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**A SURVEY OF ORGANIC
ELECTROLYTIC PROCESSES
Contract No. 31-109-38-4209**

by

ELECTROCHEMICAL TECHNOLOGY CORP.

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS
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FINAL REPORT ON

A SURVEY OF ORGANIC ELECTROLYTIC PROCESSES

PREPARED FOR

THE OFFICE FOR ELECTROCHEMICAL PROJECT MANAGEMENT
ARGONNE NATIONAL LABORATORY
UNDER CONTRACT NO. 31-109-38-4209

BY

ELECTROCHEMICAL TECHNOLOGY CORPORATION
SEATTLE, WASHINGTON 98107

NOVEMBER 1979

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ABSTRACT

The basic objectives of this study were to review the literature to determine the commercial status of electroorganic processes and to estimate whether there would be significant possible energy savings by introduction of electroorganic processes to replace conventional chemical processes for production of certain large-tonnage organic chemicals. A list was compiled of the 220 organic chemicals that were produced at greater than 10,000 tons per year in 1975 in the United States. Search of the Swann and of the Fichter Bibliographies of electroorganic literature yielded references on 95 of these compounds. By application of selection rules to obtain promising candidates, nine chemicals with diverse electrochemical processes were chosen for detailed process energy calculations. Parallel calculations were made for presently-used commercial chemical routes to these products. Two of the nine electrochemical processes, adiponitrile and methyl ethyl ketone, had energy savings in comparison to the corresponding chemical processes. Other more-energy-efficient electrochemical processes are likely among the above 95, although they remain to be identified.

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1.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The basic objectives of this study were to review the literature to determine the commercial status of electroorganic processes and to estimate whether there would be significant possible energy savings by introduction of electroorganic processes to replace conventional chemical processes for production of the highest-tonnage organic chemicals.

The first task was to compile a list of the organic chemicals that were produced at greater than 10,000 tons per year in the United States in 1975. About 220 chemicals are in the list. The Swann Bibliography of electroorganic literature was then machine searched for these compounds by Professor R. C. Alkire and associates at the University of Illinois. A total of 95 chemicals from the above list had electroorganic literature citations. A tabulation of piloted or commercialized electroorganic processes was subsequently prepared by Dr. N. L. Weinberg of the Electrosynthesis Company and is presented in Appendix A of this report. By application of a formulated set of selection rules, Dr. Weinberg also chose eighteen chemicals from the 95 to be considered for process energy calculations and provided from the electroorganic literature a compilation of process reactions, conditions, yields, current efficiencies, and other pertinent data. These process data are given in Appendix B.

Material and energy balances were made at Electrochemical Technology Corp. for chemical and electrochemical processes to produce nine representative chemicals out of the eighteen. Flowsheets and results are given in Section 6. Professor M. A. Stadtherr provided material and energy consumption data compiled from chemical industry sources, presented in Appendix C. He also assessed the potential impact of six of the nine electrochemical processes on the U. S. petrochemical industry as a whole by means of computations with a linear-programming model; results are given in Section 7.

Interest in electroorganic chemical processes has been high during the past two decades; several new processes have been introduced and many more have been patented. Large-scale production of adiponitrile by electroreductive coupling of acrylonitrile was introduced by Monsanto in 1963 and

capacity has since been increased. An electrochemical tetraalkyl lead process has also been introduced, but it is becoming less important because of declining production of tetraalkyl lead compounds for environmental reasons. The BASF Company has recently introduced several electroorganic processes with capacities from a few tons per year up to 500 tons per year in their Ludwigshafen, Germany, plant.

Generally, electroorganic processes can be favorable when the product molecular weight is high, there are fewer than four electrons in the electrolysis step, the yield is high compared to a corresponding chemical route, and the raw materials are less expensive than for the chemical synthesis. The electroorganic route may be the only way to make some desirable products in reasonable yield, and often there are fewer processing steps and fewer pollutants. Many opportunities exist for profitable electroorganic syntheses for some of the many thousands of organic chemicals produced in the world. The increased understanding of electroorganic reactions, the development of electrochemical engineering as a quantitative discipline to quantitatively design cells and processes, and the increasing awareness of electrochemical processing by chemical engineers will lead to more electroorganic processing.

The nine chemicals for which detailed estimation of process energy requirements were made in this study were selected because they were considered to have a reasonable chance of a more-energy-efficient electrochemical route or because they illustrated a particular class of electrochemical reaction. The nine pairs of chemical and electrochemical processes are presented in Table 1.1 with main reactions. 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 to go back to the same raw materials or to basic building blocks such as petroleum-derived hydrocarbons and to ammonia, hydrocyanic acid, etc.

A summary of the process energy requirements for the nine chemicals is given in Table 1.2. The energy requirements include those for chemical and electrochemical reactors and for separation processes. Electrical energy

Table 1.1

Summary of Overall Chemical and
Electrochemical Process Routes and Chemical Reactions

ADIPONITRILE

Chemical Electrochemical

Table 1.1 (continued)

Summary of Overall Chemical and Electrochemical Process Routes and Chemical Reactions

ANILINE

Chemical #1 Chemical #2 Electrochemical

Table 1.1 (continued)

Summary of Overall Chemical and
Electrochemical Process Routes and Chemical Reactions

SORBITOL

Chemical Electrochemical

TEREPHTHALIC ACID

Chemical Electrochemical

Table 1.1 (continued)

Summary of Overall Chemical and
Electrochemical Process Routes and Chemical Reactions

PHENOL

Chemical Electrochemical

Table 1.1 (continued)

**Summary of Overall Chemical and
Electrochemical Process Routes and Chemical Reactions**

METHYL ETHYL KETONE (2-BUTANONE)

Chemical

Electrochemical

MELAMINE

Chemical

Electrochemical

Table 1.1 (continued)

Summary of Overall Chemical and
Electrochemical Process Routes and Chemical Reactions

HYDROQUINONE

Chemical Electrochemical

Table 1.1 (continued)

Summary of Overall Chemical and
Electrochemical Process Routes and Chemical Reactions

DICHLOROETHANE

Chemical #1 Chemical #2 Electrochemical

Table 1.2

Summary of Process Energy Requirements

Chemical		kcal/kg		
		Electro- chem	Chem	
Adiponitrile	1	43,177	65,808	2
Aniline				
Nitrobenzene Route	1	36,172	13,919	
Phenol Route	1	-	16,736	2
Sorbitol		9,649	958	
Terephthalic Acid		17,382	700	
Phenol	1	35,592	12,251	2
Methyl Ethyl Ketone		6,187	6,690	
			3,233	2
Melamine	1	30,159	15,472	
Hydroquinone	1	52,739	30,814	
Dichloroethane				
HCl Route	1	17,773	6,131	
Cl ₂ Route	1		14,819	2

1 Energy charged for hydrocarbon raw materials (different compounds)

2 Chemical route energy from Rudd, et al. (Appendix C, ref 4)

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 assessed 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 1.2. Energy calculations for various raw materials and products are given in Appendix C.

This report gives the first extensive comparison of energy requirements for a significant number of electrochemical versus chemical processes treated in a consistent manner. Some rather firm conclusions can be drawn from the results in Table 1.2 but other conclusions may be regarded as tentative at this time within the accuracy of the results.

The overall errors of the calculations for each process are judged to be less than $\pm 50\%$ based on the level of effort allotted to each process. Only major items of process equipment were considered and many engineering judgements were made as to, for example, the best separation methods and conditions. At most, only one iterative step was made toward optimization for each chemical.

Although every effort was made to make the comparisons based on state-of-the-art technology the information available was not always complete. Chemical process flowsheets were 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 and from recent patents and papers back to a 40 year old process. Thus the "balance sheet" in Table 1.2 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 better 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 by at least 6,600 kcal/kg, and that improvements have been made in the electrochemical process.

It is quite clear from the study results that electrochemical reductions to make aniline and sorbitol are far more energy intensive than catalytic hydrogenations. In fact, the generalization can be made that with the present energy picture and current technology, electrochemical reductions are not competitive on an energy basis with 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 significant energy.

Electrochemical oxidations are likewise at an energy disadvantage to high-yield catalytic air oxidations. The particular case of terephthalic acid was chosen for the purpose of examining an indirect oxidation using the chromic/dichromate couple. One of the process selection rules was broken in this case in that the electrochemical oxidation route requires an overall 12 electrons per mole of terephthalic acid. The final distillation to make polymer-grade material was omitted for simplification for both routes so the energy requirements are low compared to that required for commercial chemical plants.

The electrochemical route to phenol is clearly not attractive on an energy basis. Furthermore, the reported bench scale current densities are low so that electrochemical plant capital cost would be high.

Production of methyl ethyl ketone in an electrochemical fuel cell does appear attractive on an energy basis. 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 but, in principle, it could generate electricity in the electrogenerative mode and increase the energy advantage in respect to the chemical route.

It is clear that the chemical route to melamine is less energy intensive than the electrochemical route. The case is less certain for hydroquinone. Benzene is oxidized to the intermediate, benzoquinone,

electrochemically in a single step in contrast to a multi-step chemical route to this intermediate. Reported current efficiencies are only 40%, however. If the current efficiency could be increased through R&D to 100%, the energy required for the electrochemical route would be at breakeven with the chemical route. On the other hand, newer chemical routes have been put into production; process information was not available to determine their energy requirements.

In-cell halogenations, as used to make dichloroethane, are close to breakeven with the chemical routes which use electrolytically-produced chlorine. More detailed analyses and calculations are required for definitive relative energy requirements for the two routes.

In order to interpret accurately the further conclusions reported below, it is important to recognize that various restraints were set on the scope of this study in order to focus squarely on energy consumption aspects. Therefore the conclusions reached by this DOE study may not correspond to a more balanced perspective with which candidate processes are normally evaluated by the industrial sector. In particular, only large-tonnage organic processes (>10,000 T/yr) were evaluated for energy consumption, without consideration of wastewater treatment, or economics of operating and capital costs.

Within the constraints specified for this study, the electrochemical routes offered energy savings in two of the nine processes summarized in Table 1.2 (adiponitrile and methyl ethyl ketone). Energy savings were particularly significant for adiponitrile, a compound which is presently synthesized commercially by electrolysis.

Energy consumption in large-tonnage electrolysis operations has been found to be associated primarily with two effects:

1. Use of aqueous electrolytes requires large heat loads to separate products by distillation from dilute cell effluents.
2. Electrical energy is currently more expensive than fossil-fuel derived energy by a factor of about three.

Use of separation methods other than solvent distillation, or development of non-aqueous electrolytes, could thus substantially improve energy consumption of electrolytic processes. In the future, electricity will undoubtedly replace fossil fuel as the primary form of energy leading thereby to ever-improved prospects for electrochemical synthesis routes.

Considerable research and development effort has been devoted to current large-tonnage chemical processes to make them economically competitive. With even modest development efforts, it therefore seems reasonable that the energy efficiencies for electroorganic processes estimated here could also be substantially improved.

This study has utilized a previously unavailable data base of electroorganic synthesis processes not previously reported in the literature. Although the constraints on this study were limited to energy efficiency considerations alone, the data base and the methods of evaluation could 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 will surely emerge, not only in the large-tonnage arena considered here but also in the lower-tonnage categories.

The following recommendations are made for further work:

1. Study a larger number of pairs of chemical and electrochemical processes using a computer-implemented process design program to provide a larger data base for development of more rigorous selection criteria for energy-efficient electroorganic processes.
2. Examine the effect of projected future availability and costs of chemical feedstocks and electrical energy on the attractiveness of electroorganic processes.
3. Develop general engineering methods for design of optimum types of cell configurations and operating conditions and for scale-up of electroorganic processes from laboratory data; develop laboratory and pilot plant procedures to obtain the correct type of data required for translation of synthesis concepts into industrial processes.

2.0 INTRODUCTION

A flowsheet based on the proposal (1) showing inputs, operations, and outputs for this study is given in Fig. 2.1. The location at which the work was to be done is indicated under operations; ETC = Electrochemical Technology Corp., U of I = University of Illinois (R. C. Alkire and M. A. Stadtherr), and TEC = The Electrosynthesis Co. (N. L. Weinberg).

A compilation of organic chemicals produced at greater than 10,000 T/yr, operation 1, is given in Table 3.1 in Section 3 of this report. A description of the Swann Bibliography on the electroorganic literature is given in Section 4. The compilation of all electroorganic processes that have been commercialized, past and present, is presented in Appendix A.

Through process selection criteria given in Table 3.2, eighteen of the chemicals from Table 3.1 were selected for further study. A summary of best process data - raw materials, products, yields, current efficiency, etc. - for the eighteen chemicals is presented in Appendix B.

The number of products was narrowed down to nine for further, detailed calculations of material and energy balances for the electrochemical and chemical routes by application of further selection criteria, namely, choosing only one reaction of a class of reactions such as halogenations and weighting more heavily the highest tonnage chemicals. These nine chemicals finally selected are given in Table 1.2. Data for the chemical routes were obtained from an Environmental Protection Agency report (2) and from the open literature.

Methods of calculation are described in Section 5. Certain process-design and calculation rules were developed and codified early in the work in order to treat all processes in a consistent manner. Process descriptions, flowsheets, and results of the energy calculations are presented in Section 6. Overall impact on the United States organic chemical economy of using the more energy-efficient electroorganic processes is given in Section 7. Results are from the computer model of M. A. Stadtherr (U of I). Compilation of by-products from the chemical and electrochemical routes and their environmental impact are given in Section 8.

Figure 2.1 Flowsheet showing steps to achieve study objectives. Inputs, outputs, and location of work are shown.

3.0 CHEMICAL PRODUCTION DATA

A list of organic chemicals produced at greater than 10,000 T/yr (20,000,000 lb/yr) in 1975, compiled from a publication of the United States International Trade Commission (3), is shown in Table 3.1. A few additional chemicals were inserted at the end of Table 3.1 from the compilation for 1976 which became available after this study was initiated. Chemicals were ranked in decreasing order of production and serially numbered for identification in subsequent literature searches.

Regarding the source (3),

"The report consists of fourteen sections, each covering a specified group (based principally on use) of organic chemicals as follows: Tar and tar crudes; crude products from petroleum and natural gas; intermediates; dyes; pigments; medicinal chemicals; flavor and perfume materials; plastics and resin materials; rubber-processing chemicals; elastomers; plasticizers; surface-active agents; pesticides and related products; and miscellaneous organic chemicals. Data have been supplied by approximately 800 producers.

The first table in each section gives statistics on products and groups of products in as great detail as is possible without revealing the operations of individual producers. Statistics for an individual chemical or group of chemicals are given only when there are three or more producers, no one or two of which may be predominant. Moreover, even when there are three or more producers, statistics are not given if there is any possibility that their publication would violate the statutory provisions relating to unlawful disclosure of information accepted in confidence by the Commission.

Data are reported by producers for only those items where the volume of production or sales exceeds 1,000 pounds or the value of sales exceeds \$1,000. They are usually given in terms of undiluted materials; however, products of 95 percent or more purity are considered to be 100 percent pure. Commercial concentrations are applied to dyes, certain plastics and resins, and a few solvents; such concentrations are specifically noted.

The statistics given in this report include data from all known domestic producers of the items covered and include the total output of each company's plants, i.e., the quantities produced for consumption within the producing plant, as well as the quantities produced for domestic and foreign sale. The quantities reported as produced, therefore, generally exceed the quantities reported as sold. Some of these differences, however, are attributable to changes in inventory."

Numbers of citations found in the Swann (4) and Fichter (5) Bibliographies for each compound are shown in the last two columns of Table 3.1. (See Section 4 for description of the bibliographies.) A blank denotes no citations. An "R" in the table indicates generic materials not listed as such in the Swann Bibliography.

The underlined 18 compounds in Table 3.1 are those chosen by Dr. Weinberg for analysis based on selection criteria in Table 3.2. Electrochemical process details for these chemicals are found in Appendix B.

Table 3.1

INDUSTRIAL ORGANIC CHEMICAL PRODUCTION

(1) Chemical	1975 Production (1000 lb/yr)	(2) No. of Swann Citations	No. of Fichter Citations
1 Ethylene	20,499,399	6	4
2 Benzene	7,500,000 (3)	10	1
3 Xylene	4,800,000 (3)		2
4 Toluene	5,000,000 (3)	3	
5 Propylene	8,709,332	4	2
6 <u>1,2-Dichloroethane</u>	7,977,096	9	
7 Urea	7,597,734		7
8 Polyethylene & copolymers resins	7,482,746	R	
9 Ethane	6,304,505	17	6
10 Propane	5,848,797	15	4
11 Methanol	5,176,292	6	1
12 Tar	5,164,296	R	
13 Ethylbenzene	4,822,071	4	1
14 Styrene	4,673,095	2	1
15 <u>Terephthalic acid</u>	4,614,497		11
16 Formaldehyde	4,558,127	17	6
17 Vinyl Resins	4,536,061	R	
18 Ethylene Oxide	4,466,854	2	
19 Vinyl Chloride	4,196,250		
20 Styrene plastics materials	3,877,292	R	
21 Ethylene Glycol	3,809,003	5	2
22 1,2-Butadiene	3,353,153		
23 Styrene-Butadiene type elastomers	2,607,907	R	
24 n-Butane	2,459,999	8	7
25 Acetic Acid	2,197,423	10	7
26 Cumene	2,002,703		

(1) Chemical	1975 Production (1000 lb/yr)	(2) No. of Swann Citations	No. of Fichter Citations
27 Polypropylene resins	1,903,429	R	
28 Polyethylene Terephthalate	1,822,546	1	
29 <u>Phenol</u>	1,746,027	3	1
30 Cyclohexane	1,733,650	3	
31 Acetone	1,650,187	10	2
32 Crude Light Oil	1,558,512	R	
33 <u>Propylene oxide</u>	1,523,613	1	
34 Isopropyl alcohol	1,521,492	16	10
35 Nylon (<u>But add ADN intermed.</u>)	1,504,472	(R)	
36 Acetic Anhydride	1,457,873		
37 1-Butene & 2-Butene	1,451,230	4	7
38 Ethyl alcohol	1,428,764	5	6
39 n-Paraffins	1,360,592	R	
40 Adipic Acid	1,342,942	1	2
41 Vinyl Acetate	1,290,450		
42 Phenolic & other tar acid resins	1,274,869	R	
43 Acrylonitrile	1,214,550	1	
44 Stereo Elastomers	978,324	R	
45 Ligninsulfonates	945,462	R	
46 Creosole oil	918,680	R	
47 Urea-formaldehyde resins	909,243	R	
48 Carbon Tetrachloride	906,489	3	1
49 Polyester resins	802,126	R	
50 Phosgene	796,141		1
51 Acrylic resins	773,342	R	
52 1,6-Hexanediamine	749,589	5	

(1) <u>Chemical</u>		1975 <u>Production</u> (1000 lb/yr)	(2) <u>No. of</u> <u>Swann</u> <u>Citations</u>	<u>No. of</u> <u>Fichter</u> <u>Citations</u>
53	Isobutane	746,038	1	
54	Cellulose Acetate	725,925	R	
55	Caprolactam	713,293		
56	Phthalic Anhydride	702,186	1	
57	Tetrachloroethylene	679,140		1
58	Isobutylene, 2-butene & mixed butylenes	640,558	2	
59	Phthalic anhydride type alkyd resins	614,776	R	
60	Mixtures of alcohol	575,777		
61	Chloroethane	575,174	1	
62	Cyclohexanone	553,663	5	3
63	Methyl Methacrylate	545,624		
64	Butyraldehyde	532,661	2	2
65	Polyacrylonitrile & acrylonitrile copolymers	528,670	18	
66	Dichloromethane	497,119	3	6
67	Alkyl Benzenes	495,248		
68	n-Butyl Alcohol	489,616	5	3
69	Carbon Disulfide	479,289		
70	Toluene 2,4- & 2,6-diisocyanate	478,790		
71	<u>2-Butanone</u>	424,929	3	
72	1,1,1-Trichloroethane	458,763		
73	Nitrobenzene	414,288	8	2
74	<u>Aniline</u>	406,930	16	8
75	Dichlorodifluoromethane	393,098		1
76	Propylene Glycol	390,836	2	

(1)	1975	(2)	
<u>Chemical</u>	<u>Production</u>	<u>No. of</u>	<u>No. of</u>
	<u>(1000 lb/yr)</u>	<u>Swann</u>	<u>Fichter</u>
		<u>Citations</u>	<u>Citations</u>
77 2-Ethyl-1-hexanol	387,232		
78 Chloromethane	366,449	2	
79 Dodecylbenzenesulfonic acid Na ⁺	331,551		
80 Alpha Olefins	327,754	R	
81 Diethylene Glycol	322,622		
82 Tallow acids, Na ⁺	315,521	R	
83 Tetraethyl lead	314,589		
84 2,4-Dinitrotoluene	308,257		
85 <u>Chlorobenzene</u>	306,030	4	5
86 Di(2-ethylhexyl)phthalate	301,492		
87 Petroleum hydrocarbon resins	299,030	R	
88 4,4'-Isopropylidenediphenol	292,909		
89 Trichloroethylene	292,714		1
90 Nonene	287,702		
91 Dodecene	287,238		
92 <u>1,2-Dibromoethane</u>	275,156	1	
93 Acetylene	272,914		
94 2,4 & 2,6 Dinitrotoluene	272,610		
95 Trichlorofluoromethane	269,611		
96 Oil-soluble petroleum sulfonates	265,617	R	
97 Engineering Plastics	266,007	R	
98 Chloroform	261,740	6	3
99 Hexane	251,552	5	5
100 Polymethylene polyphenylisocyanate	247,242		
101 Isoprene	243,586	1	
102 Ethyl Acrylate	239,978		1

	(1) <u>Chemical</u>	1975 <u>Production</u> <u>(1000 lb/yr)</u>	(2)	No. of Fichter Citations
			No. of Swann Citations	
103	Heptanes	224,262	2	5
104	Maleic Anhydride	215,828	1	
105	Acrylic Acid	215,195	3	8
106	<u>Toluene-2,4-diamine</u>	191,009	3	2
107	Unmodified Epoxy Resins	182,807	R	
108	Isobutylene-isoprene type elastomers	182,039	R	
109	Butyl Acrylate	178,554		
110	2-Ethoxyethanol	178,537		
111	Polyurethane and diisocyanate resins and urethane type elastomers	177,141	R	
112	Ethyl acetate	171,162		7
113	Dodecylbenzenesulfonic acid	169,241		
114	Isobutyl alcohol	157,609		1
115	Cellulosic plastics & resins	156,840	R	
116	4-Methyl-2-pentanone	150,190		
117	Melamine-formaldehyde resins	147,852	R	
118	Glycerol	136,259	2	
119	<u>Sorbitol</u>	133,643	5	1
120	Chlorodifluoromethane	131,913	1	
121	2-Butoxyethanol	130,558		
122	Coconut oil acids, Na ⁺	129,222	R	
123	Tar, refined	127,696	R	
124	Phosphorodithionates	121,842	R	
125	Polyamide resins	119,719	R	
126	Acrylonitrile-butadiene type	118,767	R	

		(2)		
(1)		1975	No. of	No. of
<u>Chemical</u>		<u>Production</u>	<u>Swann</u>	<u>Fichter</u>
		<u>(1000 lb/yr)</u>	<u>Citations</u>	<u>Citations</u>
127	Propyl Alcohol	115,989	2	4
128	Naphthalene	109,919	2	
129	Diisodecyl Phthalate	105,668		
130	Pentaerythritol	100,598	1	
131	2-Methoxyethanol	90,389		
132	Cresols	93,220	2	12
133	Triethanolamine	89,457		
134	Triethylene Glycol	88,528		
135	Melamine	85,894		
136	2,2'-Aminodiethanol	85,599		
137	1,2-Dichloropropane	84,233		
138	2-Aminoethanol	82,678		
139	n-Butyl Acetate	80,341		
140	Dicyclopentadiene	77,823		
141	Epoxidized soya oils	77,621	R	
142	Polyester resins	76,765	R	
143	Phenol Salts	70,704	2	
144	α & β Pirene	70,215	R	
145	Heptenes	67,565	2	
146	Silicone Fluids	67,462	R	
147	Polyethylene Glycol	64,822		
148	Rosin Modifications	64,196	R	
149	Benzoic Acid	63,216	9	15
150	Sodium Carboxymethyl cellulose	63,325	R	
151	Hexamethylenetetramine	61,619		

(1) <u>Chemical</u>	1975 <u>Production</u> <u>(1000 lb/yr)</u>	(2) <u>No. of</u> <u>Swann</u> <u>Citations</u>	<u>No. of</u> <u>Fichter</u> <u>Citations</u>
152 Coumarone-indene resins	60,949	R	
153 Stearic Acid salts	58,187		11
154 o-Dichlorobenzene	54,679		1
155 o,o-Dimethyl-O-p-nitrophenyl phosphorothioate	53,668	R	
156 Propionic Acid	50,892	1	6
157 (Ethylenedinitrilo) tetraacetic acid, tetrasodium salt	50,070		
158 Biphenyl	47,956	6	5
159 Bis(hydrogenated tallow alkyl) dimethylammonium chloride	46,539	R	
160 p-dichlorobenzene	45,755		
161 4-Methyl-3-penten-2-one	45,685		
162 Cresylic Acid	44,852		
163 Crude tar acid oils	42,352	R	
164 Naphthenic acid	41,873		
165 Dithiocarbamic acid salts	40,666		
166 4-Hydroxy-4-methyl-2-pentanone	39,522		
167 Intermediate light oil	39,472	R	
168 Pentachlorophenol	39,447		
169 Dipropylene Glycol	39,005		
170 2-[2-(2-methoxyethoxy)ethoxy] ethanol	38,967		
171 Choline Chloride	38,702		
172 Advanced Epoxy resins	37,067	R	
173 Dimethylamine	37,011	1	1
174 Methylbromide	36,048		

	(1) <u>Chemical</u>	1975 <u>Production</u> <u>(1000 lb/yr)</u>	(2)	
			<u>No. of</u> <u>Swann</u> <u>Citations</u>	<u>No. of</u> <u>Fichter</u> <u>Citations</u>
175	Propyl Acetate	35,398		
176	Polypropylene Glycol	34,863		
177	Xylenesulfonic acid, sodium salt	33,820		
178	Formic Acid, Na ⁺	33,235	16	
179	Polybasic acid type alkyd resins	32,638	R	
180	2-2-(Ethoxyethoxy)ethanol	32,376		
181	2-Ethyl-1-hexyl-acrylate	32,308		
182	Silicone type elastomers	31,221	R	
183	<u>Salicylic acid</u>	30,605	1	5
184	N-(1,3-Dimethylbutyl)-N'-phenyl- p-phenylene diamine	30,525		
185	Di-(2ethylhexyl)adipate	30,302		
186	α Methylstyrene	29,856		
187	Styrene-butadiene-vinylpyridine type elastomers	29,500	R	
188	2-[2-(2-ethoxyethoxy)ethoxy] ethanol	27,716		
189	Ethyl Ether	27,629		
190	Toluenesulfonic acid, K ⁺ & Na ⁺	27,379		2
191	2-2(Butoxyethoxy)ethanol	26,759		
192	Styrene alkyd polyester resins	26,736	R	
193	Polyacrylamide	26,276	9	
194	2,4-Dichlorophenoxyacetic acid, dimethylamine salt	25,697		
195	Aspirin	25,434		
196	Polyamide resins	24,362	R	
197	Glycerol Monostearate	23,029		

(1)	1975	(2)	
<u>Chemicals</u>	<u>Production</u>	No. of	No. of
	<u>(1000 lb/yr)</u>	<u>Swann</u>	<u>Fichter</u>
		<u>Citations</u>	<u>Citations</u>
198 Acetic Acid Salts	22,356	1	
199 Coconut oil acids	21,660	R	
200 Butylamines	21,086	3	
201 Fumaric Acid	20,817	1	
202 p-tert-Butylphenol	18,041		
203 <u>Tetrafluoroethylene</u>	17,296	1	
204 2,6-Ditertbutyl-p-cresol	17,100		
205 Dodecyl sulfate	16,853		
206 <u>Hydroquinone</u>	16,575	23	16
207 <u>2,2'-Dithiobis(benzothiazole)</u>	16,368	1	
208 Naphtha	16,360	R	
209 2(2-Methoxyethoxy)ethanol	15,673		
210 Di-tridecylphthalate	15,664		
211 Tetraethylene Glycol	15,005		
212 Trimethylamine	14,163	1	

Notes:

- (1) Underlined chemicals - electroorganic energy studies to be made
- (2) R indicates rejection from Swann Bibliography search because not a specific compound
- (3) Chemicals out of order in production sequence.

ADDITIONAL CHEMICALS

(1) <u>Chemical</u>	1976 Production (1000 lb/yr)	(2) No. of Swann Citations	No. of Fichter Citations
213 Isobutyraldehyde	372,071	1	
214 Polybutene	283,256	R	
215 Monoethylamine	36,806	2	
216 Monoisopropylamine	33,353	1	2
217 <u>Quinone (intermediate for Hydroquinone)</u>		28	15
218 Phenyl hydrazine		5	
219 O-amino benzyl alcohol		2	
220 1, 4-cyclohexadiene		5	
221 Semicarbazide		5	
222			
223			
224 Phthalide		3	

Table 3.2

Process Selection Rules

(For the 18 chemicals in Appendix B)

- Only processes for which product cost is greater than raw materials costs.
- Only processes for which there is published electroorganic literature sufficient to formulate a flowsheet.
- Only processes for which there are fewer than 6-8 electrons per molecule, and product molecular weight is reasonably high.
- No hydrocarbons which are produced by efficient catalytic routes.
- No polymers, except nylon which is based on adiponitrile.
- No pollutants presently being phased out, e.g., tetraalkyl lead.

4.0 SWANN BIBLIOGRAPHY LITERATURE SEARCH

4.1 Description of Data Base

- 4.1.1 "Bibliography of Electro-organic Synthesis Literature, 1801-1975", S. Swann, Jr. and R. Alkire, Electrochemical Society, Princeton, N.J., 1979.

The Swann Bibliography contains approximately 12,000 citations which had been compiled from various sources. Citations of original articles and patents were examined for the present contract (31-109-38-4209-Organic).

Original article citations after 1907 were obtained from Chemical Abstracts (6) Sections as follows:

Biology	#6, 9, 10
Organic	#21 - 34
Polymers	#35
Applied Chemistry	#60
Physical Chemistry	#72, 80

Earlier abstract sources which predate Chemical Abstracts include:

Annales de Chimie

Chemisches Zentralblatt

Jahrsbericht "über die Fortschritte der reinen pharmaceutischen und technischen Chemie (1849 - 1910)

Abstracts of the Journal of the Chemical Society (1873 - 1907)

Abstracts of the Société Chimique de France (1897 - 1907)

In addition, raw literature was scanned for all pertinent journals not covered by the foregoing abstracting services, and for journals which pre-dated the foregoing services.

