Industrial Organic Chemistry

Translated by Charlet R. Lindley

Third Completely Revised Edition
Preface to the Third Edition

In the few years that have passed since the publication of the 2nd English edition, it has become clear that interest in Industrial Inorganic Chemistry has continued to grow, making a new English edition necessary.

In the meantime, further translations have been published or are in preparation, and new editions have appeared.

The availability of large amounts of new information and up-to-date numerical data has prompted us to modernize and expand the book, at the same time increasing its scientific value. Apart from the scientific literature, a major help in our endeavors was the support of colleagues from Hoechst AG and numerous other chemical companies. Once again we thank VCH Publishers for the excellent cooperation.

February 1997

K. Weissermel
H.-J. Arpe
Preface to the Second Edition

The translation of "Industrial Organic Chemistry" into seven languages has proved the worldwide interest in this book. The positive feedback from readers with regard to the informational content and the didactic outline, together with the outstanding success of the similar work "Industrial Inorganic Chemistry" have encouraged us to produce this new revised edition.

The text has been greatly extended. Developmental possibilities appearing in the 1st Edition have now been revised and updated to the current situation. The increasingly international outlook of the 1st Edition has been further extended to cover areas of worldwide interest. Appropriate alterations in nomenclature and style have also been implemented.

A special thank you is extended to the Market Research Department of Hoechst AG for their help in the collection of numerical data. It is also a pleasure to express our gratitude to VCH Verlagsgesellschaft for their kind cooperation and for the successful organization and presentation of the books.

February 1993

K. Weissemel
H.-J. Arpe
Preface to the First Edition

Industrial organic chemistry is exhaustively treated in a whole series of encyclopedias and standard works as well as, to an increasing extent, in monographs. However, it is not always simple to rapidly grasp the present status of knowledge from these sources.

There was thus a growing demand for a text describing in a concise manner the most important precursors and intermediates of industrial organic chemistry. The authors have endeavored to review the material and to present it in a form, indicative of their daily confrontation with problems arising from research and development, which can be readily understood by the reader. In pursuing this aim they could rely, apart from their industrial knowledge, on teaching experience derived from university lectures, and on stimulating discussions with many colleagues.

This book addresses itself to a wide range of readers: the chemistry student should be able to appreciate from it the chemistry of important precursors and intermediates as well as to follow the development of manufacturing processes which he might one day help to improve. The university or college lecturer can glean information about applied organic syntheses and the constant change of manufacturing processes and feedstocks along with the resulting research objectives. Chemists and their colleagues from other disciplines in the chemical industry – such as engineers, marketing specialists, lawyers and industrial economists – will be presented with a treatise dealing with the complex technological, scientific and economic interrelationships and their potential developments.

This book is arranged into 14 chapters in which precursors and intermediates are combined according to their tightest possible correlation to a particular group. A certain amount of arbitrariness was, of course, unavoidable. The introductory chapter reviews the present and future energy and feedstock supply.

As a rule, the manufacturing processes are treated after general description of the historical development and significance of a product, emphasis being placed on the conventional processes and the applications of the product and its important deriva-
The sections relating to heavy industrial organic products are frequently followed by a prognosis concerning potential developments. Deficiencies of existing technological or chemical processes, as well as possible future improvements or changes to other more economic or more readily available feedstocks are briefly discussed.

The authors endeavored to provide a high degree of quality and quantity of information. Three types of information are at the reader's disposal:

1. The main text.
2. The synopsis of the main text in the margin.
3. Flow diagrams illustrating the interrelationship of the products in each chapter.

These three types of presentation were derived from the widespread habit of many readers of underlining or making brief notes when studying a text. The reader has been relieved of this work by the marginal notes which briefly present all essential points of the main text in a logical sequence thereby enabling him to be rapidly informed without having to study the main text.

The formula or process scheme (flow diagram) pertaining to each chapter can be folded out whilst reading a section in order that its overall relevance can be readily appreciated. There are no diagrams of individual processes in the main text as this would result in frequent repetition arising from recurring process steps. Instead, the reader is informed about the significant features of a process.

The index, containing numerous key words, enables the reader to rapidly find the required information.

A first version of this book was originally published in the German language in 1976. Many colleagues inside and outside Hoechst AG gave us their support by carefully reading parts of the manuscript and providing valuable suggestions thereby ensuring the validity of the numerous technological and chemical facts. In particular, we would like to express our thanks to Dr. H. Frit, Dr. W. Reif (BASF); Dr. R. Streck, Dr. H. Weber (Hüls AG); Dr. W. Jordan (Phenolchemie); Dr. B. Cornils, Dr. J. Falbe, Dr. W. Payer (Ruhrchemie AG); Dr. K. H. Berg, Dr. I. F. Hudson (Shell); Dr. G. König, Dr. R. Kühn, Dr. H. Tetteroo (UK-Wesel).

We are also indebted to many colleagues and fellow employees of Hoechst AG who assisted by reading individual chapters, expanding the numerical data, preparing the formula diagrams.
and typing the manuscript. In particular we would like to thank Dr. U. Dettmeier, M. Keller, Dr. E. I. Leupold, Dr. H. Meidert, and Prof. R. Steiner who all carefully read and corrected or expanded large sections of the manuscript. However, decisive for the choice of material was the access to the experience and the world-wide information sources of Hoechst AG.

Furthermore, the patience and consideration of our immediate families and close friends made an important contribution during the long months when the manuscript was written and revised.

In less than a year after the first appearance of ‘Industrielle Organische Chemie’ the second edition has now been published. The positive response enjoyed by the book places both an obligation on us as well as being an incentive to produce the second edition in not only a revised, but also an expanded form. This second edition of the German language version has also been the basis of the present English edition in which the numerical data were updated and, where possible, enriched by data from several leading industrial nations in order to stress the international scope.

