OPTIMIZATION OF ELECTROLYTIC CELLS AND PROCESSES

State-of-the-art methods are reviewed for process simulation and for optimization of steady-state electrochemical systems which exhibit large numbers of variables. Three categories of examples are discussed: (1) cell models based on algebraic equations, (2) cell models based on differential equations, and (3) process flowsheets. The purpose of this paper is to provide a general overview of how simulation and optimization methods are employed in electrochemical research and engineering.

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Optimization of a system requires a formal description of the problem as well as of the choices one is free to make in order to achieve a specific goal. Optimization procedures are used to evaluate the best position when there are trade-offs to be made, and thus invariably involve economic features. The purpose of this paper is to provide an introductory survey of the field of optimization with emphasis on electrolytic applications.

Published works on electrochemical process optimization have to date used analytical or graphical methods for differentiating a cost equation with respect to one or two variables while holding all other variables constant. The literature has been recently surveyed (1) and is also discussed elsewhere in this volume in papers by Ford and by Jansson.

Electrolytic optimization papers have by and large simulated cell behavior by using models obtained from operating experience. In most cases, the cell models are essentially empirical. However, the modeling of electrochemical reactors by application of fundamental principles has reached an advanced level of sophistication in recent years. Rigorous models are now available for many of the more common cell configurations (2-4). These models are based on current and potential distribution phenomena within cells, and are therefore able to clarify the scientific principles which influence cell behavior (5).

Computer-aided process simulation is by now commonplace in large petroleum and chemical companies. Process simulators such as Monsanto's FLOWTRAN have been in industrial use for nearly two decades, and have proven useful and easy to use. To set up a steady-state process simulation problem the user must first supply a process flowsheet, i.e., he must specify what unit operations are present and how they are connected to each other. For each unit operation, values for a number of equipment parameters must then be specified. The parameters provided must be sufficient to permit the computation of the outputs from each unit operation given the inputs. Finally each feed stream to the process must be described. This requires values for c+2 independent variables for each feed stream, often the temperature, pressure, and flowrates of the c components present. Given the process flowsheet, the equipment parameters, and the feed stream data, the process simulator will then compute values describing each product and intermediate stream, i.e., their temperature, pressure, composition, flowrate, enthalpy, vapor fraction, etc. Also computed is performance data, utility requirements for example, for the appropriate unit operations. In other words, in a simulation problem, one essentially computes the performance of a process given its design.

Often a more interesting and useful

problem to solve is to compute the design of a process given a desired performance. In this so-called "controlled simulation" or design problem, one supplies most of the same information required to solve a simulation problem. However, in the design problem certain equipment parameters or feed stream values are left unknown and instead design specifications on output or intermediate streams are provided. The program then computes the unknown equipment or feed stream values that satisfy the design specifications. It should be noted that the traditional numerical methods still used in most process simulators today are often much less efficient in solving the design problem than the simulation problem. This has prompted considerable recent interest in alternative numerical methods. These methods as well as the traditional ones for process simulation and design have been discussed in a number of recent reviews (6-9). Also the monograph of Westerberg et al. (10) provides an excellent introduction to the field of computer-aided process simulation and design (flowsheeting).

Most process simulators were developed for use in the petroleum industry, and were therefore originally equipped to simulate vapor-liquid equilibria of hydrocarbon mixtures. The methods used for such mixtures, however, are not suitable for electrolytic solutions. Within the past two decades, significant advances have been made in the thermodynamics of electrolytes (11-16). These have been recently incorporated in at least one general-purpose flowsheeting package (ASPEN). Some stand-alone programs are also available for handling electrolytes in certain separation operations (17).

While simulation of process flowsheets has become routine in certain industries, process optimization has lagged behind (18,19). To a large extent, the reason for this situation was that the mathematical methods used originally for flowsheet simulation and still used predominantly today are very inefficient when coupled to optimization methods (18,20). Alternative numerical methods have therefore been vigorously explored (20-26). These alternative methods generally rely on recent advances in the field of nonlinear programming, in particular the development of successive quadratic programming algorithms (27-32). Using such techniques, process optimization studies can be conducted much more cheaply and efficiently than ever before possible.