Patents were obtained by search in the U. S. Patent Office up to such dates that they began to be included in Chemical Abstracts. The patent offices of certain foreign countries were visited in order to scan for early patents not contained in the collection of the U. S. Patent Office. These countries included Italy (prior to 1927), France (prior to 1903), England, and Canada. Every attempt was made to arrive at a complete list of U. S. patents, and patents in the English language.

The foregoing bibliography is a sequel to that of Fr. Fichter, cited below, and thus contains none of the references given by Fichter except duplicates which appeared in another language than the citation given by Fichter. The Swann Bibliography contains a number of early references not reported by Fichter.

- 4.1.2 "Organische Electrochemie," Fr. Fichter, Steinkopff, Dresden, 1942; reprinted by Edwards Bros., Ann Arbor, MI, 1946; available from University of Microfilms International, Ann Arbor, MI. (5)

The bibliographic compilation of Fichter is organized with respect to the reaction which occurs: electrolysis of organic acids, enolate and metalorganic reactions, oxidations, substitutions, reduction of nitro-derivatives, and other reductions. In addition, an author index and subject index are provided. However, Fichter does not provide Chemical Abstract reference data for any citations.

4.2 Use of Data Base

4.2.1 Scientific Publications

The Swann Bibliography was, at the time of this contract, in the process of being indexed for computer retrieval of data. In particular, all reaction products reported in yields of 10% or more were collected in a Product Index. Such data were obtained from notes kept by Swann and/or by examination of Chemical Abstracts. No attempt was made to re-scan raw literature. Nomenclature for reaction product names followed IUPAC convention except in cases where trivial names (Merck Index) were clear.

Some of the high-tonnage chemicals listed by the U. S. Tariff Commission (3) were generic by nature (tar, crude light oils, silicone fluids, stereo elastomers, etc.) and therefore did not appear in the Product Index of the Swann Bibliography. Citations for such syntheses were therefore not obtained; these compounds are denoted by "R" in Table 3.1.

For each citation identified in the above manner, the notes of Swann and/or Chemical Abstracts were examined. The Fichter Bibliography

search also began by using the Subject Index for each compound of interest. Processes involved obviously unattractive feedstock material or reaction conditions were recorded but not examined further (for example, production of chloroform from the potassium salt of hexanoic acid). For the remaining citations, the notes of Swann and/or copy of Chemical Abstract was forwarded to Dr. Weinberg. At his request, copies of original articles were made and distributed. The numbers of citations found in the Swann and Fichter Bibliographies which made reference to high-tonnage chemical candidates are listed in Table 3-1.

4.2.2 Patents

The Swann Bibliography contains approximately 2,800 patent citations; the patents are not indexed for reaction product information. A listing of patents was provided to Dr. Weinberg who indicated those for which additional information was desired. Copies of the notes of Swann and/or Chemical Abstracts were made and forwarded to Dr. Weinberg.

5.0 ENERGY CALCULATIONS - METHODS

The basic flowsheet for an electroorganic process is shown in Fig. 5.1. The cells and the separation and purification steps are energy intensive. Electricity is generally the only energy applied to the cells; it causes the electrochemical reactions to occur and generates by-product heat, often requiring cooling. Thermal energy is used for the separations and purifications. Feed preparation usually requires a minor amount of energy, such as for mixing, and was usually neglected. In the case of chemical processes, the cells are replaced by a reactor that may require thermal energy.

During the calculations, a set of process design rules shown on Table 5.1 were formulated to help meet the objective of consistent treatment of each process. A current chemical route was used for comparison to each electrochemical route. The current chemical routes were obtained where possible from a recent Environmental Protection Agency report on the organic chemicals industry (2). When there was a choice of more than one currently active chemical process, one was chosen that was as similar as possible to the electrochemical process in order to obtain a more accurate energy comparison.

The electrochemical processes were based on the largest scale data available; plant, pilot plant, and laboratory, in that order. All electrochemical process calculations were based on continuous processes, even if the data were from batch experiments. Cell designs were based on state-of-the-art technology, such as metal anodes and membranes, even if the data were for older technology. Membranes or other separators were not used if they could be avoided because of voltage penalty and a necessity to remove water transported through membranes with the conducting ion. Three moles of water per hydrogen ion passing through a membrane were usually assumed for acid electrolytes (7). Hydrogen by-product was credited at the gross heat of combustion, assuming it would be burned under a boiler. No energy credit was given for oxygen by-product because it is not generally economic to collect from cells.

Product separation energy requirements were calculated for each separation process. Energy requirements for liquid-liquid extraction and

Fig. 5.1 Electrochemical Process Material and Energy Streams

Table 5.1

Process Design Rules

- Current chemical route insofar as known used for comparison.
- Electrochemical and chemical routes as similar as possible.
- Electrochemical processes will be based on largest scale data available because in general these are more complete and accurate.
- All electrochemical processes will be continuous.
- Cells will be based on state-of-the-art technology, e.g., metal anodes, membranes.
- Membranes or other separators are not used unless essential.
- Cation membranes are preferred because they have reached a higher state of art.
- Atmospheric pressure cells used unless otherwise specified.
- Hydrogen by-product will be credited at $\Delta H_{\text{combust}}$ thermal.
- No credit for oxygen by-product.
- Product separation energy requirements based on key component binary separation.
- When thermodynamics dictates that a reaction does not go to completion, 100% of the equilibrium conversion will be assumed.
- All compressors and pumps are electrically driven.
- Only consider pumps and compressors for high-pressure reaction; no transfer pumps.
- Neglect energy cost of vacuum.

for phase separations were assumed negligible. Energy requirements for distillation were based on heat required for boiling the bottoms for a column with constant reflux ratio.

In chemical reactors an equilibrium conversion was assumed when thermodynamics indicated that the reaction did not go to completion.

For auxiliary equipment, only pumps and compressors for high-pressure reactors were considered; no transfer or recycle pumps were considered. Compressors were assumed to be electrically driven for the purpose of energy calculations. Energy cost of obtaining a vacuum for stills and evaporators was not considered because it is usually small.

In some cases the chemical and electrochemical processes use entirely different raw materials. It was then necessary to assign energy costs to the raw materials to put both routes on a consistent basis. A list of energy costs for common raw materials is given in Table 5.2. These costs were based on published process energy data, and calculations are given in Appendix C. Hydrocarbons were assessed their gross heat of combustion; if they had not been used in the process they could have been burned under a boiler to produce steam. Although steam boiler efficiency is about 82% and, therefore, hydrocarbons might be assessed 82% of their heat of combustion, there are also drilling, pumping, and refining energy costs (not estimated). For these reasons it was decided to assess at the full heat of combustion.

An energy balance for a continuous electrochemical reactor at steady state is given in Fig. 5.2. The algebraic sum of the enthalpies of formation of reactants and products and the electrical and thermal energy is zero. The heat of reaction is the sum of the products of the component flow rates and their heats of formation. Usually a cell reaction is endothermic; the electrical potential applied drives a reaction that would otherwise require a higher temperature. Usually the electrical energy into the cell exceeds the endothermic heat of reaction due to ohmic and activation overpotentials, and a net amount of heat is generated that must be removed by heat exchange or boiling the electrolyte.

Table 5.2

Assigned Thermal Energy Costs of Chemical Raw Materials

<u>Chemical</u>	<u>kcal/kg</u>
Hydrocarbons	$\Delta H_{\text{combustion}}^*$
Hydrogen	
steam reforming of hydrocarbons	49,000
water electrolysis (at 1.5 V)	105,770
NH ₃	9,000
HCN	18,000
HNO ₃	3,100
Urea	6,400
O ₂ from air	964
Chlorine (prorated 50% with NaOH)	5,875
NaOH (prorated 50% with Cl ₂)	5,875
H ₂ SO ₄	29
Iron	4,050
Air	zero
Water	zero
MnO ₂	zero

* Table C-1, Appendix C

Fig. 5.2 ENERGY BALANCE FOR CONTINUOUS REACTOR
AT STEADY STATE

$$q_r + q_p + EI + Q = 0$$

$$q = \sum_{i=1}^n N_i \Delta H_{fi} \quad \begin{array}{l} N_{ri} \text{ is } + \\ N_{pi} \text{ is } - \end{array}$$

$$\Delta H_f = \Delta H_{fg} - \Delta H_v$$

Heats of formation of most organic compounds have not been experimentally determined, including most of the compounds used or produced in the processes under study in this report. Fortunately, the American Society for Testing and Materials (ASTM) had available a program called CHETAH - Chemical Thermodynamic and Energy Release Evaluation Program (8) - which allowed estimation of values of ΔH_f . The program furnishes good to excellent estimates of the enthalpy, entropy, and heat capacities from 300°K to 1500°K for a virtually unlimited number of organic and organometallic compounds. CHETAH is based on the second order method of Benson (9) and the method of group equations; it determines the foregoing properties for the ideal gas state. Heats of vaporization must, therefore, also be estimated for compounds that are liquid or solid at the reaction temperatures.

Specific dc electrical energy consumption for an electrochemical product is related to cell voltage and current efficiency by

$$\text{Sp. E.} = \frac{z_1 F V}{3600 e M} = 26.806 \frac{z_1 V}{e M} \text{ kWh/kg, or } 23,060 \frac{z_1 V}{e M} \text{ kcal/kg} \quad (1)$$

The cell voltage is composed of the equilibrium thermodynamic potential and the irreversible potentials due to slow kinetics, mass transport, and to ohmic losses in electrolyte, separators, electrodes and buswork,

$$V = E_e + \eta_q + \eta_c + \eta_r \quad (2)$$

Various sources of current inefficiency are shown in Fig. 5.3. The desired product is P_1 from reactant R_1 produced by a z_1 electron reaction. Product P_1 may further react to form by-product P_1' by a z_1' electron reaction, or reactant R_1 may be consumed by a parallel z_1'' reaction to give by-product P_1'' . Either case results in a loss in yield. Another source of current inefficiency is another solution component (such as the solvent), R_2 reacting by a z_2 electron reaction to form by-product P_2 . A third source of current inefficiency is a redox couple R_3/P_3 which cycles back and forth between electrodes giving no overall chemical change but using electrons and generating heat. Electronic conduction by the electrolyte is rare and was not considered for organic processes. Short circuits through electrolyte conduits between cells also cause effective current efficiency losses in

Fig. 5.3 Definitions

(electronic conduction not considered)

Short circuits through electrolyte conduits between cells also cause effective current efficiency losses in series cell lines and in bipolar electrode cells.

series cell lines and in bipolar electrode cells. Current efficiency is then

$$\epsilon_1 = \frac{z_1 N_{p1}}{\sum_i z_i N_{pi}} \quad (3)$$

Overall yield or conversion per pass may be defined by

$$Y = \frac{N_{p1} \text{ (actual)}}{N_{p1} \text{ (stoichiometric from } R_1)} \quad (4)$$

Knowing desired production rate and product current efficiency, the cell current can be calculated from

$$I = \frac{z_1^{FN} N_{p1}}{\epsilon_1} \quad \text{Amperes} \quad (5)$$

Electrical energy consumption rate is

$$VI = \frac{z_1^{FVN} N_{p1}}{\epsilon_1} = 23,060 \frac{z_1^{VN} N_{p1}}{\epsilon_1} \quad \text{kW} \quad (6)$$

The calculations for the chemical and electrochemical processes in this report were done manually. It was discovered too late in the study that a chemical process design program called FLOWTRAN was available to DOE contractors. Use of FLOWTRAN should be considered if further process comparisons are to be made.

The following guidelines were used throughout for process equipment calculations unless there existed a compelling reason for changing the procedure:

1. Thermodynamic Data:

The required thermodynamic information was obtained from many sources. The following source list is in decreasing order of preference:

- a. JANAF Thermochemical Tables, 2nd Ed. (10)
- b. The Chemical Thermodynamics of Organic Compounds (11)
- c. The Properties of Gases and Liquids (12)
- d. Chemical Engineers Handbook (13)

- e. Physical Properties (14)
- f. Lange's Handbook of Chemistry (15)
- g. The Merck Index (16)
- h. CHETAH Program (8)
- i. Thermochemical Kinetics (9)
- j. Kirk - Othmer (17)
- k. Lowenheim (18).

Heat of vaporization data were obtained wherever possible from the above sources. When the temperature dependence of the heat of vaporization was needed, the Watson relation was used:

$$\Delta H_{v2} = \Delta H_{v1} \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38} \quad (7)$$

in which T_r is reduced temperature.

Critical properties were taken from Michael and Thodos (19), and Kudchadker, Alani, and Zwalinski (20), in addition to the above listed sources. Where critical properties were unavailable, Lydersen's method of group contributions was used. Where required, vapor pressure data were obtained by integrating the Clausius - Clapeyron equation in the following form:

$$\ln \frac{P_2}{P_1} = \frac{\lambda}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8)$$

from the normal boiling point to the required temperature (T_2). In some cases the integration was from 298°K to T_2 . The smallest temperature difference was always used. When no heat of vaporization data were available they were estimated using the Riedel method (21).

Wherever possible the heats of formation were obtained for the physical states [solid (c), aqueous (aq), etc.] of the compounds as they exist in the process equipment. In some cases this was not possible; the heats of formation were unavailable for several compounds in solution (sorbitol for instance). Most of the compounds in this category probably exhibit small heats of solution, so the heat of formation of the compound in the crystalline

or liquid state was used. This procedure ignores the heat of solution.

The temperature variation of the heat capacity was ignored in most instances.

2. Phase Equilibria:

Solubility data were taken from Seidell (22) as well as those sources listed under thermodynamic information.

In aqueous and organic phases the complex phase equilibrium of multicomponent mixes is generally unknown. Where binary data were available they were used irrespective of the concentration of other components. No salting out or other ternary effects were considered.

In liquid phases ideal vapor-liquid equilibrium was assumed, i.e., Raoult's law was assumed valid.

Solid phases were assumed to be present as pure compounds.

3. Separation Methods:

The separation methods considered in this study include filtering, centrifuging, settling, phase separation (either liquid-liquid or gas-liquid), and distillation.

Filtering and Washing Operations. In filtering centrifuges the residual moisture was assumed to be 10% by weight.

The wash water for these processes was assumed to be 1 kg wash water/1 kg product.

Sedimentation type separators were assumed to produce underflow streams at 20% by volume solids.

Liquid-Liquid Phase Separators. Aqueous solutions were assumed to be immiscible in organic phases unless other information was available.

Distillation. All the distillation separations were handled as binary separations even if multicomponent systems were involved. The basic approach is outlined in Treybal (23), and the following equation has been used to calculate the minimum reflux ratio (R_m):

$$R_m = \frac{1}{\alpha - 1} \left[\frac{X_D}{X_F} - \frac{\alpha(1 - X_D)}{1 - X_F} \right] \quad (9)$$

where X_D and X_F are the mole fractions of the light component in the distillate and feed respectively, and α is the relative volatility of the light component. When dealing with multicomponent systems, X_D and X_F were based on the light and heavy key components as though they were the only compounds present. The key components have been assumed, not evaluated, in each case. After the minimum reflux ratio was known, the actual reflux ratio was calculated as 1.25 times R_m . The reboiler duty (Q_{reb}) was then calculated as,

$$Q_{reb} = \lambda_{Ave} (R + 1) D$$

where

D = distillate rate (mole/sec),

R = actual reflux ratio ($1.25 R_m$), and

λ_{Ave} = average heat of vaporization, all individual lambdas calculated at the average column temperature.

The average column temperature was taken as the mean of the top and bottom temperatures.

The preceding equation applies to liquid feed at the bubble point. No attempt to calculate bubble points was made in this study. The heat loads on the reboilers may be in error by a few kcal/sec. The sensible heat to bring the feed to the bubble point was ignored.

4. Definitions:

Yield was used below to indicate the fraction of primary reactant ultimately converted to desired product. It refers to the overall plant process and is independent of recycle streams. Conversion, on the other hand, is concerned with the reactor or cell. It represents the fraction of limiting reactant which is converted to product on each pass through the reactor. Both the conversion and yield are affected by side reactions, but the conversion can be lower than the yield when recycle is used.

5. Optimization:

Processes were not optimized. At most only one iterative step was made toward optimization for each chemical.

6.0 ENERGY CALCULATIONS - RESULTS

Chemical products chosen for study based on the process selection rules in Table 3.2 are shown in Table 6.0. The chemicals are categorized by cathodic, anodic, and anodic-halogenation reactions to produce them. Within each category they are ranked in decreasing order of production rate according to Table 3.1; the rank from Table 3.1 is indicated. Present chemical processes for these chemicals were taken from the EPA compilation (2) if available there; the EPA numbers are noted. Descriptions of electrochemical processes to produce these chemicals are presented in Appendix B.

After the material and energy balance calculations were underway it was apparent that only about one-half of the list could be considered in the detail necessary for valid comparisons of energy requirements for the chemical and electrochemical routes, within the time and budget allowed. The final selection (with asterisk in Table 6.0) was based on the further criteria: selection of various representative types of electrochemical reactions, and weighting the selection toward the higher-production chemicals. Thus, only one halogenation was selected as representative of this class of reactions. Aniline was selected over toluene-2,4-diamine based on higher production and similarly for phenol over salicylic acid. Ethylene oxide was studied previously (24) and the electrochemical route was found to have a slight advantage in respect to energy required. Propylene oxide should have a similar advantage for the electrochemical route.

Flowsheets, stream conditions, and results of the energy calculations for the chemical and electrochemical routes to the nine selected chemicals are given in the following subsections 6.1 through 6.9. Each flowsheet has associated with it a table of stream conditions with the same number.

Table 6.0
Processes Chosen

	<u>No.</u>		<u>EPA No.</u>
<u>Cathodic</u>	*	35 (Nylon) Adiponitrile	
	*	74 Aniline	31
		106 Toluene-2,4-diamine	343
	*	119 Sorbitol	
<u>Anodic</u>	*	15 Terephthalic Acid	362A, B
	*	29 Phenol	37, 295
		33 Propylene Oxide	286, 328
	*	71 Methyl Ethyl Ketone (2 Butanone)	55, 56
	*	135 Melamine	
		183 Salicylic Acid	303A, B
	*	206 Hydroquinone (Anodic to Quinone 6 e ⁻)	16
		207 Dithiobis (2,2-Dithiobisbenzothiazole)	
<u>Anodic Halogenation</u>			
	*	6 Dichloroethane	131, 132
		85 Chlorobenzene	4
		92 1,2-Dibromoethane	
		137 1,2-Dichloropropane	
		203 Tetrafluoroethane	
	-	2,4-Dichlorophenol	

*Processes chosen for detailed material and energy balance calculations given in subsections 6.1 through 6.9.

6.1 Adiponitrile from Acrylonitrile (Electrochemical)

The electrochemical production of adiponitrile from acrylonitrile is a commercial process. The process description was obtained from Weinberg (Appendix B, adiponitrile), Brubaker, et al. (25), Danly and Giblin (26), Campbell and Johnson (27), and Danly (28). The flowsheet is given in Fig. 6.1 and the stream conditions in Table 6.1.1.

The reaction sequence for this process is as follows:

Anode

Cathode

Primary Overall

The heat of reaction for the primary overall reaction at 298°K is

$$\Delta H_{298} = 53.36 \text{ kcal/mole adiponitrile.}$$

The secondary reaction producing propionitrile has a heat of reaction,

$$\Delta H_{298} = 35.86 \text{ kcal/mole propionitrile.}$$

These reactions are carried out in a membrane cell which is assumed to pass three moles of water per mole of hydrogen ions. The catholyte consists of an aqueous mixture of adiponitrile, acrylonitrile, and a quaternary ammonium salt (assumed to be tetra-ammonium-para-toluene sulfonate, for which an aqueous phase heat capacity of 0.38 cal/g°C was assigned). The quaternary ammonium salt (QAS) increases both the solubility of organic compounds and the conductivity of the catholyte. The cells are assumed to operate at 6 V.

Fig. 6.1 Electrochemical Route to Adiponitrile

Table 6.1.1

Stream Conditions for Adiponitrile Process
Electrochemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6
Flows						
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
Stream No.	7	8	9	10	11	12
Flows						
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			
Stream No.	13	14	15	16	17	18
Flows						
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
Stream No.	19	20	21	22	23	
Flows						
C ₃ H ₃ N	138.19	18.69				
H ₂ O					75.00	
C ₆ H ₈ N ₂				9.26		
C ₃ H ₅ N	8.13	1.10	1.10			

Equipment Conditions

	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

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.

Acrylonitrile forms an azeotrope with water. This fact was ignored in the water evaporator and third distillation column calculations since no information on this mixture was available.

Energy requirements for the chemical and electrochemical routes to adiponitrile are given in Table 6.1.2. The energy for the chemical route was based on a compilation by Rudd and Stadtherr (40); time available did not allow a complete calculation on this process. The energy requirement figure in Table 6.1.2 is based on data given in Table C-0 and on p C24 of Appendix C. The total of 65,808 kcal/kg includes the energy required to make butadiene and the gross heating value of its butylene feedstock. A newer process, commercialized in 1972, that does not use chlorine (42) has superseded the older process for which data are tabulated. Not using chlorine would save 6,668 kcal/kg and decrease the energy for the chemical route to 59,140 kcal/kg, but the overall energy savings for the newer process were not calculated due to lack of sufficient information.

The energy requirement calculated for the electrochemical route agreed with the data of Rudd and Stadtherr (40) for fuel oil equivalent energy to within 8%. To put the electrochemical route on a comparable basis as 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. The electrochemical route appears to have a significant saving in energy as compared to the chemical route.

Table 6.1.2

Adiponitrile Energy Requirements

Basis: 1 kg (9.26 g mol)

<u>Chemical Route</u>	<u>kcal</u>
du Pont adiponitrile from butadiene	
ADN	65,808*

<u>Electrochemical Route</u>		
Cell	(2,868/0.325)	= 8,825
Evaporator (H ₂ O)		1,730
Distillation No. 1		1,229
Distillation No. 2		358
<u>Distillation No. 3</u>		<u>773</u>
Total		12,915

Comparison to data from Appendix Table C-0

<u>Electrochemical Route</u>		
FOE	(1.14) (10,430)	= 11,890
Sohio acrylonitrile from propylene		
<u>AN</u>	(1.09) (28,704)*	= <u>31,287</u>
Total		43,177

*Appendix C-12, p C24

6.2.1 Aniline from Nitrobenzene (Chemical)

The production of aniline from nitrobenzene is outlined by Lowenheim (18). Other sources include Kirk-Othmer (17), Hydrocarbon Processing (29), and EPA 600 Report (2).

The process flowsheet in Fig. 6.2.1 shows the process to be a fairly simple one with one phase separator, an absorber, and a distillation column. The reactor is operated at about 270°C and 2.35 atmospheres of pressure. The primary reaction is

The heat of reaction at 298°K is

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

The same heat of reaction has been assumed at 270°C. The conversion per pass has been assumed to be 100%, and the yield has likewise been assumed to be 100%.

From the reactor the product stream, containing aniline, passes through a cooler where aniline and water are condensed out. Hydrogen is recycled from the cooler to the reactor. After the cooler the aniline-water mixture enters a phase separator from which the organic aniline-rich phase passes to the aniline still. In the still, aniline is separated as bottoms product; and the distillate, water rich, is recycled to the phase separator. The water rich phase from the separator is stripped of aniline by fresh nitrobenzene feed which is then sent to the reactor.

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 distillation column and preheat the nitrobenzene feed. The condenser with cooling to 100°C could generate 223 kcal/sec of usable heat, and the heat of reaction (1051 kcal/sec) is available at 270°C. Since the overall process is highly exothermic, this energy would have to be sold to a consumer outside the plant.

Fig. 6.2.1 Aniline from Nitrobenzene, Chemical

Table 6.2.1

Stream Conditions for Aniline from Nitrobenzene
Chemical Route - Flow units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
H ₂ O						21.50	21.50
C ₆ H ₅ NO ₂	10.75	10.75					
H ₂			32.25	64.50	96.75	64.50	
C ₆ H ₅ NH ₂		0.15				10.90	10.90
Stream No.	8	9	10	11	12	13	
Flows							
H ₂ O	4.16	21.06	4.16	21.50	21.50		
C ₆ H ₅ NH ₂	5.38	16.28	16.13	0.15		10.75	

Equipment Conditions

	Reactor	Condenser Cooler	Phase Sep.	Liq-Liq Ext.	Aniline Dist.
T (°C)	270	25	25	25	141-185
P (atm)	2.35	1	1	1	1
Q (kcal/sec)	-1051	-509			13.5

6.2.2 Nitrobenzene from Benzene and Nitric Acid (Chemical)

The nitrobenzene process is described in the EPA 600 Report (2).

The process flowsheet is given in Fig. 6.2.2. This is an extremely simple process involving only the phase separator and one distillation column. The reactor operates at 50°C and one atmosphere pressure. The reaction is

At 298°K the heat of reaction is

$$\Delta H_{298} = -31.60 \text{ kcal/mole nitrobenzene.}$$

The conversion and yield have each been assumed to be 100%. No correction was made for the heat of reaction at 50°C.

The phase separator splits the aqueous phase away from the nitrobenzene phase which, without further purification, is suitable for use as feed for the aniline process. The water generated in the reactor is removed by distillation, and the sulfuric acid catalyst is recycled to the reactor. The water-still bottoms are used to preheat the column feed.

Fig. 6.2.2 Nitrobenzene from Benzene, Chemical

Table 6.2.2

Stream Conditions for Nitrobenzene from Benzene
Chemical Route - Flow units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
C_6H_6	8.13						
HNO_3		8.13					
H_2SO_4			mu*	7.36	7.36	7.36	
H_2O				5.82	5.82	13.95	
$C_6H_5NO_2$						8.13	8.13
Stream No.	8	9	10	11			
Flows							
H_2SO_4	7.36	7.36	7.36				
H_2O	13.95	13.95	5.82	8.13			

Equipment Conditions

	Reactor	Phase Sep.	H_2O Dist.
T ($^{\circ}C$)	50	25	100-246
P (atm)	1	1	1
Q (kcal/sec)	-257		104

* Makeup

6.2.3 Aniline from Nitrobenzene (Electrochemical)

The electrochemical production of aniline as described by Weinberg (Appendix B), and Swaminathan (Appendix B, Aniline, 5), is presented in the flowsheet in Fig. 6.2.3.

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

Anode

Cathode

Primary Overall

The heat of reaction for the overall reaction at 298°K is

$$\Delta H_{298} = 71.94 \text{ kcal/mole aniline.}$$

Solubility data for para-aminophenol and aniline were taken from the Merck Index (16), as was the vapor pressure of aniline. The heat capacity of para-aminophenol has been assumed equal to that for aniline on a weight basis.

The calculations for the individual equipment pieces are straight forward. No energy credit has been given for the heat evolved in the acid neutralizer. If the neutralizer operated at a higher temperature than 25°C, some of that heat could be used in the aniline evaporator.

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.

Fig. 6.2.3 Aniline from Nitrobenzene, Electrochemical

Table 6.2.3

Stream Conditions for Aniline from Nitrobenzene
Electrochemical Route - Flow units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
C ₆ H ₅ NO ₂	11.45			11.45			
H ₂ SO ₄		5.73	5.25	10.98	5.25	5.25	
H ₂ O			305.80	305.80	294.00	252.05	64.38
C ₆ H ₅ NH ₂ Sulf.			1.29	1.29	12.04	12.04	
P Amino Phenol Sulf.			15.78	15.78	16.48	16.48	
TiO ₂			0.63	0.63	0.63	0.63	
Stream No.	8	9	10	11	12	13	14
Flows							
H ₂ O	59.72	4.66	5.97	127.00	4.24		148.67
C ₆ H ₅ NH ₂ Sulf.			10.75				
P Amino Phenol Sulf.			0.70				
P Amino Phenol						0.70	
NaOH				11.46			
C ₆ H ₅ NH ₂					2.00	12.75	
Na ₂ SO ₄							5.73
Stream No.	15	16	17	18	19	20	
Flows							
H ₂ O	0.42					41.95	
P Amino Phenol	0.70	0.70					
C ₆ H ₅ NH ₂		2.00	10.75				
H ₂					0.34		
O ₂				17.00			

Equipment Conditions

	Cell	Xtallizer	Centrif Wash 1	Acid Neut	Centrif Wash 2	Aniline Evap.
T (°C)	25	25	25	25	25	102
P (atm)	1		1		1	0.07
VI (kcal/sec)	7839					
Q (kcal/sec)	-7027	441		-153		179

Energy requirements for the chemical and electrochemical routes to aniline are compared in Table 6.2.4. The electrochemical route has a decided energy disadvantage compared to the chemical route, primarily because of the high energy requirement for the cells.

Table 6.2.4

Aniline Energy Requirements

Chemical Route to Nitrobenzenekcal

(Basis: 1 kg = 8.13 g mol)

Benzene	(8.13)(78.12)(10.117) =	6,425
HNO ₃	(8.13)(63.01)(3.100) =	1,588
H ₂ SO ₄	(recycled)	-
<u>H₂O Distillation</u>		<u>104</u>
Total		8,117

Chemical Route to Aniline

(Basis: 1 kg = 10.75 g mol)

Nitrobenzene (10.75 g mol)	(10.75/8.13)(8,117) =	10,733
Hydrogen (32.25 g mol)	(32.25)(2.016)(49.000) =	3,186
<u>No thermal credit taken</u>		<u>-</u>
Total		13,919

Electrochemical Route to Aniline

Cell	(7,839/0.325) =	24,120
Crystallizer		441
<u>Aniline evaporator</u>		<u>179</u>
Process energy		24,740
<u>Nitrobenzene (11.45 g mol)</u>	(11.45/8.13)(8,117) =	<u>11,432</u>
Total		36,172

6.3.1 Sorbitol from Glucose (Chemical)

The production of sorbitol from glucose is described by Lowenheim (18), and Fedor, et al. (30). The flowsheet is given in Fig. 6.3.1.

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

The heat of reaction at 298°K is

$$\Delta H_{298} = -16.15 \text{ kcal/mole sorbitol.}$$

No correction was made for the heat of reaction at 200°C. The conversion and yield of this reaction were both assumed to be 100%.