Additional products were included along with their manufacturing processes. New facts were often supplemented with mechanistic details to facilitate the reader’s comprehension of basic industrial processes.

The book was translated by Dr. A. Mullen (Ruhrchemie AG) to whom we are particularly grateful for assuming this arduous task which he accomplished by keeping as closely as possible to the original text whilst also managing to evolve his own style. We would like to thank the Board of Ruhrchemie AG for supporting this venture by placing the company’s facilities at Dr. Mullen’s disposal.

We are also indebted to Dr. T. F. Leahy, a colleague from the American Hoechst Corporation, who played an essential part by meticulously reading the manuscript.

Verlag Chemie must also be thanked — in particular Dr. H. F. Ebel — for its support and for ensuring that the English edition should have the best possible presentation.

Hoechst, in January 1978

K. Weissermel
H.-J. Arpe
This Page Intentionally Left Blank
Contents

1. Various Aspects of the Energy and Raw Material Supply ........................................... 1
   1.1. Present and Predictable Energy Requirements .................................................. 2
   1.2. Availability of Individual Sources ...................................................................... 3
       1.2.1. Oil ........................................................................................................... 3
       1.2.2. Natural Gas ............................................................................................. 4
       1.2.3. Coal .......................................................................................................... 5
       1.2.4. Nuclear Fuels ............................................................................................ 5
   1.3. Prospects for the Future Energy Supply ............................................................... 7
   1.4. Present and Anticipated Raw Material Situation ................................................... 8
       1.4.1. Petrochemical Primary Products ................................................................. 8
       1.4.2. Coal Conversion Products ....................................................................... 11

2. Basic Products of Industrial Syntheses ...................................................................... 13
   2.1. Synthesis Gas ...................................................................................................... 13
       2.1.1. Generation of Synthesis Gas ..................................................................... 13
       2.1.1.1. Synthesis Gas via Coal Gasification ....................................................... 14
       2.1.1.2. Synthesis Gas via Cracking of Natural Gas and Oil ............................... 17
       2.1.2. Synthesis Gas Purification and Use ............................................................ 19
   2.2. Production of the Pure Synthesis Gas Components ............................................. 21
       2.2.1. Carbon Monoxide ...................................................................................... 21
       2.2.2. Hydrogen .................................................................................................. 24
   2.3. C1-Units .............................................................................................................. 27
       2.3.1. Methanol .................................................................................................... 27
       2.3.1.1. Manufacture of Methanol ..................................................................... 28
       2.3.1.2. Applications and Potential Applications of Methanol ......................... 30
       2.3.2. Formaldehyde ........................................................................................... 35
       2.3.2.1. Formaldehyde from Methanol ................................................................. 36
       2.3.2.2. Uses and Potential Uses of Formaldehyde .............................................. 38
       2.3.3. Formic Acid ............................................................................................... 40
       2.3.4. Hydrocyanic Acid ...................................................................................... 44
       2.3.5. Methylamines ............................................................................................. 49
       2.3.6. Halogen Derivatives of Methane ................................................................. 50
       2.3.6.1. Chloromethanes ..................................................................................... 50
       2.3.6.2. Chlorofluoromethanes ......................................................................... 55
## Contents

3. **Olefins**  
   3.1. Historical Development of Olefin Chemistry  
   3.2. Olefins via Cracking of Hydrocarbons  
   3.3. Special Manufacturing Processes for Olefins  
      3.3.1. Ethylene, Propene  
      3.3.2. Butenes  
      3.3.3. Higher Olefins  
         3.3.3.1. Unbranched Higher Olefins  
         3.3.3.2. Branched Higher Olefins  
   3.4. Olefin Metathesis  

4. **Acetylene**  
   4.1. Present Significance of Acetylene  
   4.2. Manufacturing Processes for Acetylene  
      4.2.1. Manufacture Based on Calcium Carbide  
      4.2.2. Thermal Processes  
   4.3. Utilization of Acetylene  

5. **1,3-Diolefins**  
   5.1. 1,3-Butadiene  
      5.1.1. Traditional Syntheses of 1,3-Butadiene  
      5.1.2. 1,3-Butadiene from C₄ Cracking Fractions  
      5.1.3. 1,3-Butadiene from C₄ Alkanes and Alkenes  
      5.1.4. Utilization of 1,3-Butadiene  
   5.2. Isoprene  
      5.2.1. Isoprene from C₅ Cracking Fractions  
      5.2.2. Isoprene from Synthetic Reactions  
   5.3. Chloroprene  
   5.4. Cyclopentadiene  

6. **Syntheses Involving Carbon Monoxide**  
   6.1. Hydroformylation of Olefins  
      6.1.1. The Chemical Basis of Hydroformylation  
      6.1.2. Industrial Operation of Hydroformylation  
      6.1.3. Catalyst Modifications in Hydroformylation  
      6.1.4. Utilization of ‘Oxo’ Products  
         6.1.4.1. ‘Oxo’ Alcohols  
         6.1.4.2. ‘Oxo’ Carboxylic Acids  
         6.1.4.3. Aldol and Condensation Products of the ‘Oxo’ Aldehydes  
   6.2. Carbonylation of Olefins  
   6.3. The Koch Carboxylic Acid Synthesis