In summary, advances have very recently been made in electrochemical modeling, in chemical process engineering, in thermodynamics of electrolyte solutions, and in applied mathematics. These will have profound influence on the optimization of electrochemical systems.

FORMULATION OF A MODEL FOR OPTIMIZATION

It is important first to define the objective of an optimization study and to anticipate the kinds of answers which are to be sought. In addition, it is important to recognize restrictions which limit the freedom of action of our attempts to optimize the situation. For example before building a plant, one may investigate how to optimize a certain cell, but once the cells are built, it becomes substantially more difficult to re-optimize except by retrofit.

The next step is to establish a model of the system. There are six basic steps to this task as described in the following paragraphs. Many of these tasks are carried out automatically by most process simulators so that there is no need to carry them out manually.

Material Balances

Material balances including heat balances need to be made for each piece of equipment involved in the process flowsheet. These equations along with physical property data and phase equilibria data are used to determine the composition and temperature of all process streams (33).

Cell Model

For the electrolytic cell, some sort of chemical description is needed to determine conversions. The model may be extremely simple, or may be empirically based on past experience, or may be built upon fundamental principles of electrochemical science. In the latter case, the model could include elements of mass transport, ohmic resistance, fluid mechanics, membrane transport, charge-transfer kinetics, and thermodynamics.

Thermodynamics of Separation Processes

Data concerning phase equilibrium and enthalpy changes are needed to establish simple models of separation units. Until recently, process simulators had libraries of data which did not include solutions of electrolytes. This deficiency has recently

been remedied by recent developments as indicated previously, thus enabling simulation of electrolytic processes to move forward.

Equipment Sizing

Various decisions need to be made on the size of equipment such as the number of trays in a distillation tower, or the surface area in a heat exchanger. Most simulators include sizing models for the common units in a flowsheet, but not for an electrochemical cell. Therefore some type of design model is required in order to establish the size of an electrochemical cell.

Capital Cost

Evaluation of equipment cost must be performed under various conditions in order to identify the economic optimum. There is very little in the way of literature sources for such information in the electrolytic area (34), although data on other unit processes is built into simulators for the most common unit operations.

Economics

Some kind of accounting procedure must be chosen to generate an economic assessment of the system. The common choice would be a rate-of-return criterion, of which there are several variations. A good review of economic objectives with respect to chemical engineering applications is available (35).

TYPES OF OPTIMIZATION PROBLEMS

There are basically four types of optimization endeavors, and the techniques associated with these classes are substantially different from each other.

Process Design

Elsewhere in this volume, Jansson emphasized the value of simple economic models in process design of electro-organic synthesis systems. That article contains references to about a dozen electrolytic process design case studies. In addition, Beck, et al. (36) evaluated a number of electro-organic process routes by computing the energy consumption of the entire process. These works represent important case studies for specific processes, and provide clear justification for the need of more robust methods of electrolytic flowsheet simulation and optimization.

None of the methods used in these studies employed computer-assisted flowsheet simulations. In comparison with the widespread use of computer methods for process design in chemical and petrochemical industries, it is reasonable to suggest that substantial improvements in methodology could be developed for electrochemical processes.

The previous paper, by Chen and Boston, highlights the electrolyte capability of ASPEN PLUS, a computer-aided chemical process simulator. This capability represents a significant advancement in the state of the art of process simulation.

In a recent study, Cera (37) used ASPEN and ASPEN PLUS to simulate and optimize a process for electrolytic production of methyl ethyl ketone by oxidation of butyl alcohol in an undivided parallel plate cell. The flowsheet given in Fig. 1 is similar to those in the early patents of Worsham (38). Butene is contacted with 65 % wt H_2SO_4 and is sulfonated and hydrolyzed to butyl alcohol which is fed to the electrolytic cell. At the anode, alcohol adsorbs according to a Temkin isotherm and reacts with 100% current efficiency; hydrogen evolution occurs at the cathode. The cell was modeled by writing balances on species, heat, voltage and charge.