The reaction products flow from the reactor to a filter and phase separator where the hydrogen is collected and recycled to the reactor. The nickel catalyst is filtered off (20% solids assumed) and recycled to the reactor as well. The sorbitol-water solution then passes to an evaporator where the water is driven off to produce the product, 83% sorbitol, mixture.

The product stream leaving the reactor was assumed to preheat the inlet reactants.

Hydrogen gas was assumed to be available at one atmosphere pressure, and a four-stage compressor with intercooling to 25°C was used to raise the pressure to 140 atmospheres.

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

Fig. 6.3.1 Sorbitol from Glucose, Chemical

Table 6.3.1

Stream Conditions for Sorbitol Process
Chemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6
T (°C)	25					
P (atm)	1					
Flows						
H ₂	5.49				5.49	5.49
C ₆ H ₁₂ O ₆		5.49			5.49	5.49
H ₂ O			54.90		54.90	54.90
Ni (cat.)				0.34	0.34	0.34
C ₆ H ₁₄ O ₆				0.49	0.49	0.49
Stream No.	7	8	9	10	11	12
T (°C)	161	120	153	200		95
P (atm)	175	175	175			
Flows						
H ₂	5.49	1.43	6.92	1.43	1.43	1.43
H ₂ O				55.39	55.39	
Ni (cat.)				0.34	0.34	
C ₆ H ₁₄ O ₆				5.49	5.49	
Stream No.	13	14	15			
Flows						
H ₂ O	54.90	43.53	11.37			
C ₆ H ₁₄ O ₆	5.49		5.49			

Equipment Conditions

	Reactor	Filter Sep.	Evap.	Comp. 1	Comp. 2
T (°C)	200	95	95		
P (atm)	140	140	1		
W (kcal/sec)				20.4	0.24
Q (kcal/sec)			352		

6.3.2 Sorbitol from Glucose (Electrochemical)

The electrochemical reduction of glucose to sorbitol is described by Creighton (Appendix B, sorbitol, U.S. Patent No. 1,990,582), Taylor (Appendix B, sorbitol, 2), Creighton (Appendix B, sorbitol, 4), Sanders and Holes (Appendix B, sorbitol, 5) and by Mantell (Appendix B, sorbitol, 6). The flowsheet is given in Fig. 6.3.2.

The chemical reaction sequence is:

Anode

Cathode

Primary Overall

The heat of reaction for the primary overall reaction at 298°K is

$$\Delta\text{H}_{298} = 52.16 \text{ kcal/mole sorbitol.}$$

The reactor conditions are stated to be (Weinberg, Appendix B): $T = 25^\circ\text{C}$, and one atmosphere pressure. A conversion of 100% has been assumed for the reactor. The conversion to sorbitol takes place in the cathode compartment of the cell, which has been assumed to contain a cation membrane. The membrane passes three moles of water for each mole of hydrogen ions. The cells are assumed to operate at 6 V with cation membranes in contrast to 20 V for the earlier commercial cells with alundum tube separators.

From the cathode the product stream passes to a crystallizer-filter where sodium sulfate is extracted as a solid. The sorbitol is extracted, in this same equipment, with ethanol. The ethanol-sorbitol mix then passes to the ethanol evaporator where the alcohol is driven off and the sorbitol goes through another water wash to eliminate the final traces of alcohol.

Fig. 6.3.2 Sorbitol from Glucose, Electrochemical

Table 6.3.2

Stream Conditions for Sorbitol Process
Electrochemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6
Flows						
$C_6H_{12}O_6$	5.49			5.49		
H_2O		96.20	8.20	104.40	141.00	42.70
Na_2SO_4			1.93	1.93	1.93	
$C_6H_{14}O_6$					5.49	
C_2H_5OH			4.84	4.84	4.84	
Stream No.	7	8	9	10	11	12
Flows						
H_2O	27.75	70.45	166.65			9.32
C_2H_5OH						83.35
H_2				0.61		
O_2					3.05	
Stream No.	13	14	15	16	17	18
Flows						
H_2O	142.12	125.56	267.68	116.61	151.07	141.75
$C_6H_{14}O_6$	5.49	16.15	21.64	21.64		
C_2H_5OH	83.85	7.43	91.28	7.43	83.85	
Stream No.	19	20	21	22		
Flows						
H_2O	7.43	149.18	18.80	11.37		
$C_6H_{14}O_6$			5.49	5.49		

Equipment Conditions

	Cell	Xtallizer Filter	Ethanol Evap.	Dist	Dry
T ($^{\circ}C$)	25	25	89	78 - 100	100
P (atm)	1	1	1	1	1
VI (kcal/sec)	1688				
Q (kcal/sec)			2539	1795	121

A centrifuge and dryer are then used to produce the final 83% sorbitol product.

This process is quite straightforward and the primary energy demand, other than 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.

Energy requirements for the chemical and electrochemical routes to sorbitol are compared in Table 6.3.3. 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.

Table 6.3.3

Sorbitol Energy Requirements

Basis: 1 kg (5.49 g mol)

<u>Chemical Route</u>			<u>kcal</u>
Compressor No. 1	(20.4/0.325)	=	63
Compressor No. 2	(0.24/0.325)	=	1
H ₂ O evaporation			352
H ₂	(5.49) (2.016) (49.000)	=	542
<u>Total</u>			<u>958</u>
<u>Electrochemical Route</u>			
Cell	(1,688/0.325)	=	5,194
Ethanol evaporation			2,539
Ethanol distillation			1,795
<u>Dryer</u>			<u>121</u>
<u>Total</u>			<u>9,649</u>

6.4.1 Terephthalic Acid from Xylene (Chemical)

The production of terephthalic acid (TPA) from para-xylene is discussed in the EPA 600 Report (2), and Hydrocarbon Processing (31), as well as by Lowenheim (18), and Sherwood (32). The flowsheet is given in Fig. 6.4.1.

The reaction involved is the air oxidation of para-xylene to TPA,

The enthalpy of reaction at 298°K is

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

This reaction takes place in a reactor operating at 200°C and 27 atmospheres pressure. The reaction is conducted in the liquid phase with an acetic acid solvent. All thermodynamics involving the mixing process have been ignored. The conversion in the reactor has been assumed to be 50% with the ultimate yield, based on xylene, of 100%. An acetic acid-xylene ratio of one has been assumed for the stream leaving the reactor.

When the products exit the reactor, they are cooled in a crystallizer where the TPA precipitates from solution. No allowance was made for the solubility of TPA in the water-xylene-acetic acid mixture at 40°C. The solid TPA containing some residual solution is then washed, first with acetic acid, then with water, after which it is dried to the final crystalline form.

The solution from the crystallizer contains water, xylene, and acetic acid. Water and some of the acetic acid are separated by distillation, and the remaining mix is recycled to the reactor.

The largest energy requirements for this process are from the first distillation column and the air compressor, for which three stages have been assumed. No credit has been given for the heat of reaction which is more than enough to make this process energy self-sufficient. Use should be made of this heat since the reactor is the highest temperature unit in the process.

Fig. 6.4.1 Terephthalic Acid from p-Xylene, Chemical

Table 6.4.1

Stream Conditions for Terephthalic Acid Process
Chemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6
T (°C)	25	25	127	200	128	200
P (atm)	27	1	27			
Flows						
C ₈ H ₁₀	6.02			6.02	6.02	
H ₂ O				12.04		
acetic acid				6.02	6.02	
C ₈ H ₆ O ₄				6.02		
O ₂		20.07	20.07			2.01
N ₂		75.44	75.44			75.44
Stream No.	7	8	9	10	11	12
T (°C)	40	25				
P (atm)	1	1	1	1	1	1
Flows						
C ₈ H ₁₀	0.25					
H ₂ O	0.50					0.50
acetic acid	0.25	0.95	1.00	1.95	0.95	1.25
C ₈ H ₆ O ₄	6.02				6.02	0.25
Stream No.	13	14	15	16	17	18
T (°C)		20	20			100
P (atm)	1	1	1	1	1	1
Flows						
C ₈ H ₁₀				5.77	6.02	
H ₂ O	231.20	231.10	3.02	11.54	12.04	12.04
acetic acid		0.95	6.02	5.77	7.02	
Stream No.	19	20	21	22	23	24
T (°C)	128					
P (atm)	1	1	1	1	1	1
Flows						
C ₈ H ₁₀	6.02	5.16	0.86	0.86		
H ₂ O					3.02	
acetic acid	7.02	6.02	1.00			
C ₈ H ₆ O ₄						6.02

Equipment Conditions

	Compress.	Dryer	Dist. 1	Dist. 2
T (°C)	127	100	100 - 128	118 - 138
P (atm)	27	1	1	1
Q (kcal/sec)	206	64	411	19

6.4.2 Terephthalic Acid from p-Xylene (Electrochemical)

The electrochemical production of terephthalic acid (TPA) is discussed by Weinberg (Appendix B, terephthalic acid) and by Engelbrecht (Appendix B, terephthalic acid, 6), Bondarenko and Tomilov (Appendix B, terephthalic acid, 7), Mantell (Appendix B, terephthalic acid, 8), and McKee and Leo (33). The flowsheet is given in Fig. 6.4.2.

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:

Anode

Cathode

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. It is assumed that some type of porous synthetic coating could be applied to the cathode to prevent reduction of dichromate in acid solution like the action of chromic hydroxide in neutral solutions.

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

The heat of reaction for this reaction is

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

Fig. 6.4.2 Terephthalic Acid from p-Xylene, Electrochemical

Table 6.4.2

Stream Conditions for Terephthalic Acid Process
Electrochemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6	7
T (°C)	25	40	32.5	55	35	100	40
P (atm)	1	1	1	1	1	1	1
Flows							
C_8H_{10}	6.02	6.02	12.04			6.02	
H_2O				1140.00		1188.16	1188.16
H_2SO_4				209.45		173.30	173.30
$Cr(SO_4)_{1.5}$				24.10		48.20	48.20
CrO_3				24.10		0	0
$C_8H_8O_2$					6.02	6.02	6.02
$C_8H_6O_4$						6.02	6.02
Stream No.	8	9	10	11	12	13	14
T (°C)	25	40	55	130	137	60	55
P (atm)	1	1	1	1	1	1	1
Flows							
H_2O	48.40	1235.55	100.00	100.00	84.72	84.72	
H_2SO_4		173.30	18.37	18.37	18.37	18.37	
$Cr(SO_4)_{1.5}$		48.20	2.11	2.11	2.11	2.11	
CrO_3		0	2.11	2.11	2.11	2.11	
O_2							4.02
Stream No.	15	16	17	18	19	20	21
T (°C)	55	40	7	35			7
P (atm)	1	1	1	1	1	1	1
Flows							
H_2O		1.01					1.01
$C_8H_8O_2$		6.02	6.02				
$C_8H_6O_4$		6.02					6.02
H_2	44.15						
Ether			6.02	6.02	1.49	7.51	1.49
Stream No.	22	23	24	25			
T (°C)			137				
P (atm)	1	1	1	1			
Flows							
H_2O	1.01	1.01	15.20				
Ether	1.49						
$C_8H_6O_4$				6.02			

Equipment Conditions

	Cell	Reactor	Boiler	Eth. Evap.	Refrig.	Dryer
T (°C)	55	100	137	35	-73	100
P (atm)	1	1	1	1	1	1
VI (kcal/sec)	6180					
Q (kcal/sec)	(-2196)	(-2185)	160	48	364	60

The enthalpies of formation of aqueous chromium ions were taken from Latimer (34). The primary overall reaction for the entire process is

The enthalpy of reaction is

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

The second reactor operates at a chromic acid conversion per pass of 100%, but on a xylene basis 50% conversion was assumed.

After leaving the reactor the product stream is cooled, and the solid TPA is filtered out of solution. The solution is then recycled to the cell; the solid phase, consisting of terephthalic acid, partially converted para-toluic acid, and entrained water, is then washed with ether. The toluic acid passes into solution in the ether, but the TPA does not. After subsequent ether evaporation the toluic acid is recycled to the reactor where the conversion to TPA is completed. The TPA leaving the ether wash is dried to produce the final product. Ether is recycled.

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. The water wash has been assumed to be 0.4 kg water for each kg of solid.

Energy requirements for the chemical and electrochemical routes to terephthalic acid are compared in Table 6.4.3. Only the process energies are listed because 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 Table C-0 in Appendix C, based on plant data. The reason for the higher actual 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

Table 6.4.3

Terephthalic Acid Energy Requirements

Basis: 1 kg (6.02 g mol)

<u>Chemical Route</u>		<u>kcal</u>
Compressor		206
Dryer		64
Distillation No. 1		411
<u>Distillation No. 2</u>		<u>19</u>
Total		700
 <u>Electrochemical Route</u>		
Cell	(6,180/0.325)	= 19,015
Boiler		160
Ether evaporation		48
Refrigeration	(364/0.325)	= 1,120
Dryer		60
<u>Hydrogen credit</u>	(44.15) (2.016) (33.944)	= <u>-3,021</u>
Total		17,382

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 6-0. 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.

6.5 Phenol from Benzene (Electrochemical)

The electrochemical conversion of benzene to phenol is reviewed by Weinberg (Appendix B, phenol, electrochemical), by Tomat and Vecchi (Appendix B, phenol, 2), and Steckhan and Wellmann (Appendix B, phenol, 6). The process flowsheet is given in Fig. 6.5.

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

Anode

Cathode

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,

This reaction has an exothermic heat,

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

A conversion of 4% has been used for the cell with a yield of 100%. As in the previous cases, three waters per hydrogen ion are assumed to pass through the membrane.

Fig. 6.5 Phenol from Benzene, Electrochemical

Table 6.5.1

Stream Conditions for Phenol from Benzene
Electrochemical Route - Flow units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
O ₂	5.34	18.77	24.11				
H ₂ O				262.55		225.00	
C ₆ H ₆							10.64
H ⁺					75.09		
Stream No.	8	9	10	11	12	13	14
Flows							
H ₂ O	3737.45		3737.45	4000.00	4000.00		262.55
C ₆ H ₆		269.90	286.54	270.00		270.00	
H ₂ SO ₄	25.00		25.00	25.00	25.00		
FeSO ₄	0.80		0.80	0.80	0.00		
C ₆ H ₅ OH	52.00	10.69	62.69	73.33	52.00	21.33	
Stream No.	15	16	17	18	19	20	
Flows							
C ₆ H ₆	133.71	135.22	136.19	0.97	0.97		
C ₆ H ₅ OH		10.69	10.69		10.64	10.64	

Equipment Conditions

	Cell	Phase Sep	H ₂ O Evap.	Xtallize Centrif	Dry
T (°C)	50	25	50	25	25
P (atm)	1	1		0.12	0.12
VI (kcal/sec)	6928				
Q (kcal/sec)	-7472		4610	1083	8

From the cell the catholyte enters a phase separator which splits off the organic phase of benzene and phenol. The aqueous phase is recycled to the cathode compartment after water has been removed by evaporation. The organic phase enters the crystallizer section where benzene is evaporated. The solid phenol is separated by centrifuge, washed, and dried to form the final product. All the benzene is recycled to the cathode compartment of the cell.

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.

Energy requirements for the chemical and electrochemical routes to phenol are compared in Table 6.5.2. The chemical route is based on ref 40. 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 sizeable cell energy requirement for an overall six-electron reaction.

Table 6.5.2

Phenol Energy Requirements

Basis: 1 kg (10.64 g mol)

		<u>kcal</u>
<u>Chemical Route via Cumene</u>		12,251*
<u>Electrochemical Route</u>		
Cell	(6,928/0.325)	= 21,317
H ₂ O evaporation		4,610
Crystallizer - centrifuge		1,083
Dryer		8
Benzene	(10.64) (78.12) (10.117)	= 8,409
<u>Oxygen</u>	(5.34) (32.00) (0.964)	= <u>165</u>
Total		35,592

*Appendix C-12

6.6.1 Methyl Ethyl Ketone from Butene (Chemical)

The thermochemical production of methyl ethyl ketone (MEK) from butene is discussed in the EPA 600 Report (2), and Lowenheim (18). The process flowsheet is shown in Fig. 6.6.1.

The first reaction occurs in the aqueous phase as the absorption of butene in concentrated (75%) sulfuric acid. The reactor is operated at 25°C and 6.8 atmospheres. The reaction is

No heat of formation was found for the product. A conversion of 100% was assumed.

The second reaction is merely the hydrolysis of the butyl hydrogen sulfate to form butanol,

A conversion and yield of 84% was taken as appropriate for this reaction. The remainder of the butyl hydrogen sulfate was assumed to be converted to a heavy tar.

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 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 thence to a gas phase catalytic reactor. The aqueous phase is recycled to the hydrolysis reactor.

The gas phase reactor operates at 450°C and one atmosphere with the reaction

Fig. 6.6.1 Methyl Ethyl Ketone from n-Butene, Chemical

Table 6.6.1

Stream Conditions for n-butanone Process
Chemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6	7
T (°C)	25						
P (atm)	6.8						
Flows							
C ₄ H ₈	16.50						
C ₄ Sulfate					16.50		
H ₂ O		32.83	59.77	26.94	59.77	88.20	285.69
H ₂ SO ₄		3.30	32.99	29.69	16.50		
C ₄ H ₁₀ O							8.68
Tar			7.33	7.33	7.33		
Stream No.	8	9	10	11	12	13	14
T (°C)		27	27	102		132	25
P (atm)		1	1	1			
Flows							
C ₈ H ₁₈ O		0.91					
H ₂ O	373.89		359.01	359.01	285.69	73.32	
H ₂ SO ₄			32.99	32.99		32.99	
C ₄ H ₁₀ O	8.68		22.55	22.55	22.55		13.87
Tar			8.14	8.14		8.14	
Stream No.	15	16	17	18	19	20	21
T (°C)	25	25	341	450	350	100	182
Flows							
H ₂ O						43.38	29.94
H ₂ SO ₄							32.99
C ₄ H ₁₀ O	2.45	16.32	16.32	2.45	2.45		
C ₄ H ₈ O				13.87	13.87		
Tar							8.14
H ₂				13.87	13.87		
Stream No.	22	23	24	25			
T (°C)	182	182					
Flows							
H ₂ O	3.00						
H ₂ SO ₄	3.30						
C ₄ H ₈ O		13.87		13.87			
Tar	0.81						
H ₂			13.87				
C ₄ H ₁₀ O		2.45					

Equipment Conditions

	HX	Reactor	Dist. 1	Dist. 2	Dist. 3
Q (kcal/sec)	623.01	276.61	4907.01	480.04	1352.26

The heat of reaction at 700°K is

$$\Delta H_{700} = 13.81 \text{ kcal/mole MEK.}$$

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 butene feed was assumed to be a liquid, and no compressor costs were assigned.

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.

6.6.2 Methyl Ethyl Ketone from Butene (Electrochemical)

The electrochemical production of 2-butanone (MEK) from butene is discussed in a series of patents by Worsham (Appendix B, methyl ketones, 9), and by Griffin (35). The process flowsheet is given in Fig. 6.6.2.

The cation membrane electrochemical cell operates at about 80°C, and at one atmosphere pressure. The reaction sequence is:

Anode

Cathode

Primary Overall

The heat of reaction for this overall reaction is

$$\Delta H_{350} = -64.4 \text{ kcal/mole MEK.}$$

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

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

Fig. 6.6.2 Methyl Ethyl Ketone from Butene, Electrochemical

Table 6.6.2

Stream Conditions for 2-butanone Process
Electrochemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6	7
T (°C)	25	80	151	80	170	80	
P (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			
Stream No.	8	9	10	11	12	13	
T (°C)	80	80	25				
P (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						

Equipment Conditions

	Cell	Vac. Still	Dist. 1	Dist. 2
T (°C)	80			
P (atm)	1	14 mm	1	3
VI (kcal/sec)	0			
Q (kcal/sec)	0	3300	1710	47

been given, i.e., 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 6.6.3. 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 reasons for the difference between the plant data from Table C-0 in Appenidx C and the study calculations for the chemical route are not known.

Table 6.6.3

Methyl Ethyl Ketone Energy Requirements

Basis: 1 kg (13.87 g mol)

<u>Chemical Route</u>	<u>kcal</u>
Heat exchanger	623
Reactor	277
Distillation No. 1	4,907
Distillation No. 2	480
Distillation No. 3	1,352
<u>H₂ credit</u>	<u>(13.87)(2.016)(33.944) = - 949</u>
Total	6,690
Appendix C-12 (comparison)	3,233*

<u>Electrochemical Route</u>	
Cell (short circuit fuel cell)	-
Vacuum Distillation	3,300
Distillation No. 1	1,710
<u>Distillation No. 2</u>	<u>47</u>
Total	5,057

*Appendix C-12

6.7.1 Melamine from Urea (Chemical)

The process producing melamine from urea is described by Kirk-Othmer (36), Lowenheim (18), and Mackay (37). The process discussed here is represented in the flowsheet in Fig. 6.7.1.

The primary reaction produces cyanamide, ammonia, and carbon dioxide from urea. The cyanamide trimerizes in excess ammonia to yield melamine. The overall reaction is

The heat of reaction at 298°K is

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

Melamine is a volatile solid; however, no information on the vapor pressure was available. The heat of sublimation was not calculated since Benson's (9) estimation methods produced unreasonable results. The heat of formation for crystalline melamine was taken from Stull (11). The conversion and yield in the reactor were assumed to be 92% with the remaining 8% of urea forming biuret. The reactor operates at 350°C and 8 atmospheres with a solid catalyst. The reactants and products are assumed to all be in the gas phase inside the reactor; however, no adjustment has been made for the heat of reaction given above because of the limited information available for melamine.

From the reactor the gaseous products move to a gas scrubber where they are cooled. The carbon dioxide and ammonia are absorbed by water as ammonium carbamate ($\text{CH}_6\text{N}_2\text{O}_2$). The solubility and vapor pressure of this chemical are unknown. The solubility has been assumed high, and the vapor pressure is probably low. Excess ammonia passes out the top of the gas scrubber and is recycled to the reactor.

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 moves 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

Fig. 6.7.1 Melamine from Urea and NH_3 , Chemical

Table 6.7.1

Stream Conditions for Melamine from Urea
Chemical Route - Flow units are in g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
$(\text{NH}_2)_2\text{CO}$	51.76						
NH_3		mu	27.00	27.00			
H_2O					61.04	14.34	75.38
Stream No.	8	9	10	11	12	13	14
Flows							
NH_3	76.69	49.69	49.69	tr	49.69	tr	
H_2O		75.38	7.54	6.80	14.34	67.84	61.04
CO_2	23.81	23.81	23.81	tr	23.81	tr	
Biuret	2.07	2.07				2.07	2.07
$\text{C}_3\text{N}_3(\text{NH}_2)_3$	7.94	7.94				7.94	7.94
Stream No.	15	16	17	18	19	20	21
Flows							
NH_3	46.69						
H_2O				61.04	5.55	5.55	
CO_2	23.81						
Biuret			2.07				
$\text{C}_3\text{N}_3(\text{NH}_2)_3$					7.94		7.94

Equipment Conditions

	Reactor	Gas Scrub	Thickener	Dist.	Cond.	Xtalliz	Dry
T ($^{\circ}\text{C}$)	350	25	60	60-	60		100
P (atm)	8	8	1			0.13	1
Q (kcal/sec)	1378		1007	69	-145	610	00

driven off and the solid product separated by a centrifugal filter. After drying the final product is formed.

The ammonia-carbon dioxide stream produced over the thickener is assumed to be recycled to a urea plant where it will ultimately be recycled to the urea feed. A credit has, therefore, been given for the thickener off-gasses.

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

6.7.2 Melamine from Hydrogen Cyanide (Electrochemical)

The electrochemical production of melamine from cyanide is reviewed by Weinberg (Appendix B, melamine), and discussed by Forman and Sprague (Appendix B, melamine, 1); and Sprague, et al., (Appendix B, melamine, 3). The process discussed below is presented in the flowsheet of Fig. 6.7.2.

The reactions in the electrochemical cell are:

Anode

Cathode

In order to maintain the required acid/base balance in the cell it is operated under conditions whereby one mole of NH_3 per mole of H_2 leaves the cathode compartment in the gas stream. A chemical reaction takes place in the anolyte

The primary overall reaction can thus be written,

The overall reaction heat at 298°K is

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

The electrochemical cell is assumed to contain a membrane which passes three water molecules for each cation. 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,

Fig. 6.7.2 Melamine from HCN and NH₃, Electrochemical

Table 6.7.2

Stream Conditions for the Melamine Process
Electrochemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
HCN	23.78			23.73			
H ₂ O		142.68	1745.00	1887.68	1745.00		1745.00
NH ₄ Br			173.00	173.00	149.22	23.78	173.00
HBr			18.65	18.65	18.65		18.65
CNBr					23.78		23.78
THF						2.88	2.88
Stream No.	8	9	10	11	12	13	14
Flows							
H ₂ O		142.68		261.58	119.00		261.58
CNBr	23.78						
THF	2.88						
NH ₃		23.78		23.78		23.78	
H ₂		23.78	23.78				
Stream No.	15	16	17	18	19	20	21
Flows							
NH ₄ Br		23.78					
THF	43.79	46.82	43.94	43.94		43.94	43.94
NH ₃	23.78				23.78	23.78	23.78
CN ₂ H ₂		23.78	23.78	23.78			
Melamine						7.93	7.93
Stream No.	22	23	24	25	26	27	28
Flows							
H ₂ O			5.55		5.55		
Melamine	7.93		7.93				7.93
Stream No.	29	30	31				
Flows							
H ⁺	23.78						
NH ₄ ⁺		23.78					
H ₂ O			142.68				

Table 6.7.2 (continued)

Stream Conditions for the Melamine Process
Electrochemecal Route - Flow Units are g mol/sec

Equipment Conditions

	<u>Cell</u>	<u>Abs.</u>	<u>Dist.</u>	<u>Strip</u>	<u>Reactor 1</u>	<u>Centrif. 1</u>	<u>Reactor 2</u>
T (°C)	25	25	16 - 167	63 - 105	43	25	200
P (atm)	1	1	7.3		1	1	100
VI (kcal/sec)	3400						
Q (kcal/sec)	(-2244)		183	4932	(-1389)		(-453)

	<u>Centrif. 2</u>	<u>Xtallizer</u>
	<u>Dry</u>	<u>Dry</u>
T (°C)	25	100
P (atm)	3.2	1
Q (kcal/sec)	15	88

The heat of reaction at 298°K is

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

The conversion is assumed to be 100%. 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,

The heat of reaction is

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

One hundred percent conversion is assumed.

The melamine is separated from the tetrahydrofuran in a centrifuge and then dried. After a water wash and final drying the product is ready for sale.

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.

Energy requirements for the chemical and electrochemical routes to melamine are compared in Table 6.7.3. The electrochemical energy requirements are significantly greater than those of the chemical route largely because of the cell and the CNBr stripper.

Table 6.7.3

Melamine Energy Requirements

Basis: 1 kg (7.93 g mol)

<u>Chemical Route</u>	<u>kcal</u>
Reactor	1,378
Thickener	1,009
Steam stripper	69
Crystallizer	618
<u>Dryer</u>	<u>88</u>
Total	3,162
<u>Credit (heat exchange)</u>	<u>- 410</u>
Net	2,752
Urea	(51.76) (60.0) (6.400) = 19,876
<u>NH₃ credit</u>	<u>(46.69) (17.03) (9.000) = -7,156</u>
Total	15,472

Electrochemical Route

Cell	(3,400/0.325)	= 10,462
CNBr stripper		4,932
NH ₃ still		183
THF dryer		15
<u>H₂O evaporator</u>		<u>88</u>
Total		15,680
<u>Credits (heat exchange)</u>		<u>- 736</u>
Net		14,944
HCN	(23.78) (27.03) (18.000)	= 11,570
<u>NH₃</u>	<u>(23.78) (17.03) (9.000)</u>	<u>= 3,645</u>
Total		30,159

6.8.1 Hydroquinone from Benzoquinone (Chemical)

This process is described in the EPA 600 Report (2) and additionally in the same references quoted for the benzoquinone chemical route. The flowsheet is given in Fig. 6.8.1. The reaction takes place at 70°C and one atmosphere with the consumption of iron,

The heat of reaction at 298°K is

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

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

No attempt to separate the iron oxide from iron was made. The process is characterized by a large volume of water due to the low solubility of hydroquinone. Solubility data were taken from Lange's Chemical Handbook. The solubility of hydroquinone at 70°C was assumed to be 9% by weight.

The vacuum evaporator was assumed to run at the reactor temperature of 70°C.

The process might be ended after the first vacuum evaporator, but in the more realistic situation, the hydroquinone is washed with dilute sulfuric acid solution. The dissolver is at a higher temperature than the precipitator; however, no energy charge was made for this equipment since it was assumed that the heat from the water evaporator could be utilized. The precipitator is an exothermic unit. The literature gave no data on the volume of sulfuric acid present in the wash loop. This secondary wash process consumes about 546 kcal/sec of thermal energy.

Fig. 6.8.1 Hydroquinone from Benzoquinone, Chemical

Table 6.8.1

Stream Conditions for the Hydroquinone Process
Chemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6
Flows						
C ₆ H ₄ O ₂	9.08			5.44	5.44	
Fe		11.64			5.59	
H ₂ O	4.58		1292.41	48.67	1336.58	50.00
Fe ₂ O ₃					3.03	
C ₆ H ₆ O ₂			11.37		20.45	
Stream No.	7	8	9	10	11	12
Flows						
C ₆ H ₄ O ₂	5.44					
Fe	5.59					
H ₂ O	50.00	1336.58	1437.15	144.74	111.01	10.44
Fe ₂ O ₃	3.03					
C ₆ H ₆ O ₂		20.45	11.37			9.08
Stream No.	13	14	15			
Flows						
Fe			5.59			
H ₂ O	10.44		1.33			
Fe ₂ O ₃			3.03			
C ₆ H ₆ O ₂		9.08				

Equipment Conditions

	Reactor	Crystallizer	Evap	Vac Dry
T (°C)	70	15	70	
P (atm)	1	1		
Q (kcal/sec)			2979	147.39

6.8.2 para-Benzoquinone from Aniline (Chemical)

The process describing the manufacture of benzoquinone from aniline is described in the EPA 600 Report (2). Other sources include Kirk-Othmer (17) volumes 2, 11, 18 (manganese compounds), and 16. The basic flowsheet is given in Fig. 6.8.2.

The reactor operates at 25°C and at atmospheric pressure. The primary reaction is

The heat of reaction at 298°K is calculated to be

$$\Delta H_{298} = -59.3 \text{ kcal/mole benzoquinone.}$$

The reactor conversion and yield were both assumed to be 100%.

