Abstract
Process Economics Program Report 6D
ACRYLIC ACIDS AND ESTERS
(July 2003)

For many years, acrylic acid has been an important building block in the production of many industrial and consumer products. Because of the importance of acrylic acid, several PEP reports have evaluated processes for the production of acrylic acid and related esters. Since the last PEP update in 1987, there have been substantial process improvements, resulting in lower production costs and reduced capital investment costs for new acrylic acid and ester plants. Recent changes in the catalyst allow much higher reactor space-time yield of acrylic acid. Because of these important changes, we have updated the process to produce acrylic acid by vapor phase oxidation of propylene. We also evaluated the production of n-butyl acrylate based on a recent BASF patent. The process economics for a new grass-root acrylic acid plant and n-butyl acrylate plant were evaluated and compared with earlier processes. In addition, we have summarize relevant new patents and the current state of the acrylic acid and ester industry. Because of the significant reduction in capital investment and production costs with these process improvements, this report will be of great interest to producers of acrylic acid and esters. Although this report principally addresses new grass-root acrylic acid and ester production plants, the retrofitting of existing plants with these process improvements is feasible with relatively small capital investment.
## CONTENTS

GLOSSARY ..............................................................................................................................................................................

1 INTRODUCTION ........................................................................................................................................................................ 1-1

2 SUMMARY .................................................................................................................................................................................. 2-1

   INDUSTRIAL ASPECTS ............................................................................................................................................................... 2-1

   TECHNICAL ASPECTS ............................................................................................................................................................... 2-3

   Acrylic Acid Production Process ........................................................................................................................................ 2-3

   n-Butyl Acrylate Production Process .................................................................................................................................. 2-6

   ECONOMIC ASPECTS ............................................................................................................................................................... 2-7

   Acrylic Acid Production Process ........................................................................................................................................ 2-7

   n-Butyl Acrylate Production Process .................................................................................................................................. 2-11

3 INDUSTRY STATUS ................................................................................................................................................................. 3-1

   INTRODUCTION ........................................................................................................................................................................ 3-1

   PRODUCERS ............................................................................................................................................................................. 3-1

   CONSUMPTION AND GROWTH .................................................................................................................................................. 3-7

   Acrylic Acid ............................................................................................................................................................................... 3-7

   Acrylic Esters ........................................................................................................................................................................... 3-8

   Growth ..................................................................................................................................................................................... 3-9

   ACRYLIC ACID AND ESTER PRICES ........................................................................................................................................ 3-10

4 CHEMISTRY AND PATENT REVIEW ......................................................................................................................................... 4-1

   INTRODUCTION ........................................................................................................................................................................ 4-1

   TWO-STAGE PROPYLENE OXIDATION PROCESS .................................................................................................................... 4-2

   Oxidation of Propylene to Acrolein and Acrylic Acid ............................................................................................................. 4-2

   Oxidation of Acrolein to Acrylic Acid ....................................................................................................................................... 4-6

   Separation and Recovery of Acrylic Acid ................................................................................................................................. 4-9

       Nippon Shokubai Acrylic Acid Recovery Process ............................................................................................................... 4-9
CONTENTS (Continued)

BASF Aktiengesellschaft Acrylic Acid Recovery Process ........................................... 4-10
PROPAWAY OXIDATION PROCESS ................................................................. 4-11
ESTERIFICATION PROCESS ............................................................................. 4-11

5 ACRYLIC ACID PRODUCTION ........................................................................ 5-1
INTRODUCTION ................................................................................................. 5-1
NIPPON SHOKUBAI ACRYLIC ACID PROCESS .................................................. 5-1
Process Description .......................................................................................... 5-8
Section 100: Reaction Section ........................................................................... 5-8
Section 200: Crude Acrylic Acid Recovery Section .............................................. 5-9
Section 300: Glacial Acrylic Acid Production Section .......................................... 5-9
Capital Investment ............................................................................................. 5-10
Production Costs ............................................................................................... 5-18
BASF ACRYLIC ACID PROCESS ...................................................................... 5-23
Process Description .......................................................................................... 5-30
Section 100: Reaction Section ........................................................................... 5-30
Section 200: Crude Acrylic Acid Recovery Section .............................................. 5-31
Capital Investment ............................................................................................. 5-31
Production Costs ............................................................................................... 5-38
COMPARISON OF COSTS FOR ACRYLIC ACID PRODUCTION PROCESSES ... 5-43

