

422 ELECTRODES FOR SMALL-SCALE ELECTROORGANIC PROCESSES

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Chapter IX

**ELECTROCHEMICAL ENGINEERING OF
ELECTROORGANIC PROCESSES:**

**ILLUSTRATED BY AN ENERGY ASSESSMENT OF
SOME LARGE-TONNAGE PROCESS CHEMICALS**

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1 INTRODUCTION

The industrial synthesis of organic chemicals has always been practiced in the presence of uncertainty. Therefore it is necessary constantly to evaluate new candidate processes in the search for those that will be compatible with the future. Included among routes to the synthesis of many organic compounds are those involving electrolysis. The purpose of this chapter is to describe progress in various electrochemical fields related to industrial organic synthesis and to present new calculations of energy usage for both electrochemical and chemical routes of several high-tonnage organic chemicals.

The pace of electrochemical science and technology quickened during the very recent past. There have been major advances in the elucidation of electrochemical fundamentals in areas of reaction mechanisms, solvent effects, and the influence of the electrode on the course of reaction. A large number of experimental techniques have only recently become available for the study of electrochemical processes, many of which were triggered by concurrent

developments in electronics, computer data processing, and catalytic science. Engineering methodologies have advanced rapidly as principles of current and potential distribution phenomena have been shaped into strategies for engineering design, scale-up, and optimization of electrolytic systems. New materials for electrodes, membranes, process sensors, and other cell components have appeared, often with extraordinary impact, as in the case of metal anodes and ion-selective membranes. Electrochemical science and engineering is coming of age, and those who practice electrochemistry are increasingly able to describe their knowledge in a manner that promotes rational engineering evaluation and design.

The field of electroorganic synthesis has seen steady growth since the earliest days of chemical synthesis. The annual publication of electroorganic synthesis documents during the past three decades is given in Fig. 9.1. These citations include scientific publications, patents, books, reviews, laboratory manuals, and dissertations [1]. It may be seen that the rate of publication has doubled every 8 years over the past 3 decades. Even *without any further increase* in the publication rate, the entire body of knowledge, which dates back to 1801, will have doubled again between 1975 and 1990.

By 1975 there were some 8000 organic compounds for which electrochemical synthesis routes were available [1, 2]. In view of electrochemical activities in general, and electroorganic synthesis in particular, it seems inevitable that new industrial technologies will emerge based on electrolytic routes for synthesis of organic compounds.

This chapter is divided into three main parts. In the first (Section 2), a historical perspective is presented by compiling the known industrial syntheses along with the advantages and disadvantages commonly associated with electroorganic process technologies. In the second part (Section 3), various specific areas of electrochemical science and engineering are discussed briefly, since knowledge from these areas will contribute to the emergence of new technology. The third part (Section 4) reports on engineering methodologies for predicting energy consumption from both electrochemical and chemical routes to synthesis of certain large-tonnage organic compounds [3] (see also Chapter V). These example evaluations are only preliminary in the sense that no process optimization has been attempted.

Not included in the comparison of electrochemical *versus* chemical routes (Section 4) are considerations of operating or investment costs, wastewater treatment credits for the electrochemical routes, and compounds produced at rates below 7000 tons/year. That is, the conclusions reached in Section 4 may not correspond to the more balanced perspective by which candidate processes are evaluated by the industrial sector. However, the purpose of this chapter is to contribute a general engineering perspective that, by further refinement and expansion, would lead to rational assessment of electro-

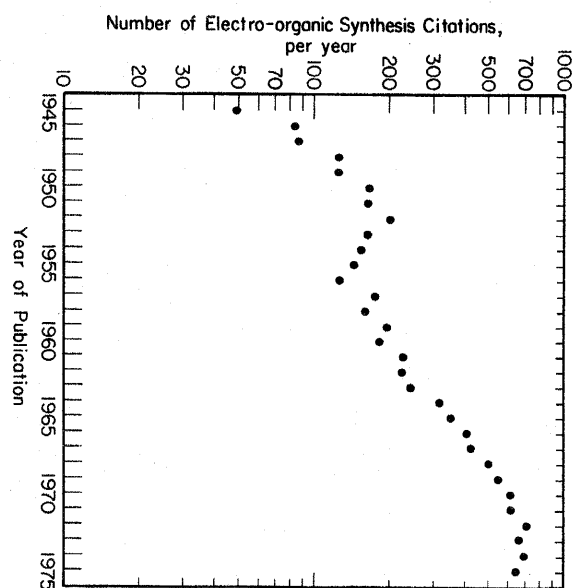


Fig. 9.1. Publication rate during the last three decades; data include papers, review, books, patents, and dissertations [1].

organic process routes, not only in the large-tonnage arena considered below, but also in other categories of intermediate and fine chemicals.

2 INDUSTRIAL ELECTROORGANIC PROCESSES

Current and Previously Used Processes

Industrial electroorganic synthesis has been practiced for many years and with various degrees of success. A measure of perspective is thus afforded by examining current and previously used processes. Table 9.1 provides a brief description of known processes. These include oxidation processes, reduction processes, and miscellaneous processes. The following symbols are used in the column marked "status" in Table 9.1.

P, pilot studies believed to be currently in progress.
EP, pilot studies that were begun and that are believed to have been abandoned.

C, commercial production currently in progress.

EC, commercial production that has been abandoned.

Table 9.1

| Oxidations | | | | | | |
|--|------------------------------|------------------|------------------------|---------------------------|-----------------------|----------------|
| Starting Material (Electrolyte) | Product(s) | Anode | Current Efficiency (%) | Energy Usage ^a | Status | Ref. |
| Anthracene (H ₂ O, Cr ⁺ ₆ , H ₂ SO ₄) ^b | Anthraquinone | PbO ₂ | 80 | [4.8] | C—Holliday | 4-7 |
| Benzene (H ₂ O, H ₂ SO ₄) | Hydroquinone (quinone) | PbO ₂ | 40-60 | 15 | P—Stavely, Carus, etc | 8-10, 70 |
| Butynediol (H ₂ O, H ₂ SO ₄) | Acetylenedicarboxylic acid | PbO ₂ | 75 | [12.4] | P—BASF | 11, 12, 69, 71 |
| Cyanuric acid (H ₂ O, 20% KCl) | Pot. dichlorocyanurate | Pt/Ti | High | [3-5] | EP—Monsanto | 13, 14 |
| Dimethyldithiocarbamate (H ₂ O, sodium salt) | Tetramethylthiuram disulfide | Pt | 90 | 1.7 | P—Dupont | 15, 16 |
| Dimethyl sulfide (H ₂ O, DMSO, 5% H ₂ SO ₄) | Dimethyl sulfoxide | Pt/Ti | 100 | 0.7-1.3 | P—Glanzstoff, Akzo? | 17-20 |
| Ethyl alcohol (H ₂ O, EtOH, NaOH, KI) | Iodoform | Pt | 93-95 | 2 | EC—Schering | 21-23 |
| Ethyl alcohol (H ₂ O, HCl) | Chloral | C | High | [8-10] | EC—Schering | 24 |
| Furan (CH ₃ OH, NaBr or NH ₄ Br) | Dimethoxydihydrofuran | C | 85 | 2.5 | C—BASF | 25, 26, 69, 71 |
| Glucose (H ₂ O, NaBr, CaCO ₃) | Calcium gluconate | C | High | [2] | C—Sandoz, Chefaro? | 27-29 |
| Hydrogen cyanide (H ₂ O, NH ₄ Br) | Melamine | C | 98 | 1.5-2 | P—Sohio | 30-31 |
| Isobutanol (H ₂ O, 10% H ₂ SO ₄) | Isobutyric acid | PbO ₂ | 45 | [14] | P—USSR | 32-33 |
| p-Methoxytoluene (H ₂ O, redox reagent, H ₂ SO ₄) ^b | Anisaldehyde | PbO ₂ | High | [2.2] | P—Oxy | 34 |
| Methyl (ethyl) chloride (THF/diglyme, RMgCl) | Tetraalkyl lead | Pb | 92 | 4-8 | C—Nalco | 35, 36 |
| 2-Methylnaphthalene (HOAc, NaOAc) | 2-Methyl-a-naphthol acetate | C | Good | [1.9] | EP?—Socony EP—BASF | 37, 69, 71 |
| Monomethyl adipate (CH ₃ OH, sod. salt of acid) | Dimethylsebacate | Pt/Ti | 75-85 | 5 | EP—BASF | 38-41, 69 |

Table 9.1. Continued

| Oxidations | | | | | | |
|--|--|-----------------------|------------------------|---------------------------|---------------------------------|-----------|
| Starting Material (Electrolyte) | Product(s) | Anode | Current Efficiency (%) | Energy Usage ^a | Status | Ref. |
| Naphthalene | 1-Naphthylacetate | C | | [1.6] | P—BASF | 69, 71 |
| <i>p</i> -Nitrotoluene | <i>p</i> -Nitrobenzoic acid | PbO ₂ | 98 | 7.5 | P—India | 42–44 |
| (H ₂ O, Cr ⁺⁶ , H ₂ SO ₄) ^b | | | | | | |
| Oleic acid (H ₂ O, Cr ⁺⁶ , H ₂ SO ₄) ^b | Azelaic acid, pelargonic acid | PbO ₂ | High | [4] | EC—Energy | 45–46 |
| Phenol (H ₂ O, 3% H ₂ SO ₄) | Hydroquinone (quinone) | PbO ₂ | 50 | [8–12] | P? Union Carbide, Eastman Kodak | 47 |
| Propargyl alcohol | Propiolic acid | | | [8.5] | P—BASF | 69 |
| Potassium alkylaluminum (melt) | Tetraalkyl lead | Pb | 100 | 1 | P—MPI | 48 |
| Propylene (H ₂ O, NaCl or NaBr) | Propylene oxide | C, DSA ^R | 70–88 | 4–6 | P—Bayer, Kellogg, EP—BASF | 49–52, 69 |
| Quinoline (H ₂ O, H ₂ SO ₄) | Nicotinic acid | PbO ₂ | 40 | 25 | ? | 53 |
| Starch (H ₂ O, NaOH, periodate) ^b | Dialdehyde starch | PbO ₂ | High | [1.5–2] | C—Miles | 54–58 |
| Toluene (H ₂ O, H ₂ SO ₄ , Ce ⁺⁴) ^b | Benzaldehyde | PbO ₂ , Pt | 90 | [6] | P—ETH | 59, 60 |
| <i>o</i> -Toluenesulfonamide | Saccharin | PbO ₂ | 78 | [6] | EP—Boots | 61, 62 |
| (H ₂ O, Cr ⁺⁶ , H ₂ SO ₄) ^b | | | | | | |
| Various organics (HF, KF) | Perfluoroorganics | Ni | Low | High | C—3M | 63–65 |
| Various organics (KF·2HF melt) | Perfluorinated and partially fluorinated Organics ^c | C | Fair | High | EP—Phillips | 166–68 |

Reductions

| Starting Material (Electrolyte) | Product(s) | Cathode | Current Efficiency (%) | Energy Usage ^a | Status | Ref. |
|--|---------------------------------------|-----------------|------------------------|---------------------------|----------------------------------|------------|
| Acetone (H ₂ O, H ₂ SO ₄ , Cu ²⁺) | Pinacol | Pb | 70–75 | 3.3 | EP—BASF, Bayer, Diamond Shamrock | 69, 71–73 |
| Acrylonitrile (H ₂ O, quat. salt) | Adiponitrile | Pb alloy | 90–92 | 3–6 | C—Monsanto, Asahi | 74–77 |
| Adiponitrile (H ₂ O, HCl) | 1,6-Hexanediamine | Ni(Cu) | 60 | [15.8] | P—USSR | 78–79 |
| Ammonium phthalamate | Phthalide | Pb | 70 | [5.7] | EP—BASF | 71, 80, 81 |
| (H ₂ O, phthalamate salt) | | | | | | |
| Anthranilic acid | <i>o</i> -Aminobenzyl alcohol | | | | P—BASF | 69 |
| Benzene (NH ₃ or CH ₃ NH ₂ , NaCl or LiCl) | 1,4-Cyclohexadiene | C, Al | 80 | [4.2] | EP—Esso Res | 82–84 |
| Benzenediazonium chloride (H ₂ O, HCl) | Phenylhydrazine hydrochloride | Hg | 70 | 5 | ? | 85 |
| Benzoic acid (H ₂ O, C ₂ H ₅ OH, H ₂ SO ₄) | Benzyl alcohol | Pb | 93 | 4.1 | P?—India | 86, 87 |
| Benzyl cyanide (H ₂ O, HCl) | β -Phenethylamine hydrochloride | Pd | 35–42 | [12] | P—India | 88, 89 |
| Diazoaminobenzene (H ₂ O, CH ₃ OH, THF, NaOH) | Phenylhydrazine | C | 82 | [7] | EP—Hoechst | 71, 90, 91 |
| <i>N, N</i> -Dimethylaminoethyltetra-chlorophthalimide (H ₂ O, HOAc, H ₂ SO ₄) | Corresponding isoindole | Hg | 78 | [2] | EP?—Ciba | 92–94 |
| <i>m</i> -Dimethylaminobenzoic acid | <i>m</i> -Dimethylaminobenzyl alcohol | | | [3.9] | P—BASF | 69 |
| <i>m</i> -Dinitrobenzene (H ₂ O, H ₂ SO ₄) | 2,4-Diaminophenol | Hg ^b | 60 | [18] | P—India | 95, 96 |
| Dimethyl terephthalate | <i>p</i> -Carbomethoxybenzyl alcohol | | | [3.6] | P—Hoechst | 70, 132 |