The critical pressure and volume of benzoquinone were calculated by group contributions as previously discussed. The critical compressibility (z_c) was then assumed to be equal to 0.26, and the critical temperature calculated. The hypothetical boiling point was calculated using Lydersen's equation for the critical temperature. The heat of sublimation was calculated assuming the Riedel model was valid for the sublimation process. Finally, the Watson relation was used and also assumed valid for sublimations. The preceeding method yielded the following vapor pressure data for benzoquinone:

<u>T(°C)</u>	<u>P°(mm)</u>
100	2.8
150	29.4
200	172
255	760

From the reactor the product stream is pumped to the acid neutralizer, where hydrated lime is added. The hydrated lime slurry entering the acid neutralizer was assumed to 40% solids by weight. The acid neutralizer was assumed to operate adiabatically with a temperature rise to 76°C. From the

Fig. 6.8.2 Benzoquinone from Aniline, Chemical

Table 6.8.2

Stream Conditions for the Quinone Process
Chemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6
Flows						
C ₆ H ₇ N	9.25					
H ₂ O		277.52			296.02	
MnO ₂			28.30		9.80	
H ₂ SO ₄				42.73	19.60	
C ₆ H ₄ O ₂					9.25	
MnSO ₄					18.50	
(NH ₄) ₂ SO ₄					4.63	
Ca(OH) ₂						19.60
Stream No.	7	8	9	10	11	12
T (°C)				330		
P (atm)				3.4		
Flows						
H ₂ O	201.51	536.73	536.73	863.27	1000.00	1000.00
MnO ₂		9.80	9.80			
C ₆ H ₄ O ₂		9.25	9.25		9.25	9.25
MnSO ₄		18.50	18.50			
(NH ₄) ₂ SO ₄		4.63	4.63			
CaSO ₄		19.60	19.60			
Stream No.	13	14	15			
Flows						
H ₂ O	4.67	995.33	400.00			
C ₆ H ₄ O ₂	9.25					
MnO ₂			9.80			
MnSO ₄			18.50			
(NH ₄) ₂ SO ₄			4.63			
CaSO ₄			19.60			

Equipment Conditions

	Reactor	Acid Neut	Steam Strip	Cool Filter
T (°C)	25	76	150	25
P (atm)	1	1	3.4	1

neutralizer the product is pumped to a steam stripping unit where benzoquinone is volatilized out of the solution. The aqueous phase contains valuable by-product salts which can be further used.

The slurry leaving the bottom of the steam stripper was assumed to be 20% solids by volume. The steam benzoquinone stream is cooled to 25°C and the benzoquinone separated by filtration. The wet benzoquinone is suitable for use as feed for the hydroquinone process.

6.8.3 Hydroquinone from Benzene (Electrochemical)

The electrochemical production of hydroquinone from benzene has been described by Fremery, Hoefer, and Schwarzlose (Appendix B, hydroquinone, 4). Further, the process was evaluated according to Weinberg's suggestions (Appendix B, hydroquinone). The process flowsheet is shown in Fig. 6.8.3.

The reaction of benzene to produce hydroquinone proceeds by the following reaction sequence:

Anode

Cathode

Basic Overall

The heat of reaction for the entire reaction sequence with the above mentioned current efficiencies is

$$\Delta H_{298} = 139.39 \text{ kcal/mole hydroquinone.}$$

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. For this cell, three water molecules have been assumed to cross the membrane as waters of hydration with each hydrogen ion. The acid content of the anolyte is known to be higher than that of the

Fig. 6.8.3 Hydroquinone from Benzene, Electrochemical

Table 6.8.3

Stream Conditions for Hydroquinone Process
Electrochemical Route - Flow Units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
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
Stream No.	8	9	10	11	12	13	14
Flows							
C ₆ H ₆	540.00	540.00				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
Stream No.	15	16	17	18	19	20	21
Flows							
C ₆ H ₆	17.49	494.79					
H ₂ O	515.83	14,593.72	14,593.72	66.28	12.76	32.45	9.28
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		
Stream No.	22	23	24	25	26	27	28
Flows							
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			
Stream No.	29	30	31	32	33	34	35
Flows							
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							

Table 6.8.3 (continued)

Stream Conditions for Hydroquinone Process
Electrochemical Route - Flow Units are g mol/sec

Stream No.	36	37	38	39	40
Flows					
C ₆ H ₆		9.97	27.72	35.69	
H ₂ O					349.91
Oil					
H ⁺					136.25

Equipment Conditions

	<u>Cell</u>	<u>Phase Sep. 1</u>	<u>Phase Sep. 2</u>	<u>Phase Sep. 3</u>	<u>Vac Evap</u>	<u>Vac Cryat</u>	<u>Dryer</u>	<u>Strip 1</u>	<u>Strip 2</u>	<u>Dist</u>
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)					3,244	1,430	93			233

catholyte; therefore osmotic pressure drives some water from the catholyte to the anolyte across the membrane. The flow has been evaluated using typical diffusion coefficients for water in Nafion membranes (38).

After leaving the cell, the hydroquinone is pumped to a phase separator 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 and centrifuged again, and finally dried to produce the final product.

The water which is passed through the membrane to the catholyte with the hydrogen ions must somehow be removed. A vacuum evaporator is used for this purpose, 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 (43). Soluble organic impurities build up in the electrolyte and cause a progressive decline in current efficiency to the point where sulfuric acid must either be replaced or purified. Not enough technical information was available to make an estimate of the energy requirement for sulfuric acid purification.

Energy requirements for the chemical and electrochemical routes to hydroquinone are compared in Table 6.8.4. The chemical route has a lower energy requirement according to these calculations but the case is not clear cut because the calculations were based on rather sketchy process information and the results are sensitive to the assumptions made. Factors which could increase the energy consumption for the chemical process are (43):

Table 6.8.4

Hydroquinone Energy Requirements

Basis: 1 kg (9.08 g mol)

<u>Chemical Route</u>		<u>kcal</u>
H ₂ O evaporation		2,979
Dryer		147
Iron	(11.64)(55.85)(4.050) =	2,633
Benzoquinone (9.08 g mol)		
steam stripper	(9.08/9.25)(11,257) =	11,050
<u>aniline from benzene</u>	(9.08)(93.13)(16.736) =	<u>14,152</u>
Total		30,961
<u>Electrochemical Route</u>		
Cell	(12,600/0.325) =	38,769
Vacuum evaporation		3,244
Vacuum crystallizer		1,430
Dryer		93
Distillation		233
<u>Benzene</u>	(11.35)(78.12)(10.117) =	<u>8,970</u>
Total		52,739

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 stream 15 in Fig. 6.8.2 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 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 40% used in the calculations to a higher figure through more R&D. The 12,600 kcal/kg electrical for the cell in Table 6.8.4 is in good agreement with 15 kWh/kg or 12,900 kcal/kg given in reference (41).

Millington (41) has made calculations which show that the electrochemical process is more favorable on an energy basis than the chemical process. He shows 43,950 kWh(thermal)/ton (41,600 kcal/kg) for the electrochemical route 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. He clearly shows an advantage for the electrochemical route. His overall energy requirement of 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. His overall energy requirement is higher for the chemical route because:

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

The chemical route to hydroquinone given in the EPA report (2) and used as a basis in this study is also old technology. Two newer processes (43) are: chemical oxidation of phenol to hydroquinone and catechol, and

hydroperoxidation of p-di-isopropylbenzene leading to hydroquinone and acetone.

6.9.1 Dichloroethane from Ethylene (Chemical)

The gas phase production of dichloroethane (DCE) from ethylene and hydrogen chloride (HCl) is discussed in the EPA 600 Report (2) and Hydrocarbon Processing (29). The flowsheet is given in Fig. 6.9.1.

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

The heat of reaction is

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

The yield and conversion are both 98% with the remaining 2% forming other chloroalkanes (monochloroethane assumed).

Upon leaving the reactor the hot gasses are used to preheat the reactor feed, then further cooled and collected in a phase separator. In the separator an acidic aqueous phase forms which is drawn off, neutralized with caustic (NaOH), and purged from the process. An organic phase is also withdrawn from the separator. After neutralization of the dissolved acid, this stream is considered product. The vapor phase off the separator contains nitrogen, unreacted oxygen, DCE, and most of the reaction product water. The DCE is absorbed from the gas stream with a heavy organic oil. The clean nitrogen stream is then vented to the atmosphere. The DCE is stripped from the oil and added to the product stream. The oil is recycled to the absorber.

No compressor for HCl was used since it was assumed that HCl would be purchased as a pressurized liquid. 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.

Fig. 6.9.1 Dichloroethane from Ethylene and HCl, Chemical

Table 6.9.1

Stream Conditions for Dichloroethane from Ethylene and HCl
Chemical Route - Flow units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
O ₂	6.94			6.94	6.94	1.89	1.89
N ₂	26.22			26.22	26.22	26.22	26.22
HCl		20.60		20.60	20.20	0.20	0.20
C ₂ H ₄			10.30	10.30	10.30		
H ₂ O						10.10	10.10
C ₂ H ₅ Cl						0.20	0.20
C ₂ H ₄ Cl ₂						10.10	10.10
Stream No.	8	9	10	11	12	13	14
Flows							
O ₂	1.89				1.89		
N ₂	26.22				26.22		
HCl		0.19	0.01				
H ₂ O	2.76	7.34			2.76		
C ₂ H ₅ Cl			0.20				
C ₂ H ₄ Cl ₂	5.45		4.65			5.45	5.45
Oil				4.63		4.63	
Stream No.	15	16	17	18	19	20	21
Flows							
H ₂ O			0.40	7.60	8.00	0.41	15.13
C ₂ H ₅ Cl	0.20	0.20					
C ₂ H ₄ Cl ₂	4.65	10.10					
NaOH			0.01	0.19	0.20		
NaCl						0.01	0.19

Equipment Conditions

	Reactor	Phase Sep.	DCE Abs	DCE Strip	Scrub	Acid Neut
T (°C)	300	75	60	215	25	25
P (atm)	5.5	5	1	1	1	1
Q (kcal/sec)	-578	-66		47		

6.9.2 Dichloroethane from Ethylene (Electrochemical)

The electrochemical production of dichloroethane (DCE) from ethylene and hydrogen chloride (HCl) is discussed by Weinberg (Appendix B, dichloroethane). A flowsheet for this process is given in Fig. 6.9.2.

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

Cathode

The overall electrochemical reaction can thus be written,

The hydrogen gas passes out of the cell through a hydrogen collector system and thence to the HCl recovery plant before exiting the process. The chlorine gas, on the other hand, 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 63% based on ethylene. Ethylene chlorohydrin is the primary by-product. The cells are assumed to operate at 2.2 V, similar to commercial HCl electrolysis cells.

Dichloroethane, ethylene, HCl, and chlorohydrin leave the cell in the gas phase. This stream is compressed to about three atmospheres pressure and cooled to 25°C. The mixture is then sent to a phase separator where the water phase (a trace component) is split off and recycled to the chlorohydrin still. The organic phase from the separator is primarily DCE containing traces of monochloroethane, and trichloroethane. This stream was considered as product without further purification. Ethylene, oxygen, and some HCl

Table 6.9.2

Stream Conditions for Dichloroethane from Ethylene and HCl
Electrochemical Route - Flow units are g mol/sec

Stream No.	1	2	3	4	5	6	7
Flows							
H ₂ O	2.92		0.09			3.02	
C ₂ H ₄				13.29			2.67
HCl			0.27		23.43	0.27	1.48
H ₂		13.28	13.28				
Stream No.	8	9	10	11	12	13	14
Flows							
H ₂ O	17.25	205.65	225.92	221.61	0.74	222.35	222.35
C ₂ H ₄			15.96				
HCl	4.19	37.20	66.57	40.05	0.17	40.22	40.22
ClC ₂ H ₄ OH				2.62	0.05	2.67	
Polymer				0.07		0.07	
Stream No.	15	16	17	18	19	20	21
Flows							
H ₂ O	16.70	0.64	0.74		0.74		
C ₂ H ₄			2.67		2.67	2.67	
HCl	3.02	1.44	1.65		1.65	1.48	
ClC ₂ H ₄ OH			0.05	2.67	0.05		
Polymer				0.07			
H ₂		13.28					
O ₂			0.13		0.13	0.13	
C ₂ H ₅ Cl			0.27		0.27		0.27
C ₂ H ₄ Cl ₂			10.00		10.00		10.00
C ₂ H ₃ Cl ₃			0.07		0.07		0.07
Stream No.	22	23	24	25	26		
Flows							
C ₂ H ₄	2.67	2.67	2.67		2.67		
HCl	1.48	1.48	1.48		1.48		
O ₂	0.13	0.13	0.13	0.13			

Equipment Conditions

	Cell	HCl Abs. 1	HCl Abs. 2	Dist.	Comp. 1	Phase Sep. 1	Comp. 2	Refrig.	Phase Sep. 2
T (°C)	50	20	20	108-128	25	25	25-185	-100-40	-100
P. (atm)	1	1	1	1	1-3	3	3-50	50	50
VI (kcal/sec)	1348								
W (kcal/sec)					3		10		
Q (kcal/sec)	-1341			5753					

exit the separator in the gas phase, and are compressed a second time to about 50 atmospheres. After the second compression the ethylene and acid are separated from the oxygen by refrigeration.

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.

Energy requirements for the chemical and electrochemical routes to dichloroethane are compared in Table 6.9.3. Although both the HCl and chlorine 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 (2). 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 could be decreased below that of the chemical route if formation of the by-product chlorohydrin could be suppressed. This is because conventional NaCl brine diaphragm cells which supply the chlorine for the chemical process operate at 3.5 V versus 2.2 V for HCl electrolysis.

Table 6.9.3

Dichloroethane Energy Requirements

Basis: 1 kg (10.10 g mol)

<u>Chemical Route from HCl</u>		<u>kcal</u>
Compressors and refrigerator	(37.84/0.325)	= 116
Process heat	zero	-
<u>Ethylene</u>	(10.30) (28.05) (20.817)	= <u>6,014</u>
Total		6,130
<u>Chemical Route from Cl₂</u>		14,819*
<u>Electrochemical Route</u>		
Cell	(1,348/0.325)	= 4,148
Compressor No. 1	(2.9/0.325)	= 9
Compressor No. 2	(9.9/0.325)	= 30
Refrigeration	(23.7/0.325)	= 73
Chlorohydrin distillation		5,753
Ethylene	(13.29) (20.05) (20.817)	- 7,760
<u>HCl - no cost</u>		<u>-</u>
Total		17,773

*Appendix C-12

7.0 OVERALL IMPACT

A linear-programming model of the U.S. petrochemical industry has been used to evaluate the energy-efficiency of the candidate electrochemical processes and to assess their potential impact on the industry as a whole. The model is formulated and described in detail by Stadtherr and Rudd (39). It can be used to determine the structure of the industry optimal with respect to resource use. That is, the model can be 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 (39) accounts for feedstock consumption only. For purposes of this study, the process energy data of Rudd et al. (40) has also been incorporated in the model. Thus, the objective function in the version of the model used here is minimum energy consumption, counting both energy consumed as utilities and as feedstock (feedstock energy consumption is measured using their gross heating values).

The energy-efficiency of the electrochemical processes can be evaluated by adding the processes to the model and noting which processes, if any, are 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 performs a 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 if any other route changes occur in the energy-optimal industry due to 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 1.2. This is the case 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 1.2 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 here than in Table 1.2 because those figures account for process energy only. Since the electrochemical process has a higher yield on butylene compared to the chemical route, there is a significant savings in feedstock energy.

The adoption of these processes does not result in any other route changes 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 via a cyclohexane intermediate. Thus, both monomers for Nylon 66, could be derived from propylene via 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 byproduct propylene, the effect of the electrochemical technology on propylene supplies does not seem significant.

8.0 ENVIRONMENTAL IMPACT

The primary purpose of the process calculations was to determine energy requirements, and simplifications were made in order to achieve that end. Therefore only major by-products were considered and the environmental impact considerations will deal only with handling and disposal of such major items. Reference 2 gives detailed pollution data on those chemical processes noted in Table 6.0.

Adiponitrile

The electrochemical process gives about 12% by-product 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.

Aniline

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 Reference 2.

Sorbitol

The chemical and electrochemical routes should be similar in terms of by-products.

Terephthalic Acid

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.

Phenol

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

Methyl Ethyl Ketone

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

Melamine

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

Hydroquinone

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

Dichloroethane

The electrochemical process produces about 25% chlorohydrin which is a saleable product. The chemical routes are relatively clean.

9.0 REFERENCES

1. Electrochemical Technology Corp. Proposal No. 7709 to Argonne National Laboratory, "A Survey of Organic Electrolytic Processes," October, 1977.
2. R. Liepins, et al., "Industrial Profiles for Environmental Use, Chapter 6, The Industrial Organic Chemicals Industry," EPA Contract No. 68-02-1319, Document No. EPA-600/2-77-023f, February, 1977.
3. United States International Trade Commission, "Synthetic Organic Chemicals, United States Production and Sales, 1975," USITC Publication 804, U.S. Government Printing Office, Washington, DC, 1977.
4. S. Swann, Jr., and R. C. Alkire, "Bibliography of Electro-organic Synthesis Literature, 1801-1975," The Electrochemical Society, Princeton, NJ, 1979.
5. Fr. Fichter, "Organische Elektrochemie," Dresden, 1942; reprinted by Edwards Bros., Ann Arbor, MI, 1946.
6. Chemical Abstracts, The American Chemical Society.
7. D. E. Danly, Monsanto Co., Pensacola, FL, personal communication.
8. W. H. Seaton, E. Freedman, and D. N. Treweek, "CHETAH - The ASTM Chemical Thermodynamic and Energy Release Evaluation Program," ASTM DS 51, Philadelphia, PA, 1974.
9. S. W. Benson, Thermochemical Kinetics, 2nd ed., John Wiley and Sons, Inc., New York, NY, 1976.
10. D. R. Stull, and H. Prophet, JANAF Thermochemical Tables, 2nd ed., Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37, July, 1970.
11. D. R. Stull, E. F. Westrum, and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, John Wiley and Sons, Inc., New York, NY, 1969.
12. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, The Properties of Gasses and Liquids, 3rd ed., McGraw-Hill Book Co., New York, NY, 1977.
13. R. H. Perry and C. H. Chilton, Ed., Chemical Engineers' Handbook, 5th ed., McGraw-Hill Book Co., New York, NY, 1973.
14. C. L. Yaws, Physical Properties, McGraw-Hill Publishing Co., New York, NY, 1977.
15. N. A. Lange, Ed., Handbook of Chemistry, 10th ed., McGraw-Hill Book Co., New York, NY, 1969.

16. M. Windholz, Ed., The Merck Index, 9th ed., Merck and Co., Inc., Rahway, NJ, 1976.
17. Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed., Vol 2, Interscience Publishers, New York, NY, 1963,
18. F. A. Lowenheim and M. K. Moran, Industrial Chemicals, 4th ed., Wiley Interscience, New York, NY, 1975 (previous authors: W. L. Faith, D. B. Keyes, and R. L. Clark).
19. G. V. Michael, and G. Thodos, Critical Temperatures and Pressures of Hydrocarbons, Chem. Eng. Prog. Symp. Ser., 49(7), 131 (1953).
20. A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, Chemical Reviews, 68, 659 (1968).
21. Ref 12, p 208.
22. A. Seidell, and W. F. Linke, Solubilities, Organic and Metal-Organic Compounds, 4th ed., Americal Chemical Society, Washington, DC, 1965.
23. R. E. Treybal, Mass-Transfer Operations, 2nd ed., Chapter 9, McGraw-Hill Book Company, New York, NY, 1968.
24. T. R. Beck, "Final Report on Improvements in Energy Efficiency of Industrial Electrochemical Processes," ANL/OEPM-77-2, January, 1977.
25. D. W. Brubaker, C. R. Campbell, D. E. Danly, R. Johnson, and F. S. Riordan, "The Electrohydrodimerization of Acrylonitrile to Adiponitrile," presented to The Electrochemical Society, San Francisco, CA, May 10, 1965.
26. D. E. Danly and J. F. Giblin, "A Commercial Process for Electrohydrodimerization of Acrylonitrile to Adiponitrile," presented to the Americal Chemical Society, San Francisco, CA, April 3, 1968.
27. C. R. Campbell and R. Johnson, U.S. Patent No. 3,267,131.
28. D. E. Danly, "The Discovery, Development, and Commercialization of the Electrochemical Adiponitrile Process, Part II," private communication.
29. "1975 Petrochemical Handbook Issue," Hydrocarbon Processing, November, 1975, p 114.
"1977 Petrochemical Handbook Issue," Hydrocarbon Processing, November, 1977, p 131.
30. W. S. Fedor, J. Millar, and A. J. Accola, Ed., Ind. Eng. Chem., 52(4), 282 (1960).

31. Ref 29, November, 1977, p 229.
32. P. W. Sherwood, Chem. and Ind.(London), August 27, 1096 (1960).
33. R. H. McKee and S. T. Leo, J. Ind. Eng. Chem., 12(1), 16 (1920).
34. W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, NJ, 1952.
35. L. I. Griffin and C. H. Worsham, U.S. Patent No. 3,329,593 (1967).
36. Ref 17, 3rd ed., Vol 2, p 443.
37. J. S. Mackay, U.S. Patent No. 2,760,961 (1956).
38. T. D. Gierke, "Ion Clustering in Nafion Perfluorosulfonic Acid Membranes and Its Relationship to Hydroxyl Rejection and Chlor-Alkali Current Efficiency," presented to The Electrochemical Society, October, 1977.
39. M. A. Stadtherr and D. F. Rudd, "Resource Use by the Petrochemical Industry," Chem. Eng. Sci. 33, 923 (1978).
40. D. F. Rudd, M. A. Stadtherr, et al., "Resource Management and Technology Assessment in the Petrochemical Industry," manuscript for a book in preparation.
41. J. P. Millington, Chemistry and Industry, p 783, 20 Sept. 1975.
42. D. E. Danly, reviewer comments.
43. A. H. Reidies, reviewer comments.

APPENDIX A

COMPILATION OF PAST AND PRESENT
PILOTED/COMMERCIALIZED ELECTROORGANIC PROCESSES

COMPILATION OF PAST AND PRESENT PILOTED/COMMERCIALIZED
ELECTROORGANIC PROCESSES

The following tables catalogue both past and present efforts in organic electrochemical syntheses of an industrial nature. Most of the information was assembled from general treatises as well as through direct contacts with industrial sources.

Some of the information tabulated may require correction, especially with regards to the total number of conversions and their present status. We chose to err on the side of providing too many conversions rather than too few. Where a question does exist, this is so indicated.

The status of conversions is represented as follows:

P-presently being piloted

EP-pilot studies abandoned

C-presently commercial

EC-the commercial process has been abandoned.

Commercial status is taken only to mean that electrochemically derived product is being sold; no inference as to the size of the operation is suggested.

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OXIDATIONS

Starting Material (Electrolyte)	Product(s)	Anode	CE%	Energy ² Usage	Status	Refs
anthracene (H_2O , Cr^{+6} , H_2SO_4) ¹	anthraquinone	PbO_2	80	[4.8]	C-Holliday	1
benzene (H_2O , H_2SO_4)	hydroquinone (quinone)	PbO_2	40-60	15	P-Stavely, Carus, etc	2,29
butynediol (H_2O , H_2SO_4)	acetylenedicarboxylic acid	PbO_2	75	[12.4]	P-BASF	3,28,30
cyanuric acid (H_2O , 20% KCl)	pot. dichlorocyanurate	Pt/Ti	high	[3-5]	EP-Monsanto	4
dimethyldithiocarbamate (H_2O , sodium salt)	tetramethylthiuram disulfide	Pt	90	1.7	P-Dupont	5
dimethyl sulfide (H_2O , DMSO, 5% H_2SO_4)	dimethyl sulfoxide	Pt/Ti	100	0.7-1.3	P-Glanzstoff, 6 Akzo?	
ethyl alcohol (H_2O , EtOH, NaOH, KI)	iodoform	Pt	93-95	2	EC-Schering	7
ethyl alcohol (H_2O , HCl)	chloral	C	high	[8-10]	EC-Schering	8
furan (CH_3OH , NaBr or NH_4Br)	dimethoxydihydrofuran	C	85	2.5	C-BASF	9,28,30
glucose (H_2O , NaBr, $CaCO_3$)	calcium gluconate	C	high	[2]	C-Sandoz, Chefaro?	10
hydrogen cyanide (H_2O , NH_4Br)	melamine	C	98	1.5-2	P-Sohio	11
isobutanol (H_2O , 1C% H_2SO_4)	isobutyric acid	PbO_2	45	[14]	P-USSR	12
p-methoxytoluene (H_2O , redox reagent, H_2SO_4) ¹	anisaldehyde	PbO_2	high	[2.2]	P-Oxy	13
methyl (ethyl) chloride (THF/diglyme, RMgCl)	tetraalkyl lead	Pb	92	4-8	C-Nalco	14
2-methylnaphthalene (HOAc, NaOAc)	2-methyl- α -naphthol acetate	C	good	[1.9]	EP?-Socony EP-BASF	15,28,30
monomethyl adipate (CH_3OH , sod. salt of acid)	dimethyl sebacate	Pt/Ti	75-85	5	EP-BASF	16,28
naphthalene	1-naphthylacetate	C		[1.6]	P-BASF	28,30
p-nitrotoluene (H_2O , Cr^{+6} , H_2SO_4) ¹	p-nitrobenzoic acid	PbO_2	98	7.5	P-India	17
oleic acid (H_2O , Cr^{+6} , H_2SO_4) ¹	azelaic acid, pelargonic acid	PbO_2	high	[4]	EC-Energy	18

OXIDATIONS CONTD

Starting Material (Electrolyte)	Product(s)	Anode ¹	CE%	Energy ² Usage	Status	Refs
phenol (H ₂ O, 3% H ₂ SO ₄)	hydroquinone (quinone)	PbO ₂	50	[8-12]	P? Union Carbide, Eastman Kodak	19
propargyl alcohol	propiolic acid			[8.5]	P-BASF	28
potassium alkylaluminate (melt)	tetraalkyl lead	Pb	100	1	P-MPI	20
propylene (H ₂ O, NaCl or NaBr)	Propylene oxide	C, DSA ^R	70-88	4-6	P-Bayer, Kellog, EP-BASF	21
quinoline (H ₂ O, H ₂ SO ₄)	nicotinic acid	PbO ₂	40	25	?	22
starch (H ₂ O, NaOH, periodate) ¹	dialdehyde starch	PbO ₂	high	[1.5-2]	C-Miles	23
toluene (H ₂ O, H ₂ SO ₄ , Ce ⁺⁴) ¹	benzaldehyde	PbO ₂ , Pt	90	[6]	P-ETH	24
o-toluenesulfonamide (H ₂ O, Cr ⁺⁶ , H ₂ SO ₄) ¹	saccharin	PbO ₂	78	[6]	EP-Boots	25
various organics (HF, KF)	perfluoroorganics	Ni	low	high	C-3M	26
various organics (KF·2HF melt)	perfluorinated and partially fluorinated organics ³	C	fair	high	EP-Phillips	27

1. The process is a two-stage operation in which the redox reagent (Mn⁺³, Ce⁺⁴, Cr⁺⁶, periodate, hypobromite etc) is regenerated electrochemically and passed into a second reactor where the oxidant and the organic feed are contacted.
2. [], estimated value based on a cell voltage of 5 volts and current efficiency of 90% unless otherwise given. Energy usage in kwh/kg.
3. Including perfluoropropane, perfluorobutyric acid, trifluoroacetic acid, perfluoromethylether.