7. **Oxidation Products of Ethylene** ................................................................. 143
   7.1. Ethylene Oxide .................................................................................. 143
   7.1.1. Ethylene Oxide by Chlorohydrin Process .................................... 144
   7.1.2. Ethylene Oxide by Direct Oxidation ............................................. 144
       7.1.2.1. Chemical Principles .............................................................. 144
       7.1.2.2. Process Operation ................................................................. 146
       7.1.2.3. Potential Developments in Ethylene Oxide Manufacture ........ 148
   7.2. Secondary Products of Ethylene Oxide .............................................. 149
       7.2.1. Ethylene Glycol and Higher Ethylene Glycols ........................ 150
       7.2.1.1. Potential Developments in Ethylene Glycol Manufacture ....... 151
       7.2.1.2. Uses of Ethylene Glycol ........................................................ 153
       7.2.1.3. Secondary Products — Glyoxal, Dioxolane, 1,4-Dioxane ....... 154
       7.2.2. Polyethoxylates ......................................................................... 156
       7.2.3. Ethanolamines and Secondary Products .................................... 157
       7.2.4. Ethylene Glycol Ethers ............................................................... 160
       7.2.5. Additional Products from Ethylene Oxide .................................. 162
   7.3. Acetaldehyde ....................................................................................... 163
       7.3.1. Acetaldehyde via Oxidation of Ethylene .................................... 164
       7.3.1.1. Chemical Basis ...................................................................... 164
       7.3.1.2. Process Operation ................................................................. 166
       7.3.2. Acetaldehyde from Ethanol ........................................................ 167
       7.3.3. Acetaldehyde from C3/C4 Alkane Oxidation .............................. 168
   7.4. Secondary Products of Acetaldehyde .................................................... 169
       7.4.1. Acetic Acid .................................................................................. 169
       7.4.1.1. Acetic Acid by Oxidation of Acetaldehyde ............................ 170
       7.4.1.2. Acetic Acid by Oxidation of Alkanes and Alkenes ............... 172
       7.4.1.3. Carboxylation of Methanol to Acetic Acid ........................... 175
       7.4.1.4. Potential Developments in Acetic Acid Manufacture ............. 177
       7.4.1.5. Uses of Acetic Acid ................................................................. 178
       7.4.2. Acetic Anhydride and Ketene ...................................................... 180
       7.4.3. Aldol Condensation of Acetaldehyde and Secondary Products .... 184
       7.4.4. Ethyl Acetate ............................................................................... 186
       7.4.5. Pyridine and Alkylpyridines ........................................................ 188

8. **Alcohols** ................................................................................................. 191
   8.1. Lower Alcohols .................................................................................... 191
   8.1.1. Ethanol ........................................................................................... 191
   8.1.2. Isopropanol .................................................................................... 196
   8.1.3. Butanols .......................................................................................... 199
   8.1.4. Amyl Alcohols ................................................................................. 203
   8.2. Higher Alcohols .................................................................................... 203
   8.2.1. Oxidation of Paraffins to Alcohols ................................................ 207
   8.2.2. Affol Synthesis ............................................................................... 208
8.3. Polyhydric Alcohols ................................................. 210
8.3.1. Pentaerythritol ................................................. 210
8.3.2. Trimethylolpropane .............................................. 211
8.3.3. Neopentyl Glycol ................................................. 212

9.1. Vinyl–Halogen Compounds ............................................. 215
9.1.1. Vinyl Chloride .................................................... 215
9.1.1.1. Vinyl Chloride from Acetylene ................................ 216
9.1.1.2. Vinyl Chloride from Ethylene .................................. 217
9.1.1.3. Potential Developments in Vinyl Chloride Manufacture .......... 220
9.1.1.4. Uses of Vinyl Chloride and 1,2-Dichloroethane ................ 221
9.1.2. Vinylidene Chloride .............................................. 223
9.1.3. Vinyl Fluoride and Vinylidene Fluoride .......................... 223
9.1.4. Trichloro- and Tetrachloroethylene ............................. 225
9.1.5. Tetrafluoroethylene .............................................. 227

9.2. Vinyl Esters and Ethers ............................................. 228
9.2.1. Vinyl Acetate .................................................... 228
9.2.1.1. Vinyl Acetate Based on Acetylene or Acetaldehyde .......... 228
9.2.1.2. Vinyl Acetate Based on Ethylene ................................ 229
9.2.1.3. Possibilities for Development of Vinyl Acetate Manufacture .... 233
9.2.2. Vinyl Esters of Higher Carboxylic Acids .......................... 234
9.2.3. Vinyl Ethers .................................................... 235

10. Components for Polyamides ............................................ 237
10.1. Dicarboxylic Acids .................................................. 238
10.1.1. Adipic Acid ..................................................... 239
10.1.2. 1,12-Dodecanedioic Acid ....................................... 243
10.2. Diamines and Aminocarboxylic Acids ................................ 244
10.2.1. Hexamethylenediamine .......................................... 244
10.2.1.1. Manufacture of Adiponitrile ................................ 245
10.2.1.2. Hydrogenation of Adiponitrile ................................ 249
10.2.1.3. Potential Developments in Adiponitrile Manufacture .......... 250
10.2.2. ω-Aminoundecanoic Acid ....................................... 250
10.3. Lactams ............................................................ 251
10.3.1. ε-Caprolactam ................................................... 251
10.3.1.1. ε-Caprolactam from the Cyclohexanone Oxime Route .......... 252
10.3.1.2. Alternative Manufacturing Processes for ε-Caprolactam .... 256
10.3.1.3. Possibilities for Development in ε-Caprolactam Manufacture ... 258
10.3.1.4. Uses of ε-Caprolactam ....................................... 260
10.3.2. Lauryl Lactam .................................................... 262
11. Propene Conversion Products ................................................................. 265
   11.1. Oxidation Products of Propene ......................................................... 266
   11.1.1. Propylene Oxide ............................................................................. 266
   11.1.1.1. Propylene Oxide from the Chlorohydrin Process ......................... 266
   11.1.1.2. Indirect Oxidation Routes to Propylene Oxide ............................ 267
   11.1.1.3. Possibilities for Development in the Manufacture of Propylene Oxide . 271
   11.1.2. Secondary Products of Propylene Oxide ......................................... 275
   11.1.3. Acetone ......................................................................................... 276
   11.1.3.1. Direct Oxidation of Propene ....................................................... 277
   11.1.3.2. Acetone from Isopropanol .......................................................... 278
   11.1.4. Secondary Products of Acetone ...................................................... 279
   11.1.4.1. Acetone Aldolization and Secondary Products ............................ 280
   11.1.4.2. Methacrylic Acid and Ester ......................................................... 281
   11.1.5. Acrolein ......................................................................................... 285
   11.1.6. Secondary Products of Acrolein ..................................................... 287
   11.1.7. Acrylic Acid and Esters ................................................................ 289
   11.1.7.1. Traditional Acrylic Acid Manufacture ....................................... 289
   11.1.7.2. Acrylic Acid from Propene ......................................................... 291
   11.1.7.3. Possibilities for Development in Acrylic Acid Manufacture .......... 293
   11.2. Allyl Compounds and Secondary Products ......................................... 294
   11.2.1. Allyl Chloride ............................................................................... 294
   11.2.2. Allyl Alcohol and Esters ................................................................. 297
   11.2.3. Glycerol from Allyl Precursors ...................................................... 299
   11.3. Acrylonitrile ...................................................................................... 302
   11.3.1. Traditional Acrylonitrile Manufacture .......................................... 303
   11.3.2. Ammoxidation of Propene ............................................................... 304
   11.3.2.1. Sohio Acrylonitrile Process ......................................................... 305
   11.3.2.2. Other Propene/Propane Ammoxidation Processes ....................... 306
   11.3.3. Possibilities for Development of Acrylonitrile Manufacture .......... 307
   11.3.4. Uses and Secondary Products of Acrylonitrile ............................... 308

