Abstract
Process Economics Program Report 2E
PROPYLENE OXIDE
(August 1994)

This supplementary report presents the industry status of propylene oxide (PO) and reviews recent developments in PO manufacturing technologies since PEP Report 2D, *Ethylene Oxide/Propylene Oxide*, issued in 1985. In this Report we focus on the technoeconomic evaluation of commercial and selected noncommercial PO processes.

Commercial PO processes evaluated are ARCO’s and Texaco’s PO/t-butyl alcohol processes, ARCO’s and Shell’s PO/styrene processes, and the chlorohydrin processes using lime and using cell liquor. We also present the economics of selected noncommercial PO processes: four versions of the chlorohydrin process, an electrochemical process, two peracid processes, and a propylene glycol monoacetate pyrolysis process. In addition, we evaluate other noncommercial PO processes including the direct oxidation process, the hydrogen peroxide process, and the biochemical process from a qualitative perspective.

Overall, this PO report encompasses the latest technologies and process economics and provides a basis for insight into technical trends, environmental issues, and the selection of technologies.
CONTENTS (Continued)

3 INDUSTRY STATUS
   CAPACITY, PRODUCTION, AND CONSUMPTION 3-1
      United States 3-6
      Western Europe 3-6
      Japan 3-6
      Other Regions 3-7
   SOURCES AND USES OF PROPYLENE OXIDE 3-7
   MANUFACTURING PROCESSES AND TECHNOLOGY DEVELOPMENTS 3-9
   STYRENE AND T-BUTYL ALCOHOL BY-PRODUCTS 3-11
   SAFETY AND HEALTH CONSIDERATIONS 3-11

4 REVIEW OF HYDROPEROXIDATION PROCESSES 4-1
   COPRODUCTION OF PROPYLENE OXIDE AND T-BUTYL ALCOHOL 4-1
      Isobutane Oxidation 4-1
      Catalysts for Propylene Epoxidation with TBHP 4-4
         Homogeneous Catalysts 4-4
         Heterogeneous Catalysts 4-5
         Catalyst Recovery 4-6
      Propylene Epoxidation with TBHP 4-6
      Separation of the Product of Propylene Epoxidation with TBHP 4-7
      t-Butyl Alcohol Treatment 4-7
   COPRODUCTION OF PROPYLENE OXIDE AND STYRENE 4-8
      Ethylbenzene Oxidation 4-8
      Catalysts for Propylene Epoxidation with EBHP 4-9
         Homogeneous Catalysts 4-9
         Heterogeneous Catalysts 4-10
         Catalyst Recovery 4-10
      Propylene Epoxidation with EBHP 4-11
      Separating the Product of Propylene Epoxidation with EBHP 4-11
      Methyl Benzyl Alcohol Dehydration 4-11
      Acetophenone Hydrogenation 4-12
      Styrene Recovery 4-13
   OTHER HYDROPEROXIDATION PROCESSES 4-14
   PROPYLENE OXIDE PURIFICATION 4-14
CONTENTS (Continued)

5 PROPYLENE OXIDE COPRODUCTION WITH T-BUTYL ALCOHOL BY HYDROPEROXIDATION PROCESS 5-1
THE ARCO PROCESS 5-1
  Process Description 5-1
    Isobutane Oxidation 5-1
    Propylene Epoxidation 5-4
    Product Separation 5-4
    PO Purification 5-4
    Catalyst Recovery and Preparation 5-5
    TBA Treatment 5-5
  Process Discussion 5-13
  Cost Estimates 5-14
THE TEXACO PROCESS 5-22
  Process Description 5-22
    Isobutane Oxidation 5-22
    Propylene Epoxidation 5-22
    Product Separation 5-25
    PO Purification 5-25
    Catalyst Recovery and Preparation 5-25
    TBHP/TBA Treatment 5-26
  Process Discussion 5-36
  Cost Estimates 5-36
COMPARISON OF THE ARCO AND THE TEXACO PO/TBA PROCESSES 5-44

6 PROPYLENE OXIDE COPRODUCTION WITH STYRENE BY HYDROPEROXIDATION PROCESS 6-1
THE ARCO PROCESS 6-1
  Process Description 6-1
    Ethylbenzene Oxidation 6-1
    Propylene Epoxidation 6-5
    Product Separation 6-5
    PO Purification 6-5
    Styrene Production 6-5
    Catalyst Recovery and Preparation 6-6
  Process Discussion 6-19
  Cost Estimates 6-20
CONTENTS (Continued)

