process. Additional information concerning the ASPEN system is available in public documentation from the National Technical Information Center [56]. The following outline provides a general description of the methodology.

1. Process Flowsheet Synthesis
   Identify the general process flow diagram and operating conditions.
2. ASPEN Flowsheet
   Select ASPEN modules to represent the unit processes and operations. Write additional FORTRAN subroutines to model special units not covered by ASPEN modules (such as an electrolytic cell).
3. Physical Property Modeling
   Select physical property models and obtain data needed to represent the process stream. Perform regression of data for binary parameter estimation.

4. Design Specification and Convergence
   Identify design specifications to be imposed on the flowsheet along with the free variables to be adjusted to meet the specifications. Define an ASPEN convergence scheme.
5. Costing and Economic Analysis
   Choose process unit construction materials and specify cost module factors. Select parameters for desired economic analysis.

Process Flowsheet Synthesis.-- Figures 1 and 2 show the two flowsheet configurations used in this study. These flowsheets involved absorbing n-butenes into sulfuric acid before entering the electrolytic cell. These flow designs were developed from Worsham's flow diagram [53]. Figure 1 is designated as the Cell Liquor Recovery flowsheet since the MEK was recovered from the cell liquor via a four column distillation system. MEK was recovered from the cell off-gas in Figure 2 utilizing a condenser and a two column distillation system. This plant is referred to as the Cell Gas Recovery flowsheet. The distillation system designs in both flowsheets resulted from preliminary distillation simulations done in the course of this study. The butene absorber and electrochemical reactor closely followed Worsham's specifications [53,55].

Both configurations contacted n-butenes with 65 wt% sulfuric acid in an absorber. Absorber conditions were set at 140°F and 100 psia [53]. At these conditions, the n-butenes were sulfonated (1) and subsequently hydrolyzed to 2-butanol (2). The overall reaction to 2-butanol is a very fast second order reaction that proceeds quickly to equilibrium in the absorber [57].

$$(1)\quad C_4H_8 + H_2SO_4 \dashrightarrow C_4H_9OSO_3H$$

$$(2)\quad C_4H_9OSO_3H + H_2O \dashrightarrow C_4H_9OH + H_2SO_4$$

The 2-butanol/sulfuric acid mixture proceeded to the electrochemical reactor in both configurations. A two electron transfer process yields MEK at the anode (3) and hydrogen at the cathode (4). The electrolytic cell design was based on monopolar undivided cells with expanded Pt/PtO anodes (titanium substrate) and steel cathodes.

$$(3)\quad C_4H_9OH \dashrightarrow C_4H_8O + 2H^+ + 2e^-$$

$$(4)\quad 2H^+ + 2e^- \dashrightarrow H_2$$

Modeling of the electrochemical cell was based on Worsham's best operating conditions with respect to current density. He achieved 120 amp/ft^2 at 170°F with 20% conversion per pass of 2-butanol [53]. Worsham et al. [55] made successful runs up to 1:1 hydrogen ion to 2-butanol mole ratio with 65 wt% sulfuric acid. Maximum cell voltage recommended was 1.65 volts [53]. Higher voltages resulted in loss of product selectivity via overoxidation to produce carbon dioxide.

ASPEN Flowsheet.-- Figure 3 shows the ASPEN flowsheet for the Cell Liquor Recovery plant. This configuration involved recovering MEK from the cell liquor by a system of four distillations. The first distillation separated an MEK/2-butanol/water mixture near the MEK/water azeotrope (66% MEK) from the sulfuric acid. The second distillation involved drying the mixture with the addition of a small sulfuric acid stream at the top of the column. An MEK/2-butanol stream with trace water was taken from overhead to the third distillation which removed an MEK/water azeotrope from the MEK/2-butanol. The final finishing column achieved 99% MEK product by removing 2-butanol. All other streams were recycled to the butene absorber.

The ASPEN flowsheet for the Cell Gas Recovery is shown in Figure 4. This configuration involved building up the MEK concentration in the recycle to increase MEK in the hydrogen gas. Worsham [53] found that MEK concentrations of up to 22% did not adversely affect the electrochemical reaction. The MEK/hydrogen gas mixture with minor amounts of 2-butanol and water was cooled by refrigeration to 5°C. Liquid from the cooler proceeded to an azeotropic distillation to remove water and to a finishing column to attain 99% purity MEK.