The feed preparation section of the flowsheet was in essence an absorber with reaction, and was modeled in the ASPEN/ASPEN PLUS system as a series of flashes where reaction can occur. The model of the electrolytic cell was supplied to the ASPEN routine named RYIELD, a reactor module which computes output flowrates of all components based on a yield computed by a user-supplied electrochemical cell subroutine. The separation section of the flowsheet involved product distillation, and was simulated by modifying the routine RADFRC, available in ASPEN, so that it could handle electrolytes. Thermodynamic properties were obtained by regression of T-p-X-Y data (39) along with a local composition model (40) which predicted excess Gibbs energy.

Capital cost data for the cell were estimated (34) and supplied to the ASPEN routine EES which determined capital investment, plant operating cost, and proftability according to a discounted cash flow rate of return (DCFRR) method. The simulation was carried out on an IBM 4341 (ASPEN system) and an IBM 370 (ASPEN PLUS system). It was concluded that the

ASPEN/ASPEN PLUS system is extremely flexible and shows great promise for simulating electrolytic process flowsheets.

In the same study (37), a gradient method was used to optimize the DCFRR by adjustment of a single variable, the conversion (or current density). It was found that this method required about 1600 seconds to determine the optimum. It was concluded that a more efficient method of optimization must be identified. Several candidates have recently been developed (20-26), as mentioned above.

Equipment Design

The review by Beck (1) contains numerous references and examples of economic optimization of cells. In general, these methods use a cost equation in which all but one or two variables are held constant, and the optimum value of the remaining variables are obtained by analytical or gradient search methods.

Although analytical differentiation of a cost equation is simple and rapid, more sophisticated optimization methods are also available, based on nonlinear programming techniques (18,27-32,41-43). One of the more promising methods was employed recently in a study of a chlor-alkali cell (44) based on a model by MacMullin (45) of a Hooker S-4 diaphram cell. The model consisted of 37 algebraic equations based on mass, heat, voltage and profitability balances, along with two inequality constraints, namely that the anolyte and catholyte temperatures must not exceed their boiling points. The generalized reduced gradient (GRG) method of Lasdon et al. (46) was used to identify the optimal values of 42 variables in order to maximize cell profit based on the cost of raw materials and electrical power usage. In addition, the sensitivity of the optimum to variations in design and operating variables was assessed. The execution time for the optimization calculations was about 2.5 seconds on a CDC Cyber 175 computer.

Additional methods for optimizing a cell were employed by Yung (47) in a study of an electrochemical cell in which ethylene is converted to dichloroethane in the presence of aqueous hydrochloric acid. The cell consisted of a parallel plate flow cell, modeled with algebraic equations for material, voltage and economic balances. Variables which were optimized included anode-cathode gap, electrode length, flow rate, electrolyte concentration, cell voltage, and payback time. The optimal configuration was obtained with use of a successive quadratic programming (SQP) method (32).

In the foregoing two paragraphs, two examples were given which used state-of-the-art methods for optimizing electrolytic cells. In both cases, the cell models consisted of simple algebraic equations. In cells of more complex configuration, however, the potential field distribution within the cell is non-uniform, so that a more realistic cell model would require use of differential equations. Figure 2 illustrates such a cell, consisting of two flow-through porous electrodes separated by a membrane and operating under steady conditions. In a recent study, Soon (48) optimized a model cell in which differential equations of transport were used to predict reactor behavior. The model included a main reaction and a side reaction at each electrode, along with mass, voltage and economic balances. An SQP method (32) was again used to perform the optimization. The actual optimization program, SQPHP (32), used in this study and the previous one was an enhancement of the program VF02AD, commercially available in the Harwell Subroutine Library.