References - Oxidations

1. (a) E. Opperman, U.S. Pat. 323,435 (1906)
 (b) C. J. Thatcher, Can. Pat. 222,264 (1922)
 (c) S. Krishan, V.A.Vyas, M.S.V. Pathy, and H.V.K. Udupa, Bull. India Elect. Soc., 14, 32 (1964)
 (d) K. Niki, T. Sekine, and K. Sugino, J. Elect. Soc. Japan, 37, 74 (1969)
2. (a) J. P. Millington, Chem. & Ind., 780 (1975); Brit. Pat., 1,377,681 (1974)
 (b) M. Fremery, H. Hoefer, and G. Schwarzlose, Chem.-Ing.-Tech., 46, 635 (1974); Ger. Pat., 2,204,351 (1973)
 (c) F. J. Anderson and J. L. Kessler, U.S. Pat., 3,758,391 (1973)
3. (a) V. E. Wolf, Chem. Ber., 87, 668 (1954)
 (b) U. S. Pat., 2,786,022 (1955)
4. (a) J. C. Marchon and B. Rosset, Bull. Chem. Soc. France, 2776 (1965);
 (b) E. J. Matzner, U. S. Pat., 3,449,225 (1969)
5. (a) L. H. Cutler, U.S. Pat., 4,032,416 (1977);
 (b) L. H. Cutler, AICHE Meeting Abstracts, Atlanta, Georgia 1978.
6. (a) Brit. Pat. 737,576; 737,577 (1968);
 (b) Brit. Pat., 1,177,308
 (c) C. Thibault and P. Mathieu, U.S. Pat., 3,808,112 (1974)
 (d) S. J. Reddy and V. R. Krishnan, J. Electroanal. Chem., 27, 474 (1970)
7. (a) K. Elbs and W. Herz, Z. Elektrochem., 4, 113 (1897)
 (b) J. Billiter, Die Technische Elektrolyse der Nichtmetalle, Springer-Verlag, Wien (1954)
 (c) R. Ramaswamy et al, J. Electrochem. Soc., 110, 294 (1963)
8. E. Schering, Z. Elektrochem., 1, 70 (1894)
9. (a) N. Clauson-Kaas and F. Limborg, U.S. Pat., 2,714,576 (1955);
U.S. Pat. 2,801,252 (1957)
 (b) N. Clauson-Kaas, F. Limborg, and K. Glens, Acta. Chem. Scand., 6, 531 (1952)
10. (a) H. S. Isbell, Nat. Bur. Std., 914, 331 (1936)
 (b) C. G. Fink and D. B. Summers, Trans. Elect. Soc., 74, 625 (1938)
 (c) L. Mezynski and M. Pawelczak, Przem. Chem., 51, 28 (1972)
11. (a) R. W. Foreman and J. W. Sprague, Ind. Eng. Chem. Prod. Res. Dev., 2, 303 (1963)
 (b) J. W. Sprague et al, U.S. Pat. 3,294,657 (1966); 3,300,398 (1967)

References - Oxidations

12. (a) E. A. Dzhaferov et al, U.S.S.R. Pat., 143,391 (1962); C.A. 57, 9668g;
 (b) K. I. Kryshchenko et al, Khim. Prom., 45, 496 (1969);
13. O. R. Brown, S. Chandra, and J. A. Harrison, J. Electroanal Chem., 34, 505 (1972)
14. (a) D. G. Braithwaite, U.S. Pat., 3,256,161 (1966); 3,391,066, and 3,391,067 (1968)
 (b) L. L. Bott, Hydrocarbon Proc., 44, 115 (1965)
15. W. J. Koehl, Jr., U.S. 3,252,876 (1966)
16. (a) W. Himmele, N. Kutepow and W. Schwab, Ger. 1,162,347 (1964)
 (b) F. Beck, H. Nohe, and J. Haufe, Ger. Offen., 2,014,985 (1971)
 (c) E. P. Kovsman, G. N. Greidlin, and Y. M. Tyurin, Khim. Prom., 49, 16 (1973)
 (d) N. T. Kobzeva et al, Soviet Electrochem., 11, 667 (1975)
17. (a) S. Chidambaram et al, Res. & Ind. (India), 15, 215 (1970)
 (b) R. Kanakam et al, Electrochim. Acta, 16, 423 (1971)
 (c) S. Chidambaram et al, Indian J. Appl. Chem., 34, 1 (1971)
18. (a) J. D. Fitzpatrick and L. D. Myers, U.S. Pat. 2,450,858 (1943)
 (b) M. Kappel, Chem.-Ing.-Techn., 35, 386 (1963)
19. F. Covitz, U.S. Pat., 3,509,031 (1970); 3,616,323 (1971); 3,616,324 (1971)
20. K. Ziegler and H. Lehmkuhl, U.S. Pat., 3,372,097 (1968)
21. (a) J. A. M. Leduc, U.S. Pat., 3,288,692 (1966); 3,379,627 (1968); 3,342,717 (1967); 3,427,235 (1969)
 (b) Farbenfabriken Boyer, Fr. Pat., 1,540,800 (1968)
 (c) T. D. Binns and D. C. G. Cattiker, U.S. Pat., 3,635,803 (1972)
 (d) K. H. Simmrock and G. Hellemanns, Ger. Pat., 2,658,189
22. N. A. Dschabanowski and L. D. Borkhi, Russ. Pat., 166,654 and 172,330 (1963)
23. (a) H. F. Conway and V. E. Sohns, Ind. Eng. Chem., 51, 637 (1959)
 (b) H. F. Conway, E. B. Lancaster, and V. E. Sohns, Elect. Techn., 2 (1964)
 (c) M.S.V. Pathy and H. V. K. Udupa, CLRI (India), 20 (1964)
 (d) C. L. Mehlretter, U.S. Pat., 2,713,553 (1955); 2,830,941 (1958);
 (e) J. E. Slager, U.S. Pat. 3,086,969 (1963)

References - Oxidations

24. (a) B. B. Dey and R. K. Maller, J. Sci. Ind. Res. (India),
12B, 255 (1953);
(b) N. Ibl et al, Abstracts Papers, AICHE Mfg. Atlanta, Georgia, 1978
25. (a) Dutch Pat., 41,338 (1935); Chem. Abstr. 31, 8399 (1937);
(b) S. Mizuno and Y. Kohtoku, Chem. Abstr., 62, 15334g (1968)
26. (a) J. H. Simons et al, J. Electrochem. Soc., 95, 47, 53, 55, 59, 64
(1949)
(b) J. H. Simons, U.S. Pat. 2,519,983 (1950)
(c) E. A. Kauck and J. H. Simons, U.S. Pat. 2,594,272 (1952);
Brit. Pat. 666,733 (1952)
27. (a) H. M. Fox, F. N. Ruehlen, and W. V. Childs, J. Electrochem. Soc.,
118, 1246 (1971)
(b) W. V. Childs, U.S. Pat., 3,558,449 (1971); 3,617,453 (1971);
3,655,548 (1972); 3,853,737 (1974)
(c) F. N. Ruehlen, U. S. Pat., 3,620,941 (1971)
28. Private Communication from BASF (Ludwigshofen) from Drs. Reif
and Pape, 1/29/79
29. Private Communication from Hoechst (Frankfurt) from Drs. Jensen
and Lohaus, 1/17/79.
30. Private Communication from Prof. F. Beck, Gesamthochschule
Duisburg, 4/10/79.

REDUCTIONS

Starting Material (Electrolyte)	Product(s)	Cathode	CE%	Energy ² Usage	Status	Refs.
acetone (H ₂ O, H ₂ SO ₄ , Cu ⁺²)	pinacol	Pb	70-75	3.3	EP-BASF, Bayer Diamond Shamrock	1,28,31
acrylonitrile (H ₂ O, quat. salt)	adiponitrile	Pb alloy	90-92	3-6	C-Monsanto Asahi	2
adiponitrile (H ₂ O, HCl)	1,6-hexanediamine	Ni(Cu)	60	[15.8]	P-USSR	3
ammonium phthalamate (H ₂ O, phthalamate salt)	phthalide	Pb	70	[5.7]	EP-BASF	4,31
anthranilic acid	o-aminobenzyl alcohol				P-BASF	28
benzene (NH ₃ or CH ₃ NH ₂ , NaCl or LiCl)	1,4-cyclohexadiene	C, Al	80	[4.2]	EP-Esso Res	5
benzenediazonium chloride (H ₂ O, HCl)	phenylhydrazine hydrochloride	Hg	70	5	?	6
benzoic acid (H ₂ O, C ₂ H ₅ OH, H ₂ SO ₄)	benzyl alcohol	Pb	93	4.1	P?-India	7
benzyl cyanide (H ₂ O, HCl)	β-phenethylamine hydrochloride	Pd	35-42	[12]	P-India	8
diazoaminobenzene (H ₂ O, CH ₃ OH, THF, NaOH)	phenylhydrazine	C	82	[7]	EP-Hoechst	9,31
N,N-dimethylaminoethyl- tetrachlorophthalimide (H ₂ O, HOAc, H ₂ SO ₄)	corresponding isoindole	Hg	78	[2]	EP?-Ciba	10
m-dimethylaminobenzoic acid	m-dimethylamino- benzyl alcohol			[3.9]	P-BASF	28
m-dinitrobenzene (H ₂ O, H ₂ SO ₄)	2,4-diaminophenol	Hg ¹	60	[18]	P-India	11
dimethyl terephthalate	p-carbomethoxy- benzyl alcohol			[3.6]	P-Hoechst	29,30
glucose (H ₂ O, Na ₂ SO ₄)	sorbitol	Amalgamated lead	90	1.5-2	EC-Atlas	12
4-methylimidazolecarboxylic acid	4-methyl-5-hydroxy- methyl imidazole			[5.3]	P-BASF	28

Blank

REDUCTIONS CONTD

Starting Material (Electrolyte)	Product(s)	Cathode	CE%	Energy ² Usage	Status	Refs.
α -methylindole	α -methyl-dihydro-indole			[2.3]	C-BASF	28,31
N-methylpyridinium chloride (H ₂ O, sod. carbonate)	bipyridylum chloride	Pb	high	[1.2]	P-ICI	13
nitrobenzene (H ₂ O, H ₂ SO ₄)	p-aminophenol	Hg, C, Cu etc	90	[5.5]	P-Bayer, Miles CJB, India Etc.	14
nitrobenzene (H ₂ O, H ₂ SO ₄ , Ti ⁺³)	aniline	Cu, Pb	97	12.4	P?-India	15
nitrobenzene (H ₂ O, NaOH)	benzidine	NaHg, steel	good	[4-5]	EC-I.G. Farben P-India	16
nitrobenzene	p-anisidine			[4.8]	P-BASF	28
m-nitrobenzenesulfonic acid (H ₂ O, H ₂ SO ₄)	metanilic acid	Pb	80	8-13	P-L.B. Holliday, CJB, India BASF	17,28
nitronaphthalene	1-amino-4-methoxy-naphthalene			[3.5]	P-BASF	28
nitroguanidine (H ₂ O, (NH ₄) ₂ SO ₄)	aminoguanidine bicarbonate	Zn	89	[12]	P-India	18
p-nitrophenol (H ₂ O, H ₂ SO ₄)	p-aminophenol	Cu, Hg/Cu	60	5	P-India	19
nitrourea (H ₂ O, H ₂ SO ₄)	semicarbazide	Pb	good	[13]	P-USSR	20
oxalic acid (H ₂ O, H ₂ SO ₄)	glyoxylic acid	Pb	97	[3.7]	P-Rhône Poulenc others	21
phthalic acid (H ₂ O, dioxane, H ₂ SO ₄)	dihydrophthalic acid	Pb	90-95	1.6-4	EC-BASF	22,28
phthalimide (H ₂ O, HOAc, H ₂ SO ₄)	isoindole	Pb	50-55	[18]	P-Ciba	23
pyridine (H ₂ O, H ₂ SO ₄)	piperidine	Pb	90	[11]	C-Robinson Bros.	24
quinoline (H ₂ O, H ₂ SO ₄)	tetrahydro-quinoline	Pb	74	[5.4]	P?-Russ	25

REDUCTIONS CONTD

Starting Material (Electrolyte)	Product(s)	Cathode	CE%	Energy ² Usage	Status	Refs.
salicylic acid (H_2O , $NaHSO_3$, H_3BO_3)	salicylaldehyde	Hg/Cu	50	[4.4]	C-USSR, India	26
tetrahydrocarbazole (H_2O , C_2H_5OH , H_2SO_4)	hexahydro- carbazole	Pb	high	[1.8]	C-BASF	27,28,31

2. See footnote 2 under electrooxidations.

References - Reductions

1. (a) N. Shuster, K. J. O'Leary, and A. D. Babinsky, Abstracts of Papers, Electrochemical Soc. Meeting, Washington, D.C. May 2-7, p.p. 694-5 (1976)
(b) H. Nohe and F. Beck, Ger. Pat. 2,343,054 (1975)
2. (a) M. M. Baizer, J. Electrochem. Soc., 111, 215 (1964); U.S. Pat 3,193,480 and 3,193,481 (1965); 3,440,154 (1969)
(b) Asahi Chemical, Fr. Pat., 1,503,244 (1965); 1,533,472 (1968)
(c) F. Beck and H. Guthke, Chem.-Ing.-Tech. 41, 943 (1969)
(d) W. V. Childs and H. C. Walters, AIChE Meeting, Abstracts of Papers, Atlanta, Georgia, Feb. 1978
3. (a) M. Y. Fioshin and A. P. Tomilov, Usp. Elektrochimii - Organischeskikh., Soyedineniy, 256 (1966)
(b) Russ. Pat. 137,924 (1961); 445,647 (1974)
4. (a) F. Beck and F. P. Woerner, Ger. Offen Pat., 2,144,419 (1971);
(b) B. Sakurai, Bull. Chem. Soc. Japan, 7, 127 (1932)
5. (a) R. A. Benkesser et al, J. American Chem. Soc., 86, 5272 (1964)
(b) U. S. Pat. 2,182,284 (1938)
(c) Chem. Eng., 78B (1971)-Esso Res.: see F. Beck, book.
6. P. Ruetschi and G. Trumpler, Hebr. Chim. Acta, 36, 1649 (1953)
7. (a) K. Natarajan, K. S. Udupa, G. S. Subramanian, and H. V. K. Udupa, Electrochem. Tech. 2, 151 (1964)
(b) G. Schwarzlose, Ger. Offen. Pat. 2,237,612 (1974)
8. (a) V. Krishnan, K. Ragupathy and H. V. K. Udupa, Trans. SAEST, 11, 509 (1976)
(b) V. Krishnan, K. Ragupathy and H. V. K. Udupa, Electrochim. Acta, 21, 449 (1976)
9. (a) F. Beck, Ektroorganische Chemie, Verlag Chemie, Berlin 1974, p177
(b) H. Alt and H. Clasen, Ger. Offen 2,157,608 (1973); Chem. Abst., 79, 48729c
10. (a) M. J. Allen and J. Ocampo, J. Electrochem. Soc., 103, 452 (1956)
(b) M. J. Allen, Can. J. Chem., 37, 257 (1959); Brit. Pat. 817,097 (1959)
(c) J. W. Drew and G. J. Moll, Ind. Eng. Chem., 53, 948A (1961)
11. (a) Indian Pat., 60,865 (1957)
(b) H. V. K. Udupa, G.S. Subramanian and K. S. Udupa, Res. & Ind. (India), 5, 309 (1960)

References - Reductions

12. (a) H.J. Creighton, U.S. Pat., 1,612,361 (1926); 1,653,004 (1927);
1,712,952 (1929); 1,990,582 (1935)
(b) M. T. Sanders and R. A. Hales, J. Electrochem. Soc., 96, 241,
(1949)
13. J. E. Colchester and J. H. Entwistle, U.S. Pat., 3,478,042 (1966);
Brit. Pat. (ICI), 1,913,149 (1968)
14. (a) H. C. Rance and J. M. Coulson, Electrochim. Acta, 14, 283 (1969);
(b) H. V. Udupa et al, Indian Pat., 130,295 (1974)
(c) D. W. Lawson and D. S. Saltera, Ger. Offen. 2,026,039 (1970);
Chem. Abstr., 74, 42154 (1971)
15. (a) C. N. Otin, Z. Elektrochem., 16, 674 (1910);
(b) P. N. Anantharam and H. V. K. Udupa, Abstracts of Papers,
E.C.S. Meeting, Washington, D.C., May 1976, pp 708-709
16. (a) Ger. Pat. (Rohner), 181,116 (1903); 94,736 (1896)
(b) T. D. Bolakrishnan et al, Chem.-Ing.-Tech., 41, 776 (1969)
17. (a) S. Thangavelu, G. S. Subramanian, and H. V. K. Udupa, Denki
Kagaku, 39, 5 (1971)
(b) H. V. K. Udupa et al, Indian Pat. 119,015 (1974)
18. (a) M. Yamashita and K. Sugino, J. Electrochem. Soc., 104, 100 (1957);
(b) T. D. Balakrishnan et al, Ind. Eng. Chem. Proc. Des. Dev.,
10, 495 (1971); Indian Pat., 127,059 (1972)
19. (a) R. H. McKee et al, Trans. Am. Elect. Soc., 62, 203 (1932);
(b) H. V. K. Udupa and M. V. Rao, Electrochim. Acta, 12, 353 (1967)
20. (a) M. Y. Fioshin and A. P. Tomilov, Khim. Prom., 43, 243 (1967)
(b) R. Kanakam et al, Electrochim. Acta, 16, 423 (1971)
21. (a) Rhone-Poulenc, Fr. Pat. 2,151,150 (1973); Chem. Abst., 79, 60911P
(1973)
(b) D. J. Pickett and K. S. Yap, J. Appl. Electrochem., 4, 17 (1974)
(c) F. Goodridge and K. Lister, Brit. Pat., 1,411,371 (1975);
Chem. Abstr. 84, 66955f (1976)

References - Reductions

22. (a) P. C. Condit, Ind. Eng. Chem., 48, 1252 (1956);
 (b) H. Suter, H. Nohe, F. Beck, W. Bruegel, and H. Aschenbrenner,
U.S. Pat., 3,542,656 (1970)
 (c) H. Nohe, Chem.-Ing.-Tech., 46, 594 (1974)
23. (a) B. Sakurai, Bull. Chem. Soc. Japan, 5, 184 (1930)
 (b) N. Ibl, Chem.-Ing.-Tech., 33, 69 (1961); 35, 353 (1963);
36, 601 (1964)
24. Robinson Bros. and D. W. Parkes, Brit. Pat., 395,741 (1933)
25. N. A. Dschabanowski et al, Zhur. Prikl. Khim, 38, 2720 (1965)
26. (a) U.S. Army Technical Transl. FSTC-HT-23-258-68: "Industrial
 Electrosynthesis of Organic Compounds," by M. Y. Fioshin
 and A. P. Tomilov. (1966)
 (b) T. D. Balakrishnan et al, Chem. & Ind., 1969 (1970)
27. (a) M. Lukes, Chem. Listy, 27, 392 (1933).
 (b) W. H. Perkin and S. G. Plant, J. Chem. Soc. 125, 1503 (1924)
 (c) F. Beck (BASF) private communication
28. Private Communication from BASF (Ludwigs Lafen) from Drs. Reif
 and Pape, 1/29/79
29. Private Communication from Hoechst (Frankfurt) from Drs. Jensen and
 Lohaus, 1/17/79.
30. DT-OS 2,428,878 (1974); Euchem Conference on Organic Electro-
 chemistry, Pitlochry, Scotland 5/27/77
31. Private Communication from Prof. F. Beck, Gesamthochschule
 Duisburg, 4/10/79.

MISCELLANEOUS PROCESSES

Starting Material (Electrolyte)	Product(s)	Anode	Cathode	CE%	Energy Usage	Status	Refs.
sodium citrate ¹ (H ₂ O, sodium citrate)	citric acid, NaOH			high		C?-Liquichimica Biosintesi	1
cyanide waste stream (H ₂ O, various)	CO ₂ , H ₂ ²	C	Steel		12-15	C-several	2
methanol (CH ₃ OH, see footnote 3)	sodium methoxide	DSA ^R	Hg	high		C-Dynamit Nobel, Olin	3
montan wax (H ₂ O, chromic acid)	purified montan wax	PbO ₂	?			C-Hoechst	4,6
tetramethylammonium chloride ¹ (H ₂ O, quaternary chloride)	tetramethylammoniumhydroxide, chlorine	DSA ^R C	Steel	30-60		EC-Monsanto	5

1. example of electrodialysis

2. the initial products are cyanate and cyanogen

3. the process utilizes the sodium amalgam from mercury cells as follows:

References - Miscellaneous Processes

1. Brochure #EC-2, ChemomatTM, published 1976, Ionics Inc., 65 Grove St., Watertown, Mass. 02172
2. (a) J. K. Easton, J. Wat. Poll. Cont. Fed., 39, 1621 (1967)
(b) M. Tarjanyi and M. P. Strier, U. S. Pat. 3,764,497; 3,764,498 (1971)
(c) Report, 1974, Oxy Effluent Control Ltd., England
3. R. B. MacMullin, Chem. Eng. Progr. 46, 440 (1950)
4. M. Kappel, Chem.-Ing.-Tech., 35, 386 (1963)
5. (a) Monsanto Co., Brit. Pat., 1,066,930 (1967); Neth. Appl. 6,510,357 (1966); Neth. Appl. 6,603,164 (1966)
(b) G. S. Supin, USSR Pat. 132,205 (1960).
(c) Ref. 1
6. Private Communication from Hoechst (Frankfurt) from Drs. Jensen and Lohaus, 1/17/79

APPENDIX B

PROCESS DATA AND INFORMATION

The electroorganic literature is in many cases incomplete and inexact. When current efficiencies, yields, and process conditions were missing, guestimates were made by N. L. Weinberg in order to provide an informed basis for the calculations. Such parameters are annotated in Appendix B by (H) high confidence level, (U) uncertain confidence level, and (L) low confidence level.

ELECTROCHEMICAL CONVERSION OF
ACRYLONITRILE TO ADIPONITRILE AND HENCE:
1,6-HEXAMETHYLENEDIAMINE AND NYLON 66

- I. Present Electrochemical Status: Adiponitrile electrosynthesis is commercial in the USA with Monsanto (Decatur, Alabama); many other pilot scale studies have been and still are ongoing throughout the world. 1,6-Hexamethylenediamine has been piloted by electrochemical reduction of adiponitrile; however, no commercial process to replace catalytic hydrogenation of adiponitrile exists.
- II. (i) Chemical Processes: Adipic acid, synthesized from cyclohexane or its derivatives by oxidation, is converted to adiponitrile and the latter by chemical catalytic hydrogenation to 1,6-hexamethylenediamine. Reaction of adipic acid and hexamethylenediamine provides the basis for Nylon 66 synthesis.
- (ii) Production Figures: US production of Nylon 66 is expected to be about 2.7 billion lb in 1979 (C & E News, Dec. 4, page 11, 1978). Production figures for adiponitrile and 1,6-hexamethylenediamine should be closely related. Adiponitrile, considered as an intermediate, is not listed in Industrial Organic Chemical Production.
- III. Electrochemical Literature Discussion:
- A. Adiponitrile: An excellent summary of the Monsanto and competing processes is given by D. Danly in Organic Electrochemistry (Ref. 1). In the older Monsanto technology the catholyte consists of an aqueous solution of acrylonitrile, quaternary ammonium salt, and reaction products, in a divided (membrane) plate-and-frame type cell. The newer Monsanto technology (like the Phillips, Ref. 8)

requires no separation by membranes. Indirect electrochemical processes, utilizing sodium amalgam from chloralkali cells, have been described in a number of references (see Ref. 6,7).

- B. 1,6-Hexamethylenediamine: The Russians have been active in the electrochemical conversion of adiponitrile to 1,6-hexamethylene diamine and aminocapronitrile (both products are formed simultaneously with the relative yields depending on the current density primarily).

IV. Literature On Electrochemical Synthesis of Adiponitrile and

1,6-Hexamethylenediamine:

A. Adiponitrile:

1. Organic Electrochemistry, M. M. Baizer, Ed. Marcel Dekker Inc., NY: chapter by D. Danly, pp936-939 (1973).
2. M. M. Baizer, J. Electrochem. Soc., 111, 215 (1964);
US Pat. 3,193,480 (1965); US Pat. 3,193,481 (1965).
3. J. H. Prescott, Chem. Eng., Nov. 8, 238 (1965).
4. Anon., Chem. Eng. News, Oct. 2, 58 (1967).
5. F. Beck and H. Guthke, Chem. Ing.-Tech., 41, 943(1969).
6. I. L. Knunyants and N. P. Gambaryan, USP. Khim., 23, 781 (1958).
7. Anon., European Chem. News, 51, Dec. 19 26 (1969).
8. W. V. Childs and H. C. Walters, Symposium on Electroorganic Synthesis Technology, AIChE National Mtg. Atlanta, Feb/Mar. 1978.

B. 1,6-Hexamethylenediamine:

9. M. Y. Fioshin and A. P. Tomilov , USP. Electrokhimi,
Organicheskikh, Soyedineniy, pp 256-277 (1966).
10. Russ. Pat. 137,924 (1961).
11. M. Ohta, J. Chem. Soc. Japan, 63, 1762-5 (1942).
12. I. V. Kirilyns, et al., Tr. Khim. Met. Inst., Akad. Nauk Kaz SSR, 18, 105-7 (1972); USSR Pat. 445,647 (1974).

V. Organic Formulas/Physical Properties:*

		MW	bp °C/760mm
acrylonitrile	$\text{CH}_2=\text{CHCN}$	53.1	77
adiponitrile	$\text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$	108.1	295
propionitrile	$\text{CH}_3\text{CH}_2\text{CN}$	55.2	97
acrylonitrile trimer	$\begin{array}{c} \text{NC}-\text{CH}-(\text{CH}_2)_3\text{CN} \\ \\ (\text{CH}_2)_2 \\ \\ \text{CN} \end{array}$	-	-
hydroxypropionitrile	$\text{HOCH}_2\text{CH}_2\text{CN}$	71.1	228
<u>bis</u> -cyanoethylether	$\text{NC}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{CN}$	124.1	110-112 (at 0.5 mm)
quaternary ammonium salts	R_4NX^{**}	various	
1,6-hexamethylenediamine	$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$	116.2	204-5
aminocapronitrile	$\text{H}_2\text{N}(\text{CH}_2)_5\text{CN}$	-	-
Nylon 66	$[-\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}-]_n-$	-	-

VI. Electrochemical Routes:

(A) Monsanto Process for Adiponitrile

(a) Scheme:

(See Fig. 12A, Ref. 1)

*Physical Properties from: Handbook of Chemistry & Physics.

**R is usually alkyl (C_2H_5- or CH_3-) and x is usually halide, bicarbonate and p-toluenesulfonate.

Notes: The technology described here involves the use of a cation-exchange membrane, an aqueous solution of acrylonitrile containing tetraethylammonium p-toluenesulfonate as the catholyte, and dilute sulfuric acid as the anolyte. The cathode is lead and the anode lead alloy.

The newer Monsanto technology avoids the use of a separator.

(b) Reactions:

Major Side Reactions In Cathode Stream:

acrylonitrile

hydro-trimer

hydroxypropionitrile

bis-cyanoethylether

(c) Compositions of Streams:

(using separated cell)

<u>Input Stream</u>	<u>Composition</u>
	<u>wt %</u>
Catholyte:	
acrylonitrile	20
tetraethylammonium	40
p-toluenesulfonate	
water (pH: 8.5-9.0)	remainder

Anolyte:

sulfuric acid

H₂O

<u>Output Stream</u>	<u>wt %</u>
----------------------	-------------

Catholyte:

acrylonitrile

tetraethylammonium

p-toluenesulfonate

adiponitrile

propionitrile

acrylonitrile trimer

hydroxypropionitrile

bis-cyanoethylether

<1%

Anolyte:

sulfuric acid

H₂O

(d) Product CE's:

adiponitrile

95% (H)

propionitrile

5% (H)

oxygen

100% (H)

- (e) Cell Voltage: (6-12V 6V
given in lit.)
- (f) Energy Requirement: (3-6 kWh/kg 4kWh/kg
given in lit.)
- (g) Cell Temperature: 30°C
- (h) Temperature of Input: 20°C (H)
and Output Streams: 30°C(H)
- (i) Further Comments: The process examined above is that of
Monsanto's as described in the early patents.

B. 1,6-Hexamethylenediamine

- (a) Scheme:

(See Fig. 3 Ref. 9)

Notes: Two methods were developed in the USSR:

1. In Acid Medium (given here): Adiponitrile is reduced in aqueous HCl solution while chlorine is formed at the anode. The authors state that the cost of the product produced through the electrochemical route is 20% lower than via chemical hydrogenation of adiponitrile.
2. In Alkaline Medium: Although simpler technologically (no separator), product cost is higher because no chlorine is formed and the side product is formed in higher current efficiency.

- (b) Reactions:

side reactions:

(iii) unspecified organics

(c) Composition of Streams:

<u>Input Stream</u>	<u>wt % Composition</u>
to cathode:	
adiponitrile	28 (H)
HCl	20
water	remainder
nickel chloride (catalyst)	<1 (H)
to anode:	
HCl	20
water	remainder
<u>Output Stream</u>	
from cathode:	
adiponitrile	
1,6-hexanediamine • 2HCl	
aminocapronitrile • HCl	
hydrogen	
unspecified organic side products	
from anode:	
chlorine } as gas mixture	{ 98 (H)
oxygen }	{ 2 (H)
HCl	15 (M)
water	remainder

(d) Product CE's:

1 6-hexanediamine	60 (H)
aminocapronitrile	10 (H)
hydrogen	25 (M)
unspecified side products →	5 (M)
chlorine	95 (H)
oxygen	5 (H)

(e) Cell voltage: 7 (H)

(f) Energy Requirement: 16 (H)
kWh/kg

(g) Cell Temperature: 20°C

(h) Further Comments:

(i) because neutralization of product must be carried out to remove the diamine, the reaction is run in a batch process.

(ii) may not be at all competitive with catalytic hydrogenation which requires no neutralization.

ELECTROCHEMICAL CONVERSION OF
NITROBENZENE TO ANILINE

- I. Present Electrochemical Status: No known commercial process, but was piloted in India.
- II. Chemical Processes: Reduction of nitrobenzene with iron and HCl.
- III. Electrochemical Literature Review: Most of the available contemporary literature is from India.

The most favorable conditions found appear to utilize a copper cathode in aqueous acid solution having a redox reagent Ti^{+4}/Ti^{+3} present. Ti^{+3} is a powerful reducing agent. The major side-product, p-aminophenol, is generated with high temperature, high nitrobenzene concentration, and high current density.

IV. Literature:

1. M. Smialowski and H. Jarmolowica, Bull. Acad. Pol. Sci., Classe III, 3, 107 (1955).
2. H. V. K. Udupa, et al., Chem. Age of India, 15, 501 (1964).
3. P. N. Anantharaman, et al., Ind. J. Tech., 4, 274 (1966).
4. P. N. Anantharaman, et al., Bull Acad. Pol. Sci. Ser. Chim., 18, 629 (1970).
5. K. Swaminathan, et al., J. Appl. Electrochem., 2, 169 (1972).
6. A. Pourassamy, et al., Prep. Semin. Electrochem., 13th, 34-6 (1972).
7. H. V. Udupa, S. G. Subramanian, and N. Payyalur, Indian Pat., 128,412 (1974).

V. Formulas/Physical Properties:

		MW	
nitrobenzene	$C_6H_5NO_2$	123.1	mp $5.7^\circ C$ bp $211^\circ/760mm$
aniline	$C_6H_5NH_2$	93.1	mp $-6.2^\circ C$ bp $184^\circ/760mm$
p-aminophenol		109.1	mp $186^\circ C$
aniline bisulfate salt	$C_6H_5NH_2 \cdot H_2SO_4 \cdot \frac{1}{2}H_2O$	200.2	mp $162^\circ C$
aniline sulfate salt	$(C_6H_5NH_2)_2 \cdot H_2SO_4$	284.3	mp; decomposes

VI. Proposed Electrochemical Route:

(a) Scheme

According to Refs. 5 and 7.

(b) Reactions:

Side Reactions:

(c) Composition of Streams: (from batch type process)

Input: Given
 Composition

Catholyte:

nitrobenzene	240g/l	(1.95M)
sulfuric acid	10%vol/vol	
titanous sulfate	8.6g as TiO ₂	
cupric sulfate	1 g/l	
water	remainder	

Anolyte:

sulfuric acid	10% vol/vol
water	remainder

Output:Catholyte:

nitrobenzene	nil	
aniline (as H ₂ SO ₄ salt)	171g/l	(1.83M)
p-aminophenol (as H ₂ SO ₄ salt)	13 g/l	(0.12M)
sulfuric acid	10% vol/vol	
titanous sulfate	8.6 g as TiO ₂	
cupric sulfate	1g/l	
water	remainder	

Anolyte:

sulfuric acid	
oxygen	
water	remainder

(d) Product CE's:

aniline	94% (H)
p-aminophenol	5% (H)
hydrogen	1% (H)
oxygen	100% (H)

(e) Cell Voltage: 5V

(f) Energy For Cell: 9.2 kWh/kg

(g) Cell Temperature: 25-30°C

(h) Temperature of Input/Output Streams

(BatchProcess): 25-30°C

(i) The process described is a batch process based on information in Ref. 5 and 7. A continuous process would require separation of aniline sulfate and p-amino phenolsulfate from the electrolyte (crystallization?), and release of the free aromatic amines from their salts by neutralization. (Loss of H_2SO_4 electrolyte would be expensive, and likely this aspect would make the process uneconomical).