| Starting Material (Electrolyte) | Product(s) | Anode | Efficiency (%) | Energy Usage ^a | Status | Ref. |
|---|------------------------------------|------------------|----------------|---------------------------|-----------------------------------|-----------------|
| Glucose (H ₂ O, Na ₂ SO ₄) | Sorbitol | Amalgamated lead | 90 | 1.5-2 | EC—Atlas | 97, 98 |
| 4-Methylimidazolecarboxylic acid | 4-Methyl-5-hydroxymethyl imidazole | | | [5.3] | P—BASF | 69 |
| α -Methylindole | α -Methyldihydroindole | | | [2.3] | C—BASF | 69, 71 |
| N-Methylpyridinium chloride (H ₂ O, sodium carbonate) | Bipyridylum chloride | Pb | High | [1.2] | P—ICI | 99 |
| Nitrobenzene (H ₂ O, H ₂ SO ₄) | <i>p</i> -Aminophenol | Hg, C, Cu etc. | 90 | [5.5] | P—Bayer, Miles, CJB, India etc. | 100-102 |
| Nitrobenzene (H ₂ O, H ₂ SO ₄ , Ti ³⁺) | Aniline | Cu, Pb | 97 | 12.4 | P?—India | 103, 104 |
| Nitrobenzene (H ₂ O, NaOH) | Benzidine | NaHg, steel | Good | [4-5] | EC—I. G. Farben P—India | 105, 106 |
| Nitrobenzene | <i>p</i> -Anisidine | | | [4.8] | P—BASF | 69 |
| <i>m</i> -Nitrobenzenesulfonic acid (H ₂ O, H ₂ SO ₄) | Metanilic acid | Pb | 80 | 8-13 | P—L. B. Holliday, CJB, India BASF | 69, 107, 108 |
| Nitronaphthalene | 1-Amino-4-methoxynaphthalene | | | [3.5] | P—BASF | 69 |
| Nitroguanidine [H ₂ O, (NH ₄) ₂ SO ₄] | Aminoguanidine bicarbonate | Zn | 89 | [12] | P—India | 109, 110 |
| <i>p</i> -Nitrophenol (H ₂ O, H ₂ SO ₄) | <i>p</i> -Aminophenol | Cu, Hg/Cu | 60 | 5 | P—India | 111, 112 |
| Nitrourea (H ₂ O, H ₂ SO ₄) | Semicarbazide | Pb | Good | [13] | P—USSR | 113, 114 |
| Oxalic acid (H ₂ O, H ₂ SO ₄) | Glyoxylic acid | Pb | 97 | [3.7] | P—Rhône Poulenc others | 115-117 |
| Phthalic acid (H ₂ O, dioxane, H ₂ SO ₄) | Dihydrophthalic acid | Pb | 90-95 | 1.6-4 | EC—BASF | 69, 118-120 |
| Phthalimide (H ₂ O, HOAc, H ₂ SO ₄) | Isoindole | Pb | 50-55 | [18] | P—Ciba | 121, 122 |
| Pyridine (H ₂ O, H ₂ SO ₄) | Piperidine | Pb | 90 | [11] | C—Robinson Bros. | 123 |
| Quinoline (H ₂ O, H ₂ SO ₄) | Tetrahydroquinoline | Pb | 74 | [5.4] | P?—Russ | 124 |
| Salicylic acid (H ₂ O, NaHSO ₃ , H ₃ BO ₃) | Salicylaldehyde | Hg/Cu | 50 | [4.4] | C—USSR, India | 125, 126 |
| Tetrahydrocarbazole (H ₂ O, C ₂ H ₅ OH, H ₂ SO ₄) | Hexahydrocarbazole | Pb | High | [1.8] | C—BASF | 69, 71, 127-129 |

Miscellaneous Processes

| Starting Material (Electrolyte) | Product(s) | Anode | Cathode | Current Efficiency (%) | Energy Usage ^a | Status | Refs. |
|---|---|-----------------------|---------|------------------------|---------------------------|----------------------------|----------|
| Sodium citrate ^d (H ₂ O, sodium citrate) | Citric acid, NaOH | | | High | | C?—Liquichimica Biosintesi | 134 |
| Cyanide waste stream (H ₂ O, various) | CO ₂ , N ₂ ^e | C | Steel | | 12-15 | C—several | 135-137 |
| Methanol (CH ₃ OH, see footnote ^f) | Sodium methoxide | DSA ^R | Hg | High | | C—Dynamit Nobel, Olin | 138 |
| Montan wax (H ₂ O, chromic acid) | Purified montan wax | PbO ₂ | ? | | | C—Hoechst | 139, 143 |
| Tetramethylammonium chloride ^d (H ₂ O, quaternary chloride) | Tetramethylammonium-hydroxide, chlorine | DSA ^R C | Steel | 30-60 | | EC—Monsanto | 140-142 |

^a Brackets indicate estimated value based on a cell voltage of 5 V and current efficiency of 90% unless otherwise given. Energy usage in KWh/kg.

^b The process is a two-stage operation in which the redox reagent (Mn³⁺, Ce⁴⁺, Cr⁶⁺, periodate, hypobromite, etc.) is regenerated electrochemically and passed into a second reactor, where the oxidant and the organic feed are contacted.

^c Including perfluoropropane, perfluorobutyric acid, trifluoroacetic acid, and perfluoromethylether.

^d Example of electrodialysis.

^e The initial products are cyanate and cyanogen.

^f The process utilizes the sodium amalgam from mercury cells as follows: 2Na(Hg) + 2ROH → 2NaOR + H₂ + (Hg)

Commercial status indicates that an electrochemically derived product is being sold, but suggests no measure of the size of the operation. Of course it is difficult to determine the status of present activity, and Table 9.1 may thus be incomplete and/or in error in this regard. Another published compilation is available in Ref. 144.

According to Table 9.1, electrochemical routes to some 70 organic compounds have undergone evaluation under industrial constraints. Of these about 15 are believed to be commercially viable, while another three dozen are currently under active evaluation at the pilot-plant stage.

Of the roughly 50 processes currently known [130, 131, 133] to be under evaluation, well over half were known in the laboratory *at the turn of the century*. What has occurred in many of these cases is achievement of economical configuration through the development and adaptation of new cell materials (see Chapter IV) and designs.

Characteristics of Electroorganic Synthesis Processes

Experience to date with electroorganic processes has led to recognition of several advantages of electrolytic process routes:

1. Electroorganic syntheses usually require cheaper and thus more readily available feedstocks than alternate chemical process routes.
2. Electrochemical processes usually exhibit mild process conditions and low temperatures throughout so that entropy is conserved.
3. Electrochemical processes exhibit high chemical yields so that downstream recovery and purification is thus simplified.
4. Electricity is cleaner and easier to transport and handle than corrosive chemical reagents needed in many organic syntheses, so that the cost of containment materials is lower.
5. Wastewater treatment of effluents from electrolytic processes is minor owing to the absence of spent redox agents.

On the other hand, the disadvantages are as follows:

1. Operating costs are high because electricity is an expensive form of energy.
2. Investment costs are high.

These characteristics have been discussed at length by Fitzjohn [145] and Krumpelt et al. [146], who compared electrochemical and chemical processes over a range of production rates up to 500 million lb/year and concluded that investment costs per pound of product *were similar*.

In the field of industrial electrolysis, rules of thumb have come into use largely through experience with chlor-alkali, aluminum, and copper refining

systems. It would be thoughtless, however, to apply such empirical rules to the evaluation of prospective electroorganic processes without some added measure of engineering insight. Rational evaluation of new electroorganic processes must be based on sound economic assessment, not rules of thumb developed from experience in other fields of electrochemical technology.

Uncertainties in process development must also be taken into account in the evaluation of new technologies. Systematic methodologies for obtaining electrochemical data are becoming available. Improvements in methods for transferring technology from laboratory cell to pilot plant are being reported with increased frequency. As understanding of the interdisciplinary nature of the field develops, exploration of process candidates has been carried out with greater perception and with more cost-effective development programs. The material in the next section has been selected to provide access to the background literature required for the engineering development of new electroorganic process technologies.

3 DEVELOPMENTS IN ELECTROCHEMICAL SCIENCE AND ENGINEERING

New techniques for the elucidation of mechanisms have been developed within the last decade and have been vigorously applied to the study of electroorganic synthesis reactions. During the same period, a large number of excellent books and reviews containing much of the fundamental information and techniques have become available. The purpose of this section is to draw together the components needed for engineering evaluation and development of electroorganic processes intended for commercial exploitation. The chapters that make up the remainder of this volume provide more thorough coverage of many specific aspects of the broad and interdisciplinary literature presented in this section.

Background Material

The electroorganic synthesis literature through 1975 is contained in the bibliographies of Fichter [2] and of Swann and Alkire [1]. These collections include scientific publications, reviews, books, laboratory manuals, dissertations, and patents. In addition, the polarographic and other properties of many electroorganic systems have been tabulated by Meites and Zuman [147]. A selected bibliography of source materials appears in Appendix I of Ref. 148 and includes books, monograph series, journals, proceedings and special issues, reviews, abstracting services, and bibliographies.

A description of past industrial electroorganic activity is available [149, 150], while more recent activity has been the subject of a symposium publica-

tion [146] containing over 20 papers. A perspective of progress during the past 25 years was recently offered by Baizer [151].

Electrochemical Synthesis and Mechanistic Studies

Although major reviews of electroorganic chemistry have appeared for more than 50 years [152], the publications of Swann [153] and Allen [154] were particularly timely and influential. During the past decade, a remarkable number of books and major reviews have appeared of which an incomplete, but representative, list would include those by Wawzonek [155], Ebersson and Schäfer [156], Tomilov et al. [157], Fry [158], Baizer [148], F. Beck [159], Rifi and Covitz [160], Weinberg [161], Ebersson and Nybert [162], Bard [163], and Langer and Sakellariopoulos [164].

Laboratory Procedures, Apparatus, Techniques

One advantage of electroorganic synthesis is the high selectivity often achieved for the desired product, a result of proper control of electrode potential and reaction environment (electrode, solvent, electrolyte, etc.). Procedures for laboratory investigations naturally depend on the goals at hand. Organic chemists and electrochemists tend to emphasize mechanistic aspects that would lead to a fundamental understanding of the mechanism, from which it may be possible to predict optimum conditions for high yield. On the other hand, technologists often require information before there is understanding. Important initial considerations in the design of industrial processes include reaction stoichiometry, cell voltage, current density, current efficiency, and specification of the potential range over which high yields are possible. Of subsequent importance is knowledge of influence on yield of operating conditions such as temperature, solvent, electrolyte composition and concentration, reactant concentration, hydrodynamics, electrode material, and impurities in the solution phase. Knowledge of side reactions is critically important in order to design around them or, better yet, to avoid them. The decision of whether or not a separator is needed between anode and cathode can exert a major impact on process economics.

Engineering insight (see Chapter I) usually comes from knowledge of what phenomena control the behavior of the process, typical rate-limiting phenomena being ohmic resistance, mass transfer, and charge-transfer kinetics. It is invariably easier to obtain such insight from experiments conducted under controlled and reproducible conditions in continuous flow cells.

The book of Gileadi et al. [165] provides an excellent introduction to numerous electrochemical laboratory techniques. The chapter by Goodridge and King in Part I of this series [166] describes not only experimental aspects, but also more fundamental considerations involved in the choice of electrode, solvent, and electrolyte materials. Additional sources for labora-

tory methods for electroorganic investigations include Swann [153], Adams [167], Wawzonek [155], Ebersson and Schäfer [156], Fry [158], Tomilov et al. [157], Baizer (Chpt. II by Cauquis and Parker) [148], Rifi and Covitz [160], and F. Beck [159].

The elucidation of mass transfer processes often relies on electrochemical measurements by the limiting-current method for which an extensive review is available [168].

Cell Component Materials: Electrodes, Solvent, Electrolyte, Separator

Qualitative aspects of specification of electrode material (see Chapter IV) have been widely reported, but fundamental understanding is meager. It may be expected that substantial progress will be made as understanding of surface science and catalysis is applied to electrochemical systems. Even applied studies, however, should be carried out with an appreciation for the importance of metallurgical factors on the electrochemical performance of an electrode material, since, for example, the temperature at which a particular electrode is cast can influence the product spectrum obtained.

General discussion of materials suitable for various electrochemical purposes appears in a book by Kuhn [169], in the aforementioned review of Goodridge and King [166] in Part I of this series, and in Chapter IV of a book of Baizer [148]. Additional discussions appear in works by Adams [167], F. Beck [159], Ebersson and Nybert [162], and Danyl [144].

The use of a separator between anode and cathode is often required when one electrode is corroded or poisoned by components in the feed to the other electrode; separate flow systems for catholyte and anolyte are thus required. Separators are also needed when the product of one electrode would react if it were to pass into the vicinity of the other electrode. For example [155], reduction of benzene in methylaniline containing lithium chloride gives cyclohexene in a divided cell; in an undivided cell, however, the lithium methylaniline in the catholyte reacts with the methylaniline hydrochloride in the anolyte to yield dihydrotoluene. In simpler systems where homogeneous reactions are absent, careful hydrodynamic design can be used to ensure that reactants are removed from the cell before they diffuse across to the counterelectrode.

Source materials on separator materials for electrolytic cells, including ion-exchange membranes, may be found in Chapter IV of a book by Baizer [148] and in reviews by Goodridge and King [166], F. Beck [159], Ebersson and Schäfer [156], and Danyl [144]. More general coverage of membranes and membrane processes is provided by several recent books [170-176].

The choice of solvent, electrolyte, and solution additives is discussed in the works of Mann and Barnes [177], Goodridge and King [166], Baizer [148], Chapter IV], F. Beck [159], and Danyl [144]. On the practical side, the at-

tainment of high solubility of the organic, good mass transfer, and high ionic conductivity is sought in the presence of low cost, easy downstream recovery, and noncorrosive properties. The use of quaternary ammonium salts and their analogs is widely practiced in aqueous systems since these salts enhance both ionic conductivity and solubility of organic species, while, at the same time, contribute toward improved yields by hindering electrolytic breakdown of the solvent.

New Design Concepts for Electroorganic Cells

The attainment of high volumetric current density is important in order to keep investment costs at a minimum. Low power consumption is requisite to keeping operating costs down, and uniform potential distribution is needed for achieving high yields. A large number of design concepts have come forth that seek to achieve one or more of these goals. Reviews have been published by Houghton and Kuhn [178], Tomilov and Fioshin [179], Gallone [180], Goodridge and King [166], and Dany [144, 181]. The design concepts appear to fall into two general categories as described below.

The first category consists of cells wherein enhancement of mass transfer to the electrode surface is sought by manipulating electrode shape and fluid flow configurations. For example, flow-through porous electrodes exhibit high internal surface area and good mass transfer rates; recent reviews by Newman and Tiedemann [182, 183] survey the literature. There are essentially two flow configurations in use, the first having parallel directions of current and electrolyte flow [184], and the second having essentially perpendicular directions of current and electrolyte flow [185]. The latter configuration appears to be emerging as superior for applications involving electroorganic synthesis and has been used, for example, in the Braithwaite cell for tetraalkyl lead synthesis [186], for the "Swiss-roll" cell configuration of Ibl and co-workers [187], and for the "ESE" cells described by Keating and Sutlic [188]. Other methods for achieving high mass transfer rates at electrode surfaces include placement of stationary "turbulence promoting" grids on or near the electrode surface [189], use of continuously moving solid electrodes [190, 191], use of wipers that periodically disrupt the mass transfer layer [192], and various types of fluidized [193, 194] and tumbling [195] bed systems. In many electroorganic systems, the reactants include organic vapors and liquids that are only modestly soluble in polar solvents; thus various bipolar [196] and trickle-bed [197] cell designs have been suggested for enhancing gas/liquid contact, while emulsion cells [198] can be used to achieve enhanced liquid/liquid extraction rates.