From these studies, it was concluded that the GRG method is to be preferred for simple cell models while, for more sophisticated cell models, the SQP method is more advantageous.

Operations Scheduling

Achievement of flexibility and multi-purpose use of large interconnected facilities represents a class of optimization problems known as operations scheduling problems. An example of such a problem would include optimal scheduling of crude oil shipments from worldwide sources to refinery sites which serve certain markets and/or have limitations on compatibility to crudes from different sources. Though there is a large body of literature devoted to such operations research problems, for the most part this work has not appeared in the chemical engineering literature, even though there are a number of interesting chemical engineering applications. This area will not be discussed further in this review.

Process Control

The concept that a process could be

continually reoptimized by adjusting operating variables to changing (unsteady-state) conditions received widespread attention from the academic community during the past several decades. Known as optimal control theory, the field is highly mathematical and in general has yet to find wide application in chemical process control, due in part to the complexity of the models describing many chemical process units. This field will not be emphasized further in this review.

LIMITATIONS ON OPTIMIZATION EFFORTS

The main value of most optimization studies is not always in the specific numerical results but, rather, in the awareness which is thereby achieved about subtle interactions within the process. Thus prepared, one's intuition is able to operate at a higher level of insight.

There are a number of limitations on optimization activities, the most common of which are summarized here. Some limitations are imaginary since, for example, it takes only a few minutes to jot down a quick optimization model on the back of an envelope. What is needed is often not so much mathematical skill as an intuitive awareness for recognizing when elementary calculations can reveal important insight.

In some cases, it is difficult to formulate a model of the reactor owing either to limited experimental data or to uncertainty in the principles which govern behavior. It is obviously difficult to predict optimum cell size when the scale-up principles are uncertain. In addition there may be physical property data that are unknown, or stirring conditions that are ill-defined. In such cases, the goals of an optimization study cannot be too specific.

Most economic evaluations of profitability require forecasts of economic conditions which are of course unclear. Equally uncertain is the response of others to the introduction of new technology. Such forecasts fall into the realm of engineering judgment, and are not incorporated in process models.

The new developments in process simulation and optimization are based on sophisticated mathematics and computer techniques. Many of the newest and most promising techniques have not yet been reduced to user-friendly software. Therefore acquisition of optimization capability depends in part on achieving a critical mass of requisite skills. Manpower limitations may continue to be a problem in the near future since there are relatively few training centers in electrochemical engineering.

CONCLUDING REMARKS

In order to develop an understanding of electrolytic processes, an optimization approach can be used to investigate engineering strategies. These methods are direct descendants from chemical engineering experience on non-electrochemical systems.

In order to work creatively with mathematical representations of a system, it is essential to develop the intuitive link between mathematical symbols and physical processes. This link is best established by study of transport phenmomena and potential field phenomena related to electrochemical cells.

Extremely powerful new methods are available for optimizing electrolytic cells. These methods can accept mathematical models based either on extensive experimental data, or on fundamental principles of current and potential distribution phenomena. In addition, general-purpose process simulation software capable of handling electrolytic processes is just now becoming available. Utilization of these new tools by industrial practitioners is certain to expand in the near future. Efficient techniques for optimizing process flowsheets have only recently been conceived and have not yet developed to the robust state needed for widespread acceptance.

In summary, seminal advances have very recently been made in electrochemical engineering, in chemical process engineering, in thermodynamics of electrolyte solutions, and in applied mathematics. These will have a profound influence on electrochemical process technology.