12. Aromatics – Production and Conversion .................................................. 311
   12.1. Importance of Aromatics ..................................................................... 311
   12.2. Sources of Feedstocks for Aromatics ............................................... 312
   12.2.1. Aromatics from Coking of Hard Coal ............................................. 313
   12.2.2. Aromatics from Reformate and Pyrolysis Gasoline ....................... 314
   12.2.2.1. Isolation of Aromatics ................................................................. 317
   12.2.2.2. Special Separation Techniques for Non-Aromatic/Aromatic and Aromatic Mixtures . 318
   12.2.3. Possibilities for Development of Aromatic Manufacture ............... 323
   12.2.4. Condensed Aromatics ..................................................................... 324
   12.2.4.1. Naphthalene .............................................................................. 325
   12.2.4.2. Anthracene ................................................................................. 326
## Contents

12.3. Conversion Processes for Aromatics ................................................... 329
   12.3.1. Hydrodealkylation .......................................................................... 329
   12.3.2. m-Xylene Isomerization .................................................................. 330
   12.3.3. Disproportionation and Transalkylation ......................................... 332

13. Benzene Derivatives .............................................................................. 335
   13.1. Alkylation and Hydrogenation Products of Benzene .............................. 335
       13.1.1. Ethylbenzene ............................................................................. 335
       13.1.2. Styrene ....................................................................................... 339
       13.1.3. Cumene ....................................................................................... 342
       13.1.4. Higher Alkylbenzenes .................................................................. 343
       13.1.5. Cyclohexane ................................................................................. 345
   13.2. Oxidation and Secondary Products of Benzene .................................... 347
       13.2.1. Phenol ........................................................................................ 347
       13.2.1.1. Manufacturing Processes for Phenol ............................................. 348
       13.2.1.2. Potential Developments in Phenol Manufacture ............................ 355
       13.2.1.3. Uses and Secondary Products of Phenol ..................................... 358
       13.2.2. Dihydroxybenzenes .................................................................... 361
       13.2.3. Maleic Anhydride ...................................................................... 365
           13.2.3.1. Maleic Anhydride from Oxidation of Benzene ............................. 366
           13.2.3.2. Maleic Anhydride from Oxidation of Butene ............................. 368
           13.2.3.3. Maleic Anhydride from Oxidation of Butene ............................. 369
       13.2.3.4. Uses and Secondary Products of Maleic Anhydride ...................... 370
   13.3. Other Benzene Derivatives ............................................................ 373
       13.3.1. Nitrobenzene .............................................................................. 373
       13.3.2. Aniline ....................................................................................... 374
       13.3.3. Diisocyanates ............................................................................ 377

14. Oxidation Products of Xylene and Naphthalene .................................. 385
   14.1. Phthalic Anhydride .......................................................................... 385
       14.1.1. Oxidation of Naphthalene to Phthalic Anhydride ......................... 385
       14.1.2. Oxidation of o-Xylene to Phthalic Anhydride .............................. 387
       14.1.3. Esters of Phthalic Acid and Derivatives ....................................... 389
   14.2. Terephthalic Acid ........................................................................... 392
       14.2.1. Manufacture of Dimethyl Terephthalate and Terephthalic Acid ......... 393
       14.2.2. Fiber Grade Terephthalic Acid ................................................... 395
       14.2.3. Other Manufacturing Routes to Terephthalic Acid and Derivatives .... 397
       14.2.4. Uses of Terephthalic Acid and Dimethyl Terephthalate ................ 400

15. Appendix ............................................................................................ 405
   15.1. Process and Product Schemes ......................................................... 405
   15.2. Definitions of Terms used in Characterizing Chemical Reactions ......... 425
1. Various Aspects of the Energy and Raw Material Supply

The availability and price structure of energy and raw materials have always determined the technological base and thus the expansion and development of industrial chemistry. However, the oil crisis was necessary before the general public once again became aware of this relationship and its importance for the world economy.

Coal, natural gas, and oil, formed with the help of solar energy during the course of millions of years, presently cover not only the energy, but also to a large extent chemical feedstock requirements.

There is no comparable branch of industry in which there is such a complete interplay between energy and raw materials as in the chemical industry. Every variation in supply has a double impact on the chemical industry as it is one of the greatest consumers of energy. In addition to this, the non-recoverable fossil products, which are employed as raw materials, are converted into a spectrum of synthetic substances which we meet in everyday life.

