Abstract

Polyvinyl Chloride (PVC) is the second largest commodity thermoplastic in the world, after the polyethylenes. The estimated global capacity of PVC was equivalent to 33 million metric tons as of 2003, and about 27 million metric tons were produced at a capacity utilization factor of 82%. Major demand, following the usual historical pattern, was in the construction sector, which accounts for about 60% of the total PVC consumption. Despite a negative environmental image created around during the past several years because of presence of certain harmful chemicals and potentially harmful residue left on incineration, the PVC market continues to show a fairly steady growth. The overall global growth averaged at 2.8% per annum from 1998 to 2003¹. Major capacity additions in the next three or four years are taking place in Asia and Middle East because of a strong demand in the region.

PVC is industrially produced by the following four methods.

- Suspension Polymerization
- Mass or Bulk Polymerization
- Emulsion Polymerization
- Solution Polymerization

Of the above four processes, the solution technology has been so far used on a very limited scale. On the other hand, suspension polymerization, mainly driven by the market, is the most common and relatively the fastest growing technology today. Its share in production of rigid and flexible PVC polymer is about 90% on global basis.

This report examines in detail the first three technologies as they stand today, and evaluates their capital and production economics in the typical PEP format. The report also presents manufacturing routes details and economics for ethylene dichloride (EDC) and vinyl chloride monomer (VCM)—precursors of PVC. Economic results for EDC-PVC chain integration are also included. In addition, economic analysis of an ethane to VCM route, based on the experimental work of Dow Chemical, also forms part of the report. The results and economics conclusions of our study are summarized in Chapter 2.

¹ World Petrochemicals—SRI Consulting
VINYL POLYMERS

by SYED NAQVI

SEPTEMBER 2004

A private report by the
PROCESS ECONOMICS PROGRAM

Menlo Park, California 94025
SRIC agrees to assign professionally qualified personnel to the preparation of the Process Economics Program’s reports and will perform the work in conformance with generally accepted professional standards. No other warranties expressed or implied are made. Because the reports are of an advisory nature, neither SRIC nor its employees will assume any liability for the special or consequential damages arising from the Client’s use of the results contained in the reports. The Client agrees to indemnify, defend, and hold SRIC, its officers, and employees harmless from any liability to any third party resulting directly or indirectly from the Client’s use of the reports or other deliverables produced by SRIC pursuant to this agreement.

For detailed marketing data and information, the reader is referred to one of the SRI Consulting programs specializing in marketing research. THE CHEMICAL ECONOMICS HANDBOOK Program covers most major chemicals and chemical products produced in the United States and the WORLD PETROCHEMICALS PROGRAM covers major hydrocarbons and their derivatives on a worldwide basis. In addition the SRIC DIRECTORY OF CHEMICAL PRODUCERS services provide detailed lists of chemical producers by company, product, and plant for the United States, Western Europe, Canada, and East Asia, South America and Mexico.


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

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

   COMMERCIAL OVERVIEW ....................................................................................... 2-1

   PRODUCTION METHODOLOGIES .......................................................................... 2-2

   Production Technologies for EDC from Ethylene ....................................................... 2-2
   
   Direct Chlorination of Ethylene — Liquid-phase .................................................... 2-3
   Reaction Chemistry ......................................................................................... 2-3
   Reaction Conditions — High-Temperature Chlorination .......................................... 2-3
   Reaction Conditions — Low-Temperature Chlorination .......................................... 2-3
   Reactors ........................................................................................................... 2-4
   Feedstock & Byproducts .................................................................................. 2-4
   EDC Recovery ................................................................................................. 2-4
   
   Ethylene Oxychlorination ...................................................................................... 2-4
   Reaction Chemistry ......................................................................................... 2-4
   Reaction Conditions ......................................................................................... 2-4
   Reactors ........................................................................................................... 2-5
   Feedstock & Byproducts .................................................................................. 2-5
   EDC Recovery ................................................................................................. 2-5

   Process Economics for EDC Production from Ethylene ........................................ 2-6

   Production Technologies for VCM from EDC ............................................................. 2-8
   
   Reaction Conditions ......................................................................................... 2-8
   Reactors ........................................................................................................... 2-8
   Feedstock & Byproducts .................................................................................. 2-8
   VCM Recovery ................................................................................................. 2-8

   Process Economics for EDC Production from Ethylene ........................................ 2-9

   Production Technologies for VCM from EDC ............................................................. 2-10
   