The effluent hydrogen stream was passed through a refrigerated water absorber in both flowsheets. The absorber removed trace amounts of MEK and 2-butanol for recycle back into the process. The relatively pure hydrogen stream was credited as by-product fuel gas.

Physical Property Modeling.-- Two physical property routines were used in the MEK flowsheet. Both routines calculated vapor properties from the Redlich-Kwong equation of state. The NRTL model was used for liquid mixture properties in areas of the flowsheet that did not contain electrolytes. Chen's local composition model was used for liquid mixture properties in flowsheet sections involving electrolytes.

The ASPEN Data Regression System (DRS) with our modification determined binary interaction parameters from literature data. Aqueous sulfuric acid VLE and heat of mixing data were used to estimate ion-water binary parameters [58,59]. Binary VLE data for each solvent-solvent pair were used for solvent-solvent parameters with ternary data used to "fine-tune" the regression [60,61].

Design Specification and Convergence.-- The specifications for the flowsheets were a 1:1 hydrogen ion to 2-butanol mole ratio and 65 wt% sulfuric acid in the cell feed. Immediately preceeding the REACT block, an ASPEN Fortran Block adjusted the H_2SO_4 moleflow to maintain the H^+/2-butanol ratio. This treatment handled the specification as an equipment parameter rather than an actual design specification. An ASPEN Design Specification Block controlled the ABSR2 water flow to achieve 65 wt% sulfuric acid entering the cell. The design specification was considered converged when there was less than 0.001 kmol/hr change in the absorber water flow between iterations.

Costing and Economic Analysis.-- Capital and operating costs were estimated using the ASPEN Cost Estimation System (CES). The CES was designed to yield a "preliminary-study grade" estimate from flowsheet heat and mass balance results. The system was based on Guthrie's modular concept for capital estimation [62]. The CES contained information to determine process equipment costs (except for the electrochemical section which is discussed later). Factors to estimate the installation and indirect costs [62] were added in the ASPEN input file. Economic analysis calculated the MEK product selling price based on a 20% discounted cash flow rate of return.

The capital costs of the electrochemical reactor section were based on the work of Keating and Sutlic [47]. Their cost module accounted for the cell bank, rectifier and busing, pumps, and common facilities associated with the electrochemical reactor section. Their design involved a divided membrane cell with a chlorinated polyvinyl chloride body, a precious metal oxide anode (titanium substrate), and a mild steel cathode. The costs were adjusted for this study since only an undivided cell design was needed. The overall cost per square foot of electrode surface was $1091 (1984$) which included 40% indirect field costs.

Plant life was 20 years with declining balance depreciation, 13% interest on borrowed capital, 10% salvage value, and 5% yearly inflation. CES defaults [56] were used for other economic parameters such as tax rates. Construction year was 1985 in a Midwest location with production beginning in 1987. Materials of construction were Incoloy 825 and Hastelloy for all process units (except the electrolytic cells) with sulfuric acid present [63]. Units with no electrolytes were constructed of carbon steel. Plant capacity ranged from 25 to 45 kton/yr MEK produced [64].

RESULTS AND DISCUSSION

Table 1 lists several example runs made in this study. MEK selling prices at 20% discounted cash flow rate of return were calculated for different plant configurations and capacities. These results are compared with the 1984 MEK price of $0.36/lb. Capital and utility cost comparisons were made with the conventional oxidation of n-butenes to MEK (Table 2). These comparisons were based on conventional capital and utility costs estimated by Rudd et al. [65].

Typical computer run time statistics for the two flowsheet configurations are shown in Table 3. Runs were made on an IBM 4341 model L10 computer at the University of Illinois. Core memory requirements were 4 megabytes running under the VM/SP Release 3 operating system. A simulation of Cell Liquor Recovery required 12 iterations to converge while taking 31 CPU minutes at a cost of $37. Cell Gas Recovery runs took 12 CPU minutes for 19 iterations at a cost of $14. Reduction of distillation computation time could bring computations to the level of microcomputer simulation.