The second general category of design concept emphasizes manipulation of the potential field distribution. Minimization of ohmic resistance losses has been achieved with the use of capillary-gap cells, developed originally by

Beck and Guthke [199], in which the anode/cathode gap spacing is very small; such cells have been extensively developed [200] and have been employed in pilot-plant operations in both divided and undivided configurations. Hydrodynamic and mass transfer conditions within capillary-gap cells have been modeled [201] in order to predict operating conditions under which such cells may operate in undivided configurations [202]. Along different lines, manipulation of the potential field to achieve bipolarity along an electrode surface [203] has been used for a variety of applications to electroorganic synthesis processes [195, 204].

To select a reactor concept appropriate for a given application it is important to bear in mind several elements of overall perspective. Electrochemical cells, for example, are always carefully designed to match the process chemistry. Adaptation of a concept to actual hardware involves countless decisions that must be based on the process chemistry. Also, the relative importance of investment capital, electric power cost, and chemical yield depends greatly on the selling price. Appropriate design concepts must therefore be responsive to the economic constraints under which the process will eventually be judged. In addition, the economic evaluation of various reactor configurations must incorporate the entire array of peripheral equipment, including electrical distribution, flow devices, and cooling equipment; thus seeming advantages in cell operation may be offset by nonelectrochemical considerations.

Engineering Methods, Modeling, and Economic Assessment*

The papers of MacMullin provide general discussions of engineering procedures and considerations involved in scale-up of electroorganic and other electrolytic processes, as well as of the design and materials of construction of cells, of innovation, and of the use of computer simulation in design [204]. The use of analytical and numerical methods for simulation of cell processes based on current and potential distribution phenomena represented an important development in the mathematical modeling of electrochemical processes [205].

The elucidation of fundamental principles of electrochemical engineering has led to improved ability to predict electrochemical behavior from knowledge of operating parameters. Principles of thermodynamics, double-layer phenomena, electrode kinetics, ohmic resistance, fluid mechanics, heat, and mass transport form the underlying concepts needed for electrochemical engineering [206]. While mathematical complications may be formidable for highly exact results, the deft use of simple limiting cases can often result in cost-effective improvements. In many cases it is not necessary to solve equa-

*See Chapter I for details.

tions, but only to recognize the dimensionless variables that dominate behavior of the process. That is, modeling electrochemical processes provides a methodology for dealing with the unknown. Perhaps the greatest value of such endeavors is the quantitative and rational thought processes thereby promoted.

A book by Hine [207] provides an excellent general introduction, while that by Newman [206] is rigorous and detailed. Concepts involved in electrochemical reactor design are described from a chemical engineering viewpoint by Pickett [208].

The application of current and potential distribution concepts to electroorganic synthesis cells promises to provide added leverage needed to design and optimize reactors. For example, one major advantage of electroorganic syntheses is the high degree of selectivity for a desired reaction product that can be achieved through careful control of the potential along the electrode surface. However, to achieve large reaction rates per unit volume, it is necessary to optimize around competing needs for large surface area, adequate mass transfer, and low ohmic resistance, in addition to uniform potential distribution. Defining the optimum process conditions that achieve both high selectivity and high reaction rate is clearly an important engineering design consideration [209]. In electroorganic syntheses, where multiple reactions occur, the use of modeling techniques appears to be especially important to avoid loss of intuition.

In the near future it seems reasonable to expect that modeling activities will continue to expand in scope so that entire cells will be included within the model. Examples to date include nonelectroorganic processes [204, 210-212], although the extension of such methods to electroorganic systems is clearly within grasp. The consequence of this development would be to greatly enhance the capability for accurate engineering evaluation and design.

Use of simple models in optimization of electrochemical systems has been extensively reviewed by Beck [213], who provides many references and examples of specific design trade-offs. Fitzjohn [145, 214] and Danyl [144] provide discussion and references on additional economic considerations involving investment and operating costs.

It is generally agreed that investment costs for electrolytic cells scale with a power between 0.9 and 1.0. Other (nonelectrolytic) components of the process scale with a 0.5 to 0.6 power and can often represent a significant fraction of total investment [144, 145, 214], so that the overall process may exhibit substantial economies of scale. While the exponents cited above are generally accepted, the literature is nearly devoid of data on actual investments required. The examples reported by Fitzjohn [145, 214], Danyl [144], and Keating and Sutlic [188] therefore represent particularly important contributions. Additional data on methods for investment cost estima-

tion would be extremely beneficial in promoting the accuracy with which electroorganic process economics may be evaluated.

4 ENERGY USAGE OF LARGE-TONNAGE ORGANIC ELECTROLYTIC PROCESSES

The objective of this section is to demonstrate the use of chemical engineering methods for evaluation of energy consumption to be expected of electroorganic processes in comparison with chemical processes. Additional details may be found in Ref. 3.

No attempt was made to iterate the process calculations to achieve optimized electrochemical designs. The results reported below could undoubtedly be improved upon by simple optimization procedures and by better pilot-plant data. Only synthesis of large-tonnage organic chemicals was evaluated. Many additional low-tonnage process candidates exist. Other important engineering considerations not introduced in the discussion below include economics of operating and investment costs, wastewater treatment, and synthesis of lower-tonnage chemicals for which electrochemical routes are also available.

There should be no question whatsoever that additional and broader engineering studies are needed before arriving at firm conclusions on the question of electrochemical versus chemical process selection. The chemical engineering methods described below can easily be expanded to embrace a wider range of considerations, as well as a larger population of process candidates. By such refinement and expansion, a more realistic engineering assessment of electroorganic process routes would surely emerge.

Organic chemicals produced and sold at greater than 7000 tons/year in the United States number about 220, of which 95 were found to have electrochemical synthesis routes. The literature was examined and a group of compounds was chosen for which engineering estimates were made on process reaction conditions, yields, current efficiencies, and so on. Of these, the nine chemicals for which the most complete data were available were then chosen for detailed evaluation as reported below. Material and energy balances were made for both chemical and electrochemical routes for each compound; the energy consumption (kcal/kg) for both process routes was compared. Also, the potential impact that large-tonnage electrochemical processes might have on the U.S. petrochemical industry was simulated using a mathematical model of that industry.

Identification of Candidate Electroorganic Reactions

Candidates for evaluation were selected from a list of organic chemicals produced and sold in the United States in amounts exceeding 7000 tons/year in 1975 [215]. This list does not contain organic intermediates and, because

of the difficulties in obtaining this often proprietary information, organic intermediates were excluded from evaluation except in the case of adiponitrile. For each compound, two bibliographic collections [1,2] were examined to obtain literature citations on the electrolytic synthesis. The bibliographic data base covered the period 1801 to 1975 and included the patent literature. Some of the chemicals, however, were generic in nature (e.g., tar) and were not listed as such in the bibliographic sources. Any literature reference that involved obviously unattractive feedstock material or untenable reaction conditions was discarded from further evaluation. The compounds that survived this preliminary screening step are shown in Table 9.2. *Electrochemical synthesis routes were found for 95 compounds, or 57% of the nongeneric large-tonnage compounds.*

To narrow the list of candidate processes, additional selection rules were established as follows:

1. There should be sufficient published electroorganic literature to make reasonable estimates of process conditions. Thus promising but speculative process routes were not considered.
2. Hydrocarbons currently synthesized by efficient catalytic routes should not be evaluated.
3. Polymers should not be evaluated.
4. Pollutants presently being phased out should not be evaluated (e.g., tetraalkyl lead compounds).
5. The product molecular weight should be high, and there should be fewer than eight electrons transferred per molecule.
6. The product cost should be greater than the cost of raw materials.

The application of these rules to the 95 compounds in Table 9.2 led to the selection of 18 compounds listed in Table 9.3. Of these, the 9 compounds given in capital letters were selected for detailed evaluation reported below, since they had the most complete and accurate process data files.

The 9 compounds selected for detailed evaluation represent several types of electrochemical reactions and include oxidations, halogenations, and reductions. The EPA numbers cited in Table 9.3 refer to information on chemical process routes [216] that, along with information in the open literature, was used in making process calculations.

Methods Used for Making Calculations

The basic flowsheet for a typical electroorganic process is shown in Fig. 9.2. The cells and the separation and purification steps are most often energy intensive. Electricity is generally the only energy applied to the cells, and cooling is usually required. Thermal energy is used for the separation and

Table 9.2. Large-Tonnage^a Organic Chemicals Having Electrochemical Synthesis Routes

| | | |
|-------------------------------|------------------------------|--|
| Acetic acid | 2,2'-Dithiobis | Phenol |
| Acetic acid salts | (benzothiazole) | Phenol salts |
| Acetone | Ethane | Phenyl hydrazine |
| Acrylic acid | Ethyl acetate | Phosgene |
| Acrylonitrile | Ethyl acrylate | Phthalic anhydride |
| Adipic acid | Ethyl alcohol | Phthalide |
| <i>o</i> -Aminobenzyl alcohol | Ethylbenzene | Polyacrylamide |
| Aniline | Ethylene | Polyacrylonitrile and acrylonitrile |
| Benzene | Ethylene glycol | copolymers |
| Benzoic acid | Ethylene oxide | Polyethylene terephthalate |
| Biphenyl | Formaldehyde | Propane |
| <i>n</i> -Butane | Formic acid, Na ⁺ | Propionic acid |
| 2-Butanone | Fumaric acid | Propyl alcohol |
| 1-Butene and 2-butene | Glycerol | Propylene |
| <i>n</i> -Butyl alcohol | Heptanes | Propylene glycol |
| Butylamines | Hexane | Propylene oxide |
| Butyraldehyde | 1,6-Hexanediamine | Quinone (intermediate for |
| Carbon tetrachloride | Heptenes | hydroquinone) |
| Chlorobenzene | Hydroquinone | Salicylic acid |
| Chlorodifluoromethane | Isobutyl alcohol | Semicarbazide |
| Chloroethane | Isobutyraldehyde | Sorbitol |
| Chloroform | Isopropyl alcohol | Stearic acid salts |
| Cyclohexanone | Isobutane | Styrene |
| Chloromethane | Isobutylene, 2-butene, | Terephthalic acid |
| Cresols | and mixed butylenes | Tetrachloroethylene |
| 1,4-Cyclohexadiene | Isoprene | Tetrafluoroethylene |
| Cyclohexane | Maleic anhydride | Toluene |
| 1,2-Dibromoethane | Methanol | Toluene-2,4-diamine |
| <i>o</i> -Dichlorobenzene | Monoethylamine | Toluenesulfonic acid, K ⁺ , and Na ⁺ |
| Dichlorodifluoromethane | Monoisopropylamine | Trichlorethylene |
| 1,2-Dichloroethane | Naphthalene | Trimethylamine |
| Dichloromethane | Nitrobenzene | Urea |
| Dimethylamine | Pentaerythritol | Xylene |

^a 14,163,000 lb/year and above.

Table 9.3. Candidate Electrochemical Processes

| Class | Product Compound | EPA Number |
|--------------|--|--|
| Reduction | ADIPONITRILE ANILINE Toluene-2,4-diamine SORBITOL TEREPHTHALIC ACID | 31 343 362A,B 37,295 286,328 |
| Oxidation | PHENOL Propylene oxide METHYL ETHYL KETONE (2-BUTANONE) MELAMINE Salicylic acid QUINONE (then to HYDROQUINONE) Dithiois(2,2-dithiobenzothiazole) DICHLOROETHANE | 303A,B 16 131,132 4 |
| Halogenation | Chlorobenzene 1,2-Dibromoethane 1,2-Dichloropropane Tetrafluoroethane 2,4-Dichlorophenol | |

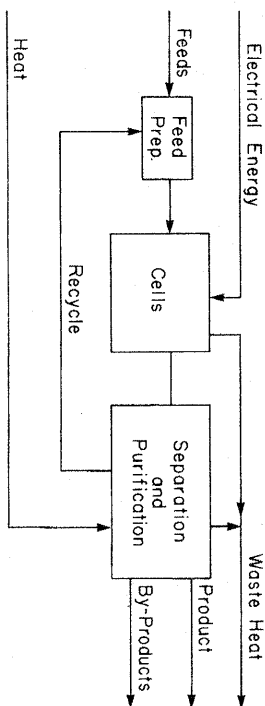


Fig. 9.2. Electrochemical process material and energy streams.

purification steps downstream from the cells. Feed preparation usually requires a minor amount of energy, such as for mixing, and therefore was usually neglected. In the case of chemical processes, chemical reactors are used for which thermal energy is most often required.

To give consistent treatment for all processes, the set of design rules shown in Table 9.4 was used. According to rule 1, current chemical routes were based on Ref. 216. According to rule 7, it was assumed that 3 moles of water per hydrogen ion passed through a membrane in acid electrolyte [217].

Table 9.4. Process Design Rules

1. Current chemical routes used for comparison with each electrochemical route
2. Electrochemical and current chemical routes are chosen that are as similar as possible
3. Electrochemical processes are based on largest-scale data available
4. All electrochemical processes are continuous
5. Cells are based on state-of-the-art technology, for example, metal anodes, membranes
6. Membranes or other separators are not used unless essential
7. Cation membranes are preferred
8. Atmospheric pressure cells are used unless otherwise specified
9. Hydrogen by-product is credited at $\Delta H_{\text{combust}}$ thermal
10. No credit is given for oxygen by-product
11. Product separation energy requirements are based on key component binary separation
12. When thermodynamics dictates that a reaction does not go to completion, 100% of the equilibrium conversion is assumed
13. All compressors and pumps are electrically driven
14. Only consider pumps and compressors for high-pressure reaction; no transfer pumps are to be considered
15. Neglect energy cost of vacuum for stills and evaporators

Following rule 11, product separation energy requirements were calculated for each separation process; energy requirements for liquid/liquid extraction and for phase separations were assumed to be negligible; and energy requirements for distillation were based on heat required for boiling the bottoms for a column with constant reflux ratio.