6 PROPYLENE OXIDE COPRODUCTION WITH STYRENE BY HYDROPEROXIDATION PROCESS (Concluded)
   THE SHELL PROCESS 6-28
      Process Description 6-28
      Process Discussion 6-40
      Cost Estimates 6-40
   COMPARISON OF THE ARCO AND THE SHELL PO/STYRENE PROCESSES 6-48

7 PROPYLENE OXIDE BY THE CHLOROHYDRIN PROCESS 7-1
   PROCESS REVIEW 7-1
   THE CHLOROHYDRIN PROCESS USING LIME (CONVENTIONAL ) 7-1
      Process Description 7-2
      Process Discussion 7-11
      Cost Estimates 7-11
   THE CHLOROHYDRIN PROCESS USING CELL LIQUOR FOR SAPONIFICATION 7-17
      Process Description 7-17
      Process Discussion 7-25
      Cost Estimates 7-25
   THE CHLOROHYDRIN PROCESS RETURNING SALINE LIQUOR TO BRINE WELLS 7-31
   THE CHLOROHYDRIN PROCESS RETURNING SALINE LIQUOR TO DISSOLVE SOLID SALT 7-31
   THE CHLOROHYDRIN PROCESS VIA T-BUTYL HYPOCHLORITE 7-32
      Process Description 7-33
      Cost Estimates 7-33
   THE CHLOROHYDRIN PROCESS VIA ALLYL CHLORIDE 7-35
      Process Discussion 7-35
      Cost Estimates 7-36
   COMPARISON OF DIFFERENT VERSIONS OF THE CHLOROHYDRIN PROCESS 7-38
CONTENTS (Concluded)

8 PROPYLENE OXIDE BY OTHER PROCESSES 8-1

PROPYLENE OXIDE BY DIRECT OXIDATION 8-1
Propylene Oxidation with Molecular Oxygen 8-1
   The BOC Group’s Technology 8-1
   Dow Chemical’s Technology 8-2
   Olin’s Technology 8-2
   Texaco’s Technology 8-3
   The Technology of VEB Chemische Werke Buna 8-3
   Other Propylene Oxidation Technologies 8-3
Propylene Oxidation with Oxygen-Containing Compounds 8-4
THE ELECTROCHEMICAL PROCESS 8-4
   The Chloride System 8-5
   The Bromide System 8-6

THE HYDROGEN PEROXIDE PROCESS 8-9

THE PERACID PROCESS 8-9
   Perpropionic Acid from Propionic Acid and Hydrogen Peroxide 8-9
   Peracetic Acid from Acetaldehyde 8-12

PROPYLENE OXIDE FROM PROPYLENE GLYCOL
MONOACETATE BY PYROLYSIS 8-14
PROPYLENE OXIDE FROM PROPYLENE GLYCOL BY DEHYDRATION 8-17
PROPYLENE OXIDE FROM (HALOGENATED) PROPYLENE CARBONATE 8-17

THE BIOCHEMICAL PROCESS 8-17
   The Cultivation and Reactivation of the Microorganisms 8-18
   The Biochemical Oxidation of Propylene to Propylene Oxide 8-18
   Process Evaluation 8-19

APPENDIX A: PATENT SUMMARY TABLES A-1
APPENDIX B: DESIGN AND COST BASES B-1
APPENDIX C: CITED REFERENCES C-1
APPENDIX D: PATENT REFERENCES BY COMPANY D-1
APPENDIX E: PROCESS FLOW DIAGRAMS E-1
## ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Propylene Oxide Consumption Patterns</td>
<td>3-8</td>
</tr>
<tr>
<td>4.1 Isobutane Oxidation: Conversion Versus Selectivity</td>
<td>4-3</td>
</tr>
<tr>
<td>5.1 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Process Flow Diagram</td>
<td>E-3</td>
</tr>
<tr>
<td>5.2 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Effect of Operating Level and Plant Capacity on Product Value</td>
<td>5-15</td>
</tr>
<tr>
<td>5.3 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Effect of Raw Material Costs and TBA Credit on Product Value</td>
<td>5-16</td>
</tr>
<tr>
<td>5.4 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process Process Flow Diagram</td>
<td>E-7</td>
</tr>
<tr>
<td>5.5 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process Effect of Operating Level and Plant Capacity on Product Value</td>
<td>5-37</td>
</tr>
<tr>
<td>5.6 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process Effect of Raw Material Costs and TBA Credit on Product Value</td>
<td>5-38</td>
</tr>
<tr>
<td>6.1 Propylene Oxide Coproduction with Styrene by the Arco Hydroperoxidation Process Process Flow Diagram</td>
<td>E-11</td>
</tr>
<tr>
<td>6.2 Propylene Oxide Coproduction with Styrene by the Arco Hydroperoxidation Process Effect of Operating Level and Plant Capacity on Product Value</td>
<td>6-21</td>
</tr>
<tr>
<td>6.3 Propylene Oxide Coproduction with Styrene by the Arco Hydroperoxidation Process Effect of Raw Material Costs and Styrene Credit on Product Value</td>
<td>6-22</td>
</tr>
<tr>
<td>6.4 Propylene Oxide Coproduction with Styrene by the Shell Hydroperoxidation Process Process Flow Diagram</td>
<td>E-15</td>
</tr>
<tr>
<td>6.5 Propylene Oxide Coproduction with Styrene by the Shell Hydroperoxidation Process Effect of Operating Level and Plant Capacity on Product Value</td>
<td>6-41</td>
</tr>
</tbody>
</table>
ILLUSTRATIONS (Concluded)