ELECTROCHEMICAL SYNTHESIS OF
TOLUENE-2,4-DIAMINE

- I. Present Electrochemical Status: no processes known to be piloted or commercial.
- II. Chemical Processes: Prepared by catalytic reduction of 2,4-dinitro-toluene.
- III. Electrochemical Literature:

Partial electrochemical reduction appears to favor formation of 4-amino-2-nitrotoluene (Ref. 3,4). Reduction can also occur to give phenylhydroxylamine derivatives, and if run too hot, a p-aminophenol derivative can be formed (Ref. 1). The electrochemical process is highly dependent on electrode potential, temperature.

IV. Selected Literature References:

1. A. Tallec and D. Peltier, C. R. Congr. Nat. Soc. Savantes, Sect. Sci., 91, 103 (1966).
2. A. Tallec, Ann. Chim. (Paris), 3, 347 (1968).
3. F. Goodridge and K. C. Nath, Electrochim. Acta, 20, 685 (1975).
4. H. Hofer, F. Jacob, Chem. Ber., 41, 3193 (1908).

V. Organic Formulas/Physical Properties:

2,4-dinitrotoluene

MW 182.14; mp. 70-1°C
bp 300°

toluene-2,4-diamine

MW 122.17; mp. 99°C

bp 292/760 mm

4-amino-2-nitrotoluene

MW 142.15; mp. 117°Cm-xylenesulfonic acid MW 186

VI. Proposed Electrochemical Route:

(a) Scheme - above

Notes on above scheme:

(1) The emulsifier unit (rapid mixing) perhaps with the presence of a suitable emulsifying agent (i.e., M-xylenesulfonic acid) would aid mass transfer of highly insoluble 2,4-dinitrotoluene.

(2) The diamine product, in the catholyte, as the soluble sulfate salt, requires separation by neutralization with caustic. On neutralization two layers would form. The upper layer would contain the free amine dissolved in starting material. The layers would be separated and distilled.

(3) On neutralization of the catholyte, Na_2SO_4 would form. This could be recovered as a product, discharged, or sent to another electrolysis cell to produce caustic and sulfuric acid.

(4) A purification setup might be needed for the recycling anolyte, especially if leakage of product occurs through the membrane.

(b) Electrochemical and Chemical Processes:

At the cathode:

(as the sulfate salt)

(assuming (ii) does

not occur)

Chemical Neutralization:

(c) Composition of Streams Mole % Composition to/from Cell:

Input

<u>catholyte</u>	2,4-dinitrotoluene	1M
	sulfuric acid	5M
	water	remainder
<u>anolyte</u>	sulfuric acid	5M
	water	remainder

Output

<u>anolyte</u>	oxygen	pure gas
	sulfuric acid	5M
	water	remainder
<u>catholyte</u>	2,4-dinitrotoluene	
	toluene-2,4-diamine*	
	water	
	hydrogen	pure gas

*as sulfate salt

(d) Current Efficiencies of Products:

toluene-2,4-diamine	90% (M)*
oxygen	100%
hydrogen	10% (M)

(e) Cell Voltage: 4V (H)

(f) Energy For Cell: 11.7 kWh/kg (M)

(g) Cell Temperature: 50°C**

(h) Temperature of Input/Output Streams: 50°C

*"optimized" current efficiency

**a higher temperature could result in aminophenol

ELECTROCHEMICAL CONVERSION OF
GLUCOSE TO SORBITOL AND MANNITOL

- I. Present Electrochemical Status: In 1937, the Atlas Powder Co. built a plant to produce about 1500 tons per year. In 1948 catalytic hydrogenation replaced the electrochemical route.
- II. Chemical Processes: High pressure hydrogenation of glucose.
- III. Electrochemical Literature Comments:
- A. Mantell (Ref. 6) provides a good overview of the process.
 - B. Cell performance data are given in Refs. 1, 4, and 5.
 - C. Mantell comments that "the Creighton electrolysis never had the benefit of continuous chemical engineering processing or good development of cell design".
 - D. A Pb/PbO₂ anode and Pb/Hg cathode were used with a ceramic separator.
- IV. Literature References:
- 1. H. J. Creighton (Atlas Powder Co.), U.S. Pat. 1,612,361 (1926) 1,653,004 (1926); 1,712,952 (1929); 1,990,582 (1935).
 - 2. R. L. Taylor, Chem. Met. Eng., 44, 588 (1937).
 - 3. D. H. Killeffer, Ind. Eng. Chem News, Ed., 15, 489 (1939).
 - 4. H. J. Creighton, Trans. Am. Electrochem. Soc., 75, 289 (1939).
 - 5. M. T. Sanders and R. A. Hales, J. Electrochem. Soc., 96, 241 (1949).
 - 6. C. L. Mantell, Electro-Organic Chemical Processing, Noyes Dev. Corp., N. J., 1968. pp 147-150.

V. Organic Formulas/Physical Properties:

Note: The monohydrate has a MW of 198.2 and is the most common form.

VI. Electrochemical Route:

(a) Scheme: see Mantell Schematic, p 149, Ref. 6.

(b) Reactions:

and

Chemical Reaction:

At higher pH's glucose isomerized to mannose, hence reduction of mannose to mannitol can occur.

(c) Compositions of Streams*:

<u>Input Streams</u>	<u>Composition</u> (a)	
<u>Catholyte:</u> (pH 8 to 9)	<u>grams/l</u>	<u>mole %</u>
glucose	325	3.8
sodium sulfate	85	1.2
sodium hydroxide	0.1	(0.0054)
water	remainder	95

Anolyte:

sulfuric acid	200	4.0
water	remainder	96

Output Streams**Catholyte:

glucose	33 (H)	0.38 (H)
sorbitol	293 (H)	3.4 (H)
mannitol	nil (H)	nil (H)
hydrogen	nil (H)	nil (H)
sodium sulfate	90 (H)	1.3 (H)
water	remainder (H)	95 (H)

Anolyte:

sulfuric acid	200 (H)	4.0 (H)
water	remainder (H)	96 (H)

(a) where appropriate, compositional data are quoted as interpolated values taken from the Handbook of Chemistry and Physics.

*The original process was a batch operation with no electrolyte recycle and significant losses through the separator of starting material, product, and electrolyte.

**The results quoted are based on Ref. 4, Table V, and assuming a highly efficient membrane (modern technology).

(d) Product CE's:

sorbitol 90 (H)

oxygen 95 (H)

Note: CE losses are expected because of membrane leakages, and oxidation of sorbitol and glucose (leaking through) at the anode. These organic oxidation products could include CO₂, oxalic acid, and higher oxidation products of sorbitol and glucose.

(e) Cell Voltage: 20V*** (current density 4A/dm²)

(f) Energy Requirement: 6500 Wh/kg

(g) Temperature Input/Output Streams: 25°C

(h) Further Comments: (1) The heat of reduction of glucose to sorbitol is given in Ref. 5 as 110 Btu/lb.

(2) Substantial savings in energy and materials might prove to be apparent if a continuous process is devised.

***An optimized cell would more realistically have a cell voltage of 5 to 10V, and closer to 5V.

ELECTROCHEMICAL SYNTHESIS OF TEREPHTHALIC ACID

I. Present Electrochemical Status: no pilot studies known.

II. Chemical Processes: p-xylene is combined with nitric acid or air (plus a catalyst) to give terephthalic acid:

III. Electrochemical Literature Review:

The electrochemical literature is sparse; however, there are three processes which merit consideration:

- A. Electrooxidation of p-xylene (Ref. 1,2)
- B. Electrooxidation of p-toluic acid (Ref. 3-6)
- C. Electrooxidation of p-xylene glycol (Ref. 7)

Of the three processes, the electrooxidation of p-xylene glycol shows the best CE (99%). Process A. starts with the least expensive starting material, but consumes the most electrical energy.

IV. Literature:

1. J. W. Shipley and M. T. Rogers, Can. J. Res., 17B, 147 (1939).
2. H. Hayashida, Chem. Abstr., 75, 36984m (1971).
3. A. J. Allmand and A. Puttick, Trans. Faraday Soc., 23, 641 (1927).
4. F. Fichter and C. Simon, Helv. Chim. Acta, 17, 717 (1934).
6. R. M. Englebrecht, J. C. Hill, and R. N. Moore, US Pat, 3,714,003 (1973).
7. E. G. Bondarenk and A. P. Tomilov, Zh. Prikl. Khim., 42, 2033 (1969); USSR Pat., 193,490 (1967).
8. C. L. Mantell, Electroorganic Chemical Processing, Noyes Dev. Corp., NJ (1968).

V. Organic Formulas/Physical Properties:

	MW	mp ^{°C}
p-xylene	106	13-4 (bp 138 ^{°C})
p-toluic acid	136	179-180
p-xylene glycol	138	112-113
terephthalic acid	166	(sublimes)
terephthalaldehydic acid	150	248-250

p-xylene

p-toluic acid

p-xylene glycol

terephthalaldehydic
acid

terephthalic acid

VI. Proposed Electrochemical Routes:

A. From p-xylene utilizing a Cr^{+6} regeneration cell.

(a) Scheme see scheme of Ibl, et al., AIChE Mtg, Mantell Book
and Millington Paper, Chem. & Ind., 780 (1975).

(b) Reactions:

in solution

side reactions:

(c) Composition of Streams/Cell (only)

(see Ref. 8, page 118, 126-133)

Input: (spent)

Composition (mole%)

At anode: $\text{Cr}_2(\text{SO}_4)_3$

26.9

H_2SO_4

12.2

Water

60.0

Output: (regenerated)

CrO_3	6.8
----------------	-----

$\text{Cr}_2(\text{SO}_4)_3$	13.2
------------------------------	------

H_2SO_4	21.9
-------------------------	------

H_2O	58.1
----------------------	------

At cathode: Hydrogen	as pure gas
----------------------	-------------

(d) CE's products:

CrO_3 (at 50% regeneration)	70% (H)
--------------------------------------	---------

oxygen

hydrogen	90% (H)
----------	---------

(e) Cell Voltage:

(f) Energy for Cell: 2.2 kWh/kg
chromic acid

(g) Cell Temperature: 55°C (h) Temperature of input/output streams: 55°C

B. From p-toluic Acid:

(a) Scheme: see Cr^{+6} cell/reactor

(b) Reactions:

in solution:

side reactions: $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$

(c) Composition of Streams/Cell (only):

(see A.)

(d) (f) (see A.)

C. From p-Xylene Glycol:

(a) Scheme: see Cr^{+6} cell

(b) Reactions:

(c) to (h) (see A.)

ELECTROCHEMICAL SYNTHESIS OF PHENOLS INCLUDING
INCLUDING PHENOL, SALICYLIC ACID, CRESOLS, P-TERTBUTYLPHENOL
2,4-DICHLOROPHENOXYACETIC ACID

I. Present Electrochemical Status: Other than piloted studies of naphthol derivatives from naphthalenes (by acyloxylation), and aryl aminophenols (from electroreduction of nitroaromatics), no piloted or commercial processes exist for phenol, salicylic acid or cresols.

II. Chemical Processes:

- A. Phenol: Obtained from coal tar or by heating monochlorobenzene with aqueous caustic under high pressure.
- B. Salicylic Acid: Obtained by heating sodium phenolate with CO_2 under pressure (see Faith, et al., Industrial Chemicals, John Wiley, 1965, pp652-655). Salicylic acid acetate (aspirin) is usually prepared by acetylation of salicylic acid with acetic anhydride and a trace of acid (H_2SO_4).
- C. Cresols (cresylic acid): The mixture of cresols in which the meta isomer predominates is usually obtained from coal tar.
- D. P-TertButyl Phenol: (see note)
- E. 2,4-D: (see note)

III. Electrochemical Literature Review:

The direct electrochemical oxidation of aromatics to phenols in aqueous media has not been a promising route for several reasons including:

- (i) very little control could be achieved on the course of reaction and many products can form including all possible isomers.

- (ii) the phenols are themselves so easily oxidized compared to the aromatics that further hydroxylations occur to give hydroquinones and quinones.

Very promising routes have been developed in recent years and these may be described generally in the two equations following:

where R and R' are electron-donating or withdrawing

where $[\cdot\text{OH}]$ is formed at the cathode and R is H or CH_3 .

IV. Selected Literature References:

1. C. M. Wright, R. F. Heck, and W. Yokoyama, Abstr. Electrochem. Soc. Mtg., New York, May, 1969, p 36.
2. R. Tomat and E. Vecchi, J. Appl. Electrochem., 1, 185 (1971).
3. N. L. Weinberg and C. N. Wu, Tetrahedron Letters, 3367 (1975).
4. N. L. Weinberg, US Pat., 4,096,044 (1978); US Pat., 4,096,052 (1978).
5. Y. So, J. Y. Becker, and L. L. Miller, J.C.S. Chem. Commun., 262 (1975).
6. E. Steckhan and J. Wellmann, Angew. Chem. - Int. Ed., 15, 1076 (1976).
7. G. Bockmair, H. P. Fritz and H. Gebauer, Electrochem. Acta, 23, 21 (1978).
8. M. I. Usanovich, et al., Elektrokhimiya, 7, 915 (1971).
9. L. Eberson, et al.: many studies. See for example in Technique of Electroorganic Synthesis, Part I, N. L. Weinberg, Ed., John Wiley, 1974, pp 265-271.
10. Y. So and L. L. Miller, Synthesis, 468 (1976).
11. Z. Blum, L. Cedheim and R. Nyberg, Acta Chem. Scand., 26, 715 (1975).

V. Organic Formulas/Physical Properties:

		MW	mp °C
benzene	C_6H_6	78.11	5.5° (bp 80.1°/760)
phenol	C_6H_5OH	94.11	43° (bp 182°/760)
benzoic acid	$C_6H_5CO_2H$	122.12	122.4° (bp 249°/760)
<u>o</u> -hydroxybenzoic acid (salicylic acid)		138.12	157-159° (bp 211°/760)
<u>m</u> -hydroxybenzoic acid		138.12	201.5°
<u>p</u> -hydroxybenzoic acid		138.12	215°
hexafluoroethane	C_2F_6	138.01	-94° (bp -79°/760)
trifluoroacetic acid	CF_3CO_2H	114.12	-15.3° (bp 72.4°/760mm)
biphenyl		154.20	70° (bp 256°/760mm)
<u>o</u> -cresol		108.13	30° (bp 191-192°/760)
<u>m</u> -cresol		108.13	11-12° (bp 202°/760mm)
<u>p</u> -cresol		108.13	35.5° (bp 202°/760mm)
toluene		92.13	-95° (bp 110.6°/760)

VI. Proposed Electrochemical Processes:

Two studies follow: the conversion of benzoic acid to salicylic acid, and the conversion of benzene to phenol. The latter study will provide a model route for toluene to cresol. Too little information exists in the literature so that much guess work is involved in providing data for "optimized" processes.

A. Benzoic Acid to Salicylic Acid:

(a) Scheme:

(b) Electrochemical and Chemical Processes:

At Anode:

major process:

(mixture of o, m, p-isomers)

minor processes:

In Solution (Chemical Reaction):

hydrolysis:

mixture of hydroxybenzoic acid isomers

Hydrolysis occurs quickly in the aqueous trifluoroacetic acid solution (electrolyte)

(c) Composition of Streams:

<u>To Cell</u>	<u>Concentration</u>	<u>Mole % Composition</u>
trifluoroacetic acid	remainder (M)	63.5 (M)
sodium trifluoroacetate	0.5 <u>M</u> (M)	2.6 (M)
water	10% (M)	28.6 (M)
benzoic acid	1.0 <u>M</u> (M)	5.3 (M)

From Cell:

Gases:	hydrogen	cathode gas	100% (H)
	oxygen		
	carbon dioxide	} anode gases	
	trifluoroethane		
	trifluoroacetic acid		
	sodium trifluoroacetate		
	water		
	benzoic acid		
	<u>o</u> -hydroxybenzoic acid		
	<u>m</u> -hydroxybenzoic acid		
	<u>p</u> -hydroxybenzoic acid		

(d) Product Current Efficiencies:

* <u>o</u> -hydroxybenzoic acid (salicylic acid)	49 (M)
<u>m</u> -hydroxybenzoic acid	13 (M)
<u>p</u> -hydroxybenzoic acid	27 (M)
hexafluoroethane	3.5 (L)
carbon dioxide	7 (L)
oxygen	0.5 (L)
hydrogen	100% (H)

(e) Cell Voltage: 7V (M)

(f) Energy For Cell: 6 kWh/kg (M)

(g) Cell Temp.: 50°C (M)

(h) Temp. of Input/Output Streams: 50°C

*The relative ratio of isomeric products is that calculated by Blum, et al.,
(Ref. 11).

B. Benzene to Phenol (via electrochemically generated Fenton's Reagent):

(a) Scheme:

The proposed scheme suggests oxygen produced at the anode becomes part of the oxygen feed to the cathode. An excess of benzene could protect the product, phenol, from further hydroxylation.

(b) Electrochemical and Chemical Processes:

At the Cathode: (2 major processes needed),

minor processes:

In the Catholyte: (chemical; two processes needed)

(Fenton's reagent)

References 2 and 6 point out the following to achieve optimal yields of phenol:

- (1) the total yield of phenol + biphenyl depends on the ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$; highest yields occur when $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1$
- (2) increasing the concentration of Fe^{3+} increases the the phenol yield
- (3) set the reduction potential at -0.35V vs SCE,
- *(4) use a low H_2SO_4 concentration

* H_2SO_4 (Ref. 2) seems to react with $\cdot\text{OH}$; HClO_4 (Ref. 6) was used alternatively.

- (5) phenol should be removed as it is formed to avoid further hydroxylation
- (6) a large excess of benzene
- (7) low operating temperature.

(c) Composition of Streams:

<u>To Cell</u>	<u>Relative Conc.</u>	<u>Composition Mole%</u>
benzene	50 ml. = 0.55 <u>M</u>	3.2(L)
sulfuric acid	0.1 <u>M</u>	0.6 (M)
ferric sulfate	0.0035 <u>M</u>	0.02 (M)
water	300 ml = 16.7 <u>M</u>	96.18 (H)
oxygen	0.001 <u>M</u> (est)	<u>0.006 (M)</u>
		100.006%
<u>From Cell</u>		
benzene		
sulfuric acid		
phenol		
biphenyl		
ferric sulfate	0.0035 <u>M</u>	
water		
oxygen (excess from catholyte		
+ gas from anolyte)		

(d) Current Efficiencies of Products:

At Anode: oxygen	100% (H)
At Cathode: phenol	85% (M)*
biphenyl	0.3% (M)
miscellaneous	14.7% (M)**

(e) Cell Voltage: 4V (M)

(f) Energy For Cell (assuming a 3e overall process): = 4.0 kWh/kg (M)

(g) Cell Temperature: 25°C

(h) Temperature of Input/Output Streams: 25°C

Notes: (1) m-Cresol formation is a poor process electrochemically using toluene as a feed. Acetoxylation would favor the o- and p-isomers, and hydroxylation with Fenton's reagent $[\text{Fe}^{2+}/\text{H}_2\text{O}_2]$ would give all the isomers. Hence m-cresol is not covered here.

(2) p-tert-Butylphenol might be prepared by the direct acyloxylation (trifluoroacetic acid/NaTFA route) or by electrochemically generated Fenton's Reagent. Either route would give the other isomers but the former might be cleaner. This product is prepared chemically from phenol:

* "optimized"

**miscellaneous processes include water formation from O_2 and H_2O_2 and conversion of Fe^{2+} to Fe^{3+} by $\cdot\text{OH}$.

ELECTROCHEMICAL SYNTHESIS OF PROPYLENE OXIDE

(AND COMMENTS ON ETHYLENE OXIDE)

I. Present Electrochemical Status: There are several pilot studies in progress in Europe for electrochemical conversion of propylene to propylene oxide.* No studies are being made on ethylene oxide.

II. A. Chemical Processes for Propylene Oxide:

(a) The oldest is the chlorohydrin process (Dow and others).

Propylene is contacted with hypochlorous acid, followed by hydrolysis of the resultant chlorohydrin with lime

This process has two problems; (i) the calcium chloride by-product can be harmful to the environment, and (ii), the chlorine is costly.

(b) Oxirane Chemical has a "direct" oxidation process in which propylene is epoxidized with an organic hydroperoxide.

Although the propylene oxide yield is about 90%, the economics of the process are strongly dependent on the availability of by-product markets.

(c) Produits Chimique Ugine Kuhlmann (PCUK, France) have recently announced a new "direct" process**. Propylene

* Information provided to NLW in private communication by J. A. M. LeDuc.

** C & E News, Dec. 11, p 24 (1978).

reacts with 70% H_2O_2 in the presence of a catalyst in a solvent. The degree of selectivity is 95%. Low-boiling propylene oxide is stripped off, while solvent and unused H_2O_2 are recycled. Metaboric acid is used to combine with the liberated water. Dehydration of the hydrate recovers the metaboric acid for reuse. The process is still undergoing development.

"Direct" oxidation using oxygen itself (as with the ethylene oxide process) has been unsuccessful. The methyl group tends to be too readily oxidized. An excellent review of chemical routes and major drawbacks is given by Simmrock in Ref. 4 (c).

B. Chemical Process for Ethylene Oxide:

Ethylene oxide is manufactured by direct catalytic oxidation of ethylene (U.S. Pat. 2,960,511; C & E News, Jan. 22, p 8, 1973). The process is operated at low concentrations of ethylene and oxygen to prevent explosions and minimize side products.

III. Electrochemical Literature Review:

The majority of the available literature has come from Pullman/Kellog (J. A. M. LeDuc) and Bayer, and their joint interaction in the late sixties. Essentially, the olefin is introduced into what amounts to a chloralkali cell. In one such method, the undivided cell causes the chlorhydrin formed at the anode to be hydrolyzed to the epoxide by base being generated at the cathode. In another process, using a compartmented cell, the chlorhydrin stream (anolyte) is contacted with base (catholyte). An alternative route (Ref. 4) couples a membrane chloralkali cell with conventional propylene chlorhydrin synthesis and hydrolysis.

IV. Selected Literature:

A. Propylene Oxide Electrosynthesis:

1. J. A. M. LeDuc, U.S. Pat. 3,288,692 (1966), 3,342,717 (1967), 3,379,627 (1968); Ger. Offen. 1,906,182 (1970); U.S. Pat. 3,427,235 (1969).
2. Farbenfabriken Bayer, Ger. Pat. 1,252,649 (1967); Fr. Pat. 1,540,800 (1968), 1,574,783 (1969); Ger. Pat. 1,258,856 and 1,258,857 (1968), 1,290,926 (1969); Ger. Offen. 2,020,590 (1969).
3. T. D. Binns and D. C. G. Gattiker, U.S. Pat. 3,635,803 (1972).
4. (a) K. H. Simmrock and G. Hellemans, Ger. Pat. 2,658,189 (1978).
 (b) C & E News, March 6, pp 20-21 (1978).
 (c) K. H. Simmrock, AIChE 84th National Mtg., Atlanta, GE, Feb. 26, 1978, Abstracts of Papers.

B. Ethylene Oxide Electrosynthesis:

Most of the above references also cover ethylene oxide electro-synthesis.

V. Organic Formulas/Physical Properties:

	<u>MW</u>	<u>bp °C/760 mm</u>
Ethylene, C_2H_4	28.05	-104
Ethylene oxide, C_2H_4O	44.05	10.7
Ethylene chlorohydrin, CH_2ClCH_2OH	80.52	128-130
Ethylene dichloride, CH_2ClCH_2Cl	98.96	84
Ethylene glycol, $\begin{array}{c} CH_2 - CH_2 \\ \quad \quad \\ OH \quad \quad OH \end{array}$	62.07	198
Propylene, C_3H_6	42.08	-47.8

	<u>MW</u>	<u>bp°C/760 mm</u>
Propylene chlorohydrin*, $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{Cl}}{\text{CH}_2}$	94.54	126-7
Propylene dichloride, $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\underset{\text{Cl}}{\text{CH}_2}$	112.99	96.2
Propylene glycol, $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}_2}$	76.10	189
Dichlorodiisopropyl ether,	165	?

VI. Proposed Electrochemical Routes (Propylene Oxide):

The process adopted for discussion here is that described in Ref. 4.

The energies associated with brine purification and especially caustic soda solution evaporation in a conventional chloralkali cell are eliminated. An oxygen-depolarized cell is also considered here in B.

* Another isomer is also formed in smaller (about 10%) amounts:

This will also hydrolyze, however, to the epoxide.

A. (a) Scheme: Conventional Chloralkali:**Propylene oxide process combines chlorohydrin synthesis with ion exchange membrane cell** (b) Electrochemical & Chemical Processes:

Chemistry in various streams:

Major Side Reactions:

(c) Composition Of Streams:

<u>Input:</u>	<u>Wt%</u>
Anolyte: salt	7
HCl	
Water	
Catholyte:	

Output:

(d) Product Current Efficiencies:

From anode reactions based on Cl ₂	Propylene oxide	88% (H)
	Propylene dichloride	9% (H)
	Propylene glycol	1% (H)
	Dichlorodiisopropyl ether	<1% (H)
	Oxygen	<1%
	Hydrogen	100%

(e) Cell Voltage: 3.75 V

(f) Energy for Cell: 5.6 kWhr/kg propylene oxide.

(g) Cell Temp.: 55°C

(h) Temp. of Input/Output Streams: ?

B. (a) Scheme: Oxygen - Depolarized Cell:

(essentially flow scheme as in A. except O₂ is a feed to cathode space, and no H₂ is formed.)

(b) Electrochemical & Chemical Processes: Same as before except that at cathode, the reaction is:

(c) Composition of Streams: Same as before, except oxygen is introduced at the cathode and no hydrogen is formed.

- (d) Product CE's: Same as before, but eliminate value for hydrogen.
- (e) Cell Voltage: Assume a saving of 1.00 V using air-depolarized cell: 2.75 V (H)
- (f) Energy for Cell: 4.1 kwh/kg
- (g) Cell Temp.: 55°C
- (h) Temp. of Input/Output Streams: ?

Additional Comments:

1. Much of the input/output compositional data could be extrapolated from the chloralkali process.
2. While the electrochemical ethylene oxide process does not look feasible because of the success of the chemical route, a comparison on an energy basis might be interesting.

ELECTROCHEMICAL CONVERSION OF OLEFINS TO METHYL KETONES

A. Propylene to Acetone

B. 1- and 2-Butenes to 2-Butanone

I. Present Electrochemical Status: No known pilot or commercial processes at present. In 1971 Esso (Exxon) was to build a plant for methyl ethyl ketone from 1- and 2-butenes: plans were abandoned.

II. Chemical Processes: Ketones are produced commercially in these steps:

A. Reaction of olefin with conc. H_2SO_4 with formation of an organic sulfate

B. Hydrolysis of the sulfate to the alcohol, followed by separation

C. Catalytic dehydrogenation of the purified alcohol in vapor phase by a solid catalyst at high temperature (650 - 900 °F)

III. Electrochemical Literature Review:

Direct electrochemical processes starting from olefins (Ref. 1-4, 8-13) should be more attractive than from alcohols (Ref. 5-7). The most available studies published by Esso Res. during the mid 60's involve direct electrochemical oxidation of the olefin in aqueous sulfuric acid solution at a platinum coated anode. In one description,

the process is operated in a fuel cell mode, utilizing an oxygen depolarized cathode (Ref. 9).

An alternative process (Ref. 11) is described in which the olefin is oxidized via redox reagents (Tl^{+3} solution containing Ce^{+4} and a noble metal salt).

VI. Literature:

Acetone, from Propylene:

1. M. Fleischmann, D. Pletcher, and G. M. Race, J. Electroanal. Chem., 23, 369 (1969).
2. G. E. Nelson, U.S. Pat., 3,419,483 (1968).
3. O. G. Tyurikova, N. B. Miller and V. I. Veselovskii, Elektrokhimiya, 8, 618 (1972); USSR Pat. 390,063 (1973).
4. V. A. Shepelin, Novosti Elektrokhim. Ors. Soedim Tezisy Dokl. Vses. Soveshch, 8th, 19-20 (1973).

Acetone, from Isopropyl Alcohol:

5. G. Horanyi, P. Konig, and I. Telcs, Magy. Kem. Foly., 77, 432 (1971).
6. K. Elbs and O. Brunner, Z. Elektrochem., 6, 604 (1900).
7. T. Kurenniemi, et al., Chem. Abstr., 31, 1299 (1937).

2-Butanone, from 1, & 2-Butenes:

8. European Chemical News, 15 (1969).
9. C. H. Worsham (to Esso Res), U.S. Pat., 3,219, 562 (1965),
3,247,084 (1966); 3,247,085 (1966); Brit. Pat., 935,236 (1963).
10. L. I. Griffin, Jr., J. V. Clarke, Jr., and C. H. Worsham,
(to Esso Res) U.S. Pat., 3,324,593 (1967).
11. A. F. Maclean and A. L. Stantzenberger, (to Celanese), U.S. Pat.,
3,479,262 (1969).

12. Farbwerke Hoechst, Belg. Pat., 648,304 (1964); Chem. Abstr.,
63, 130821 (1965).
13. See Ref. 2 above.

V. Organic Formulas/Physical Properties:

	<u>MW</u>	<u>bp °C/760 mm</u>
propylene $\text{CH}_3\text{CH}=\text{CH}_2$	42.1	-47.8
1-butene $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	56.1	-6.3
2-butene $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	56.1	{ 3.7 (cis) 0.9 (trans)
acetone CH_3COCH_3	58.1	56.2
2-butanone $\text{CH}_3\text{CH}_2\text{COCH}_3$	72.1	79.6

VI. A. Scheme:

See Exxon patents, esp. U.S. Pat. 3,247,085.