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LITERATURE CITED

1. T. R. Beck, in Techniques of Electrochemistry, E. Yeager and A. Salkind, eds., John Wiley, New York (1978).
2. D. J. Pickett, Electrochemical Reactor Design, Elsevier, Amterdam (1977).
3. J. S. Newman and W. Tiedemann, Adv. Electrochem. Engr, 11, (1978).
4. G. A. Prentice and C. W. Tobias, J. Electrochem. Soc., 129, 72 (1982).
5. R. Alkire, AIChE Symposium Ser., 204, 121 (1981).
6. R. L. Motard, M. Shacham and E. M. Rosen, AIChE J., 21, 417 (1975).
7. V. Hlavacek, Comput. Chem. Eng., 1, 75 (1977).
8. E. M. Rosen, ACS Symposium Series, 124 (1980).
9. L. B. Evans, in Foundations of Computer-Aided Chemical Process Design, vol. 1, R. S. H. Mah and W. D. Sieder, eds., Engineering Foundation, New York (1981).
10. A. W. Westerberg, H. P. Hutchison, R. L. Motard and P. Winter, Process Flowsheeting, Cambridge University Press, Cambridge (1979).
11. C. M. Criss and J. W. Cobble, JACS, 86, 5385 (1964).
12. H. P. Meissner and J. W. Tester, I&EC Proc. Des. Devl, 11, 128 (1972).
13. L. A. Bromley, AIChE J., 19, 313 (1973).
14. K. S. Pitzer , J. Phys. Chem., 77, 268 (1973).
15. J. L. Cruz and H. Renon, AIChE J., 24, 817 (1978).
16. C. C. Chen, H. I. Britt, J. F. Boston, and L. B. Evans, AIChE J., 25, 820 (1979).
17. J. F. Zemaitis, ACS Symposium Series, 124, 309 (1980).
18. A. W. Westerberg, in Foundations of Computer-Aided Chemical Process Design, vol. 1, R. S. H. Mah and W. D. Seider, eds., Engineering Foundation, New York (1981).
19. G. E. Blau, ibid. (1981).
20. S. Jirapongphan, Ph. D. Thesis, Massachusetts Institute of Technology, Cambridge (1980).
21. L. T. Biegler and R. R. Hughes, Chem. Eng. Prog., 77(4), 76 (1981).
22. L. T. Biegler and R. R. Hughes, AIChE J., 28, 994 (1982).
23. L. T. Biegler and R. R. Hughes, Comput. Chem. Eng., in press (1983).
24. T. J. Berna, M. H. Locke and A. W. Westerberg, AIChE J., 26, 37 (1980).
25. M. H. Locke and A. W. Westerberg, paper #23c, presented at AIChE National Meeting, Los Angeles (1982).
26. M. A. Stadtherr and H. S. Chen, paper presented at Second International Conference on Foundations of Computer-Aided Process Design, Snowmass, Colo., proceedings to be published (1983).
27. S. P. Han, Math. Prog., 11, 263 (1976).
28. S. P. Han, J. Opt. Theory Appl, 22, 297 (1977).
29. M. J. D. Powell, in Numerical Analysis-Dundee 1977, ed. G. A. Watson, Lecture Notes in Mathematics, vol. 630, Springer-Verlag (1978).
30. M. J. D. Powell, Math. Prog., 14, 225 (1978).
31. M. J. D. Powell, in Nonlinear Programming Symposium 3, O. L. Mangasarian, R. R. Meyer and S. M. Robinson, eds., Academic Press, NY (1978).
32. H. S. Chen and M. A. Stadtherr, Comput. Chem. Eng., to be published (1984).
33. R. M. Felder and R. W. Rousseau, Elementary Principles of Chemical Processes, Wiley, New York (1978).

34. K. Keating and V. D. Sutlic, in Techniques of Chemistry, Vol. V, Part 3, N. L. Weinberg and B. V. Tilak, eds., Wiley-Interscience, New York (1982).

35. M. S. Peters and K. D. Timmerhaus, Plant Design and Economics for Chemical Engineers, McGraw Hill, New York (1980).

36. T. Beck, R. Alkire, N. Weinberg, R. Ruggeri and M. Stadtherr, in Techniques of Chemistry, vol V, Part 3, N. L. Weinberg and B. V. Tilak, eds., Wiley-Interscience, New York (1982).