The constantly increasing demand for raw materials and the limited reserves point out the importance of safeguarding future energy and raw material supplies.

All short- and medium-term efforts will have to concentrate on the basic problem as to how the flexibility of the raw material supply for the chemical industry on the one hand, and the energy sector on the other hand, can be increased with the available resources. In the long term, this double function of the fossil fuels will be terminated in order to maintain this attractive source of supply for the chemical industry for as long as possible.

In order to better evaluate the present situation and understand the future consumption of primary energy sources and raw materials, both aspects will be reviewed together with the individual energy sources.

fossil fuels
- natural gas, petroleum, coal
  - have two functions:
    1. energy source
    2. raw material for chemical products

long range aims for securing industrial raw material and energy supply:
1. extending the period of use of the fossil raw materials
2. replacing the fossil raw materials in the energy sector
primary energy consumption (in 10^{12} kwhr)  

<table>
<thead>
<tr>
<th>Year</th>
<th>World</th>
<th>USA</th>
<th>W.Europe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1964</td>
<td>41.3</td>
<td>12.5</td>
<td>7.9</td>
</tr>
<tr>
<td>1974</td>
<td>67.5</td>
<td>15.4</td>
<td>10.7</td>
</tr>
<tr>
<td>1984</td>
<td>82.6</td>
<td>19.5</td>
<td>11.6</td>
</tr>
<tr>
<td>1989</td>
<td>95.2</td>
<td>23.6</td>
<td>13.0</td>
</tr>
<tr>
<td>1994</td>
<td>93.6</td>
<td>24.0</td>
<td>13.2</td>
</tr>
</tbody>
</table>

energy consumption of the chemical industry:  
6% of total consumption, i.e., second greatest industrial consumer

changes in primary energy distribution worldwide (in %):  

<table>
<thead>
<tr>
<th>Year</th>
<th>1964</th>
<th>1974</th>
<th>1984</th>
<th>1995</th>
</tr>
</thead>
<tbody>
<tr>
<td>oil</td>
<td>41</td>
<td>48</td>
<td>42</td>
<td>38</td>
</tr>
<tr>
<td>coal</td>
<td>37</td>
<td>28</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>natural gas</td>
<td>15</td>
<td>18</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>nuclear energy</td>
<td>6</td>
<td>6</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>water power/ others</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>14</td>
</tr>
</tbody>
</table>

(others include, e.g., biomass)

reasons for preferred use of oil and natural gas as energy source:  
1. economic recovery  
2. versatile applicability  
3. low transportation and distribution costs  
4. restructuring of energy consumption not possible in the short term  
5. oil remains main energy source for the near future

1.1. Present and Predictable Energy Requirements

During the last twenty-five years, the world energy demand has more than doubled and in 1995 it reached $94.4 \times 10^{12}$ kwhr, corresponding to the energy from $8.12 \times 10^9$ tonnes of oil (1 tonne oil =11620 kwhr = $10 \times 10^6$ kcal = $41.8 \times 10^6$ kJ). The average annual increase before 1974 was about 5%, which decreased through the end of the 1980s, as the numbers in the adjacent table illustrate. In the 1990s, primary energy consumption has hardly changed due to the drop in energy demand caused by the economic recession following the radical changes in the former East Bloc.

However, according to the latest prediction of the International Energy Agency (IEA), global population will grow from the current 5.6 to $7 \times 10^9$ people by the year 2010, causing the world energy demand to increase to $130 \times 10^{12}$ kwhr.

In 1989, the consumption of primary energy in the OECD (Organization for Economic Cooperation and Development) countries was distributed as follows:

- 31% for transport
- 34% for industrial use
- 35% for domestic and agricultural use, and other sectors

The chemical industry accounts for 6% of the total energy consumption and thereby assumes second place in the energy consumption scale after the iron processing industry.

Between 1950 and 1995, the worldwide pattern of primary energy consumption changed drastically. Coal's share decreased from ca. 60% in 1950 to the values shown in the accompanying table. In China and some of the former Eastern Bloc countries, 40% of the energy used still comes from coal. Oil's share amounted to just 25% of world energy consumption in 1950, and reached a maximum of nearly 50% in the early 1970s. Today it has stabilized at ca. 38%, and is expected to decrease slightly to 37% by 2000.

The reasons for this energy source structure lie with the ready economic recovery of oil and natural gas and their versatile applicability as well as lower transportation and distribution costs.

In the following decades, the forecast calls for a slight decrease in the relative amounts of energy from oil and natural gas, but...
a small increase for coal and nuclear energy. An eventual transition to carbon-free and inexhaustible energy sources is desirable, but this development will be influenced by many factors.

In any event, oil and natural gas will remain the main energy sources in predictions for decades, as technological reorientation will take a long time due to the complexity of the problem.

1.2. Availability of Individual Sources

1.2.1. Oil

New data show that the proven and probable, i.e., supplementary, recoverable world oil reserves are higher than the roughly $520 \times 10^9$ tonnes, or $6040 \times 10^{12}$ kwhr, estimated in recent years. Of the proven reserves (1996), 66% are found in the Middle East, 13% in South America, 3% in North America, 2% in Western Europe and the remainder in other regions. With about 26% of the proven oil reserves, Saudi Arabia has the greatest share, leading Iraq, Kuwait and other countries principally in the Near East. In 1996, the OPEC countries accounted for ca. 77 wt% of worldwide oil production. Countries with the largest production in 1994 were Saudi Arabia and the USA.

A further crude oil supply which amounts to ten times the above-mentioned petroleum reserves is found in oil shale, tar sand, and oil sand. This source, presumed to be the same order of magnitude as mineral oil only a few years ago, far surpasses it.