Processes:

At Anode:

side processes produce CO_2 :

At Cathode:

VI. B. Stream Compositions:

Input

To Anolyte:

1-butene pure gas (excess)
aq. sulfuric acid 10 M

To Catholyte:

oxygen pure gas
aq. sulfuric acid 10 M

Output

From Anolyte:

1-butene
2-butanone (selectivity, 93%)
aq. sulfuric acid 10 M
carbon dioxide (selectivity, 7%)
oxygen

From Catholyte:

oxygen
aq. sulfuric acid 10 M

C. Yields of Products:

At Anode:

2-butanone 92% (H)
carbon dioxide 8% (M)

At Cathode: water 100% (H)

ELECTROCHEMICAL SYNTHESIS OF MELAMINE

(FROM CYANOGEN BROMIDE)

- I. Present Electrochemical Status? (Was piloted by Standard Oil Co. (Sohio) in early 60's)
- II. Chemical Processes: Commercial processes for melamine are mainly based on dicyanodiamide (or cyanoguanidine) which is produced from calcium cyanamide (Mackay, U.S. Pat. 2,737,513 (1956)).
- III. Electrochemical Literature Review: The literature is contained in a key publication (Ref. 1) and several patents (Ref. 2,3). Briefly, the process described by Sohio involves electrolysis of hydrogen cyanide in ammonium bromide solution to give cyanogen bromide. Further chemical steps are (1) ammonolysis of cyanogen bromide, and (2) trimerization of cyanamide (formed in step 2) to melamine.
- IV. Selected Literature:
1. R. W. Foreman and J. W. Sprague, Ind. Eng. Chem., Prod. Res. Dev., 2, 303 (1963).
 2. R. W. Foreman and F. Veatch, U. S. Pat., 3,119,760 (1964).
 3. J. W. Sprague, et al., U. S. Pat., 3,294,657 (1966): U. S. Pat., 3,300,398 (1967).
- V. Organic Formulas/Physical Properties:

	<u>MW</u>	<u>bp °C/760mm</u>
hydrogen cyanide, HCN	27.03	25.6
cyanogen bromide, CNBr	105.93	61-62
Melamine,	126.13	(mp < 250°C)

Cyanamide, H_2NCN

42.04

(mp 45-46 °C)

VI. Sohio Electrochemical Route:

A. Scheme: see Ref 1, Fig. 1

B. Electrochemical and Chemical Processes:

Chemical Reaction At Anode:

In CNBr Reactor: (Chemical Step)

In Trimerization Reactor: (Chemical Step)

Net Reaction:

C. Composition of Streams:

Input (Cell)

Anode Feed:	Wt%
hydrogen cyanide	2.4*
ammonium bromide	25.0*
water	72.6*

*Conditions from patent

Cathode Feed:	<u>Wt or Vol</u>
concentrated ammonium hydroxide solution	10 lbs.**
ammonium bromide	10 lbs.**
water	3 liters

**from paper

Output (Cell)

Anode Compartment:

ammonium bromide	?
cyanogen bromide	175 g
hydrogen cyanide	2.4 g
water	

Cathode Compartment:

hydrogen gas

ammonia gas

others in solution?

D. Product 'CE's:

cyanogen bromide	98%
bromine	2%
hydrogen gas	100%
ammonia	100%

E. Cell Voltage: 3.1V

F. Energy For Cell: 1.5 - 2 kWhr/kg

G. Cell Temperature: 27°C

H. Temp. of Streams (Cell):

Input ? (Probably near 25°C)

Output ? (Probably near 27°C)

I. Comments: While the literature indicated few side products,
it is possible that NC-CN (cyanogen) is produced in the cell.

ELECTROCHEMICAL CONVERSION OF BENZENE (OR PHENOL) TO HYDROQUINONE

- I. Present Electrochemical Status: Several pilot studies have been recently conducted (Electricity Council/Staveley Chemical Co. - in England; Carus Chemical Co; Union Carbide; Union Rheinische Braunkohlen Kraftstoff Aktiengesellschaft (UK)). None have yet reached commercialization.
- II. (i) Chemical Processes:
- (a) Oxidation of aniline with $\text{MnO}_2/\text{H}_2\text{SO}_4$ followed by reduction of the quinone to the product.
 - (b) Acetylene + CO (duPont)
 - (ii) Hydroquinone Production: 16,575,000 lbs/yr.
- III. Electrochemical Literature Discussion:
- Three important processes have been conducted:
- Ref. 1-3: The Electricity Council/Staveley Chemical Co., have piloted a process wherein benzene is oxidized to benzoquinone. The benzoquinone is then chemically reduced outside the cell with SO_2 .
- Ref. 4-6,8: Fremery et al. describe a small piloted process wherein benzene is oxidized to benzoquinone. The anolyte containing the benzoquinone intermediate is then brought into the cathode compartment where hydroquinone is formed. Anderson and Kessler describe a process for producing quinone. Keidel (Ref. 8) describes an interesting variation with improved yields using Redox couples.
- Ref. 7: The Union Carbide process starts with phenol and utilizes

both anode and cathode compartments.

Many additional studies emanating from many countries are not listed here.

IV. Literature on Electrosynthesis of Hydroquinone:

1. J. P. Millington, Brit. Pat., 1,377,681, (1974).
2. J. P. Millington, Chem & Ind., 780, (1975).
3. J. P. Millington and M. Trotman, Abstr. of Papers Electrochem. Soc. Meeting, Washington, D.C., May 2-7, pp 700-702, (1976).
4. M. Fremery, H. Hoever, and G. Schwarzlose, Chem. Ing. Techn., 46 645, (1974).
5. G. Schwarzlose, M. Fremery, K. Erdt, Ger. Pat., 2,204,351, (1973); Ger. Pat., 2,108,623, (1972).
6. F. J. Anderson and J. L. Kessler, U.S. Pat., 3,758,391, (1973).
7. F. Covitz, U.S. Pat., 3,616,324, (1971); U.S. Pat., 3,509,031, (1970); U.S. Pat., 3,616,323, (1971).
8. F. A. Keidel, U.S. Pat., 3,884,776, (1975).

V. Organic Formulas/Physical Properties^{*}:

		<u>MW</u>	<u>m.p. °C</u>
benzene		78.1	5.5
<u>p</u> - benzoquinone		108.1	115-117 (sublimes)

^{*} Physical properties from:

Handbook of Chemistry & Physics, 49th ed., The Chemical Rubber Co., (1968).

		MW	m.p. °C
hydroquinone	<chem>Oc1ccc(O)cc1</chem>	110.1	170
<u>o</u> - benzoquinone	<chem>O=C1C=CC(=O)C=C1</chem>	108.1	60-70 (decomposes)
catechol (pyrocatechol)	<chem>Oc1ccccc1O</chem>	110.1	105

VI. Proposed Electrochemical Routes from Benzene In a Cell Utilizing Both Anode and Cathode: (see Ref. 4,5)

(a) Scheme:

Total flow diagram for the electrochemical production of hydroquinone. a) Electrochemical cells; b) Cooler; c) Degasser; d) Two-compartment separator; e) Degasser; f) Vacuum vaporizer; g) Pump; h) Condenser; i) Receiver; k) Post-reduction; l) Separator; m) Heater; n) Vacuum crystallizer; o) Pump; p) Condenser; q) Decanter; r) Washing tower; s) Centrifuge; t) Drier; u) Heater; v) Drier; w₁, w₂) Washing columns; x) Condenser; y) Stripper; z) Condenser.

Notes: The process takes advantage of the favorable solubility of benzoquinone in benzene and of hydroquinone in aqueous sulfuric acid electrolyte. A purge stream of electrolyte from the catholyte loop after being subjected to cathodic postreduction and concentration gave crystalline hydroquinone which upon washing was industrially pure. All process streams are completely recycled with no discharge to the environment.

(b) Reactions:

secondary reactions:

Secondary reactions:

(c) Compositions of Streams:

Input (anolyte)

Composition

	<u>Wt %</u>
benzene	10
sulfuric acid	20
water	remainder

Output (catholyte)

hydroquinone	7
--------------	---

	<u>Wt %</u>	<u>Composition</u>
catechol	trace	
benzene	1.9	
sulfuric acid	15	
benzoquinone		

Gases: Output

Anode	{ Oxygen <10% (by volume)	
	{ Carbon dioxide + CO 90% (by volume)	

Hydrogen

(d) Product CE's:

hydroquinone	40
oxygen + carbon dioxide	50 (L)
hydrogen	50 (L)

(e) Cell Voltage: 4 V

(f) Energy Requirement: 15 kWh/kg

(g) Cell Temperature: 40°C

(h) Temperature of Input and Output Streams:

anolyte, 40°C

catholyte, 40°C

ELECTROCHEMICAL SYNTHESIS OF 2,2'-DITHIOBISBENZOTHAZOLE (DITHIOBIS)

- I. Electrochemical Status: No present (or past) pilot/commercial studies.
- II. Chemical Process: Oxidation of 2-mercaptobenzothiazole.
- III. Literature Review: Only a few references could be found. Ref. 1 utilizes anhydrous electrooxidation conditions.

IV. Literature: (Selected)

1. H. Berge, N. Millat, and B. Struling, Z. Chem., 15, 37, (1975).
2. J. Chambers, P. R. Moses, R. N. Rhelton, and D. L. Coffen, J. Electroanalytical Chem., 38, 245, (1972).

V. Organic Formulas/Physical Properties:

		<u>MW</u>	<u>mp</u> ⁶ C
2-mercaptobenzothiazole,		167.25	181.7°
2,2'-dithiobis,		332.46	180°

Note: 2-mercaptobenzothiazole and the product 2,2'-dithiobis are highly insoluble in water. The starting material (2-mercaptobenzothiazole) is soluble in aqueous alkaling media, but the product is not. The scheme following is based on these solubility differences. The solid product is filtered from the anolyte.

VI. Proposed Electrochemical Route:

(a) Scheme:

(b) Electrochemical & Chemical Processes:

Chemical Reaction in Premixer:

(neutralization)

Note: The solid, 2,2'-dithiobis, is likely pure enough, after a brief water rinse, and drying (air) to be used without further purification.

* R is

(c) Composition of Streams^{**}:

<u>Input</u>		<u>Mole%</u>
Anolyte:	sodium hydroxide	8.1
	2-mercaptobenzothiazole	4.1
	water	87.8
Catholyte:	sodium hydroxide	8.4
	water	91.6
<u>Output</u>		
Anolyte:	sodium hydroxide	8.2
	2,2'-dithiobis	2.1
	2-mercaptobenzothiazole	1.0
	water	88.7
Catholyte:	sodium hydroxide	
	water	
	hydrogen	100%

(d) Product Current Efficiencies^{*}:

2,2'-dithiobis	100% (H)
hydrogen	100% (H)
sodium hydroxide	100% (H)

(e) Cell Voltage: 2.5 V (H)

(f) Energy for Cell: 0.40 kWhr/kg (H)

(g) Temperature of Cell: 50°C (M)

(h) Temperature of Input/Output Streams: ?

(i) Further Comments: 1. The process should proceed very well since the literature gives an almost quantitative CE for the dimerization. 2. Take H₂ credit.

^{**} The values given represent a hypothetical possibility

^{*} "optimized"

ELECTROCHEMICAL CONVERSION OF ETHYLENE
TO DICHLOROETHANE (DCE) AND VINYL CHLORIDE MONOMER (VCM)

I. Present Electrochemical Status: No pilot studies known.

II. Chemical Processes: Two steps.

1. Chlorination of ethylene to ethylene dichloride (EDC).
2. Pyrolysis of ethylene dichloride to VCM + HCl.

See: L. F. Albright, Chem. Eng., 219, (1967).

VCM production: 10 billion lbs./year worldwide

Note: Major use of chlorine, an electrochemical product, is in manufacture of VCM.

III. Electrochemical Literature: See references 1-7 and literature references therein. The most extensive research in this area was done by Russian workers, on a small scale basis.

- (1) Using a porous graphite anode for admitting ethylene gas into the 27% waste HCl electrolyte. Electrolysis temperature was 50-55°C; cd 0.3 A/cm². Dichloroethane was formed in 94-97% yields. Non-diaphragm cell (Ref. 3). See IV. 1. below.
- (2) Ref. 2 shows that the amount of 1,2-dichloroethane formed, in contrast to chlorohydrin, increases with increase in CD, T, and concentration of chlorohydrin in solution, when the electrolyte is 2N HCl and the anode graphite. With NaCl, the CE of 1,2-dichloroethane is 44%. See IV. 2. below.
- (3) Ref. 5 chlorinates ethylene in concentrated HCl at 80-90°C in a cell with diaphragm and graphite anode: cd 12.5-50 A/dm². The products were 1,2-DCE, trichloroethane, higher chlorination products. See IV. 1. below.

- (4) Ref. 3 discusses electrolysis at a porous graphite anode and a solid graphite cathode. Electrolyte 27% HCl, 50°C, 67% CE of chlorination products, 0.1 A/cm². Other useful anode is Pt. Additional products noted are halohydrin and ethyl chloride.

IV. Literature On Electro-Chlorination of Ethylene:

1. P. Askenasy, Z. Electrochemie, 15, 773, (1909).
2. M. A. Kalinin and V. V. Stender, J. Appl. Chem. USSR, 19, 1045, (1946); Chem. Abstr., 41, 4767 c.
3. G. S. Tedoradze, V. A. Paprotskaya, and A. P. Tomilov, Boinet Electrochem., 10, 1047, (1974); ibid, 10, 1239, (1974); ibid, 10, 612, (1974); ibid, 12, 206, (1976).
4. B. A. Tedoradze, V. A. Paprotskaya, N. B. Vladimirova, Yu. A. Yuzbekov, Elektrokhimiya, 11, 502, (1975).
5. Belgian Patent, 648997, (1964).
6. U. S. Patent, 1,253,615; 1,253,616, (1918); 1,295,339, 1308797 (1919).
7. A. P. Tomilov, Yu. D. Smirnov, and M. I. Kolutma, Zh. Prikl.Khim, 38, 2123, (1965).

V. Organic Formulas/Physical Properties^{*}:

	<u>MW</u>	<u>bp°C/760mm</u>
Ethylene: CH ₂ =CH ₂	28	-104
Ethylene dichloride: ClCH ₂ -CH ₂ Cl (DCE)	99	84

^{*}Physical properties from:

Handbook of Chemistry & Physics, 49th ed., The Chemical Rubber Co., 1968.

	MW	bp°C/760mm
Vinyl Chloride: $\text{CH}_2=\text{CHCl}$ (VCM)	62.5	-13.9
Ethylene chlorohydrin: $\text{HOCH}_2\text{CH}_2\text{Cl}$	80.5	1.28
Trichloroethane: $\text{ClCH}_2\text{CHCl}_2$	133.4	113
Ethyl chloride: $\text{CH}_3\text{CH}_2\text{Cl}$	64.5	13.1

VI. Proposed Electrochemical Routes:

A. In concentrated aqueous HCl solution:

(a) Scheme:

Notes on separations: With the cell temperature at 80-90°C, ethylene, oxygen, DCE, $\text{C}_2\text{H}_5\text{Cl}$, and likely $\text{C}_2\text{H}_3\text{Cl}_3$ will be volatile. The organics should be easily separated by trapping (cold) the $\text{C}_2\text{H}_3\text{Cl}_3$, and then the (DCE + $\text{C}_2\text{H}_5\text{Cl}$) as a mixture. This would then leave separation of ethylene and oxygen. The low $\text{C}_2\text{H}_5\text{Cl}$ level in the DCE product should be acceptable for VCM production. The separation of chlorinated polymers from the anolyte stream could be done by filtration since these will likely be solids. Ethylene chlorohydrin will require

separation before the HCl stream is returned for recycle. DCE may need to be dried.

(b) Reactions:

Chemical, In Anolyte:

(c) Compositions of Streams

<u>Input Streams</u>	<u>Mole % Composition</u>
ethylene	as pure gas
concentrated HCl	15
water	85
<u>Output Streams</u>	
anolyte volatiles:	
ethylene	20 (U)
DCE	75 (U)
$\text{C}_2\text{H}_5\text{Cl}$	2 (H)
$\text{C}_2\text{H}_3\text{Cl}_3$	~1 (H)
oxygen	2 (U)

anolyte:

$\text{HOCH}_2\text{CH}_2\text{Cl}$	1 (U)
concentrated HCl	22 (U)
polymer (chlorinated)	1 (H)

catholyte volatiles:

hydrogen	98 (H)
other	2 (H)

catholyte:

concentrated HCl	25 (H)
------------------	--------

(d) Product CE's:

DCE	75 (H)
$[\text{C}_2\text{H}_5\text{Cl}]$	1 (H)
$\text{HOCH}_2\text{CH}_2\text{Cl}$	20 (U)
$\text{C}_2\text{H}_3\text{Cl}_3$	1 (H)
oxygen	2 (H)
polymer (chlorinated)	1 (H)
hydrogen	98 (H)

(e) Cell Voltage: 2.2 V (?)

(f) Energy Requirement For Cell: 1500 kWh/ton Cl_2

(See A. T. Kuhn, Industrial Electrochemical Processes,
Elsevier Publishing Co., 1971, p 92.)

(g) Cell Temperature: 80-90°C

(h) Temperature of Input/Output Streams: 80-90°C

(i) Additional Notes: The hydrogen value energy equivalent should be taken.

B. In Concentrated Aqueous Brine (Chloralkali Cell):

(a) Scheme:

Notes on Separations:

See notes in VI. A. (a).

With the membrane cell, caustic is generated directly in 30% concentration.

(b) Reactions:

At Anode: See VI. A. (b), these are identical

(c) Compositions of Streams:

Input Streams

ethylene

brine

Mole% Composition

as pure gas

25 (H)

Output Streams

anolyte volatiles: See VI. A. (c)

anolyte:

HOCH₂CH₂Cl 1 (U)

brine (H)

polymer (chlorinated) 1 (H)

catholyte volatiles:

hydrogen 98 (H)

catholyte:

caustic 30 (H)

(d) Product CE's:

See VI. A.(d)

add caustic 90 (H)

(e) Cell Voltage: 3.5 V

(f) Energy Requirement for Cell: ?

(g) Cell Temperature: 90-95°C

(h) Temperature of Input/Output Streams: 90-95°C

C. In O₂-Depolarized Chloralkali Cell:

(a) Scheme:

The scheme is essentially that shown in VI. B.(a), except for O₂ storage and input to the cell, and no hydrogen product.

(b) Reactions:

At Anode: Same as VI. A.(b)

At Cathode: $O_2 + 2H_2O + 4e \longrightarrow 4OH^-$

(c) Compositions of Streams:

Input StreamsMole% Composition

ethylene as pure gas

oxygen as pure gas

brine 25 (H)

Output Streams: Same as VI. B.(c) except that no hydrogen is produced.

(d) Product CE's:

See VI. B.(d)

(e) Cell Voltage: 2.7 V (H)

(f) Energy Requirement for Cell: ?

(g) Cell Temperature: 90-95°C

(h) Temperature of Input/Output Stream: 90-95°C

(i) Additional Notes:

No example exists of an oxygen-depolarized chloralkali cell for formation of DCE

VII. Further Comments:

Scheme VI. C. will be more energy efficient than VI. B. The data for all three schemes are based on reliable chloralkali information except where the organics are involved.

ELECTROCHEMICAL CONVERSION OF BENZENE TO CHLOROBENZENE

- I. Present Electrochemical Status: No known commercial or pilot studies ongoing.
- II. Chemical Processes: Chlorobenzene is produced by liquid phase chlorination of benzene in the presence of a catalyst. A review of manufacture, properties, and use is found in Faith, Keyes, & Clark's Industrial Chemicals, John Wiley, New York, 4th Ed., 1975, pp 258-265.
- III. Electrochemical Literature Review: A comprehensive review of electrohologeneration as given in Ref. 1. Benzene has been electrochlorinated at graphite, porous carbon, Pt, and magnetite electrodes in aqueous chloride media. Catalysts, including iodine, FeCl_3 , cyanuric acid, UV light, etc., serve to raise the current efficiency substantially.
- IV. Literature:
 1. Technique of Electroorganic Synthesis, Part II, N. L. Weinberg ed., John Wiley & Sons, New York, NY, (1975), pp 1-82.
 2. A. Lowy and H. S. Frank, Trans. Am. Elect. Soc., 43, 107, (1923).
 3. A. Hering, Ger. Pat., 903, 451, (1954); Chem Abstr., 52, 7914e, (1958).
 4. C. G. Schleuderberg, J. Phys. Chem., 12, 583, (1908).
 5. J. C. Ghoshetal, J. Sci. Indust. Res. India, 11B, 361, (1952); Current Sci., 16, 87, (1947).
 6. G. Bionda and M. Civera, Ann. Chim. (Rome), 41, 814, (1951).
 7. W. B. Mather and E. R. Kerr, U.S. Pat., 3,692,646, (1972).

V. Organic Formulas/Physical Properties:

		MW	bp°C/760mm
Benzene	C_6H_6	78.1	80.1
Chlorobenzene	C_6H_5Cl	112.6	131-132
<u>p</u> - Dichlorobenzene	$C_6H_4Cl_2$	147	174
<u>o</u> - Dichlorobenzene	$C_6H_4Cl_2$	147	180.5

VI. Proposed Schemes:

(see schemes for dichloroethane)

A. (a) In Concentrated Aqueous HCl Solution

(b) Processes:

(c) Compositions of Streams:

<u>Input</u>	<u>Mole%</u>
benzene	
aqueous HCl: 12 <u>N</u>	
catalyst (say FeCl_3): 0.5% (estimate)	
water: remainder	
<u>Output</u>	
benzene	
chlorobenzene	
dichlorobenzene (<u>o/p</u>)	
aqueous HCl	
water	
oxygen	
hydrogen	100%

(d) Product CE's:

chlorobenzene	90% (H)
dichlorobenzenes	8% (H)
oxygen	2% (H)
hydrogen	100% (H)

(e) Cell Voltage: 2.2 V

(f) Energy Requirement for Cell: 1500 kW/ton Cl_2

(g) Cell Temperature: 50°C (H)

(h) Temperature of Input/Output Streams: 50°C

(i) Additional Notes: Consider H_2 value.

B. In Concentrated Aqueous Brine, see Dichloroethane

C. In O_2 - Depolarized Chloralkali Cell, see Dichloroethane

ELECTROCHEMICAL SYNTHESIS OF 1,2 DIBROMOETHANE

I. Present Electrochemical Status: No process known to be piloted or commercial.

II. Chemical Processes:

(1) Bromination of ethylene

(2) Reaction of acetylene with HBr

III. Electrochemical Literature:

Very few studies have been conducted on electrobromination of olefins. Most of these are electroanalytical methods for olefin determination.

IV. Selected Literature References:

1. F. Cuta and Z. Kucera, Chem. Abstr., 48, 3850, (1954).
2. J. W. Miller and D. D. Deford, Anal. Chem., 29, 475, (1957).
3. A. D. Miller, Diss. Abstr. Int. B, 34, 1088, (1973); Chem. Abstr., 80, 9795.
4. See literature for electrochlorination of olefins.

V. Organic Formulas/Physical Properties:

	<u>MW</u>	<u>bp°C/760mm</u>
ethylene, $\text{CH}_2=\text{CH}$	28.05	-102.4° (700mm)
1,2-dibromoethane, $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$	187.88	131-132°
ethylene bromohydrin, $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{Br} \end{array}$	124.98	149-150°

VI. Proposed Electrochemical Route:

(a) Scheme: In Concentrated Aqueous NaBr Solution

(see Chloralkali Scheme B for electrosynthesis of 1,2-dichloroethane).

(b) Electrochemical & Chemical Processes:

In Anolyte (Chemical Reactions)

Note: Since the above was used as an electroanalytical procedure for olefin determination, the minor route (2) must have been quite insignificant. Hence for the purposes of these calculations, the minor process is ignored.

(c) Composition of Streams To/From Cell:

<u>Input</u>	<u>Mole% Composition</u>
anolyte: ethylene (large excess)	pure gas
sodium bromide	
water	
catholyte: water	100%
<u>Output</u>	
anolyte volatiles:	
ethylene	
1,2-dibromoethane	
sodium bromide	
water	
catholyte: sodium hydroxide (30%) 9.96 <u>M</u>	16.2%
water (remainder) 929 g/l, 51.6 <u>M</u>	83.8%

(d) Product Current Efficiencies:

1,2-dibromoethane	100% (H)*	
hydrogen	100% (H)	
sodium hydroxide	90% (H)	(10% represents losses through membrane)

(e) Cell Voltage: 3.1 V (H)

(f) Energy Requirement for Cell: 0.88 kWhr/kg (H)

(g) Cell Temperature: 70°C (M)

(h) Temperature of Input/Output Streams: ?

(i) Additional Notes: Take H₂ credit.

* "optimized" current efficiencies

ELECTROCHEMICAL SYNTHESIS OF TETRAFLUORETHYLENE

- I. Present Electrochemical Status: No pilot or commercial processes in progress.
- II. Chemical Process:
- III. Literature Review: Several methods are suggested from the literature.
- (a) Perfluorination of 1,2-dichlorethane followed by dechlorination (Ref. 3 f).
- (b) Perfluorination of tetrafluorocyclobutane, followed by pyrolysis:

then condense a portion of $\text{C}_2\text{F}_4 + \text{C}_2\text{H}_4$ to recycle the feed (Ref. 3).

- (c) Electrochemical reduction of CF_2Cl_2 in molten salt solution (Ref. 4).

IV. Selected Literature:

1. General Review of Electrofluorination, N. L. Weinberg in Technique of Electroorganic Synthesis, John Wiley, NY, 1975, Part II, pp 1-82.
2. H. M. Fox, F. N. Ruehlen, and W. V. Childs, J. Elect. Soc., **118**, 1246, (1971).
3. H. M. Fox, W. V. Childs, E. H. Gray et al., (a) U.S. Pat., 3,511,760, (1970); (b) 3,551,307, (1970); (c) 3,558,449, (1971);

(d) 3,620,941, (1971); (e) 3,616,336, (1971); (f) 3,645,863, (1972); (g) 3,720,597, (1973).

4. R. Dietz and M. E. Peover, J. Appl. Electrochem., **3**, 143, (1973).

V. Organic Formulas/Physical Properties:

	<u>MW</u>	<u>bp°C/760mm</u>
1,2-dichlorethane, $\text{ClCH}_2\text{CH}_2\text{Cl}$	98.96	84°
1,2-dichlorotetrofluoroethane		
$\text{ClCF}_2\text{CF}_2\text{Cl}$	171.0	?
tetrafluorethylene, $\text{CF}_2=\text{CF}_2$	100.02	-76.3°
chloropentafluorethane, ClCF_2CF_3	154.48	-38°
1,1,2-trichlorotrifluoroethane		
$\text{Cl}_2\text{CFCF}_2\text{Cl}$	187.38	47.7°
difluorodichloromethane, CF_2Cl_2	120.91	-29°
chlorotrifluoromethane, CF_3Cl	104.46	-81.1°

VI. Proposed Electrochemical Routes:

Two routes are presented: IIIa and IIIc

A. (a) Scheme: Perfluorination of 1,2-dichlorethane, followed by dechlorination.

see scheme, Ref. 3(a), 3(b).

(b) Electrochemical & Chemical Processes:

At Cathode: $2\text{H}^+ + 2\text{e} \longrightarrow \text{H}_2$

At Anode: main process:

minor processes:

(c) Composition of Streams/Cell:

Input

hydrogen fluoride

potassium fluoride

1,2-dichlorethane

Output

hydrogen fluoride

potassium fluoride

1,2-dichloroethane

1,2-dichlorotetrafluoroethane

1,1,2-trichlorotrifluoroethane

chloropentafluoroethane

hydrogen

(d) Current Efficiencies of Products*:

hydrogen 100% (H)

1,2-dichlorotetrafluoroethane 90% (M)

chloropentafluoroethane 5% (L)

1,1,2-trichlorotrifluoroethane 5% (L)

(e) Cell Voltage: 8 V (H)

(f) Energy/Cell: 11.2 kWh/kg (M)

(g) Temperature of Cell: 90°C

(h) Temperature of Input/Output Streams: ?

* optimized.

- (i) Additional Notes: The conversion of 1,2-dichlorotetrafluorethane to tetrafluorethylene needs to be described:

or

- B. (a) Scheme: Electrochemical Reduction of CF_2Cl_2 in Molten Salt (see Ref. 4).

- (b) Electrochemical/Chemical Processes:

- (c) Composition of Streams:

<u>Input</u>	<u>Mole% Comp</u>
dichlorodifluoromethane	100 (H)
<u>Output</u>	
chlorine - at anode	100 (H)
tetrafluorethylene	3.1 (M)
chlorotrifluoromethane	0.2 (M)

- (d) Product Current Efficiencies:

chlorine 100% (H)

tetrafluoroethylene 100% (H)

(chlorotrifluoromethane may be produced chemically?)

- (e) Cell Voltage: 5 V
- (f) Energy/Cell: 5.4 kWh/kg (M)
- (g) Temperature of Cell: 500°C (H)
- (h) Temperature of Input/Output: ?

ELECTROCHEMICAL SYNTHESIS OF 2,4-DICHLOROPHENOL
(FOR 2,4-DICHLOROPHENOXYACETIC ACID)

I. Present Electrochemical Status: No

Studies for electrosynthesis of 2,4-dichlorophenoxyacetic acid.

II. Chemical Process:

1,2,4-Trichlorobenzene is heated with caustic to give a mixture of phenols including 2,4-dichlorophenol. The latter is then treated with chloroacetic acid in aq. caustic to give 2,4-dichlorophenoxyacetic acid (2,4-D).

III/IV. As before: the best route appears to be via 1,3-dichlorobenzene acyloxylation.

V. Organic Formulas/Physical Properties:

1,3-dichlorobenzene,

MW 147.01

bp 173°/760 mm
mp -24.8°

2,4-dichlorophenol,

MW 163.01

bp 208°/760 mm
mp 45°

2,6-dichlorophenol,

MW 163.01

bp 220°/760 mm
mp 68-9°

3,5-dichlorophenol,

MW 163.01

bp 233°/760 mm
mp 68°2,4-dichlorophenoxyacetic
acid

MW 221.04

bp 160°/0.1 mm
mp 138°**VI. Proposed Electrochemical Route:**

(a) Scheme:

Then: Chemical Process

(b) Electrochemical and Chemical Processes:

At Cathode: $2\text{H}^+ + 2\text{e}$

At Anode:

(mixture of isomers)

minor processes:

In Solution (chemical Reaction):

hydrolysis:

mixture of dichlorophenols.

Hydrolysis occurs quickly in the aqueous TFA electrolyte.