6 ESTERIFICATION OF ACRYLIC ACID .......................................................... 6-1
INTRODUCTION ................................................................................................. 6-1
PROCESS REVIEW ............................................................................................... 6-1
BASF ESTERIFICATION PROCESS .................................................................. 6-2
Process Description ............................................................................................ 6-7
Capital Investment ............................................................................................. 6-8
Production Costs ............................................................................................... 6-13
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 DIAGRAM.................................................. E-1
FIGURES

2.1 Total Capital Investment at Different Acrylic Acid Production Capacities .......... 2-9
2.2 Comparison of Equipment Costs for Acrylic Acid Production Plant .................. 2-9
4.1 Shell-and-Tube Reactor ..................................................................................... 4-3
5.1 Nippon Shokubai Acrylic Acid Process ......................................................... E-3
5.2 BASF Acrylic Acid Process .............................................................................. E-9
6.1 n-Butyl Acrylate Production Process ............................................................... E-13
TABLES

2.1 Capacity of Crude Acrylic Acid and Acrylic Ester by Company – 2000 ................. 2-2
2.2 U.S. Consumption of Acrylic Acid by End-Use – 2000.............................................. 2-2
2.3 Comparison of Current Design Bases and Prior PEP Report Design Bases for Acrylic Acid Production .................................................................................... 2-4
2.4 Comparison of Nippon Shokubai and BASF Processes for Acrylic Acid Production .................................................................................................................. 2-6
2.5 Comparison of Current Design Bases and Prior PEP Report Design Bases for n-Butyl Acrylate Production ............................................................... 2-7
2.6 Comparison of Capital Investments for Crude Acrylic Acid Plant with Current Design Bases and Prior PEP Report Design Bases ............................................. 2-8
2.7 Comparison of Production Costs for Crude Acrylic Acid Plant with Current Design Bases and Prior PEP Report Design Bases ............................................. 2-10
2.8 Glacial Acrylic Acid Production Costs ........................................................................ 2-11
2.9 Comparison of Capital Investments for n-Butyl Acrylate with Current Design Bases and Prior PEP Report Design Bases ......................................................... 2-11
2.10 N-Butyl Acrylate Production Costs ........................................................................... 2-12
3.1 Worldwide Capacity for Acrylic Acid and Esters ....................................................... 3-1
3.2 Producers of Acrylic Acid and Esters ........................................................................ 3-3
3.3 Capacity of Crude Acrylic Acid and Acrylic Ester by Company – 2000 ................. 3-6
3.4 Physical Properties of Acrylic Acid ................................................................................ 3-7
3.5 U.S. Consumption of Acrylic Acid by End-Use – 2000............................................ 3-8
3.6 Physical Properties of Acrylic Esters ........................................................................... 3-9
3.7 U.S. Consumption of Acrylic Esters by End-Use – 2000 .......................................... 3-9