In some cases the chemical and electrochemical routes used different raw materials. It was then necessary to assign energy costs to the various raw materials to compare both routes on a consistent basis. Energy costs for common raw materials are given in Table 9.5. These data are based on published process energy data [218-220], and calculations are available in Ref. 3. Table 9.5 gives energy costs for organic raw materials and products as calculated from data given in Ref. 221. By-product hydrocarbons were credited at an energy cost equal to the heat of combustion [222], since they could have been burned under a boiler to produce steam.

An energy balance for a continuous electrochemical reactor at steady state is given in Fig. 9.3. The algebraic sum of the enthalpies of formation of reactants and products, and the electrical and thermal energy is zero.

$$q_r + q_p + EI + Q = 0 \quad (1)$$

Table 9.5. Thermal Energy Costs Assigned to Chemical Raw Materials

| Chemical | $\Delta H_{\text{combustion}}$ (kcal/kg) |
|---|---|
| Hydrocarbons | |
| Carbon | 7,824 |
| Hydrogen | 33,944 |
| Methane | 13,266 |
| Ethane | 12,400 |
| Propane | 12,034 |
| n-Butane | 11,838 |
| Ethylene | 12,024 |
| Propylene | 11,689 |
| n-Butene | 11,578 |
| Isobutene | 11,517 |
| Benzene | 10,117 |
| Toluene | 10,244 |
| Xylene | 10,361 |
| Fuel oil | 10,430 |
| Hydrogen | |
| Steam reforming of hydrocarbons | 49,000 |
| Water electrolysis (at 1.5 V) | 105,770 |
| Ammonia | 9,000 |
| Hydrogen cyanide | 18,000 |
| Nitric acid | 3,100 |
| Urea | 6,400 |
| Oxygen from air | 964 |
| Chlorine (prorated 50% with NaOH) | 5,875 |
| Sodium hydroxide (prorated 50% with Cl_2) | 5,875 |
| Sulfuric acid | 29 |
| Iron | 4,050 |
| Air | Zero |
| Water | Zero |
| Manganese dioxide | Zero |

The heat of reaction is the sum of the products of the component flow rates and their heats of formation.

$$q = \sum_{i=1}^n N_i \Delta H_{fi} \quad N_i \text{ is } + \quad (2)$$

N_{pi} is -

$$\Delta H_f = \Delta H_{fg} - \Delta H_v \quad (3)$$

where

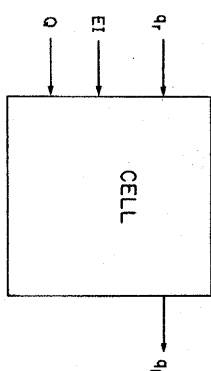


Fig. 9.3. Energy balance for continuous reactor at steady state.

Usually a cell reaction is endothermic; the electrical potential applied drives a reaction that would otherwise require a higher temperature. Generally the electrical energy delivered to the cell exceeds the endothermic heat of reaction owing to irreversible effects, so that heat is generated and must be removed by exchange or by evaporation of electrolyte.

Heats of formation of most organic compounds studied below are not experimentally known. The ASTM program (CHETAH: Chemical Thermodynamic and Energy Release Evaluation Program) [223] was used to estimate values of H_f for the ideal gas state.

Additional thermodynamic data were obtained from the following reference sources which are listed in decreasing order of preference of use [224-234]. Additional sources were used for critical properties [233, 234], heat of vaporization estimates [235], and solubility data [224-232, 236].

Phase equilibria between multicomponent mixtures of aqueous and organic phases are generally unknown. Where binary data were available, they were used without consideration of other components or ternary effects. In liquid phases, ideal vapor/liquid equilibria were assumed to be valid. Solid phases were assumed to be present as pure compounds.

Several separation methods were employed in the flowsheets discussed below, including filtering, centrifuging, settling, liquid/liquid extraction, and distillation. Of these, the distillations were usually the most energy intensive. All distillations were handled as binary separations [237] for which a reflux ratio of 1.25 times the minimum was used.

Yield was used in the calculations below to indicate the fraction of primary reactant ultimately converted to the desired product and refers to the overall plant process independent of recycle streams. Conversion, on the other hand, represents the fraction of limiting reactant converted to product on each pass through the reactor or cell.

While the foregoing procedures were used in the example process evaluations that follow, it is possible to make very quick estimates of energy consumption of the electrolysis cells. Based on Faraday's law, the power consumption in engineering units of an electrochemical cell can be determined with the formula

$$\frac{12.6n V_{\text{cell}}}{M_w \eta_e} \text{ kWh/lb product}$$

where

n = number of electrons per g·mole of product

V_{cell} = cell voltage, V

M_w = molecular weight of product

η_e = current efficiency.

These results may be connected to equivalent fossil fuel values with the factor 0.325. Thus an electroorganic process with an equivalent weight (M_w/n) of 50, $V_{\text{cell}} = 5$ V, $\eta_e = 0.90$, would consume 1.36 kWh/lb product in electricity or 1.36/0.325 = 4.18 kWh/lb in fossil fuel at the generating station.

Energy Calculations for Specific Chemicals

Descriptions of electrochemical processes are available [3] for those chemicals listed in Table 9.2. Still more detailed evaluation is given below for the nine chemicals given in capital letters in Table 9.3. For each capitalized chemical, flowsheets, stream conditions, and energy calculations for both chemical and electrochemical process routes are available [3] and are summarized below. The comparison of energy consumptions for various processes is given in Table 9.18.

Adiponitrile

Adiponitrile is a chemical intermediate and therefore is not included in the production figures cited in Ref. 216. However, its production rate should be closely related to that of nylon 66 which, in the United States, is expected to be about 2.7 billion lb in 1979 [238, 239].

CHEMICAL PROCESS (ADN FROM BUTADIENE)

The energy required for the chemical route to adiponitrile from butadiene is based on data reported by Rudd et al [221]. The figure reported in Table 9.7 (65,808 kcal/kg) includes the energy required to make butadiene, as well as the gross heating value of the butylene feedstock. A more recent chemical process route, commercialized in 1972, does not use chlorine [220] and has superseded the older process for which data were available. Avoiding the use of chlorine would save 6668 kcal/kg and would probably therefore decrease the energy for the chemical route to 59,140 kcal/kg. Detailed calculations for the newer process are not possible owing to lack of sufficient information.

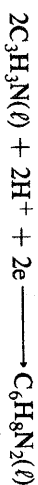
ELECTROCHEMICAL PROCESS (ADN FROM ACRYLONITRILE)

The electrochemical production of adiponitrile from acrylonitrile is commercially practiced by Monsanto and has been described in numerous publi-

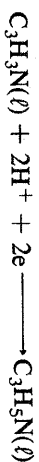
cations [240-247] (see also Chapter VII). The process chosen for evaluation in this study corresponds to the early Monsanto patents; it is to be expected that even lower energy consumption would be exhibited by more recent processes. Electrolysis is carried out in a cation-exchange membrane cell in a plate-and-frame type assembly. The catholyte consists of an aqueous mixture of adiponitrile, acrylonitrile, and a quaternary ammonium salt. The following reactions occur:

Current
Efficiency

Cathode reactions:

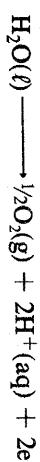


89%



11%

Anode reactions



100%

Primary overall reaction



The quaternary ammonium salt, assumed to be tetraammonium-p-toluene sulfonate, increases both the solubility of organic compounds and the conductivity of the solution. The cells are assumed to operate at 6 V.

The flowsheet for the electrochemical process, shown in Fig. 9.4, has associated with it Table 9.6, in which stream conditions at each numbered position are provided. From the reactor, the catholyte is pumped to an extractor where acrylonitrile is used to strip adiponitrile from the aqueous phase. The resulting organic phase contains appreciable QAS, which is removed using fresh water in the QAS extractor. The resultant organic stream containing adiponitrile, propionitrile, and acrylonitrile is sent to the first of two distillation towers, where the adiponitrile is separated as the bottom stream. The distillate stream is split, with part being recycled to the solvent extractor and part entering the propionitrile distillation column where the by-product, propionitrile, is separated. The acrylonitrile is the distillate and is recycled to the cell.

The energy requirement calculated for the electrochemical route agreed with the data of Rudd et al. [221] for fuel oil equivalent energy to within 8%. To put the electrochemical route on a comparable basis with the chemical route, the energy required to manufacture acrylonitrile and the gross heating value of the propylene feedstock are added to give a total of 43,177 kcal/kg.

Energy data for various process routes are compiled in Table 9.7. The electrochemical route has a significant saving in energy as compared to the chemical route. The electrochemical process gives about 12% by-product

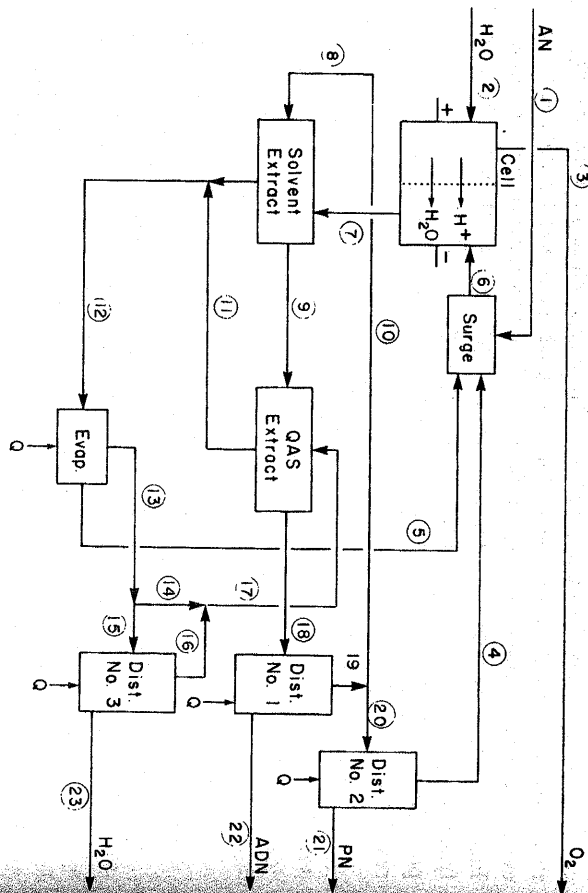


Fig. 9.4. Electrochemical route to adiponitrile.

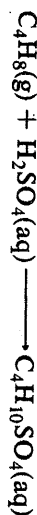
propionitrile, which is presumably a saleable product. No information was obtained on by-products of the chemical route, but hydrogen cyanide, a hazardous chemical to transport, is a chemical raw material.

Methyl Ethyl Ketone

CHEMICAL ROUTES (MEK FROM BUTENE)

The thermochemical production of methyl ethyl keton (MEK) from butene is discussed in the *EPA 600 Report* [216] and by Lowenheim and Moran [232]. The process flowsheet is shown in Fig. 9.5.

The first reaction is the absorption of butene in concentrated (75%) sulfuric acid:



A conversion of 100% was assumed. The second reaction is the hydrolysis of the butyl hydrogen sulfate to form butanol,



A conversion and yield of 84% was used.

The butanol and most of the water are separated from the sulfuric acid by distillation in the first column. The acid bottoms is sent to a second column, where more water is removed as overhead product. The concentrated acid

Table 9.6. Stream Conditions for Adiponitrile Process Electrochemical Route (Flow Units are g·mole/sec)

| | Stream No. | | | | | |
|--|------------|--------|--------|-------|-------|--------|
| Flows | 1 | 2 | 3 | 4 | 5 | 6 |
| C ₃ H ₃ N | 19.62 | | | 18.69 | | 38.31 |
| H ₂ O | | 85.36 | | | 50.00 | 50.00 |
| O ₂ | | | 5.18 | | | |
| QAS | | | | | 8.60 | 8.60 |
| Flows | 7 | 8 | 9 | 10 | 11 | 12 |
| C ₃ H ₃ N | 18.69 | 119.50 | 133.69 | 4.5 | 1.50 | 6.00 |
| H ₂ O | 125.00 | | | 125.0 | 58.41 | 183.41 |
| QAS | 8.60 | | 1.01 | 7.59 | 1.01 | 8.60 |
| C ₆ H ₈ N ₂ | 9.26 | | 9.26 | | | |
| C ₃ H ₅ N | 1.10 | 7.03 | 8.13 | | | |
| Flows | 13 | 14 | 15 | 16 | 17 | 18 |
| C ₃ H ₃ N | 6.00 | 2.40 | 3.60 | 3.60 | 6.00 | 138.19 |
| H ₂ O | 133.41 | 53.36 | 80.05 | 5.05 | 58.41 | |
| C ₆ H ₈ N ₂ | | | | | | 9.26 |
| C ₃ H ₅ N | | | | | | 8.13 |
| Flows | 19 | 20 | 21 | 22 | 23 | |
| C ₃ H ₃ N | 138.19 | 18.69 | | | 75.00 | |
| H ₂ O | | | | 9.26 | | |
| C ₆ H ₈ N ₂ | | | | | | |
| C ₃ H ₅ N | 8.13 | 1.10 | 1.10 | | | |

| Equipment Condition | Cell | Solvent Extractor | QAS Extractor | Dist. 1 | Dist. 2 | Dist. 3 | H ₂ O Evap. |
|---------------------|-------|----------------------|------------------|---------|---------|---------|---------------------------|
| T (°C) | 50 | 25 | 25 | 87-200 | 77-97 | 75-100 | 112 |
| P (atm) | 1 | 1 | 1 | 0.07 | 1 | 1 | 1 |
| VI (kcal/sec) | 2868 | | | | | | |
| Q(kcal/sec) | -2288 | | | 1229 | 358 | 773 | 1730 |

Table 9.7. Adiponitrile Energy Requirements (kcal) [Basis: 1 kg (9.26 g·moles)]

| Chemical Route (Refs. 221 and 3 p. C24) | | |
|--|--|--------|
| Adiponitrile from butadiene (duPont) | | 65,808 |
| <i>Electrochemical Route</i> | | |
| 1. Process Energy | | |
| a. As computed in Ref. 3 | | |
| Cell | | 8,825 |
| Evaporator (H ₂ O) | | 1,730 |
| Distillation no. 1 | | 1,229 |
| Distillation no. 2 | | 358 |
| Distillation no. 3 | | 773 |
| Total | | 12,915 |
| b. As reported in Ref. 221; see also Ref. 3, Table C-O | | |
| Average process energy from parts a and b | | 11,890 |
| 2. Energy to normalize feedstock to common basis as chemical route above | | 12,402 |
| a. Acrylonitrile from propylene (Sohio) | | 31,267 |
| Total for Electrochemical route | | 43,690 |

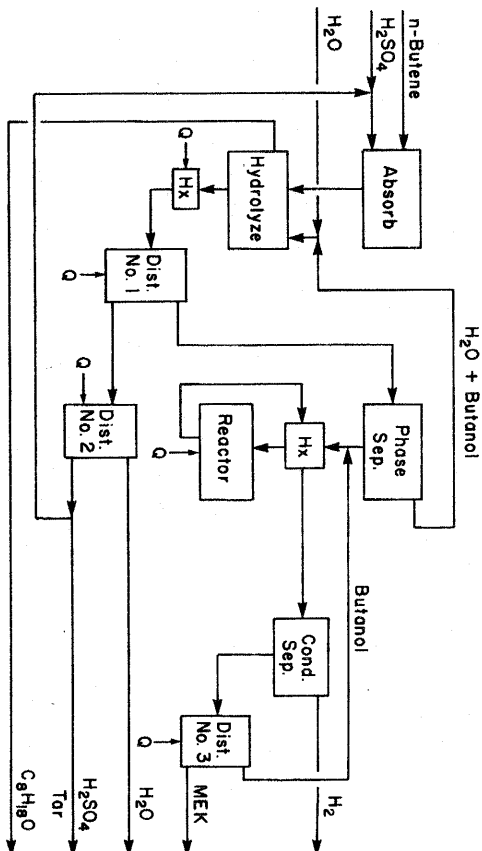
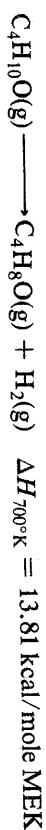


Fig. 9.5. Methyl ethyl ketone from *n*-butene, chemical.

stream contains the tar, which must be purged from the process. The remaining acid with dissolved tar is recycled to the butene absorber.