CONCLUSIONS AND RECOMMENDATIONS

A methodology was developed for the computer-aided simulation and design of electrolytic process flowsheets. The electrochemical production of methyl ethyl ketone (MEK) was used as an example. The methodology outlined opened avenues for detailed design and economic evaluation of electrochemical processes. The framework constructed in this study laid the foundation upon which a process flowsheet package capable of electrolytic process optimization could be developed. This work illustrated the use of a user-supplied FORTRAN subroutine to describe an electrolytic cell in an ASPEN flowsheet.

The public version of ASPEN with this study's enhancements provided a great degree of reliability and portability while remaining adaptable to future research. The enhancements included rigorous distillation with electrolytes and data regression capability for electrolyte thermodynamic model parameters. Future goals include microcomputing and optimization capabilities.

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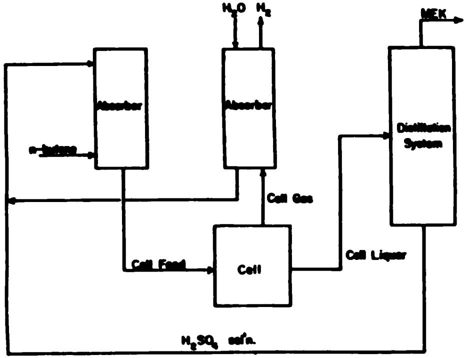
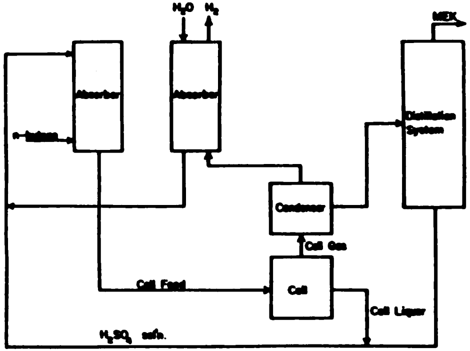
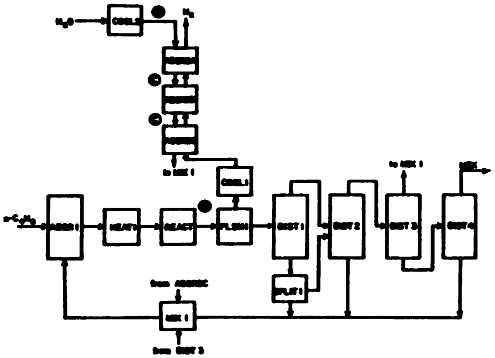


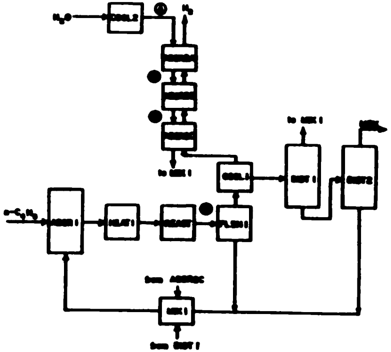
CELL LIQUOR RECOVERY
Figure 1



CELL GAS RECOVERY
Figure 2



ASPEN Flowsheet for CELL LIQUOR RECOVERY
Figure 3



ASPEN Flowsheet for CELL GAS RECOVERY
Figure 4

Table 1
ECONOMIC ANALYSIS RESULTS

Capacity (kton/yr)	MEK recovery	MEK price ($/lb)
25	cell liquor	$ 0.424
45	cell liquor	0.406
25	cell gas	0.406
45	cell gas	0.391

1984 MEK Price	$ 0.36

Table 2
CAPITAL AND UTILITY COST COMPARISON
(1984$)

	Capital Cost (MM$)	Relative Yearly Utility Cost
Conventional oxidation of n-butenes	36.66	1.00
Cell liquor recovery	51.40	1.06
Cell gas recovery	48.47	0.65

Table 3
TYPICAL RUN TIME STATISTICS

Cell Liquor Recovery 12 iterations		$37
2 electrolyte distillations	1397	(116/iteration)
2 non-electrolyte distillations	372	(31/iteration)
all other computations	75	

	1844	CPU seconds
Cell Gas Recovery 19 iterations		$14
2 non-electrolyte distillations	631	(33/iteration)
all other computations	99	

	730	CPU seconds

COMPUTER: IBM 4341 Model L10