ABSTRACT
Process Economics Program Report 9D
TEREPHTHALIC ACID AND DIMETHYL TEREPTHALATE
(November 1990)

This study presents designs and economics for the production of terephthalic acid (TPA) and dimethyl terephthalate (DMT) from processes that are of current industry importance. No new processes have been commercialized since our last report was issued in 1976; however the processes presented here are updated from those presented in previous reports to reflect current technology.

Most of the TPA currently produced is made by oxidation of \( p \)-xylene in a process similar to the one presented, while the bulk of the DMT produced commercially is made by a process using successive oxidations and esterifications such as the one we have evaluated.

In addition, the report includes the present status of the TPA and DMT industries, with a list of estimated plant capacities, and a discussion of the chemistry entailed in the various manufacturing processes. Patents issued on TPA and DMT since our 1976 update on the subject, PEP Report 9C, are also discussed.
## CONTENTS

1 **INTRODUCTION** 1-1

2 **SUMMARY** 2-1
   - **INDUSTRY STATUS** 2-1
   - **TECHNICAL ASPECTS** 2-1
     - Process Summaries 2-2
       - TPA from p-Xylene by Bromine-Promoted Catalytic Air Oxidation 2-2
       - DMT from p-Xylene by Successive Oxidations and Esterifications 2-2
       - DMT from Crude TPA by Esterification with Methanol 2-3
   - **CAPITAL AND PRODUCTION COSTS** 2-3

3 **INDUSTRY STATUS** 3-1
   - MARKET AND PRODUCTION DATA 3-1
   - PRICES (JANUARY 1990) 3-2

4 **CHEMISTRY** 4-1
   - **TPA BY OXIDATION OF P-XYLENE** 4-1
   - **DMT FROM P-XYLENE** 4-2
     - First Oxidation 4-2
     - First Esterification 4-3
     - Second Oxidation 4-3
     - Second Esterification 4-3
   - **DMT BY ESTERIFICATION WITH METHANOL** 4-3

5 **TEREPHTHALIC ACID FROM P-XYLENE** 5-1
   - **BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION** 5-1
     - **PROCESS REVIEW** 5-1
       - p-Xylene Oxidation 5-1
       - Terephthalic Acid Purification and Recovery 5-2
       - Oxidation Catalyst Recovery 5-3
       - Other 5-3
       - Design Basis Patent Selection 5-3
     - **PROCESS DESCRIPTION** 5-3
CONTENTS (Continued)

5 TEREPHTHALIC ACID FROM P-XYLENE
BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION (Concluded)

PROCESS DISCUSSION 5-16
Reactor Design 5-16
Crystallization 5-16
Acetic Acid Recovery 5-16
Hydrogenation 5-16
Catalyst Recovery 5-17
Materials of Construction 5-17
CAPITAL AND PRODUCTION COSTS 5-17
CATALYST COST 5-18

6 DIMETHYL TEREPHTHALATE FROM P-XYLENE
BY SUCCESSIVE OXIDATIONS AND ESTERIFICATIONS 6-1

PROCESS REVIEW 6-1
DESIGN BASES 6-1
PROCESS DESCRIPTION 6-3
PROCESS DISCUSSION 6-13
Catalyst Recovery 6-13
CAPITAL AND PRODUCTION COSTS 6-13

7 DIMETHYL TEREPHTHALATE FROM CRUDE TEREPHTHALIC ACID
BY ESTERIFICATION WITH METHANOL 7-1

PROCESS REVIEW 7-1
DESIGN BASES 7-1
PROCESS DESCRIPTION 7-2
PROCESS DISCUSSION 7-8
Raw Material Usages 7-8
Utility Usages 7-8
Materials of Construction 7-8
CAPITAL AND PRODUCTION COSTS 7-8
Factors Affecting Costs 7-9

APPENDIX A: PATENT SUMMARY A-1
CONTENTS (Concluded)

APPENDIX B: DESIGN AND COST BASES B-1
    DESIGN CONDITIONS B-3
    COST BASES B-3
    CAPITAL INVESTMENT B-3
    PRODUCTION COSTS B-4
    EFFECT OF OPERATING LEVEL ON PRODUCTION COSTS B-5

APPENDIX C: CITED REFERENCES C-1

APPENDIX D: PATENT REFERENCES D-1

APPENDIX E: PROCESS FLOW DIAGRAMS E-1
ILLUSTRATIONS

5.1 TEREPHTHALIC ACID FROM P-XYLENE
BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION E-3

5.2 TEREPHTHALIC ACID FROM P-XYLENE
BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION
PRODUCT VALUE AS A FUNCTION OF P-XYLENE PRICE 5-23

5.3 TEREPHTHALIC ACID FROM P-XYLENE
BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION
EFFECT OF OPERATING LEVEL AND PLANT CAPACITY
ON PRODUCTION COST 5-24

6.1 DIMETHYL TEREPHTHALATE FROM P-XYLENE
BY SUCCESSIVE OXIDATIONS AND ESTERIFICATIONS E-9

6.2 DIMETHYL TEREPHTHALATE FROM P-XYLENE
BY SUCCESSIVE OXIDATIONS AND ESTERIFICATIONS
PRODUCT VALUE AS A FUNCTION OF P-XYLENE PRICE 6-20

6.3 DIMETHYL TEREPHTHALATE FROM P-XYLENE
BY SUCCESSIVE OXIDATIONS AND ESTERIFICATIONS
EFFECT OF OPERATING LEVEL AND PLANT CAPACITY
ON PRODUCTION COST 6-21