The butanol and water mix from the first distillation column is separated in the liquid phase; the butanol proceeds first to a heat exchanger, where it is boiled, and then to a gas phase catalytic reactor. The aqueous phase is recycled to the hydrolysis reactor.

The gas phase reactor operates at 450°C and 1 atm according to the reaction



The reactor conversion is 85% and the yield is assumed to be 100%.

The exit stream from the gas phase reactor is cooled and the hydrogen gas is separated off. The MEK-butanol mix is separated in a third distillation column. The light butanol is recycled to the gas reactor feed. The final product, MEK, makes up the column bottoms. The overall process yield is 84%.

The largest energy requirement is for the first distillation column, which vaporizes a large quantity of water and butanol. The gas phase reactor requires a small amount of heat, but the temperature is moderately high. Part of this heat is recovered by preheating the reactants with the hot product stream.

Process energy calculations for the chemical route to MEK [3] are compared with those for the electrochemical route in Table 9.8.

ELECTROCHEMICAL ROUTE (MEK FROM BUTENE)

The electrochemical production of 2-butanone (MEK) from butene is discussed in a series of patents by Worsham [248] and by Griffin and Worsham [249]. Other related citations include Refs. 250 to 254. The process flowsheet is given in Fig. 9.6, with stream conditions specified in Table 9.9.

The cation membrane electrochemical cell operates at about 80°C and at 1 atm pressure. The reaction sequence is as follows:

Anode reaction



Cathode reaction



Primary overall



The conversion per pass through the cell was assumed to be 81% based on butene.

Table 9.8 Methyl Ethyl Ketone Energy Requirements (kcal) [Basis: 1 kg (13.87 g·mole)]

| Chemical Route | |
|--|-------------------|
| Process calculations in Ref. 3 | |
| Heat exchanger | 623 |
| Reactor | 277 |
| Distillation no. 1 | 4907 |
| Distillation no. 2 | 480 |
| Distillation no. 3 | 1352 |
| H ₂ credit | -949 |
| Total | 6690 |
| Data reported in Ref. 221; see also Ref. 3 App. C-12 | 3233 ^a |
| Electrochemical Route | |
| Cell (short-circuited fuel cell) | |
| Vacuum distillation | — |
| Distillation no. 1 | 3300 |
| Distillation no. 2 | 1710 |
| Total | 47 |
| | 5057 |

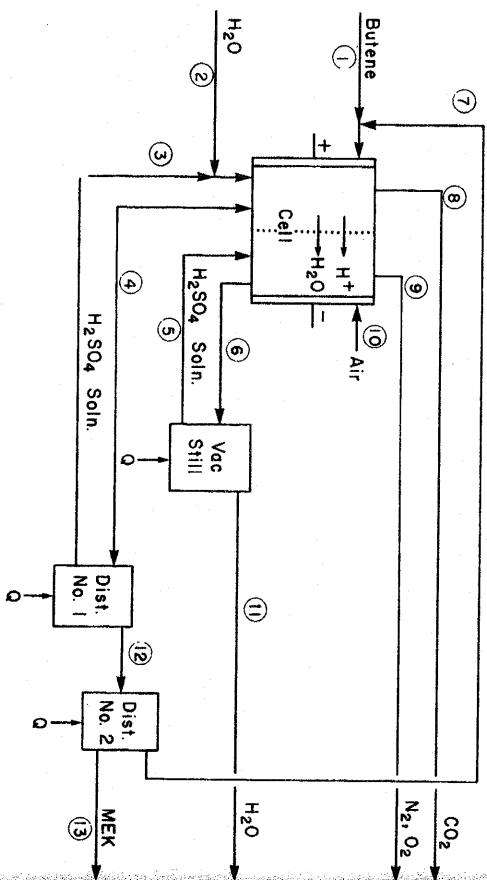


Fig. 9.6. Methyl ethyl ketone from butene, electrochemical.

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The aqueous reaction products pass out of the cell into the first distillation column, where the lighter organic products form the distillate, and the organic-free bottoms are recycled to the anode compartment. The organic phase is further separated in a second column, with the butene distillate being recycled to the cell while the bottoms stream constitutes the product MEK.

The water passing through the membrane with the hydrogen ions is purged from the system after separation from the acid solution by vacuum distillation.

The solubility of butene in sulfuric acid has been assumed to be 0.5 mole butene for each mole of acid. Since the overall chemical reaction is exothermic, the cell should be able to produce energy. No energy credit has been given, that is, a short-circuited cell has been assumed. Based on these assumptions, the vacuum still requires more energy than any other single unit, about 65% of the total process energy.

Energy requirements for the chemical and electrochemical routes to methyl ethyl ketone are compared in Table 9.9. Only the process energies are listed because both processes use the same raw materials. The electrochemical route, based on the study calculations, has a lower energy requirement than the chemical route. It has the further potential advantage of generating a net amount of energy in the electrogenerative mode rather than the short-circuit mode.

The chemical route produces waste sulfuric acid, tar, and dibutyl ethers. The electrochemical route oxidizes a part of the butene feed to CO₂.

Hydroquinone

CHEMICAL PROCESS (HYDROQUINONE FROM BENZOQUINONE)

This process is described in the *EPA 600 Report* [216] and in Volumes 2, 11, 16, and 18 of Ref. 231. The flowsheet and process conditions are described in Fig. 9.7. The reaction takes place at 70°C and 1 atm with the consumption of iron.



$$\Delta H_{298} = -40.32 \text{ kcal/mole hydroquinone}$$

The reaction proceeds with a conversion per pass of 79% and a yield of 100%.

It is characterized by a large volume of water because of the low solubility of hydroquinone. The solubility of hydroquinone at 70°C was assumed to be 9% by weight [229].

ELECTROCHEMICAL ROUTE (HYDROQUINONE FROM BENZENE)

The electrochemical production of hydroquinone from benzene has been described by Fremery et al. [255]. Further, the process was evaluated [3,

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---------------------------------|-------------|-------------------|----------------|----------------|-------|--------|------|
| <i>T</i> (°C) | 25 | 80 | 151 | 80 | 170 | 80 | |
| <i>P</i> (atm) | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Flows | | | | | | | |
| C ₄ H ₈ | 15.07 | | | 3.47 | | | 3.47 |
| H ₂ O | | 227.00 | 40.79 | 40.79 | 17.92 | 184.24 | |
| H ₂ SO ₄ | | | 13.87 | 13.87 | 62.65 | 62.65 | |
| C ₄ H ₈ O | | | | 13.87 | | | |
| | 8 | 9 | 10 | 11 | 12 | 13 | |
| <i>T</i> (°C) | 80 | 80 | 25 | | | | |
| <i>P</i> (atm) | 1 | 1 | 1 | 1 | 1 | 1 | |
| Flows | | | | | | | |
| C ₄ H ₈ | | | | | 3.47 | | |
| H ₂ O | 0.32 | 8.51 | | 166.32 | | | |
| N ₂ | | 112.86 | 112.86 | | | | |
| O ₂ | | 15.83 | 30.00 | | | | |
| C ₄ H ₈ O | | | | | 13.87 | 13.87 | |
| CO ₂ | 4.82 | | | | | | |
| <i>Equipment Condition</i> | <i>Cell</i> | <i>Vac. Still</i> | <i>Dist. 1</i> | <i>Dist. 2</i> | | | |
| <i>T</i> (°C) | 80 | | | | | | |
| <i>P</i> (atm) | 1 | 14 mm | 1 | 3 | | | |
| <i>VI</i> (kcal/sec) | 0 | | | | | | |
| <i>Q</i> (kcal/sec) | 0 | 3300 | 1710 | 47 | | | |

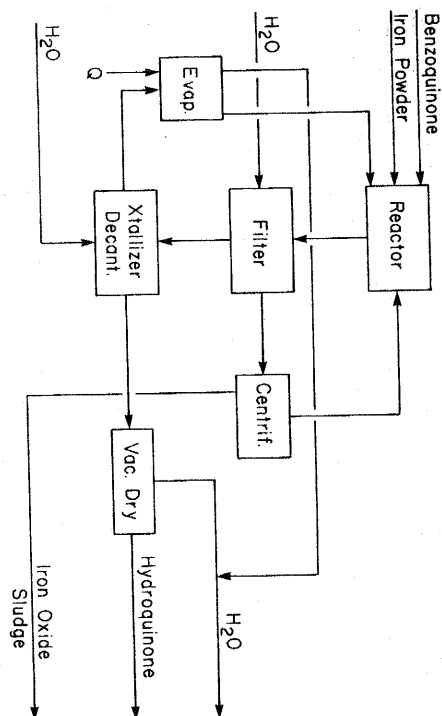
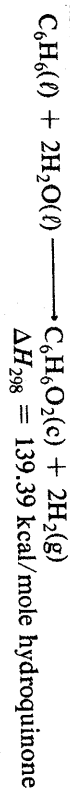
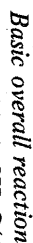
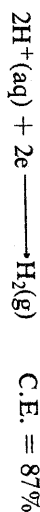
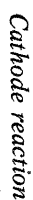
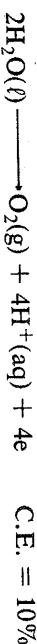
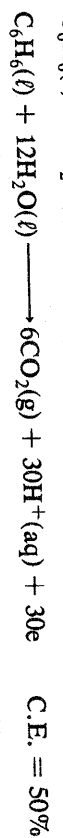
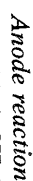


Fig. 9.7. Hydroquinone from benzoquinone, chemical...

App. B] according to suggestions based on Refs. 256 to 262. The process flowsheet is shown in Fig. 9.8 and stream conditions appear in Table 9.10. The reaction of benzene to produce hydroquinone proceeds by the following reaction sequence:



The cell for this process has been assumed to contain a cation-exchange membrane. As the chemical reactions above indicate, benzoquinone is formed at the anode along with hydrogen ions. The benzoquinone is pumped to the cathode compartment, where it is reduced to hydroquinone. The hydrogen ions traverse the ion-exchange membrane and replace those that are consumed at the cathode surface.

After leaving the cell, the hydroquinone is pumped to a phase separator

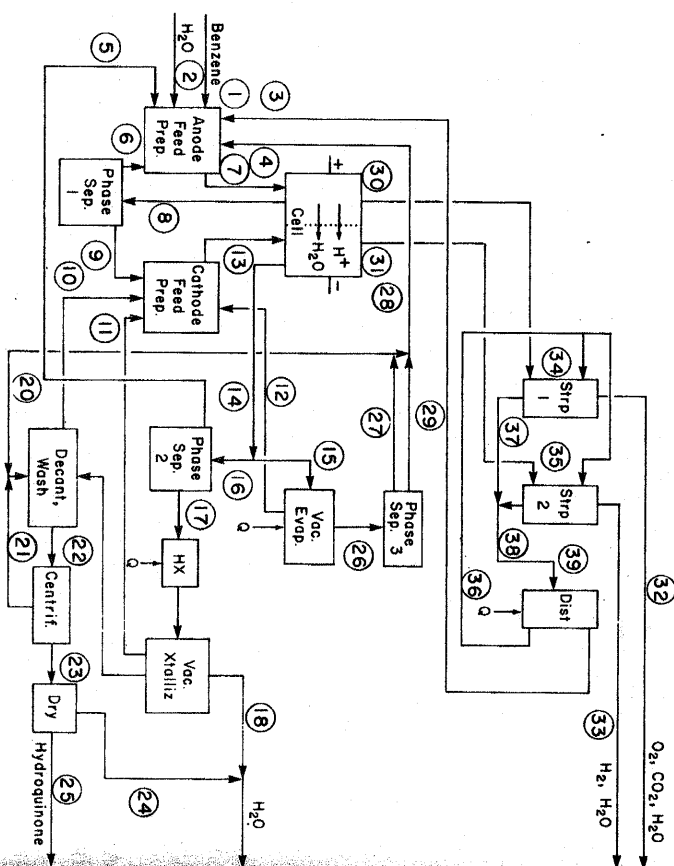


Fig. 9.8. Hydroquinone from benzene, electrochemical.

where the benzene floats and is recycled to the anode compartment. The aqueous phase containing hydroquinone is heated and flashed to a vacuum crystallizer, where the solid hydroquinone is centrifugally filtered out. The solid hydroquinone is then washed, centrifuged again, and dried to produce the final product.

The water that is passed through the membrane to the catholyte with the hydrogen ions is removed by vacuum evaporation and the resulting benzene/water mixture is recycled to the anode compartment.

The off-gases, hydrogen, oxygen, and carbon dioxide, contain benzene, which is absorbed in oil in the gas plant. The benzene is then stripped out of the heavy oil and recycled to the cell feed.

The water evaporator in this process consumes about one-fourth the energy of the cell. The high cost of recycling the water carried across the membrane with hydrogen ions is typical of membrane cell systems.