(c) Composition of Streams:

To CellMole% Comp.

trifluoroacetic acid (TFA)	63.5 (M)
sodium trifluoroacetate	2.6 (M)
water	28.6 (M)
1,3-dichlorobenzene	5.3 (M)

From Cell

Gases: hydrogen cathode gas 100% (H)

oxygen

carbon dioxide

trifluoroethane

} anode gas

trifluoroacetic acid

sodium trifluoroacetate

water

1,3-dichlorobenzene

2,4-dichlorophenol

2,6-dichlorophenol

3,5-dichlorophenol

(d) Product Current Efficiencies (%):

2,4-dichlorophenol 60 (L)*

2,6-dichlorophenol 10 (L)

3,5-dichlorophenol 19 (L)

hexafluoroethane 3.5 (L)

carbon dioxide 7 (L)

oxygen 0.5 (L)

hydrogen 100 (H)

(e) Cell Voltage: 7V (M)

(f) Energy For Cell: 3.8 kWh/kg (L)

(g) Cell Temp: 50°C (M)

(h) Temperature of Input/Output Streams: 50°C

*the "optimized" current efficiencies are a best guess.

APPENDIX C

ENERGY COSTS OF CHEMICAL RAW MATERIALS
AND PRODUCTS

APPENDIX C

ENERGY COSTS OF CHEMICAL RAW MATERIALS AND PRODUCTS

Not all of the pairs of chemical and electrochemical processes to produce a given product use the same raw materials. It was therefore necessary to have energy costs of raw materials to put the processes on the same basis. These energy costs of raw materials are summarized in Table 5-2 in the text and the methods of calculation are given here.

Data for calculating energy costs were from several sources including Shreve (1)*, Kirk-Othmer (2), Faith, Keys, and Clark (3), and Rudd, et al., (4). The source is indicated on each table of calculations. The compilation of material and energy requirements given in Table C-0, provided by Prof. Stadtherr from ref (4), was particularly valuable for estimation of energy costs of chemicals and intermediates in the processes studied in this report.

C-1. HYDROCARBONS - HEATS OF COMBUSTION

Hydrocarbon raw materials could be burned in a boiler to produce steam at an 82% efficiency. On that basis, hydrocarbon energy costs should be $0.82 \Delta H_{\text{combustion}}$. On the other hand, there are costs of drilling, refining, and transportation to use site. Arbitrarily it was decided to charge hydrocarbon at an energy cost equal to $\Delta H_{\text{combustion}}$. Heats of combustion in Table C-1 are from Perry (5) in units of Btu/lb; they were converted to kcal/kg by dividing by 1.8.

*References are given at the end of this section.

Table C-0

Material and Energy Requirements for Chemical Processes (4)

Product Basis: 1 lb	Feedstock lbs		Byproducts lbs		Utilities* lb FOE
Acrylonitrile	NH ₃	0.52	HCN	0.1	0.09
	C ₃ H ₄	1.23			
	H ₂ SO ₄	0.46			
Ammonia	H ₂	0.2			0.63
Hydrogen by reforming	CH ₄	2.32	CO	2.41	2.17
			CO ₂	2.84	
Hydrogen by water gas shift	CO	14.7	CO ₂	22	1.58
Adiponitrile	C ₄ H ₆	0.82	HCl	0.68	0.49
	Cl ₂	0.75	H ₂	0.03	
	HCN	0.57			
Butadiene	C ₄ H ₈	1.46			2.44
	H ₂ SO ₄	0.01			
HCN	NH ₃	0.83			0.13
	CH ₄	0.82			
Chlorine	NaCl	1.83	NaOH	1.14	0.95
			H ₂	0.03	
Adiponitrile (Monsanto process)	Acrylonitrile	1.09			1.14
Phenol	Cumene	1.42	Acetone	0.60	0.49
Cumene	Benzene	0.79			0.04
	C ₃ H ₆	0.41			
Aniline	Phenol	1.1			0.14
	NH ₃	0.2			
Nitrobenzene	Benzene	0.65			0.16
	HNO ₃	0.53			
Nitric Acid	NH ₃	0.29			0.1
Terephthalic Acid	P-Xylene	0.67			0.40
Methyl Ethyl Ketone	Butanol	1.1			0.31
Butanol	Butylene	1.14			0.58
	H ₂ SO ₄	0.01			
	NaOH	0.02			
Urea	NH ₃	0.58			0.09
	CO ₂	0.76			

Table C-0 (continued)

Material and Energy Requirements for Chemical Processes (4)

Product Basis: 1 lb	Feedstock lbs		Byproducts lbs		Utilities* lb FOE
Dichloroethane	C_2H_4	0.30			0.14
	Cl_2	0.80			
Acetone dehydrogenation	Iso- C_3H_7OH	1.26	H_2	0.03	0.42
Isopropanol	C_3H_6	0.72			0.45
Butylene	C_4H_{10}	1.53	C_4H_6	0.09	0.65
Ethylene	C_2H_6	1.25	pyro- gasoline	0.04	0.55
Ethylene	C_3H_8	2.29	C_3H_6	0.29	0.23
			C_4H_8	0.07	
			pyro- gasoline	0.27	
Ethylene	C_4H_{10}	2.56	C_3H_6	0.38	0.86
			C_4H_8	0.1	
			pyro- gasoline	0.20	

* FOE = fuel oil equivalent at 18,775 Btu/lb or 10,430 kcal/kg

Electric utility equivalent used was 10,320 Btu/kWh (compared to 10,500 Btu/kWh used for calculations elsewhere in this report).

Table C-1

Gross Heat of Combustion of Hydrocarbons

	<u>Btu/lb</u>	<u>kcal/kg</u>
Carbon	14,093	7,824
Hydrogen	61,100	33,944
Methane	23,879	13,266
Ethane	22,320	12,400
Propane	21,661	12,034
n-Butane	21,308	11,838
Ethylene	21,644	12,024
Propylene	21,041	11,689
n-Butene	20,840	11,578
Isobutene	20,730	11,517
Benzene	18,210	10,117
Toluene	18,440	10,244
Xylene	18,650	10,361
*Fuel oil	18,775	10,430

* See Table C-0

C-2. HYDROGEN

Sources of hydrogen are steam reforming of hydrocarbons, cracking of ammonia (produced from hydrogen made by steam reforming), and electrolysis of water. The thermodynamic energy cost of steam-reformed hydrogen from methane is calculated in Table C-2.1, and the actual energy costs determined from literature sources are given in Table C-2.2. An average value of 49,000 kcal/kg H₂ is used for energy calculations in this report. The energy cost of hydrogen by water electrolysis is calculated in Table C-2.3 based on a fuel cell operated in a reverse electrolytic mode (6).

C-3. AMMONIA

Ammonia is produced by catalytic combination of hydrogen produced by steam reforming of hydrocarbons and nitrogen from the air used in the reforming process. The thermodynamic energy cost of ammonia is calculated in Table C-3.1, and actual energy costs determined from the literature are given in Table C-3.2. An average value of 9,000 kcal/kg NH₃ is used for energy calculations in this report.

C-4. HYDROGEN CYANIDE

Hydrogen cyanide is produced by catalytic combustion of ammonia and methane with a controlled amount of air,

The energy cost of HCN is calculated in Table C-4.

Table C-2.1

Thermodynamic Energy Cost of Hydrogen
Produced by Steam Reforming and Water Gas Shift from Methane

1. Steam reforming

2. Water gas shift

3. Total

$$\begin{array}{ccccccc} & & & & & \Sigma \Delta H_{298}^\circ & \\ & & & & & \hline \Delta H_{298}^\circ & -17.889 & 2(-68.317) & -94.0518 & 0 & +60.47 \frac{\text{kcal}}{\text{g mol}} & (7) \end{array}$$

4. Combustion

$$\Delta H_{298}^\circ \quad -17.889 \quad 0 \quad -94.0518 \quad 2(-68.317) \quad -212.80 \frac{\text{kcal}}{\text{g mol}}$$

Basis: 1 g mol H₂ product

Feed (Rx 3) 0.2500 g mol CH₄

Minimum fuel (60.47)/(212.80)(4) = 0.0710

Total CH₄ 0.3210 g mol CH₄

$$\frac{\left(0.3210 \frac{\text{g mol CH}_4}{\text{g mol H}_2}\right) \left(212.80 \frac{\text{kcal}}{\text{g mol CH}_4}\right)}{\left(2.016 \times 10^{-3} \frac{\text{kg H}_2}{\text{g mol H}_2}\right)} = 33,833 \frac{\text{kcal}}{\text{kg H}_2}$$

Table C-2.2

Energy Cost of Hydrogen Produced by Steam Reforming of Natural Gas

A. Basis: 1,000 ft³ H₂ Shreve (1) p 101
 $v = 187.723 \text{ ft}^3/\text{lb}$ Perry (5) p 9-16
 $\therefore w = 5.347 \text{ lb}$

	<u>Btu</u>
Natural gas: 250 ft ³ @ 1,000 Btu/ft ³	250,000
Fuel:	215,000
Steam: 70 psig (85 psia) - 240 lb	
Enthalpy of vapor = 1,185 Btu/lb	
Enthalpy of feed	
water @ 75°F <u>43</u>	
1,142 Btu/lb	
(240)(1,142) = 274,100 Btu	-
(assumed internally generated)	
Power: 0.5 kWh x 10,500 Btu/kWh	<u>5,250</u>
Total	470,250

$$\frac{470,250}{5.327} = 88,277 \text{ Btu/lb}$$

$$\frac{88,277}{1.8} = 49,043 \text{ kcal/kg}$$

Table C-2.2 (Continued)

Energy Cost of Hydrogen Produced by Steam Reforming of Natural Gas

B. Basis: Table C-0

		Reaction FOE	Allocated FOE
1. Reforming			
	$\text{CH}_4 + \text{H}_2\text{O} \longrightarrow 3\text{H}_2 + \text{CO}$	2.17	2.17
kg	2.32 1 2.41		
2. Water gas shift			
kg	$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{CO}_2$	1.58	
	14.7 1 22		

Basis: 1 kg H_2 from Rx 1

$$\text{H}_2 \text{ from Rx 2, } (1)(2.41/14.7) = \underline{0.164 \text{ kg}}$$

$$\text{Total H}_2 \quad \quad \quad 0.164 \text{ kg}$$

$$\underline{\text{FOE for Rx 2, } (1.58)(2.41/14.7) = \underline{0.26}}$$

$$\text{Total FOE} \quad \quad \quad 2.43$$

$$\text{Energy of CH}_4, \quad (2.32)(13,266) = 30,777 \text{ kcal}$$

$$\underline{\text{Energy of FOE, } (2.43)(10,430) = \underline{25,345}}$$

$$\text{Total energy} \quad \quad \quad 56,122 \text{ kcal}$$

$$\text{Specific energy} = 56,122/1.164 = 48,215 \text{ kcal/kg H}_2$$

Table C-2.2 (Continued)

Energy Cost of Hydrogen Produced by Steam Reforming of Natural Gas

C. Kirk-Othmer (2), 2nd ed., p 351

Basis: 1,000 SCF H_2 = 5.347 lb
(Table C-2.2A)

Process feed: CH_4 11.9 lb
 CH_4 7.9 lb

19.8 lb

Power: 0.4 kWh

Feed and fuel: $(19.8 \text{ kg } CH_4)(13,266)/5.347 \text{ kg } H_2 = 49,124 \text{ kcal/kg}$

Power:
$$\frac{(0.4 \text{ kWh})(10,500 \text{ Btu/kWh})}{(5.347 \text{ lb } H_2) \left(1.8 \frac{\text{Btu/lb}}{\text{kcal/kg}}\right)} = \frac{436}{49,560 \text{ kcal/kg } H_2}$$

An average of 49,000 kcal/kg H_2 will be used for calculations
in this report.

Table C-2.3

Hydrogen from Water Electrolysis

$$p = 26.806 \frac{zV}{\epsilon M} \quad (\text{equation 1, text})$$

$$z = 2$$

$$V = 1.5 \text{ volts based on best fuel cell} \\ \text{operated in electrolytic mode (6)}$$

$$\epsilon = 1.00$$

$$M = 2.016$$

$$p = \frac{(26.806)(2)(1.5)}{(1.00)(2.016)} = 39.89 \text{ kWh/kg}$$

$$\frac{(39.89)(10,500)}{(2.20)(1.8)} = \underline{\underline{105,770 \text{ kcal/kg}}}$$

Table C-3.1

Thermodynamic Energy Cost of Ammonia from Methane

Reaction:

Free energy change is also negative so that the reaction should be spontaneous, but kinetics are slow and high pressure and elevated temperatures are used.

Thermodynamic minimum based on hydrogen from methane

(Table C-2.1) is:

$$\frac{(3 \times 2.016 \text{ kg H}_2)(33,883 \text{ kcal/kg H}_2)}{(2 \times 17.03 \text{ kg NH}_3)} = 6,016 \text{ kcal/kg NH}_3$$

The value based on actual energy cost of methane (neglecting $\text{N}_2 + \text{H}_2$ compression) is:

$$\frac{(3 \times 2.016 \text{ kg H}_2)(49,000 \text{ kcal/kg H}_2)}{(2 \times 17.03 \text{ kg NH}_3)} = 8,700 \text{ kcal/kg NH}_3$$

Table C-3.2

Energy Cost of Ammonia from Natural Gas

A. Basis:	1,000 x 2,000 lb/day NH ₃	Shreve (1) p 283
		<u>Btu/lb</u>
Natural Gas:	850 x 10 ⁶ Btu/hr	10,200
Fuel:	440 x 10 ⁶ Btu/hr	5,280
Power:	640 kW	
	<u>(640)(24)(10,500)</u>	<u>81</u>
	(2 x 10 ⁶)	<u>15,561</u>

$$\frac{15,561}{1.8} = 8,645 \text{ kcal/kg}$$

B. Kirk-Othmer (2) 3rd ed., p 487

Typical requirement for feed and fuel

Natural gas reforming 37.2 GJ/t

$$\frac{(37.2 \text{ GJ/t})(0.949 \times 10^6 \text{ Btu/GJ})}{(2,000 \text{ lb/t})(1.8)} = 9,806 \text{ kcal/kg}$$

C. Kirk-Othmer (2) 3rd ed., p 507

Natural gas feed + fuel

$$(\$70.56/\text{t})/(\$2/10^6 \text{ Btu}) = 3.528 \times 10^7 \text{ Btu/t}$$

Power

$$\frac{(\$0.39/\text{t})(10,500 \text{ Btu/kWh})}{(\$0.02/\text{kWh})} = \frac{0.0205 \times 10^7 \text{ Btu/t}}{3.548 \times 10^7 \text{ Btu/t}}$$

$$\frac{(3.548 \times 10^7 \text{ Btu/t})}{(2,000 \text{ lb/t})(1.8)} = 9,857 \text{ kcal/kg}$$

Table C-3.2 (Continued)

Energy Cost of Ammonia from Natural Gas

D. Chemical Engineering, Oct. 24, 1977, p 82 (8)

New Bechtel design of ammonia plant has a requirement of 28.2 million Btu/ton of ammonia; of this total, 10.2 million Btu is for fuel.

$$\frac{(28.2 \times 10^6 \text{ Btu})}{(2,000 \text{ lb})(1.8)} = \underline{7,833 \text{ kcal/kg NH}_3}$$

An average of 9,000 kcal/kg NH₃ will be used for calculations in this report.

Table C-4

Energy Cost of Hydrogen Cyanide from Ammonia, Methane, and Air

A. Kirk-Othmer (2) 2nd ed., V 6, p 577

Methane, ammonia, and air are mixed in the ratio of 1:0.9:6 and catalytically burned. Air is assumed to be 21% O_2 . Yield based on NH_3 is 0.873; remaining NH_3 goes to N_2 and H_2 . The ratio of gaseous reactants used requires some H_2 , CO , or CO_2 to be formed by stoichiometry, but there is a lack of specific information. Electrical energy used, heat recovered, and hydrogen formed will therefore be neglected.

Reaction:

MW 16.04 17.03 27.03

Ratio 1 0.9 6 air
 (1.26 O_2)

Basis: 1 kg mol CH_4 , 0.9 kg mol NH_3 and 1.26 kg mol O_2

HCN produced = $(0.9)(0.873) = 0.786$ kg mol

Thermal energy of CH_4

$$(16.04 \text{ kg})(13,266 \text{ kcal/kg})^* = 212,787 \text{ kcal}$$

Thermal energy cost of NH_3

$$(0.9 \times 17.03 \text{ kg})(9,000 \text{ kcal/kg})^{**} = \underline{137,943 \text{ kcal}}$$

350,730 kcal

Thermal energy cost of HCN

$$\frac{(350,730 \text{ kcal})}{(0.786 \times 27.03 \text{ kg})} = \underline{16,508 \text{ kcal/kg}}$$

*Table C1

** Table C-3.2

Table C-4 (Continued)

Energy Cost of Hydrogen Cyanide from Ammonia, Methane, and Air

B. Basis: Table C-0

NH ₃	(0.83 kg) (9,000)	=	7,470
CH ₄	(0.82 kg) (13,266)	=	10,878
FOE	(0.13) (10,430)	=	<u>1,356</u>
			19,704 kcal/kg HCN

An average of 18,000 kcal/kg HCN will be used in this report.

C-5. NITRIC ACID

Nitric acid is made by catalytic oxidation of ammonia to NO_2 followed by reaction of NO_2 with water. The overall reactions are exothermic. The energy cost of nitric acid is calculated in Table C-5.

C-6. UREA

Urea is made by reacting ammonia with carbon dioxide to form ammonium carbamate, followed by decomposition of the carbamate. The energy cost of urea is calculated in Table C-6.

C-7. OXYGEN FROM AIR

Oxygen is separated from air by liquifaction and distillation from the nitrogen. The main energy requirement is electrical to drive the compressors. The energy cost of 95% pure oxygen is calculated in Table C-7.

C-8. CHLORINE AND SODIUM HYDROXIDE

Chlorine is made by electrolysis of sodium chloride brine. Energy costs were determined in a previous contract (9). For the diaphragm cell process the total energy requirement in fossil fuel equivalent units is 42.4×10^6 Btu/T or

$$\frac{(42.4 \times 10^6 \text{ Btu/T})(2.20 \text{ lb/kg})(0.252 \text{ kcal/Btu})}{(2,000 \text{ lb/T})} = 11,750 \text{ kcal/kg.}$$

The energy cost of the process will be allocated 50:50 to chlorine and to sodium hydroxide.

Table C-5

Energy Cost of Nitric Acid
by Catalytic Oxidation of Ammonia

A. Basis: 1 short ton of 100% HNO_3
Shreve (1) p 291

NH_3 required: 574 lb

Electrical energy used: 9 kWh

Process thermal heat is generated but will not be credited.

Thermal energy cost of NH_3

$$\frac{(574 \text{ lb})(9,000 \text{ kcal/kg})^*}{(2.20 \text{ lb/kg})} = 2,348,182 \text{ kcal}$$

Electrical equivalent

$$(9 \text{ kWh})(10,500 \text{ Btu/kWh})(0.252 \text{ kcal/Btu}) = \underline{23,814}$$

$$2,371,995 \text{ kcal}$$

Thermal energy cost of HNO_3

$$\frac{(2,371,995 \text{ kcal})(2.20 \text{ lb/kg})}{(2,000 \text{ lb})} = \underline{2,609 \text{ kcal/kg}}$$

B. Basis: Table C-0

$$\text{NH}_3 \quad (0.29)(9,000) = 2,610$$

$$\text{FOE} \quad (0.1)(10,430) = \underline{1,043}$$

$$\underline{3,653 \text{ kcal/kg}}$$

An average of 3,100 kcal/kg HNO_3 will be used in this report.

*Table C-3.2

Table C-6

Energy Cost of Urea by Reaction of Ammonia and Carbon Dioxide

A. <u>Basis:</u>	1 short ton of prilled urea	
	Shreve (1) p.286	
NH ₃ required:	1,180 lb	
CO ₂ required:	1,520 lb	
Electricity:	165 kWh	
Steam (150 psig sat):	4,000 lb	
Thermal energy cost of NH ₃		
	$\frac{(1,180 \text{ lb})(9,000 \text{ kcal/kg})^*}{(2.20 \text{ lb/kg})}$	= 4,827,273 kcal
Thermal energy cost of CO ₂		
	neglect	-
Electrical equivalent		
	$(165 \text{ kWh})(10,500 \text{ Btu/kWh})(0.252 \text{ kcal/Btu})$	= 436,590
Steam assume latent heat only		
	$(4,000 \text{ lb})(1,196 - 347 \text{ Btu/lb})^{**} (0.252 \text{ kcal/Btu}) =$	$\frac{855,792}{6,119,655 \text{ kcal}}$
Thermal energy cost of urea		
	$\frac{(6,119,655 \text{ kcal})(2.20 \text{ lb/kg})}{(2,000 \text{ lb})} =$	$\frac{6,732 \text{ kcal/kg}}$

B. Basis: Table C-0

NH ₃	(0.58)(9,000)	= 5,220
CO ₂	zero	
FOE	(0.09)(10,430)	= $\frac{939}{6,159 \text{ kcal/kg}}$

An average of 6,400 kcal/kg urea will be used in this report.

*Table C-3.2

**Perry (5) p 3-206

Table C-7

Energy Cost of Oxygen by Liquifaction and Separation from Air

Basis: 500 T/day of contained oxygen, 95% pure
at 5 psig, Shreve (1) p 110

Plant requirements:

Electric power	6,900 kW
Cooling water	2,000 gal/min
	(assume no energy charge)

Thermal energy cost of oxygen

$$\frac{(6,900 \text{ kW})(24 \text{ hr/day})(10,500 \text{ Btu/kWh})(0.252 \text{ kcal/Btu})(2.20 \text{ lb/kg})}{(500 \times 2,000 \text{ lb/day})}$$

$$= \underline{964 \text{ kcal/kg}}$$

C-9. SULFURIC ACID

Sulfuric acid is made in the contact process in which SO_2 is catalytically oxidized to SO_3 which is absorbed in H_2SO_4 and diluted to marketable concentrations. The only energy requirement is electrical which is given in Shreve (1) p 305 as 10 kWh/T of 100% acid. Heat is generated by the plant but will not be credited here. The equivalent fossil fuel energy requirements of the electrical energy is

$$\frac{(10\text{kWh})(10,000 \text{ Btu/kWh})(2.2 \text{ lb/kg})(0.252 \text{ kcal/Btu})}{(2,000 \text{ lb})} = 29 \text{ kcal/kg.}$$

C-11. IRON

Iron powder is used as a reducing agent in the chemical process to make hydroquinone from quinone. The source may be scrap iron, but coke was required to reduce the original iron ore to the metallic state, so the heating value of the coke will be charged to the iron. Other energy requirements such as beneficiation of taconite to blast furnace feed, transportation, and division of the iron to powder will not be considered at this time. From Statistical Abstract (10) 58,441 tons of coke were used to make 95,909 tons of pig iron in 1974, giving 0.609 T/T. The heating value of coke will be assumed 12,000 Btu/lb from Perry (5) p 9-7. The energy cost of iron is then

$$(0.609 \frac{\text{kg coke}}{\text{kg Fe}})(12,000 \frac{\text{Btu}}{\text{lb coke}})(2.20 \frac{\text{lb coke}}{\text{kg coke}})(0.252 \frac{\text{kcal}}{\text{Btu}}) = 4,050 \frac{\text{kcal}}{\text{kg}} \text{ Fe}$$

C-11. OTHER INORGANIC RAW MATERIALS

Air, water, and mined minerals such as pyrolusite (MnO_2) will not be assessed an energy charge.

C-12. ORGANIC RAW MATERIALS AND PRODUCTS

Energy costs for the following organic raw materials and products are based on data in Table C-0.

Ethylene - C_2H_4

C_2H_6	(1.25)(12,400)	=	15,500
FOE	(0.55)(10,430)	=	5,737
Pyro-gasoline credit	(0.04)(10,430)	=	- 417
			20,820 kcal/kg

Propylene - C_3H_6

About one-half of the propylene is currently produced by cracking during petroleum refining, and one-half is by-product from manufacture of ethylene from propane and from butane (11). The following calculations based on Table C-0 are an attempt to apportion a value for propylene from the ethylene syntheses. Credit for propylene is calculated by difference assuming an energy cost of 20,820 kcal/kg for ethylene.

By-product of ethylene from propane

C_3H_8	(2.29)(12,034)	=	27,558
FOE	(0.23)(10,430)	=	2,399
C_3H_6 credit	(0.29)(16,976)	=	- 4,923 (by difference)
C_4H_8 credit	(0.07)(19,977)	=	- 1,398
<u>Pyro-gasoline credit</u>	<u>(0.27)(10,430)</u>	=	<u>- 2,816</u>
C_2H_4	(1.00)(20,820)	=	20,820 kcal/kg

By-product of ethylene from butane

C_4H_{10}	(2.56)(11,838)	=	30,305
FOE	(0.86)(10,430)	=	8,970
C_3H_6 credit	(0.38)(<u>37,818</u>)	=	-14,371 (by difference)
C_4H_8 credit	(0.1)(19,977)	=	- 1,998
<u>Pyro-gasoline credit</u>	<u>(0.20)(10,430)</u>	=	<u>- 2,086</u>
C_2H_4	(1.00)(20,820)	=	20,820 kcal/kg

The energy values for propylene by difference vary widely from 16,976 to 37,818 kcal/kg. These values are respectively 1.41 and 3.14 times the heat of combustion of propane. For the process for making ethylene the energy cost of the ethylene is 1.68 times the heat of combustion of ethane. For the corresponding butylene process the energy cost of butylene is 1.69 times the heat of combustion of butane. It would seem appropriate to use this ratio also for propylene. A ratio of 1.68 times the heat of combustion of propane gives 20,217 kcal/kg which will be used as the basis energy cost of propylene in this report.

Butylene - C_4H_8

C_4H_{10}	(1.53)(11,838)	=	18,112
FOE	(0.65)(10,430)	=	6,780
C_4H_6 credit	(0.09)(54,615)	=	<u>- 4,915</u>
			19,977 kcal/kg

Butadiene - C_4H_6

C_4H_8	(1.46) (19,978)	=	29,166
H_2SO_4	(0.01) (39)	=	-
FOE	(2.44) (10,430)	=	<u>25,449</u>
			54,615 kcal/kg

Isopropanol - C_3H_7OH

C_3H_6	(0.72) (20,217)	=	14,556
FOE	(0.45) (10,430)	=	<u>4,694</u>
			19,250 kcal/kg

Acetone - C_3H_6O

C_3H_7OH	(1.26) (19,250)	=	24,255
FOE	(0.42) (10,430)	=	4,381
H_2 credit	(0.03) (33,944)	=	<u>- 1,018</u>
			27,618 kcal/kg

Butanol - C_4H_9OH

C_4H_8	(1.14) (19,977)	=	22,774
H_2SO_4	(0.01) (39)	=	-
NaOH	(0.02) (zero)	=	-
FOE	(0.58) (10,430)	=	<u>6,049</u>
			28,823 kcal/kg

Acrylonitrile

NH ₃	(0.52) (9,000)	=	4,680
C ₃ H ₆	(1.23) (20,217)	=	24,867
H ₂ SO ₄	(0.46) (39)	=	18
FOE	(0.09) (10,430)	=	939
HCN credit	(0.1) (18,000)	=	<u>- 1,800</u>
			28,704 kcal/kg

Adiponitrile (du Pont process)

C ₄ H ₆	(0.82) (54,615)	=	44,784
Cl ₂	(0.75) (8,891)	=	6,668
HCN	(0.57) (18,000)	=	10,260
FOE	(0.49) (10,430)	=	5,111
HCl credit	(0.68) (zero)	=	-
H ₂ credit	(0.03) (33,944)	=	<u>- 1,018</u>
			65,808 kcal/kg

Adiponitrile (Monsanto Process)

Acrylonitrile	(1.09) (28,704)	=	31,287
FOE	(1.14) (10,430)	=	<u>11,890</u>
			43,177 kcal/kg

Dichloroethane - C₂H₄Cl₂

C ₂ H ₄	(0.30) (20,820)	=	6,246
Cl ₂	(0.80) (8,891)	=	7,113
FOE	(0.14) (10,430)	=	<u>1,460</u>
			14,819 kcal/kg

Nitrobenzene - $C_6H_5NO_2$

Benzene	(0.65) (10,117)	=	6,576
HNO ₃	(0.53) (3,100)	=	1,643
FOE	(0.16) (10,430)	=	<u>1,669</u>
			9,888 kcal/kg

Cumene - $C_6H_5CH(CH_3)_2$

Benzene	(0.79) (10,117)	=	7,992
C ₃ H ₆	(0.41) (20,217)	=	8,289
FOE	(0.04) (10,430)	=	<u>417</u>
			16,698 kcal/kg

Phenol - C_6H_5OH

Cumene	(1.42) (16,698)	=	23,711
FOE	(0.49) (10,430)	=	5,111
Acetone credit	(0.60) (26,618)	=	<u>-16,571</u>
			12,251 kcal/kg

Aniline - $C_6H_5NH_2$

Phenol	(1.1) (12,251)	=	13,476
NH ₃	(0.2) (9,000)	=	1,800
FOE	(0.14) (10,430)	=	<u>1,460</u>
			16,736 kcal/kg

Methyl Ethyl Ketone

$$\begin{array}{rcl} \text{C}_4\text{H}_9\text{OH} & (1.1)(28,823) & = 31,705 \\ \text{FOE} & (0.31)(10,430) & = \underline{3,233} \\ & & 34,938 \text{ kcal/kg} \end{array}$$

APPENDIX C REFERENCES

1. R. N. Shreve and J. A. Brink, Jr., Chemical Process Industries, 4th ed., McGraw-Hill Book Company, New York, 1977.
2. Kirk-Othmer, Encyclopedia of Chemical Technology, Interscience Publishers, New York, 1963.
3. F. A. Lowenheim and M. K. Moran, Industrial Chemicals, Wiley Interscience, New York, 1975 (previous authors; W. L. Faith, D. B. Keyes, and R. L. Clark).
4. D. F. Rudd, M. A. Stadtherr, et al., "Resource Management and Technology Assessment in the Petrochemical Industry," (a manuscript for a book in preparation; relevant pages provided by courtesy of Prof. Stadtherr).
5. R. H. Perry and C. H. Chilton, Chemical Engineers Handbook, 5th ed, McGraw-Hill Book Company, New York, 1973.
6. Results for General Electric fuel cell, cited in Brookhaven National Laboratory report BNL 50924, September, 1978.
7. W. M. Latimer, Oxidation Potentials, Prentice Hall, Englewood Cliffs, NJ, 1952.
8. P. R. Savage, Chemical Engineering, October 24, 1977, p 82.
9. T. R. Beck, "Final Report on Improvements in Energy Efficiency of Industrial Electrochemical Processes," ANL/OEPM-77-2, January, 1977.
10. Statistical Abstract of the United States, 96th annual ed., U.S. Dept. of Commerce, U.S. Government Printing Office, Washington, DC, 1975.
11. M. A. Stadtherr, personal communication.