6.6 Propylene Oxide Coproduction with Styrene
by the Shell Hydroperoxidation Process
Effect of Raw Material Costs and Styrene Credit on Product Value 6-42

7.1 Propylene Oxide by the Chlorohydrin Process Using Lime
Process Flow Diagram E-17

7.2 Propylene Oxide by the Chlorohydrin Process Using Cell Liquor
Process Flow Diagram E-21
# TABLES

2.1 Economics of Commercial Propylene Oxide Processes 2-13
2.2 Economics of Selected Noncommercial Propylene Oxide Processes 2-14
3.1 Historical and Projected World Propylene Oxide Capacity, Production, and Consumption by Regions 3-2
3.2 Propylene Oxide Producers and Year-End Capacities Worldwide 3-3
3.3 Commercial Processes for Propylene Oxide Production 3-10
4.1 Propylene Oxide Coproduction with t-Butyl Alcohol by Hydroperoxidation Patent Summary A-3
4.2 Propylene Oxide Coproduction with Styrene by Hydroperoxidation Patent Summary A-7
4.3 Propylene Oxide by Other Hydroperoxidation Processes Patent Summary A-9
4.4 Purification of Propylene Oxide Patent Summary A-10
5.1 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Design Bases and Assumptions 5-2
5.2 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Stream Flows 5-6
5.3 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Summary of Waste Streams 5-8
5.4 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Major Equipment 5-9
5.5 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Utilities Summary 5-12
5.6 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process Total Capital Investment 5-17
TABLES (Continued)

5.7 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process
Capital Investment by Section 5-18

5.8 Propylene Oxide Coproduction with t-Butyl Alcohol by the Arco Hydroperoxidation Process
Production Costs 5-20

5.9 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Design Bases and Assumptions 5-23

5.10 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Stream Flows 5-27

5.11 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Summary of Waste Streams 5-31

5.12 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Major Equipment 5-32

5.13 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Utilities Summary 5-35

5.14 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Total Capital Investment 5-39

5.15 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Capital Investment by Section 5-40

5.16 Propylene Oxide Coproduction with t-Butyl Alcohol by the Texaco Hydroperoxidation Process
Production Costs 5-42

6.1 Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process
Design Bases and Assumptions 6-2

6.2 Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process
Stream Flows 6-7
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process Summary of Waste Streams</td>
<td>6-13</td>
</tr>
<tr>
<td>6.4</td>
<td>Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process Major Equipment</td>
<td>6-14</td>
</tr>
<tr>
<td>6.5</td>
<td>Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process Utilities Summary</td>
<td>6-18</td>
</tr>
<tr>
<td>6.6</td>
<td>Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process Total Capital Investment</td>
<td>6-23</td>
</tr>
<tr>
<td>6.7</td>
<td>Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process Capital Investment by Section</td>
<td>6-24</td>
</tr>
<tr>
<td>6.8</td>
<td>Propylene Peroxide Coproduction with Styrene by the Arco Hydroperoxidation Process Production Costs</td>
<td>6-26</td>
</tr>
<tr>
<td>6.9</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process Design Bases and Assumptions</td>
<td>6-29</td>
</tr>
<tr>
<td>6.10</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process Stream Flows</td>
<td>6-30</td>
</tr>
<tr>
<td>6.11</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process Summary of Waste Streams</td>
<td>6-35</td>
</tr>
<tr>
<td>6.12</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process Major Equipment</td>
<td>6-36</td>
</tr>
<tr>
<td>6.13</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process Utilities Summary</td>
<td>6-39</td>
</tr>
<tr>
<td>6.14</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process Total Capital Investment</td>
<td>6-43</td>
</tr>
</tbody>
</table>
### TABLES (Continued)