An additional large energy-consuming step not mentioned in the patents or publications on the process is purification of the sulfuric acid electrolyte [263]. Soluble organic impurities build up in the electrolyte and cause a pro-

Table 9.10. Stream Conditions for Hydroquinone Process Electrochemical Route (Flow Units are g·moles/sec)

| | Stream No. | | | | | | |
|--|------------|-----------|-----------|-----------|--------|-----------|-----------|
| Flows | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| C ₆ H ₆ | 11.35 | | 35.69 | 17.49 | 494.79 | | 559.32 |
| H ₂ O | | 133.56 | | 270.84 | | 936.69 | 1341.09 |
| H ₂ SO ₄ | | | | | | 43.03 | 43.03 |
| C ₆ H ₄ O ₂ | | | | | 2.64 | | 2.64 |
| Flows | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| C ₆ H ₆ | 540.00 | 540.00 | | 14,514.68 | 212.54 | 540.00 | 512.28 |
| H ₂ O | 936.69 | | 40.58 | 14,514.68 | 212.54 | 14,767.80 | 15,109.55 |
| H ₂ SO ₄ | 43.03 | | 0.44 | 472.70 | 16.73 | 489.87 | 489.87 |
| C ₆ H ₄ O ₂ | 11.72 | 11.72 | | | 0.09 | 11.81 | 2.73 |
| C ₆ H ₆ O ₂ | | | | 214.33 | 7.90 | 222.23 | 231.31 |
| Flows | 15 | 16 | 17 | 18 | 19 | 20 | 21 |
| C ₆ H ₆ | 17.49 | 494.79 | | | | | 9.28 |
| H ₂ O | 515.83 | 14,593.72 | 14,593.72 | 66.28 | 12.76 | 32.45 | |
| H ₂ SO ₄ | 16.73 | 473.14 | 473.14 | | 0.44 | | |
| C ₆ H ₄ O ₂ | 0.09 | 2.64 | | | | | |
| C ₆ H ₆ O ₂ | 7.90 | 223.41 | 223.41 | | 9.08 | | |
| Flows | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
| C ₆ H ₆ | | | | | 17.49 | | |
| H ₂ O | 13.91 | 4.63 | 4.63 | | 303.29 | 303.29 | 270.84 |
| C ₆ H ₆ O ₂ | 9.08 | 9.08 | | 9.08 | | | |

gressive decline in current efficiency to the point where sulfuric acid must either be replaced or purified. Not enough technical information is available at present to make an estimate of the energy requirement for sulfuric acid purification.

COMPARISON (HYDROQUINONE SYNTHESIS)

Energy requirements for the chemical and electrochemical routes to hydroquinone are compared in Table 9.11. The chemical route has a lower energy requirement according to these calculations, but the case is not clearcut, because the calculations were based on rather sketchy process information and the results are sensitive to the assumptions made. The following factors can increase the energy consumption for the chemical process [263]:

1. Refrigeration may be used to operate the reactor for oxidation of aniline to benzoquinone below ambient temperature.
2. Evaporation of water from the salt solution effluent before disposal or sale of the salts for fertilizer use would require 3816 kcal/kg of hydroquinone.
3. The amount of water used in the process may be larger than that used in the calculations, thus increasing the heat loads for evaporation.

It has already been pointed out that there is an additional energy cost to the electrochemical process for sulfuric acid purification. On the other hand, the current efficiency might be increased from the 40% used in the calculations to a higher figure through more research and development. The 12,600 kcal/kg of electrical energy for the cell in Table 9.10 is in good agreement with the 14 kWh/kg or 12,900 kcal/kg given in Ref. 264.

Millington's calculations [264] show that the electrochemical process is more favorable on an energy basis than the chemical process. His data show 43,950 kWh (thermal)/ton (41,600 kcal/kg) for the electrochemical route; and 69,900 kWh (thermal)/ton (66,100 kcal/kg) for the chemical route; these numbers are exclusive of the heat of combustion of the benzene feed to each process. These results clearly show an advantage for the electrochemical route. The overall energy requirement (41,600 kcal/kg) for the electrochemical route is in reasonable agreement with the 43,769 kcal/kg (exclusive of benzene heating value) calculated here. The former exhibit a higher overall energy requirement for the chemical route because:

1. An obsolete iron-reduction method was used to make the aniline intermediate.
2. A higher energy was assigned to the iron used for reduction of nitrobenzene to aniline and benzoquinone.
3. A higher steam usage was employed in the hydroquinone part of the process, presumably for a greater water evaporation load.

458 Table 9.10. Continued

| | Stream No. | | | | | | | | | |
|-------------------------------|------------|-----------------|-----------------|-----------------|---------------|----------------|-------|------------|------------|-------|
| Flows | 29 | 30 | 31 | 32 | 33 | 34 | 35 | | | |
| C ₆ H ₆ | 17.49 | 7.97 | 27.72 | | | | | | | |
| H ₂ O | | 2.26 | 8.16 | 2.26 | 8.16 | | | | | |
| O ₂ | | 3.39 | | 3.39 | | | | | | |
| CO ₂ | | 13.64 | | 13.64 | | | | | | |
| H ₂ | | | 59.05 | | 59.05 | | | | | |
| Oil | | | | | | | | | | |
| Flows | 36 | 37 | 38 | 39 | 40 | | | | | |
| C ₆ H ₆ | | 9.97 | 27.72 | 35.69 | | | | | | |
| H ₂ O | | | | | 349.91 | | | | | |
| Oil | | | | | | | | | | |
| H ⁺ | | | | | 136.25 | | | | | |
| Equipment Conditions | Cell | Phase Sep. 1 | Phase Sep. 2 | Phase Sep. 3 | Vac. Evap. | Vac. Cryst. | Dryer | Strip 1 | Strip 2 | Dist. |
| T (°C) | 45 | | 40 | | | 20 | 100 | 25 | 25 | |
| P (atm) | 1 | 1 | 1 | 1 | 0.309 | 0.309 | 1 | 1 | 1 | 1 |
| VI (kcal/sec) | 12,600 | | | | | | | | | |
| Q (kcal/sec) | | | | | 3244 | 1430 | 93 | | | 233 |

Table 9.11. Hydroquinone Energy Requirements (kcal) [Basis: 1 kg (9.08 g·moles)]

| Chemical Route | |
|------------------------------|--------|
| H ₂ O evaporation | 2,979 |
| Dryer | 147 |
| Iron | 2,633 |
| Benzquinone (9.08 g moles) | |
| Steam stripper | 11,050 |
| Aniline from benzene | 14,152 |
| Total | 30,961 |
| Electrochemical Route | |
| Cell | 38,769 |
| Vacuum evaporation | 3,244 |
| Vacuum crystallizer | 1,430 |
| Dryer | 93 |
| Distillation | 233 |
| Benzene | 8,970 |
| Total | 52,739 |

The chemical route to hydroquinone given in the EPA report [216] and used as a basis in this study is also old technology. Two newer processes [263] are chemical oxidation of phenol to hydroquinone and catechol, and hydroperoxidation of *p*-disopropylbenzene, leading to hydroquinone and acetone.

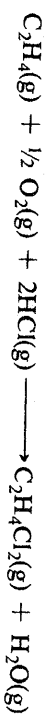
The chemical reduction of benzoquinone to hydroquinone by iron gives an iron oxide sludge that must be discarded. The chemical oxidation of aniline to benzoquinone gives calcium sulfate sludge, which must be discarded. The electrochemical route is relatively clean, although it is understood that the process is prone to produce tars.

Dichloroethane

CHEMICAL ROUTE (DICHLOROETHANE FROM ETHYLENE)

The gas phase production of dichloroethane (DCE) from ethylene and hydrogen chloride (HCl) is discussed in the *EPA 600 Report* [216] and *Hydrocarbon Processing* [265].

The catalytic reactor operates at 300°C and 5.5 atm pressure. The reaction is



$$\Delta H_{573} = -57.18 \text{ kcal/mole DCE}$$

The only energy demands for this process are made by the DCE stripper and the air compressor. The reactor operates at the highest temperature in the process, and the heat of reaction could be used in the DCE stripper. With the exception of the small requirement for the air compressor, this process is energy self-sufficient.

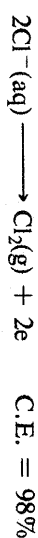
A second chemical route based on Cl₂ is also known. Energy data for both process routes are given in Table 9.12.

ELECTROCHEMICAL ROUTE (DICHLOROETHANE FROM ETHYLENE)

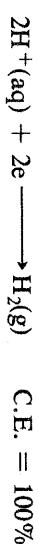
The electrochemical production of dichloroethane (DCE) from ethylene and hydrogen chloride [266-272] has led [1] to the flowsheet given in Fig. 9.9.

The diaphragm electrochemical cell used for this process converts hydrochloric acid to chlorine gas and hydrogen as shown in the following sequence of reactions:

Anode reaction



Cathode reaction



The overall electrochemical reaction can thus be written as



The chlorine gas is absorbed into solution, where it undergoes reaction with ethylene to form several compounds, with DCE constituting the primary product. About 75% of the ethylene is ultimately converted to DCE, and the conversion per pass is about 64% based on ethylene. Ethylene chlorohydrin is the primary by-product. The cells are assumed to operate at 2.2 V, which is similar to the voltage of commercial HCl electrolysis cells.

The chlorohydrin formed in the cell is absorbed primarily into the aqueous phase. Part of this phase is withdrawn from the cell and passed to a chlorohydrin still. This still is a very large energy user, primarily because of the small concentration of chlorohydrin assumed for the water phase. If the concentration of chlorohydrin is allowed to increase beyond the value assumed here, a significant energy savings will be possible. Water and HCl pass overhead from the chlorohydrin still and are recycled to the cell. The primary energy requirements for this process are for the chlorohydrin still and the electrochemical cell.

COMPARISON (DICHLOROETHANE SYNTHESIS)

Energy requirements for the chemical and electrochemical routes to dichloroethane are compared in Table 9.12. Although both the HCl and chloro-

Table 9.12. Dichloroethane Energy Requirements (kcal) [Basis: 1 kg (10.10 g·moles)]

| | |
|---|--------|
| <i>Chemical Route</i> | |
| From HCl | 116 |
| Compressors and refrigerator | — |
| Process heat | 6,014 |
| Ethylene | 6,130 |
| Total | 14,819 |
| From Cl ₂ (see Ref. 3, App C-12) | |
| <i>Electrochemical Route</i> | |
| Cell | 4,148 |
| Compressor 1 | 9 |
| Compressor 2 | 30 |
| Refrigeration | 73 |
| Chlorohydrin distillation | 5,753 |
| Ethylene | 7,760 |
| HCl—no cost | — |
| Total | 17,773 |

rine chemical routes are used commercially to make DCE, the HCl route has a clearly lower energy requirement. Over 95% of the DCE produced in the United States in 1974 was made by the "balanced process," which is a balance of these two processes with pyrolysis of DCE to produce vinyl chloride monomer [216]. The by-product HCl from the vinyl chloride process is used in the DCE process so that there is no net production of HCl. The electrochemical route has a 20% greater energy requirement than the chemical chlorine route, but this energy requirement can be decreased below that of the chemical route if formation of the by-product chlorohydrin can be suppressed. This is because conventional NaCl brine diaphragm cells that supply the chlorine for the chemical process operate at 3.5 V versus 2.2 V for HCl electrolysis. The electrochemical process produces about 25% chlorohydrin, which is a saleable product.

Melamine

CHEMICAL ROUTE (MELAMINE FROM UREA)

The process producing melamine from urea is described by Kirk-Othmer [273], Lowenheim and Moran [232], and Mackay [274].

The primary reaction produces cyanamide, ammonia, and carbon dioxide:

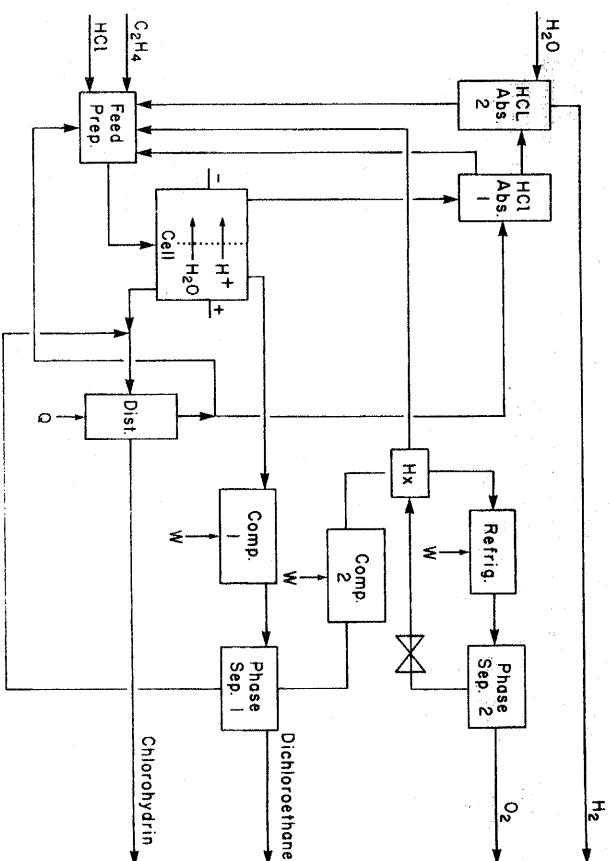
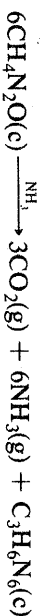


Fig. 9.9. Dichloroethane from ethylene and HCl, electrochemical.

from urea. The cyanamide trimerizes in excess ammonia to yield melamine.

The overall reaction is



$$\Delta H_{298} = 114.75 \text{ kcal/mole melamine}$$

The aqueous phase containing the melamine as crystals passes to a vacuum thickener where some water and most of the ammonia and carbon dioxide are evaporated off. The thickener bottoms then move to a steam stripper where the residual ammonia and carbon dioxide are removed. The melamine passes, as an aqueous slurry, to the crystallizer, where water is driven off and the solid product is separated by a centrifugal filter.

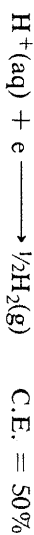
The ammonia/carbon dioxide stream is recycled to a urea plant, where it is ultimately recycled to the urea feed. A credit has therefore been given for the off-gases.

The primary energy demand for this process is the reactor. The overall reaction is highly endothermic and requires a large amount of thermal energy.