There is a great incentive for the exploitation of oil shale and oil sand. To this end, extraction and pyrolysis processes have been developed which, under favorable local conditions, are already economically feasible. Large commercial plants are being run in Canada, with a significant annual increase (for example, production in 1994 was 17% greater than in 1993), and the CIS. Although numerous pilot plants have been shut down, for instance in the USA, new ones are planned in places such as Australia. In China, oil is extracted from kerogen-containing rock strata. An additional plant with a capacity of $0.12 \times 10^6$ tonnes per year was in the last phase of construction in 1994.

At current rates of consumption, proven crude oil reserves will last an estimated 43 years (1996). If the additional supply from oil shale/oil sands is included, the supply will last for more than 100 years.
1. Various Aspects of the Energy and Raw Material Supply

However, the following factors will probably help ensure an oil supply well beyond that point: better utilization of known deposits which at present are exploited only to about 30% with conventional technology, intensified exploration activity, recovery of difficult-to-obtain reserves, the opening up of oil fields under the seabed as well as a restructuring of energy and raw material consumption.

**1.2.2. Natural Gas**

The proven and probable world natural gas reserves are somewhat larger than the oil reserves, and are currently estimated at \(368 \times 10^{12} \text{ m}^3\), or \(3390 \times 10^{12} \text{ kwhr}\). Proven reserves amount to \(1380 \times 10^{12} \text{ kwhr}\).

In 1995, 39% of these reserves were located in the CIS, 14% in Iran, 5% in Qatar, 4% in each of Abu Dhabi and Saudi Arabia, and 3% in the USA. The remaining 31% is distributed among all other natural gas-producing countries.

Based on the natural gas output for 1995 (25.2 \(\times 10^{12}\) kwhr), the proven worldwide reserves should last for almost 55 years.

In 1995, North America and Eastern Europe were the largest producers, supplying 32 and 29%, respectively, of the natural gas worldwide.

Natural gas consumption has steadily increased during the last two decades. Up until now, natural gas could only be used where the corresponding industrial infrastructure was available or where the distance to the consumer could be bridged by means of pipelines. In the meantime, gas transportation over great distances from the source of supply to the most important consumption areas can be overcome by liquefaction of natural gas (\(\text{LNG} = \text{liquefied natural gas}\)) and transportation in specially built ships as is done for example in Japan, which supplies itself almost entirely by importing LNG. In the future, natural gas could possibly be transported by first converting it into methanol — via synthesis gas — necessitating, of course, additional expenditure.

The dependence on imports, as with oil, in countries with little or no natural gas reserves is therefore resolvable. However, this situation will only fundamentally change when synthesis gas technology — based on brown (lignite) and hard coal — is established and developed. This will probably take place on a larger scale only in the distant future.
1.2. Availability of Individual Sources

1.2.3. Coal

As far as the reserves are concerned, coal is not only the most widely spread but also the most important source of fossil energy. However, it must be kept in mind that the estimates of coal deposits are based on geological studies and do not take the mining problems into account. The proven and probable world hard coal reserves are estimated to be 61,920 x 10^{12} kwhr. The proven reserves amount to 4610 x 10^{12} kwhr. Of this amount, ca. 35% is found in the USA, 6% in the CIS, 13% in the Peoples' Republic of China, 13% in Western Europe, and 11% in Africa. In 1995, 3.4 x 10^6 tonnes of hard coal were produced worldwide, with 56% coming out of the USA and China.

In 1989, the world reserves of brown coal were estimated at 6800 x 10^{12} kwhr, of which 860 x 10^{12} kwhr are proven reserves. By 1992, these proven reserves had increased by ca. 30%.

With the huge coal deposits available, the world’s energy requirements could be met for a long time to come. According to studies at several institutes, this could be for several thousand years at the current rate of growth.

1.2.4. Nuclear Fuels

Nuclear energy is — as a result of its stage of development — the only realistic solution to the energy supply problem of the next decades. Its economic viability has been proven.

The nuclear fuels offer an alternative to fossil fuels in important areas, particularly in the generation of electricity. In 1995, 17% of the electricity worldwide was produced in 437 nuclear reactors, and an additional 59 reactors are under construction. Most nuclear power plants are in the USA, followed by France and Japan. The uranium and thorium deposits are immense and are widely distributed throughout the world. In 1995, the world production of uranium was 33,000 tonnes. Canada supplied the largest portion with 9900 tonnes, followed by Australia, Niger, the USA and the CIS.

In the low and medium price range there are ca. 4.0 x 10^6 tonnes of uranium reserves, of which 2.2 x 10^6 tonnes are proven; the corresponding thorium reserves amount to around 2.2 x 10^6 tonnes.

<table>
<thead>
<tr>
<th>energy sources for electricity (in %):</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
</tr>
<tr>
<td>natural gas/oil</td>
</tr>
<tr>
<td>coal</td>
</tr>
<tr>
<td>nuclear energy</td>
</tr>
<tr>
<td>hydroelectric/others</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>reserves of nuclear fuels (in 10^6 tonnes):</th>
</tr>
</thead>
<tbody>
<tr>
<td>uranium</td>
</tr>
<tr>
<td>proven</td>
</tr>
<tr>
<td>total</td>
</tr>
<tr>
<td>n.a. = not available</td>
</tr>
</tbody>
</table>

hard coal reserves (in 10^{12} kwhr):

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>proven</td>
<td>5600</td>
<td>4090</td>
<td>5860</td>
</tr>
<tr>
<td>total</td>
<td>54500</td>
<td>58600</td>
<td>67800</td>
</tr>
</tbody>
</table>

“hard coal” also includes tar coal and anthracite.
I. Various Aspects of the Energy and Raw Material Supply

energy content of uranium reserves (in 10¹² kwhr):

- 690 with conventional reactor technology
- 80000 by full utilization via breeders

function of fast breeders (neutron capture):

\[
238\text{U} \rightarrow 239\text{Pu} \\
232\text{Th} \rightarrow 233\text{U}
\]

reactor generations:

- light-water reactors
- high temperature reactors
- breeder reactors

advantage of high temperature reactors:

- high temperature range (900 – 1000 °C)
- process heat useful for strongly endothermic chemical reactions

essential prerequisites for the use of nuclear energy:

1. reliable supply of nuclear energy
2. technically safe nuclear power stations
3. safe disposal of fission products and recycling of nuclear fuels (reprocessing)

Employing uranium in light-water reactors of conventional design in which essentially only 235U is used (up to 0.7% in natural uranium) and where about 1000 MWd/kg 235U are attained means that 4 x 10⁶ tonnes uranium correspond to ca. 690 x 10¹² kwhr. If this uranium were to be fully exploited using fast breeder reactors, then this value could be very considerably increased, namely to ca. 80000 x 10¹² kwhr. An additional 44000 x 10¹² kwhr could be obtained if the aforementioned thorium reserves were to be employed in breeder reactors. The significance of the fast breeder reactors can be readily appreciated from these figures. They operate by synthesizing the fissionable 239Pu from the nonfissionable nuclide 238U (main constituent of natural uranium, abundance 99.3%) by means of neutron capture. 238U is not fissionable using thermal neutrons. In the same way fissionable 233U can be synthesized from 232Th.

The increasing energy demand can be met for at least the next 50 years using present reactor technology.

The dominant reactor type today, and probably for the next 20 years, is the light-water reactor (boiling or pressurized water reactor) which operates at temperatures up to about 300 °C. High temperature reactors with cooling medium (helium) temperature up to nearly 1000 °C are already on the threshold of large scale development. They have the advantage that they not only supply electricity but also process heat at higher temperatures (cf. Sections 2.1.1 and 2.2.2). Breeder reactors will probably become commercially available in greater numbers as generating plants near the end of the 1990s at the earliest, since several technological problems still confront their development.

In 1995, Japan and France were the only countries that were still using and developing breeder reactors.

It is important to note that the supply situation of countries highly dependent on energy importation can be markedly improved by storing nuclear fuels due to their high energy content. The prerequisite for the successful employment of nuclear energy is not only that safe and reliable nuclear power stations are erected, but also that the whole fuel cycle is completely closed. This begins with the supply of natural uranium, the siting of suitable enrichment units, and finishes with the waste disposal of radioactive fission products and the recycling of unused and newly bred nuclear fuels.

Waste management and environmental protection will determine the rate at which the nuclear energy program can be realized.
1.3. Prospects for the Future Energy Supply

As seen in the foregoing sections, oil, natural gas, and coal will remain the most important primary energy sources for the long term. While there is currently little restriction on the availability of energy sources, in light of the importance of oil and natural gas as raw materials for the chemical industry, their use for energy should be decreased as soon as possible.

The exploitation of oil shales and oil sands will not significantly affect the situation in the long term. The substitution of oil and natural gas by other energy sources is the most prudent solution to this dilemma. By these means, the valuable fossil materials will be retained as far as possible for processing by the chemical industry.

In the medium term, the utilization of nuclear energy can decisively contribute to a relief of the fossil energy consumption. Solar energy offers an almost inexhaustible energy reserve and will only be referred to here with respect to its industrial potential. The energy which the sun annually supplies to the earth corresponds to thirty times the world’s coal reserves. Based on a simple calculation, the world’s present primary energy consumption could be covered by 0.005% of the energy supplied by the sun. Consequently, the development of solar energy technology including solar collectors and solar cell systems remains an important objective. At the same time, however, the energy storage and transportation problems must be solved.

The large scale utilization of the so-called unlimited energies — solar energy, geothermal energy, and nuclear fusion — will become important only in the distant future. Until that time, we will be dependent on an optimal use of fossil raw materials, in particular oil. In the near future, nuclear energy and coal will play a dominant role in our energy supply, in order to stretch our oil reserves as far as possible. Nuclear energy will take over the generation of electricity while coal will be increasingly used as a substitute for petroleum products.

Before the energy supply becomes independent of fossil sources — undoubtedly not until the next century — there will possibly be an intermediate period in which a combination of nuclear energy and coal will be used. This combination could utilize nuclear process heat for coal gasification leading to the greater employment of synthesis gas products (cf. Section 2.1.1).

Along with the manufacture of synthesis gas via coal gasification, nuclear energy can possibly also be used for the possible relief for fossil fuels by generation of energy from:
1. nuclear energy (medium term)
2. solar energy (long term)
3. geothermal energy (partial)
4. nuclear fusion energy (long term)

possible substitution of oil for energy generation by means of:
1. coal
2. nuclear energy
3. combination of coal and nuclear energy
4. hydrogen
1. Various Aspects of the Energy and Raw Material Supply

Various Aspects of the Energy and Raw Material Supply

1.1. Energy Supply

1.1.1. Hydrogen Technology

Manufacture of hydrogen from water via high temperature steam electrolysis or chemical cyclic processes. The same is true of water electrolysis using solar energy, which is being studied widely in several countries. This could result in a wide use of hydrogen as an energy source (hydrogen technology) and in a replacement of hydrogen manufacture from fossil materials (cf. Section 2.2.2).

This phase will lead to the situation in which energy will be won solely from renewable sources and oil and coal will be employed only as raw materials.