37. G. D. Cera, Ph. D. Thesis, Department of Chemical Engineering, University of Illinois, Urbana (1983).

38. C. W. Worsham, U. S. Patent 3,247,084 (1966).

39. R. H. Perry and C. H. Chilton, Chemical Engineers' Handbook, Fifth Edition, McGraw-Hill, New York (1973).

40. C. C. Chen, H. I. Britt, J. F. Boston, and L. B. Evans, ACS Symposium Series, 133, 61 (1980).

41. A. Waren and L. Lasdon, Operations Research, 27, 431 (1979).

42. L. Lasdon and A. Waren, ibid., 28, 1029 (1980).

43. R. W. H. Sargent, ACS Symposium Series, 124 (1980).

44. R. C. Alkire, G. D. Cera, and M. A. Stadtherr, J. Electrochem. Soc., 129, 1225 (1982).

45. R. B. MacMullin, Denki Kagaku, 38, 570 (1970).

46. L. Lasdon, A. Waren, A. Jain, and M. Ratner, ACM Trans. Mathematical Software, 4, 34 (1978).

47. E. K. Yung, Ph. D. Thesis in progress, Department of Chemical Engineering, University of Illinois, Urbana (1983).

48. S. A. Soon., M.S. Thesis, Department of Chemical Engineering, University of Illinois, Urbana (1983).

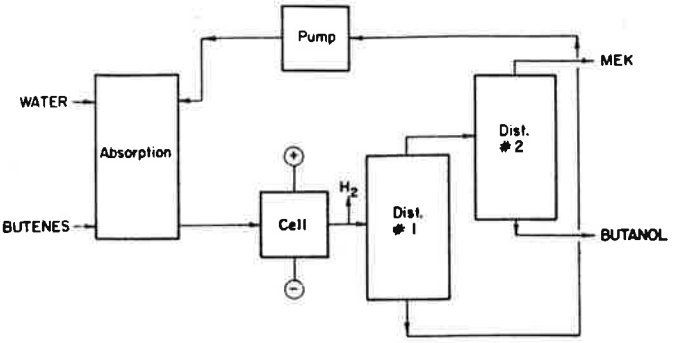

Figure 1. Flowsheet for the electrolytic production of methyl ethyl ketone from butene.

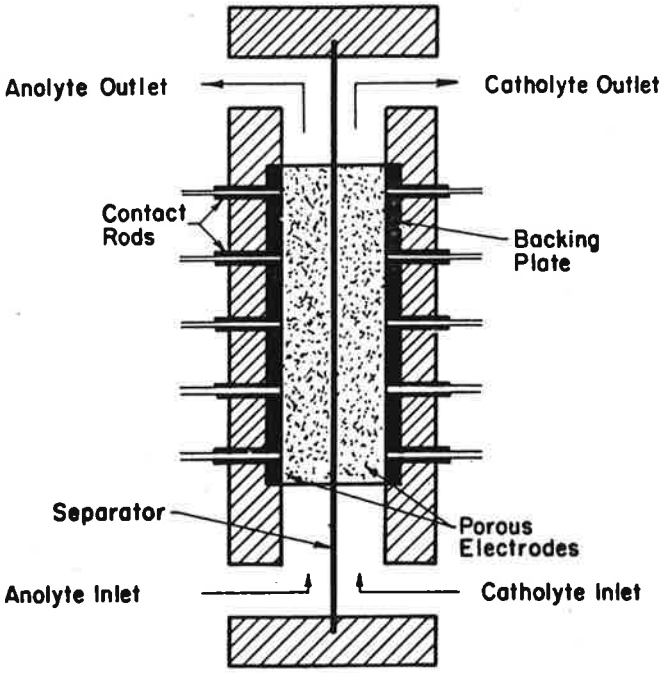

Figure 2. Flow-through porous electrode cell.