<table>
<thead>
<tr>
<th>Table Number</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.15</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Capital Investment by Section</td>
<td>6-44</td>
</tr>
<tr>
<td>6.16</td>
<td>Propylene Peroxide Coproduction with Styrene by the Shell Hydroperoxidation Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Production Costs</td>
<td>6-46</td>
</tr>
<tr>
<td>7.1</td>
<td>Propylene Oxide by the Chlorohydrin Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Patent Summary</td>
<td>A-12</td>
</tr>
<tr>
<td>7.2</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Design Bases and Assumptions</td>
<td></td>
</tr>
<tr>
<td>7.3</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Stream Flows</td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Summary of Waste Streams</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Major Equipment</td>
<td></td>
</tr>
<tr>
<td>7.6</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Utilities Summary</td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Total Capital Investment</td>
<td></td>
</tr>
<tr>
<td>7.8</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Capital Investment by Section</td>
<td></td>
</tr>
<tr>
<td>7.9</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Lime Production Costs</td>
<td></td>
</tr>
<tr>
<td>7.10</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Design Bases and Assumptions</td>
<td></td>
</tr>
<tr>
<td>7.11</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Stream Flows</td>
<td></td>
</tr>
<tr>
<td>7.12</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Summary of Waste Streams</td>
<td></td>
</tr>
<tr>
<td>7.13</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Major Equipment</td>
<td></td>
</tr>
</tbody>
</table>
### TABLES (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.14</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Utilities Summary</td>
<td>7-24</td>
</tr>
<tr>
<td>7.15</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Total Capital Investment</td>
<td>7-26</td>
</tr>
<tr>
<td>7.16</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Capital Investment by Section</td>
<td>7-27</td>
</tr>
<tr>
<td>7.17</td>
<td>Propylene Oxide by the Chlorohydrin Process Using Cell Liquor Production Costs</td>
<td>7-29</td>
</tr>
<tr>
<td>7.18</td>
<td>Propylene Oxide by the Chlorohydrin Process Via t-Butyl Hypochlorite Summary of Economics</td>
<td>7-34</td>
</tr>
<tr>
<td>7.19</td>
<td>Propylene Oxide by the Chlorohydrin Process Via Allyl Chloride Summary of Economics</td>
<td>7-37</td>
</tr>
<tr>
<td>7.20</td>
<td>Comparison of Different Versions of the Chlorohydrin Process for PO Production</td>
<td>7-39</td>
</tr>
<tr>
<td>8.1</td>
<td>Propylene Oxide by Direct Oxidation Patent Summary</td>
<td>A-14</td>
</tr>
<tr>
<td>8.2</td>
<td>Propylene Oxide by the Electrochemical Process Patent Summary</td>
<td>A-18</td>
</tr>
<tr>
<td>8.3</td>
<td>Propylene Oxide by the Kellogg-bayer Electrochemical Process Summary of Economics</td>
<td>8-8</td>
</tr>
<tr>
<td>8.4</td>
<td>Propylene Oxide by the Hydrogen Peroxide Process Patent Summary</td>
<td>A-19</td>
</tr>
<tr>
<td>8.5</td>
<td>Propylene Oxide by the Peracid Process Patent Summary</td>
<td>A-20</td>
</tr>
<tr>
<td>8.6</td>
<td>Propylene Oxide by the Bayer-Degussa Peracid Process Summary of Economics</td>
<td>8-11</td>
</tr>
<tr>
<td>8.7</td>
<td>Propylene Oxide by the Daicel Peracid Process Summary of Economics</td>
<td>8-13</td>
</tr>
<tr>
<td>8.8</td>
<td>Propylene Oxide from Propylene Glycol Monoacetate by Pyrolysis Patent Summary</td>
<td>A-21</td>
</tr>
<tr>
<td>8.9</td>
<td>Propylene Oxide from Propylene Glycol Monoacetate Summary of Economics</td>
<td>8-16</td>
</tr>
</tbody>
</table>
### TABLES (Concluded)

8.10 Propylene Oxide from Propylene Glycol by Dehydration  
Patent Summary  
A-22

8.11 Propylene Oxide from (Halogenated) Propylene Carbonate  
Patent Summary  
A-23

8.12 Propylene Oxide by the Biochemical Process  
Patent Summary  
A-24