3.8 U.S. List Price for Glacial Acrylic Acid and Acrylic Esters ........................................... 3-10
4.1 Metal Oxide Catalyst Compositions for Oxidation of Propylene to Acrolein .......... 4-5
4.2 Metal Oxide Catalyst Compositions for Oxidation of Acrolein to Acrylic Acid....... 4-8
5.1 Nippon Shokubai Acrylic Acid Process: Design Bases and Assumptions .......... 5-2
5.2 Comparison of Current Design Bases and Prior PEP Report Design Bases ...... 5-3
5.3 Nippon Shokubai Acrylic Acid Process: Stream Flows ........................................... 5-4
5.4 Nippon Shokubai Acrylic Acid Process: Major Equipment ...................................... 5-12
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Nippon Shokubai Acrylic Acid Process: Utilities Summary</td>
<td>5-15</td>
</tr>
<tr>
<td>5.6</td>
<td>Nippon Shokubai Acrylic Acid Process: Total Capital Investment</td>
<td>5-16</td>
</tr>
<tr>
<td>5.7</td>
<td>Nippon Shokubai Acrylic Acid Process: Capital Investment by Section</td>
<td>5-17</td>
</tr>
<tr>
<td>5.8</td>
<td>Nippon Shokubai Acrylic Acid Process: Production Costs for Crude Acrylic Acid</td>
<td>5-19</td>
</tr>
<tr>
<td>5.9</td>
<td>Nippon Shokubai Acrylic Acid Process: Production Costs for Glacial Acrylic Acid</td>
<td>5-21</td>
</tr>
<tr>
<td>5.10</td>
<td>BASF Acrylic Acid Process: Design Bases and Assumptions</td>
<td>5-24</td>
</tr>
<tr>
<td>5.11</td>
<td>Comparison of Reactor Conditions for Nippon Shokubai and BASF Processes</td>
<td>5-25</td>
</tr>
<tr>
<td>5.12</td>
<td>BASF Acrylic Acid Process: Stream Flows</td>
<td>5-26</td>
</tr>
<tr>
<td>5.13</td>
<td>BASF Acrylic Acid Process: Major Equipment</td>
<td>5-32</td>
</tr>
<tr>
<td>5.14</td>
<td>BASF Acrylic Acid Process: Utilities Summary</td>
<td>5-35</td>
</tr>
<tr>
<td>5.15</td>
<td>BASF Acrylic Acid Process: Total Capital Investment</td>
<td>5-36</td>
</tr>
<tr>
<td>5.16</td>
<td>BASF Acrylic Acid Process: Capital Investment by Section</td>
<td>5-37</td>
</tr>
<tr>
<td>5.17</td>
<td>BASF Acrylic Acid Process: Production Costs for Crude Acrylic Acid</td>
<td>5-39</td>
</tr>
<tr>
<td>5.18</td>
<td>BASF Acrylic Acid Process: Production Costs for Glacial Acrylic Acid</td>
<td>5-41</td>
</tr>
<tr>
<td>5.19</td>
<td>Comparison of Capital Costs for BASF and Nippon Shokubai Processes</td>
<td>5-43</td>
</tr>
<tr>
<td>5.20</td>
<td>Comparison of Crude Acrylic Acid Production Costs for BASF and Nippon Shokubai Processes</td>
<td>5-44</td>
</tr>
<tr>
<td>6.1</td>
<td>Comparison of Current Design Bases and Prior PEP Report Design Bases for n-Butyl Acrylate Production</td>
<td>6-2</td>
</tr>
<tr>
<td>6.2</td>
<td>n-Butyl Acrylate Production Process: Design Bases and Assumptions</td>
<td>6-3</td>
</tr>
<tr>
<td>6.3</td>
<td>n-Butyl Acrylate Production Process: Stream Flows</td>
<td>6-4</td>
</tr>
<tr>
<td>6.4</td>
<td>n-Butyl Acrylate Production Process: Major Equipment</td>
<td>6-9</td>
</tr>
<tr>
<td>6.5</td>
<td>n-Butyl Acrylate Production Process: Utilities Summary</td>
<td>6-11</td>
</tr>
<tr>
<td>6.6</td>
<td>n-Butyl Acrylate Production Process: Total Capital Investment</td>
<td>6-12</td>
</tr>
<tr>
<td>6.7</td>
<td>n-Butyl Acrylate Production Process: Production Costs</td>
<td>6-14</td>
</tr>
<tr>
<td>A.1</td>
<td>Oxidation of Propylene to Acrolein and Acrylic Acid</td>
<td>A-3</td>
</tr>
</tbody>
</table>
## TABLES (Concluded)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.2</td>
<td>Oxidation of Acrolein to Acrylic Acid</td>
<td>A-9</td>
</tr>
<tr>
<td>A.3</td>
<td>Separation and Recovery of Acrylic Acid</td>
<td>A-13</td>
</tr>
<tr>
<td>A.4</td>
<td>Acrylic Acid Production from Propane</td>
<td>A-18</td>
</tr>
<tr>
<td>A.5</td>
<td>Acrylic Ester Production</td>
<td>A-21</td>
</tr>
</tbody>
</table>