7.1 DIMETHYL TEREPHTHALATE FROM CRUDE TEREPHTHALIC ACID
BY ESTERIFICATION WITH METHANOL E-15

7.2 DIMETHYL TEREPHTHALATE FROM CRUDE TEREPHTHALIC ACID
BY ESTERIFICATION WITH METHANOL
PRODUCT VALUE AS A FUNCTION OF TEREPHTHALIC ACID PRICE 7-15

7.3 DIMETHYL TEREPHTHALATE FROM CRUDE TEREPHTHALIC ACID
BY ESTERIFICATION WITH METHANOL
EFFECT OF OPERATING LEVEL AND PLANT CAPACITY
ON PRODUCTION COST 7-16
# TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>SUMMARY OF CAPITAL AND PRODUCTION COSTS</td>
<td>2-4</td>
</tr>
<tr>
<td>3.1</td>
<td>DIMETHYL TEREPTHALATE AND TEREPTHALIC ACID PLANT CAPACITIES IN THE AMERICAS</td>
<td>3-3</td>
</tr>
<tr>
<td>3.2</td>
<td>DIMETHYL TEREPTHALATE AND TEREPTHALIC ACID PLANT CAPACITIES IN WESTERN EUROPE</td>
<td>3-4</td>
</tr>
<tr>
<td>3.3</td>
<td>DIMETHYL TEREPTHALATE AND TEREPTHALIC ACID PLANT CAPACITIES IN EASTERN EUROPE</td>
<td>3-5</td>
</tr>
<tr>
<td>3.4</td>
<td>DIMETHYL TEREPTHALATE AND TEREPTHALIC ACID PLANT CAPACITIES IN THE FAR EAST AND MIDDLE EAST</td>
<td>3-6</td>
</tr>
<tr>
<td>5.1</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION PATENT SUMMARY</td>
<td>A-3</td>
</tr>
<tr>
<td>5.2</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION PATENT SUMMARY</td>
<td>A-16</td>
</tr>
<tr>
<td>5.3</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION PATENT SUMMARY</td>
<td>A-29</td>
</tr>
<tr>
<td>5.4</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION PATENT SUMMARY</td>
<td>A-34</td>
</tr>
<tr>
<td>5.5</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION DESIGN BASES</td>
<td>5-4</td>
</tr>
<tr>
<td>5.6</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION MAJOR EQUIPMENT</td>
<td>5-9</td>
</tr>
<tr>
<td>5.7</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION UTILITIES SUMMARY</td>
<td>5-12</td>
</tr>
<tr>
<td>5.8</td>
<td>TEREPTHALIC ACID FROM P-XYLENE BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION STREAM FLOWS</td>
<td>5-13</td>
</tr>
</tbody>
</table>
5.9 TEREPTHALIC ACID FROM P-XYLENE
BY BROMINE-PROMOTED CATALYTIC AIR OXIDATION
TOTAL CAPITAL INVESTMENT 5-19
### TABLES (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.10</td>
<td>Terephthalic Acid from P-xylene by Bromine-promoted Catalytic Air Oxidation Capital Investment by Section</td>
</tr>
<tr>
<td>5.11</td>
<td>Terephthalic Acid from P-xylene by Bromine-promoted Catalytic Air Oxidation Production Costs</td>
</tr>
<tr>
<td>6.1</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Patent Summary</td>
</tr>
<tr>
<td>6.2</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Design Bases</td>
</tr>
<tr>
<td>6.3</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Major Equipment</td>
</tr>
<tr>
<td>6.4</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Utilities Summary</td>
</tr>
<tr>
<td>6.5</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Stream Flows</td>
</tr>
<tr>
<td>6.6</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Total Capital Investment</td>
</tr>
<tr>
<td>6.7</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Capital Investment by Section</td>
</tr>
<tr>
<td>6.8</td>
<td>Dimethyl Terephthalate from P-xylene by Successive Oxidations and Esterifications Production Costs</td>
</tr>
<tr>
<td>7.1</td>
<td>Dimethyl Terephthalate from Crude Terephthalic Acid by Esterification with Methanol Design Bases</td>
</tr>
<tr>
<td>7.2</td>
<td>Dimethyl Terephthalate from Crude Terephthalic Acid by Esterification with Methanol Major Equipment</td>
</tr>
</tbody>
</table>
### TABLES (Concluded)

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>DIMETHYL TEREPTHALATE FROM CRUDE TEREPTHALIC ACID BY ESTERIFICATION WITH METHANOL UTILITIES SUMMARY</td>
<td>7-6</td>
</tr>
<tr>
<td>7.4</td>
<td>DIMETHYL TEREPTHALATE FROM CRUDE TEREPTHALIC ACID BY ESTERIFICATION WITH METHANOL STREAM FLOWS</td>
<td>7-7</td>
</tr>
<tr>
<td>7.5</td>
<td>DIMETHYL TEREPTHALATE FROM CRUDE TEREPTHALIC ACID BY ESTERIFICATION WITH METHANOL TOTAL CAPITAL INVESTMENT</td>
<td>7-10</td>
</tr>
<tr>
<td>7.6</td>
<td>DIMETHYL TEREPTHALATE FROM CRUDE TEREPTHALIC ACID BY ESTERIFICATION WITH METHANOL CAPITAL INVESTMENT BY SECTION</td>
<td>7-11</td>
</tr>
<tr>
<td>7.7</td>
<td>DIMETHYL TEREPTHALATE FROM CRUDE TEREPTHALIC ACID BY ESTERIFICATION WITH METHANOL PRODUCTION COSTS</td>
<td>7-13</td>
</tr>
</tbody>
</table>