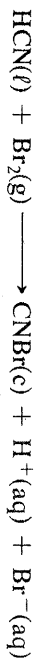
ELECTROCHEMICAL ROUTE (MELAMINE FROM HYDROGEN CYANIDE)

The electrochemical production of melamine from cyanide is reviewed [1] based on work by Forman et al. [275, 276] and by Sprague et al. [277]. The process discussed below is discussed more thoroughly in Ref. 3.

The reactions in the electrochemical cell are as follows:

Anode reaction*Cathode reaction*

A chemical reaction takes place in the anolyte:



The primary overall reaction can thus be written as



$$\Delta H_{298} = 48.62 \text{ kcal/mole cyanogen bromide}$$

The cell is operated at 3.1 V and 25°C at 100% conversion efficiency for HCN.

The product stream leaves the reactor as a slurry and enters the cyanogen bromide stripping tower where CNBr is extracted with tetrahydrofuran (THF). The THF stream is pumped to a chemical reactor, where cyanamid is formed,



$$\Delta H_{298} = -60.62 \text{ kcal/mole cyanamide}$$

The product ammonium bromide is precipitated and separated from the THF stream in a centrifuge. The centrifuge overflow is pumped to a second chemical reactor, where polymerization to melamine occurs:



$$\Delta H_{298} = -59.30 \text{ kcal/mole melamine}$$

This process contains two large energy sinks, the electrochemical cell, and the cyanogen bromide stripper. The stripper energy requirement is high because of the moderate solubility of CNBr in water.

COMPARISON (MELAMINE SYNTHESIS)

Energy requirements for the chemical and electrochemical routes to melamine are compared in Table 9.13. The electrochemical energy requirements

Table 9.13. Melamine Energy Requirements (kcal) [Basis: 1 kg (7.93 g·moles)]

| <i>Chemical Route</i> | |
|------------------------|--------|
| Reactor | 1,378 |
| Thickener | 1,009 |
| Steam stripper | 69 |
| Crystallizer | 618 |
| Dryer | 88 |
| Total | 3,162 |
| Credit (heat exchange) | -410 |
| Net | 2,752 |
| Urea | 19,876 |
| NH ₃ credit | -7,156 |
| Total | 15,472 |

| <i>Electrochemical Route</i> | |
|------------------------------|--------|
| Cell | 10,462 |
| CNBr stripper | 4,932 |
| NH ₃ still | 183 |
| THF dryer | 15 |
| H ₂ O evaporator | 88 |
| Total | 15,680 |
| Credits (heat exchange) | -736 |
| Net | 14,944 |
| HCN | 11,570 |
| NH ₃ | 3,645 |
| Total | 30,159 |

are significantly greater than those of the chemical route largely because of the cell and the CNBr stripper.

The chemical process gives about 20% biuret as a by-product, which is a saleable product.

Aniline

CHEMICAL ROUTE (ANILINE FROM NITROBENZENE)

The production of aniline from nitrobenzene is outlined by Lowenheim [232]. Other sources include Kirk-Othmer [231], *Hydrocarbon Processing* [265], and *EPA 600 Report* [216].

The process is a simple one with one phase separator, an absorber, and a distillation column. The primary reaction is



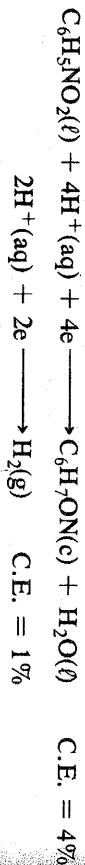
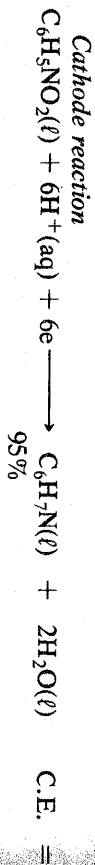
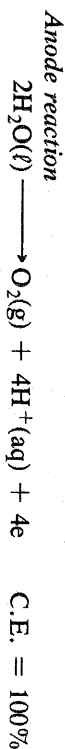
$$\Delta H_{298} = -111.34 \text{ kcal/mole aniline}$$

The equipment for this process presented no serious calculation problems. The heat, both sensible and latent, in the reactor product stream is sufficient to run the downstream separation equipment and preheat the nitrobenzene feed. Since the overall process is highly exothermic, this energy would have to be sold to a consumer outside the plant.

ELECTROCHEMICAL ROUTE (ANILINE FROM NITROBENZENE)

The electrochemical production of aniline is described in the literature [3, 278-284].

The cell operates at 25°C without a membrane and produces aniline by the following reactions:



Primary overall reaction



By far, the greatest energy cost in this process is the electrical energy going to the cell, which was assumed to operate at 5 V. Nearly all this energy is degraded to low-quality heat.

COMPARISON (ANILINE SYNTHESIS)

Energy requirements for the chemical and electrochemical routes to aniline are compared in Table 9.14. The electrochemical route has a decided energy disadvantage compared to the chemical route, primarily because of the high energy requirement for the cells.

The electrochemical route gives about 7% *p*-amino phenol by-product, which is a saleable product. Information on the corresponding chemical routes is given in Ref. 216.

Table 9.14. Aniline Energy Requirements

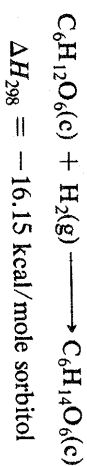
| Chemical Route | |
|-------------------------------|--------|
| (Basis: 1 kg = 10.75 g·moles) | |
| Nitrobenzene (10.75 g·moles) | 10,733 |
| Hydrogen (32.5 moles) | 3,186 |
| No thermal credit taken | — |
| Total | 13,919 |
| Electrochemical Route | |
| Cell | 24,120 |
| Crystallizer | 441 |
| Aniline evaporator | 179 |
| Process energy | 24,740 |
| Nitrobenzene (11.45 g·moles) | 11,432 |
| Total | 36,172 |

Sorbitol

CHEMICAL ROUTE (SORBITOL FROM GLUCOSE)

The production of sorbitol from glucose is described by Lowenheim and Moran [232] and Fedor et al. [285].

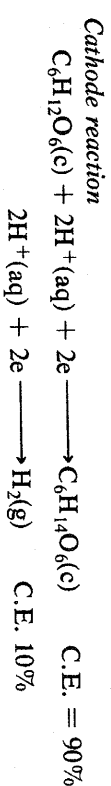
The reaction is carried out in aqueous solution at 200°C and 140 atm of pressure over a nickel catalyst. The reaction is



As with most highly hydrated processes, the primary energy demand is that required to evaporate the water.

ELECTROCHEMICAL ROUTE (SORBITOL FROM GLUCOSE)

The electrochemical reduction of glucose to sorbitol is described by various authors [286-291]. The chemical reaction sequence is as follows:



Primary overall reaction

$$\Delta H_{298} = 52.16 \text{ kcal/mole sorbitol}$$

This process is quite straightforward and the primary energy demand, other than that of the electrochemical cell, involves the removal of water. No allowance has been made for the heat of solution of glucose in water or of sorbitol in ethanol.

COMPARISON (SORBITOL SYNTHESIS)

Energy requirements for the chemical and electrochemical routes to sorbitol are compared in Table 9.15. The electrochemical route is at a substantial energy disadvantage to the chemical route because of the higher energy requirement for the cells and of the difficulty of separation of the product sorbitol from the sodium sulfate electrolyte. The chemical and electrochemical routes should be similar in terms of by-products.

Terephthalic Acid

CHEMICAL ROUTE (TEREPHTHALIC ACID FROM XYLENE)

The production of terephthalic acid (TPA) from *p*-xylene is discussed in the *EPA 600 Report* [216] and *Hydrocarbon Processing* [292], as well as by Lowenheim and Moran [232] and Sherwood [293].

The reaction involved is the air oxidation of *p*-xylene to TPA:



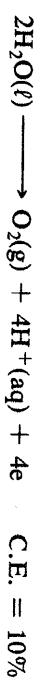
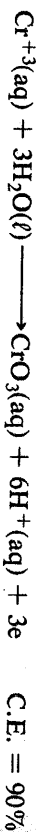
$$\Delta H_{298} = -319.78 \text{ kcal/mole TPA}$$

The largest energy requirements for this process are for distillation and the air compressor, for which three stages have been assumed.

ELECTROCHEMICAL ROUTE (TEREPHTHALIC ACID FROM *P*-XYLENE)

The electrochemical production of terephthalic acid (TPA) is discussed by various authors [3, 291, 294-300].

The chemical reactions comprising the heart of this process take place in both an electrochemical cell and an accompanying reactor. The reduction of dichromate to chromic ions drives the second reaction. Dichromate ions are regenerated in the cell. The cell reactions are as follows:

Anode reaction*Cathode reaction*

The heat of reaction for the primary reaction in the cell is

$$\Delta H_{298} = 126.1 \text{ kcal/mole chromic acid}$$

The cell operates at 55°C and atmospheric pressure without a membrane at 3.3 V.

The cell effluent, a sulfuric acid/chromic acid mix, is pumped to the second reactor, where it is mixed with *p*-xylene, and the following reaction takes place:



$$\Delta H_{298} = -417.8 \text{ kcal/mole TPA}$$

The primary overall reaction for the entire process is



$$\Delta H_{298} = 86.68 \text{ kcal/mole TPA}$$

The largest energy consumer in this process is the cell. A small amount of energy is consumed by the boiler and ether dryer. Both the cell and the reactor are highly exothermic, but they both operate at such low temperatures that this heat is unavailable for use elsewhere.

Table 9.15. Sorbitol Energy Requirements (kcal) [Basis: 1 kg (5.49 g·moles)]

| Chemical Route | |
|------------------------------|------|
| Compressor 1 | 63 |
| Compressor 2 | 1 |
| H ₂ O evaporation | 352 |
| H ₂ | 542 |
| Total | 958 |
| Electrochemical Route | |
| Cell | 5194 |
| Ethanol evaporation | 2539 |
| Ethanol distillation | 1795 |
| Dryer | 121 |
| Total | 9649 |

COMPARISON (TEREPHTHALIC ACID SYNTHESIS)

Energy requirements for the chemical and electrochemical routes to terephthalic acid are compared in Table 9.16. Both processes use the same raw materials. The energy requirement calculated for the chemical process is considerably smaller than the 4172 kcal/kg given in Ref. 221 based on plant data. The reason for the high actual value is that terephthalic acid must be very pure for polymer production; insufficient information was available for the present calculations to make an accurate estimate of distillation energy. In either case, the chemical process is overwhelmingly favored in terms of energy requirement. The catalytic air-oxidation step is exothermic and only requires a small amount of energy for compression. The electrolytic cells require a large amount of energy for the overall 12-electron reaction. One of the process selection rules was violated in this case in order to include an example of an indirect oxidation from the processes in Table 9.3. An overall one-electron process for an oxidation would have a chance of being much more competitive, but a high-yield catalytic air oxidation is very difficult competition.

The electrochemical route uses toxic sodium dichromate as an intermediate oxidizing agent and high recovery is required. The chemical route uses acetic acid as a solvent, part of which is lost in effluent streams.

Table 9.16. Terephthalic Acid Energy Requirements (kcal) [Basis: 1 kg (6.02 g·moles)]

| | |
|------------------------------|--------|
| <i>Chemical Route</i> | |
| Calculated in Ref. 3 | 206 |
| Compressor | 64 |
| Dryer | 411 |
| Distillation 1 | 19 |
| Distillation 2 | 700 |
| Total | |
| <i>Electrochemical Route</i> | |
| Cell | 19,015 |
| Boiler | 160 |
| Ether evaporation | 48 |
| Refrigeration | 1,120 |
| Dryer | 60 |
| Hydrogen credit | -3,021 |
| Total | 17,382 |

Phenol

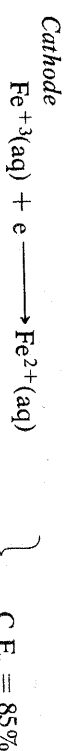
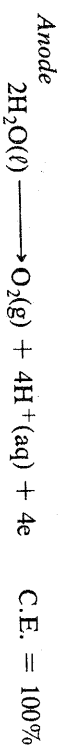
CHEMICAL ROUTE (PHENOL FROM CUMENE)

The energy requirements for phenol synthesis by way of cumene are available from the compilation of Rudd et al. [221].

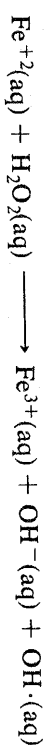
ELECTROCHEMICAL ROUTE (PHENOL FROM BENZENE)

The electrochemical conversion of benzene to phenol is reviewed in Refs. 3, 301, and 302, which describe other fundamental studies [303-311].

The cation-membrane electrochemical cell operates at 50°C. The following reaction sequence is assumed:



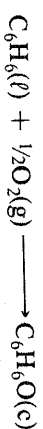
The hydrogen peroxide then reacts in solution with the ferrous ions:



The hydroxyl free radical also can react directly with benzene:



Thus the overall chemical reaction can be written



$$\Delta H_{298} = -51.16 \text{ kcal/mole phenol}$$

The cell, assumed to operate at 4 V, is by far the largest energy-consuming unit in this process; the water evaporator consumes about two-thirds as much energy as the cell.

COMPARISON (PHENOL SYNTHESIS)

Energy requirements for the chemical and electrochemical routes to phenol are compared in Table 9.17. The chemical route is based on Ref. 221. Both processes include the heat of combustion of the raw materials to put them on an equal basis. The chemical route has a sizable energy advantage because of the energy credit for readily marketable acetone by-product and because of the sizable cell energy requirement for an overall six-electron reaction.

Table 9.17. Phenol Energy Requirements (kcal) [Basis: 1 kg (10.64 g·moles)]

| Chemical Route by way of Cumene (Ref. 3, App. C-12) | |
|---|--------|
| | 12,251 |
| <i>Electrochemical Route</i> | |
| Cell | 21,317 |
| H ₂ O evaporation | 4,610 |
| Crystallizer-centrifuge | 1,083 |
| Dryer | 8 |
| Benzene | 8,409 |
| Oxygen | 165 |
| Total | 35,592 |

Biphenyl is a by-product of the electrochemical route and is presumably saleable. Acetone is a desired by-product in the chemical route.

Impact of Electrochemical Routes on Process Industry

A linear-programming model of the U.S. petrochemical industry was used to evaluate the energy efficiency of the electrochemical processes reported above and to assess their potential impact on the industry as a whole. The model was formulated and described in detail by Stadtherr and Rudd [312]. It was used to determine the optimal structure of the industry with respect to resource use. That is, the model was used to determine the combination of process alternatives that can meet the demands of the economy while consuming a minimum of feedstock and energy resources. The version of the model described by Stadtherr and Rudd [312] accounted for feedstock consumption only. For purposes of this study, the process energy data of Rudd et al. [221] were also incorporated in the model. Thus the objective function in the version of the model used here was minimum energy consumption, counting energy consumed both as utilities and as feedstock (feedstock energy consumption is measured using its gross heating values).