   Basic Chemistry — Ethane Oxychlorination ...................................................... 2-10
   Feed/Byproducts — Ethane Oxychlorination ...................................................... 2-10
   Reaction Conditions — Ethane Oxychlorination ................................................ 2-10
   VCM Recovery ................................................................................................. 2-11
### CONTENTS (Continued)

- Process Economics for VCM Production from Ethylene ................................ 2-11
- Production Technologies for PVC .............................................................. 2-12
  - Suspension Polymerization ................................................................. 2-13
  - Bulk Polymerization ........................................................................... 2-13
  - Emulsion & Microsuspension Polymerization ....................................... 2-14
  - Solution Polymerization ...................................................................... 2-14
  - Production Economics of PVC Technologies ........................................ 2-15
- ENVIRONMENTAL ASPECTS OF PVC ...................................................... 2-16

### 3 INDUSTRY STATUS

- WORLD PRODUCTION CAPACITY .......................................................... 3-2
- CONSUMPTION OVERVIEW ................................................................. 3-12

### 4 TECHNICAL REVIEW

- REVIEW OF PRODUCTION TECHNOLOGIES FOR EDC AND VCM —
  - SECTION A ....................................................................................... 4-1
  - Direct Chlorination of Ethylene — Liquid-Phase Process ..................... 4-2
    - Basic Chemistry ................................................................................ 4-2
    - Reaction Conditions ......................................................................... 4-2
    - Catalysts .......................................................................................... 4-2
    - Reactors ............................................................................................ 4-3
    - Feedstock & Byproducts ................................................................. 4-3
    - EDC Recovery .................................................................................. 4-4
  - Direct Chlorination of Ethylene Gas-Phase Process ............................... 4-5
    - Reaction Conditions ......................................................................... 4-5
  - Oxychlorination of Ethylene ................................................................. 4-6
    - Basic Chemistry ................................................................................ 4-6
    - Reaction Conditions ......................................................................... 4-6
    - Oxidation Methodology .................................................................... 4-7
    - Catalysts .......................................................................................... 4-7
CONTENTS (Continued)

Reactors ............................................................................................................... 4-8
Feedstock & Byproducts ...................................................................................... 4-9
EDC Recovery...................................................................................................... 4-9
Vinyl Chloride from Ethylene Dichloride by Pyrolysis................................................. 4-10
   Reaction Conditions ..................................................................................... 4-10
   Reactors ....................................................................................................... 4-11
   Feedstock & Byproducts ............................................................................. 4-11
   VCM Recovery ............................................................................................ 4-12
Vinyl Chloride from Ethane......................................................................................... 4-13
   Basic Chemistry — Ethane Chlorination ....................................................... 4-14
   Reaction Conditions — Ethane Chlorination.................................................. 4-14
   Basic Chemistry — Ethane Oxychlorination .................................................. 4-15
   Feedstock & Byproducts Ethane Oxychlorination.......................................... 4-16
   Unsaturateds Hydrogenation ........................................................................ 4-16
   Reaction Conditions — Ethane Oxychlorination .......................................... 4-17
Vinyl Chloride from Mixed Ethane-Ethylene Feed ..................................................... 4-18
REVIEW OF PRODUCTION TECHNOLOGIES FOR PVC — SECTION B .............. 4-21
Suspension Polymerization ..................................................................................... 4-22
   Temperature ................................................................................................. 4-23
   Dispersants ................................................................................................. 4-23
   Initiators ..................................................................................................... 4-24
   Shortstopping & Stabilizing Agents .............................................................. 4-25
   Agitation ..................................................................................................... 4-25
   Conversion .................................................................................................. 4-26
   Scale Buildup or Encrustation ................................................................... 4-26
Emulsion & Microsuspension Polymerization ........................................................ 4-27
   Polymerization Process ............................................................................. 4-27
   Emulsifiers ............................................................................................... 4-28
   Initiators ................................................................................................. 4-28
Contents (Continued)

Other Additives ................................................................. 4-29
Reaction Conditions and Reactor ........................................ 4-29
Bulk Polymerization .......................................................... 4-30
Polymerization Conditions ............................................... 4-31
Initiators ................................................................. 4-32
Solution Polymerization .................................................... 4-32