1.2. Raw Material Supply

1.2.1. Energy Supply

Long-term aim:

- Energy supply solely from renewable sources;
- Raw material supply from fossil sources

Characteristic changes in the raw material base of the chemical industry:

- Feedstocks until 1950:
  - Coal gasification products (coking products, synthesis gas)
  - Acetylene from calcium carbide

- Feedstocks after 1950:
  - Products from petroleum processing
  - Natural gas
  - Coal gasification products as well as acetylene from carbide and light hydrocarbons

1.4. Present and Anticipated Raw Material Situation

1.4.1. Petrochemical Primary Products

The manufacture of carbon monoxide and hydrogen via gasification processes together with the manufacture of carbide (for welding and some special organic intermediates), benzene, and certain polynuclear aromatics are the only remaining processes of those employed in the 1950s for the preparation of basic organic chemicals from coal. However, these account for only a minor part of the primary petrochemical products; currently ca. 95% are based on oil or natural gas. Furthermore, there is no doubt that the expansion in production of feedstocks for the manufacture of organic secondary products was only possible as a result of the changeover to oil. This rapid expansion would not have been possible with coal due to inherent mining constraints. It can thus be appreciated that only a partial substitution of oil by coal, resulting in limited broadening of the raw material base, will be possible in the future. The dependence of the chemical industry on oil will therefore be maintained.

In Japan and Western Europe, naphtha (crude gasoline) is by far the most important feedstock available to the chemical industry from the oil refineries. A decreasing availability of natural gas has also led to the increasing use of naphtha in the USA. Olefins such as ethylene, propene, butenes, and butadiene as well as the aromatics benzene, toluene, and xylene can be
obtained by cracking naphtha. Of less importance are heavy fuel oil and refinery gas which are employed together with natural gas for the manufacture of synthesis gas. The latter forms the basis for the manufacture of ammonia, methanol, acetic acid, and 'oxo' products. The process technology largely determines the content and yield of the individual cuts.

This technology has been increasingly developed since the oil crisis, so that today a complex refinery structure offers large quantities of valuable products. Thus heavy fuel oil is partially converted to lower boiling products through thermal cracking processes such as visbreaking and coking processes. Furthermore, the residue from the atmospheric distillation can, following vacuum distillation, be converted by catalytic or hydrocracking. This increases the yield of lighter products considerably, although it also increases the energy needed for processing.

The spectra of refinery products in the USA, Western Europe, and Japan are distinctly different due to the different market pressures, yet they all show the same trend toward a higher demand for lighter mineral oil fractions:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery &amp; liquid gas</td>
<td>9</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>Motor gasoline, naphtha</td>
<td>44</td>
<td>49</td>
<td>47</td>
<td>24</td>
<td>26</td>
<td>29</td>
<td>21</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>Jet fuel</td>
<td>6</td>
<td>7</td>
<td>9</td>
<td>4</td>
<td>5</td>
<td>7</td>
<td>8</td>
<td>11</td>
<td>15</td>
</tr>
<tr>
<td>Light fuel oil, diesel oil</td>
<td>19</td>
<td>20</td>
<td>20</td>
<td>32</td>
<td>38</td>
<td>37</td>
<td>12</td>
<td>17</td>
<td>32</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>16</td>
<td>9</td>
<td>8</td>
<td>33</td>
<td>22</td>
<td>21</td>
<td>50</td>
<td>33</td>
<td>23</td>
</tr>
<tr>
<td>Bitumen, oil coke</td>
<td>6</td>
<td>5</td>
<td>8</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Total refinery products (in 10^6 tonnes)</td>
<td>825 730 690</td>
<td>730 527 577</td>
<td>260 220 179</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The aforementioned development toward lower boiling products from mineral oil was influenced by the fuel sector as well as by the chemical industry. Even though in principle all refinery products are usable for the manufacture of primary chemicals such as olefins and the BTX (benzene—toluene—xylene) aromatics, there is still a considerable difference in yield. Lowering the boiling point of the feedstock of a cracking process increases not only the yield of C_2—C_4 olefins, but also alters the olefin mixture; in particular, it enhances the formation of the main product ethylene, by far the most important of the chemical building blocks (cf. adjacent table).

<table>
<thead>
<tr>
<th></th>
<th>USA naphtha oil</th>
<th>Western Europe BTX</th>
<th>Japan BTX</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>82</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>propene</td>
<td>2</td>
<td>17</td>
<td>14</td>
</tr>
<tr>
<td>C_2-olefins</td>
<td>3</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>remainder: fuel gas, gasoline from cracking, oil residue</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
saving oil as an energy source is possible in several ways:

1. increased efficiency during conversion into energy
2. gradual substitution by coal or nuclear energy
3. gradual substitution as motor fuel by, e.g., methanol, ethanol

Independent of the higher supply of refinery fractions preferred by the chemical industry through expanded processing technology, by and large the vital task of reducing and uncoupling the dual role of oil as a supplier of both energy and raw materials remains.

A first step toward saving oil could be to increase the efficiency of its conversion into electricity, heat, and motive power.

In the industrial sector, currently only 55% of the energy is actually used. Domestic and small consumers, who represent not only the largest but also the expanding consumption areas, use only 45%, while transport uses only 17%. The remainder is lost through conversion, transport, and waste heat.

The gradual replacement of oil in energy generation by coal and nuclear energy could have an even greater effect (cf. Section 1.3). This includes the partial or complete replacement of gasoline by methanol (cf. Section 2.3.1.2) or by ethanol, perhaps from a biological source (cf. Section 8.1.1).

Over and above this, there are other aspects of the future of the primary raw chemical supply for the chemical industry. First among these is the geographic transfer of petrochemical production to the oil producing countries. Saudi Arabia has emerged in the last few years as a large-scale producer of primary chemicals and the most important olefins, in order to (among other things) make use of the petroleum gas previously burned off. A number of nonindustrialized and newly industrialized nations have followed this example, so that in the future they will be able to supply not only their domestic requirements, but also the established production centers in the USA, Western Europe, and Japan.

Thus it can be expected that the capacity for production of primary chemicals in these newly industrialized countries will increase continuously. This is a challenge to the industrialized countries to increase their proportion of higher valued products.

In 1995, the world production capacity for the total area of petrochemical products was about $200 \times 10^6$ tonnes per year. Of this, about 29% was in Western Europe, 23% in the USA, 17% in Southeast Asia, 10% in Japan, and 21% in the remaining areas.