The energy efficiency of the electrochemical processes was evaluated by adding the processes to the model and noting which processes, if any, were used in the energy-optimal industry. Since the model accounts for all commercially proven processes, not just those that predominate today, use of the model in this way, in effect, provided comparison of the electrochemical routes to *all available chemical routes*. Since the various segments of the industry are highly interactive, the introduction of a more energy-efficient

route in one part of the industry, say in the manufacture of some chemical intermediate, may affect other parts of the industry, as other route changes may occur in order to make use of the more energy-efficient intermediate. The overall effect on the industry of adding the electrochemical processes may be assessed by noting whether any other route changes occur in the energy-optimal industry as a result of its adoption of an electrochemical process.

The study outlined above was performed by adding to the model industry six of the electrochemical processes, those for adiponitrile, aniline, ethylene dichloride (dichloroethane), methyl ethyl ketone, phenol, and terephthalic acid. The processes for hydroquinone, melamine, and sorbitol are not considered here since these chemicals are not manufactured on a large enough scale for their production to be accounted for explicitly in the model. Of the six processes added, two were used in the energy-optimal industry model: the electrochemical routes to adiponitrile and to methyl ethyl ketone. Addition of the adiponitrile process results in a savings of 5260 kcal/kg adiponitrile; addition of the MEK process results in a savings of 1960 kcal/kg methyl ethyl ketone.

The savings in adiponitrile manufacture are less than indicated in Table 9.18 because the chemical route used by the energy-optimal industry before the addition of the electrochemical processes is butane dehydrogenation, while the figure for the chemical route in Table 9.18 is based on butylene dehydrogenation. The butane process is more energy efficient, but is used to a lesser extent than the butylene process.

The savings in methyl ethyl ketone manufacture are greater in the present estimates than in Table 9.18 because those figures account for process energy only. Since the electrochemical process has a high yield of butylene compared to the chemical route, there is a significant savings in feedstock energy.

The adoption of this process does not result in any other route change in the energy-optimal industry. Of course, this does not rule out the development of new routes not now included in the model. For instance, it has been suggested that a route might be developed from adiponitrile to adipic acid, which is currently derived from benzene by way of a cyclohexane intermediate. Thus both monomers for nylon 66 could be derived from propylene by way of acrylonitrile and adiponitrile intermediates, using the energy-efficient electrochemical technology.

The main effect indicated by the model on the overall industry is a tightening in the supply of propylene. Since there is a trend toward increased use of heavier feedstocks (naphtha or gas oil) in the manufacture of ethylene, and this results in increased production of by-product propylene, the effect of the electrochemical technology on propylene supplies does not seem significant.

Table 9.18. Summary of Process Energy Requirements (Electrochemical Processes Are Not Optimized)

| Chemical | Energy Requirement (kcal/kg) | |
|-----------------------|---------------------------------|---------------------|
| | Electro-chemical | Chemical |
| Adiponitrile | 43,177 ^a | 65,808 ^b |
| Aniline | | |
| Nitrobenzene route | 36,172 ^a | 13,919 |
| Phenol route | — ^a | 16,736 ^b |
| Sorbitol | 9,649 | 958 |
| Terephthalic acid | 17,382 | 700 |
| Phenol | 35,592 ^a | 12,251 ^b |
| Methyl ethyl ketone | 5,057 | 6,690 |
| Melamine | | 3,233 ^b |
| Hydroquinone | 30,159 ^a | 15,472 |
| Dichloroethane | 52,739 ^a | 30,961 |
| HCl route | 17,773 ^a | 6,130 |
| Cl ₂ route | — ^a | 14,819 ^b |

^aEnergy charged for hydrocarbon raw materials (different compounds).^bChemical route energy from Reference [221].

Summary

The objective of Section 4 is to review the commercial status of electroorganic process technology and to provide methods for estimating whether energy savings might be realized by the introduction of electroorganic processes for production of high-tonnage organic chemicals.

It is important to recognize that severe restraints were set on the scope of this section. The conclusions reached here therefore may not correspond to the more balanced perspective with which candidate processes are normally evaluated by the industrial sector. In particular, only the energy consumption of large-tonnage organic processes is evaluated, without consideration of waste-water treatment or economics of operating and capital costs.

This section provides a previously unavailable data base of electroorganic synthesis processes, along with engineering methodologies needed for process evaluation. Although the constraints on this section are limited to energy-efficiency conditions of existing process candidates alone, the data base and the methods of evaluation can be readily expanded to include a wider range

of criteria and process candidates. By these additional refinements, a more realistic assessment of electroorganic process routes surely will emerge, not only in the large-tonnage arena considered here, but also in the lower-tonnage categories, where product compounds tend to be more complex, to have high molecular weight, and to be polyfunctional.

The nine chemicals for which detailed estimations of process energy requirements were made in this study were selected either because they illustrated a particular class of electrochemical reaction or because they were considered to have a reasonable chance of a more-energy-efficient electrochemical route. Within the constraints specified on this study of nine compounds, the electrochemical routes offered energy savings in two processes and came close to an even match in two other processes. In many of the cases the chemical and electrochemical processes started with different raw materials. It was therefore necessary to link more than one process in series back to the same raw materials or to basic building blocks.

A summary of the nonoptimized process energy requirements for the nine chemicals is given in Table 9.18. The energy requirements include those for chemical and electrochemical reactors and for separation processes. Electrical energy inputs to cells, compressors, and refrigerators were divided by 0.325, the U.S. average fossil fuel-to-electricity efficiency, to convert to a common fossil-fuel basis. The gross heating values of alkane and benzene feedstocks were assigned to each process when different feedstocks were used in the chemical and electrochemical routes. By-product hydrogen was credited its gross heating value and other organic by-products were credited their manufacturing energy requirements for their main synthesis route. Energy data for some of the chemical products with several series processes were obtained from the literature and are so noted in Table 9.18. Detailed calculations are available in Ref. 3.

Although every effort is made to make the comparisons based on state of the art technology, the information available was not always complete. Chemical process flowsheets are for the most part based on a 1977 survey of industrial organic processes by the Environmental Protection Agency, but even this source for reasons of industrial secrecy was not completely current. The electrochemical process calculations were based on data from bench to industrial scale, from recent patents and papers, as well as from a 40-year-old process. The electrochemical process flowsheets are *not* optimized to minimum energy consumption conditions. Thus the "balance sheet" in Table 9.18 is not for a true instant in time, but spans a number of years for the various processes.

The electrochemical route to adiponitrile shows a clear energy advantage over the chemical route. This is one of the more accurate comparisons because the electrochemical route calculations were based on a published

plant flowsheet and the chemical route result is based on production data. Qualifications are that a new chemical route introduced in 1973 probably has a lower energy requirement of at least 6600 kcal/kg, and that improvements have been made in the electrochemical process.

Production of methyl ethyl ketone in an electrochemical cell appears to be attractive on an energy basis in comparison with the current chemical route. In addition, replacement of the chemical route by the electrochemical route would offer the further advantage of conserving feedstock material by higher efficiency utilization. The cell uses an air cathode and oxidizes butene at a catalytic anode. For the calculations it was assumed that the cell operated in the short-circuited mode although it could generate electricity.

The electrochemical synthesis of hydroquinone begins with the oxidation of benzene to the quinone intermediate. While the electrochemical process involves a single step in contrast to a multistep chemical route to this intermediate, it is reported that current efficiencies are only 40%. However, if research and development activity would focus on increasing the current efficiency toward 100%, then the energy required for the electrochemical route would be competitive with that required for the existing chemical route.

In-cell halogenations, as used to make dichloroethane, are also close to breakeven with chemical routes, all of which use electrolytically produced chlorine. More detailed analyses and optimization calculations would clearly be justified to provide a better definition of the relative benefits of the two routes.

The chemical synthesis of melamine is less energy intensive than the electrochemical route owing, to an appreciable extent, to power consumption by the electrolysis cell.

The two electrochemical hydrogenation processes (aniline and sorbitol syntheses) are considerably more energy intensive than high-yield catalytic hydrogenations. Electrochemical generation of hydrogen is more energy intensive than generation from hydrocarbons by steam reforming, and separation of products from electrolytes requires more energy than that from corresponding chemical process streams. While economic considerations are not taken into account in this section, it is worth mentioning that electrochemical hydrogenations occur under very mild process conditions in comparison with some chemical routes that require very high pressure. Other types of electrochemical reductions deserve evaluation, including hydrodimerizations and electrode-specific reductions.

Terephthalic acid synthesis represents an example of indirect oxidation using the chromic/dichromate redox couple. However, one of the process selection rules (Table 9.4) was broken, since the electrochemical route requires 12 electrons per mole of product. While the resulting comparison may thus be

foreordained to favor the chemical route, it is also true that high-yield catalytic air oxidations are difficult competition for electrochemical processes. Evaluation of competing electrochemical routes would be worthwhile in cases of difficult chemical oxidation processes, which often exhibit low yields and strenuous reaction conditions.

If the electrochemical route to phenol is to become attractive on an energy basis, research must be directed to reducing the cell voltage and increasing the current density.

This section provides the first extensive comparison of energy requirements for a significant number of processes (electrochemical versus chemical) treated in a consistent manner. The overall errors of the calculations for each process are judged to be less than $\pm 50\%$, although the electrochemical processes are not optimal. Because only one iterative step is made toward optimization for each electrochemical process route, it seems undeniably clear that the results given here represent a *preliminary assessment* against which future improvements in process technologies may be measured. That is, considerable research and development effort has already been devoted to current large-tonnage chemical processes to make them economically competitive. With even modest development efforts, there is no question but that the energy efficiencies for electroorganic processes estimated here could be substantially improved.

5 CONCLUSIONS AND RECOMMENDATIONS

Many of the critical components that make up the field of electroorganic synthesis technology have recently grown into place. Chemists, for example, can synthesize many thousands of organic compounds by electrolysis and have thereby come to a deeper understanding of the molecular basis underlying many reactions. Advances in surface science and catalysts are leading to controlled study of electrode properties, which should further enhance ability to synthesize chemicals in high yields. Further, electrochemical engineers have developed reactor designs along with modeling techniques needed to guide scale-up and optimization. Chemical engineers are therefore increasingly able to assess economic aspects of process routes involving electrochemistry. It seems inevitable that consolidation of these interdisciplinary elements will continue and will promote increased effectiveness in the development of electroorganic process technologies.

Generally, electroorganic processes can be favorable when the product molecular weight is high, when there are fewer than four electrons in the electrolysis step, when the yield is high compared to a corresponding chemical route, and when the raw materials are less expensive than those used in the

chemical synthesis. In some cases the electroorganic route may be the only way to make some desirable products in reasonable yield; often there are fewer processing steps and fewer pollutants.

The task of identifying process candidates may involve widespread searching of general categories, such as the high-tonnage search described in Section 4. On the other hand, most industrial producers carry out evaluation studies based on a specific chemical of interest. In such situations, the consideration of potential electrochemical synthesis routes should be included as a matter of routine, especially if the chemical routes are cumbersome from the viewpoint of energy, feedstock, or environment. That is, electrochemical methods should be regarded as one of several tools available for the purpose of synthesis. It is no longer realistic to ignore electrochemical candidates, because the methods of evaluation and implementation of electrolytic routes have so vastly improved.

With the recent development of new electrode and membrane materials, the prospects for imaginative new process chemistry have been greatly expanded. There can be no question that the synthesis of organics from nonpetroleum feedstock is extremely important; electrolytic routes based on CO and CO₂ have been known since the mid-1800s and have been vigorously pursued in the laboratory. Similarly, the possibility of paired synthesis (where useful chemical products are made at both electrodes) could offer highly competitive process economics.

In the development of an electrochemical process route, three viewpoints are critically important, namely, those of the *organic electrochemist*, the *electrochemical engineer*, and the *process engineer*. For example, the prospect of using a nonaqueous solvent may intrigue the chemist since wholly new avenues of chemistry would be available in comparison with aqueous chemistry. The electrochemical engineer, however, may express concern over low electrolyte solubility, consequent high power consumption, and poor in-cell mass transfer. The chemical engineer might recognize still other nonelectrochemical implications, such as easier downstream solvent recovery, higher investment cost of solvent inventory, and environmental concern. In the early stages of process development, it is therefore especially critical to incorporate different viewpoints to ensure cost-effective workup.

Many important engineering questions cannot be adequately answered with data from batch-type cells. The early deployment of continuous flow cells is often an important step in obtaining an improved assessment of technical problems and realities. The early identification of gaps in needed process data can also be important. Measurement of heat capacity, enthalpy, solubility, and conductivity, for example, are often required for early evaluation and are often unavailable from literature sources.

The application of computer-based process design simulators to elec-

trochemical process studies would bring a major new engineering methodology into the industrial electrolytic field. More work is needed to identify the type of laboratory and pilot-plant data required to scale-up and design optimum cell configurations and operating conditions. Of particular importance is the need for more investment cost data and estimation procedures for various cell configurations.

The evaluation of competing process routes depends to a great extent on the relative costs of power, feedstock, capital, wastewater treatment, labor, and materials as projected over the lifetime of the process. It would therefore be helpful to examine the effect of such projected future trends on the viability of selected electroorganic processes versus chemical counterparts. Of special importance would be assessment of the effect of decoupling electricity costs from petroleum costs owing to the advent of nuclear or solar generating capability.

This chapter reviews a number of major trends that, taken together, indicate electroorganic synthesis technology has come of age. Our understanding of electroorganic chemistry has advanced toward levels that exhibit more rigorous and more scientific approaches to explaining observed behavior on the basis of molecular events. Electrochemical engineering has become established as a quantitative discipline for the design of cells and processes. As a consequence, chemical engineers are increasingly able to assess electrochemical options for organic synthesis. It is yet to be seen whether these trends will lead to substantial expansion of industrial electroorganic synthesis. It is abundantly clear, however, that the essential groundwork has been laid and the field is ripe for industrial development.

Acknowledgment

The survey of organic electrolytic processes reported in Sections 2 and 4 of this chapter was carried out under Argonne National Laboratory Contract No. 31-109-38-4209 at Electrochemical Technology Corporation. Portions of the work were subcontracted to the University of Illinois and to the Electrochemical Company.

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Chapter X

ECONOMICS OF ELECTROORGANIC SYNTHESIS

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