5 EDC AND VCM PRODUCTION ........................................ 5-1

PRODUCTION OF EDC & VCM FROM ETHYLENE — SECTION A .... 5-2
Direct Chlorination of Ethylene — Liquid-phase ................. 5-2
  Basic Chemistry ............................................................ 5-2
  Reaction Conditions — High-Temperature Chlorination ..... 5-2
  Reaction Conditions — Low-Temperature Chlorination .... 5-3
Reactors ................................................................. 5-4
Feedstock & Byproducts .................................................... 5-5
EDC Recovery ............................................................... 5-5
Ethylene Oxychlorination ................................................... 5-6
  Basic Chemistry ............................................................ 5-6
  Reaction Conditions ...................................................... 5-6
  Feed Rate ...................................................................... 5-6
  Feedstock Quality & Byproducts ..................................... 5-7
Reactors ................................................................. 5-7
EDC Recovery ............................................................... 5-8
Vinyl Chloride from Ethylene Dichloride by Pyrolysis .......... 5-9
  Reaction Conditions ...................................................... 5-9
Reactors ................................................................. 5-9
Feedstock & Byproducts .................................................... 5-9
VCM Recovery ............................................................... 5-10
Economics of EDC & VCM Production ............................. 5-15
<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRODUCTION OF VCM FROM ETHANE — SECTION B</td>
<td>5-23</td>
</tr>
<tr>
<td>Basic Chemistry — Ethane Oxychlorination</td>
<td>5-23</td>
</tr>
<tr>
<td>Feedstock/Byproducts — Ethane Oxychlorination</td>
<td>5-23</td>
</tr>
<tr>
<td>Unsaturates Hydrogenation — Ethane Oxychlorination</td>
<td>5-24</td>
</tr>
<tr>
<td>Reaction Conditions — Ethane Oxychlorination</td>
<td>5-24</td>
</tr>
<tr>
<td>VCM Recovery</td>
<td>5-25</td>
</tr>
<tr>
<td>Economics of VCM Production from Ethane</td>
<td>5-27</td>
</tr>
<tr>
<td>VCM Production by Ethane Deoxyhydrochlorination — Dow Process</td>
<td>5-30</td>
</tr>
<tr>
<td>Process Description — Dow Process</td>
<td>5-30</td>
</tr>
<tr>
<td>Ethane Oxydehydrochlorination — Section 100</td>
<td>5-30</td>
</tr>
<tr>
<td>VCM — Section 200</td>
<td>5-31</td>
</tr>
<tr>
<td>COST ESTIMATES</td>
<td>5-41</td>
</tr>
<tr>
<td>Fixed-Capital Costs</td>
<td>5-41</td>
</tr>
<tr>
<td>Production Costs</td>
<td>5-41</td>
</tr>
<tr>
<td>Economics Discussion</td>
<td>5-42</td>
</tr>
<tr>
<td>6 POLYVINYL CHLORIDE BY SUSPENSION POLYMERIZATION PROCESS</td>
<td>6-1</td>
</tr>
<tr>
<td>PROCESS DESCRIPTION</td>
<td>6-3</td>
</tr>
<tr>
<td>Section 100 — Polymerization</td>
<td>6-3</td>
</tr>
<tr>
<td>Section 200 — Monomer Recovery</td>
<td>6-4</td>
</tr>
<tr>
<td>Section 300 — Product Drying &amp; Finishing</td>
<td>6-5</td>
</tr>
<tr>
<td>Section 400 — Bulk Handling</td>
<td>6-5</td>
</tr>
<tr>
<td>PROCESS DISCUSSION</td>
<td>6-13</td>
</tr>
<tr>
<td>COST ESTIMATES</td>
<td>6-14</td>
</tr>
<tr>
<td>Fixed-Capital Costs</td>
<td>6-14</td>
</tr>
<tr>
<td>Production Costs</td>
<td>6-14</td>
</tr>
<tr>
<td>7 POLYVINYL CHLORIDE BY BULK POLYMERIZATION PROCESS</td>
<td>7-1</td>
</tr>
</tbody>
</table>
2.2 Economics of EDC Plant (Oxochlorination Processes) ........................................ 2-7
2.3 Economics of VCM Plant (EDC Noncatalytic Pyrolysis) ........................................ 2-9
2.4 Economics of VCM Plant (Ethane Oxidative Chlorination) .................................... 2-12
2.5 Economics of PVC Plant (Vinyl Chloride Polymerization) .................................... 2-16
3.1 World Capacity for PVC Resins ........................................................................ 3-3
5.1 Ethylene Dichloride by Direct Chlorination of Ethylene — Liquid Phase Total Capital Investment ........................................................................................................... 5-17
5.2 Ethylene Dichloride by Oxochlorination of Ethylene — Oxygen Based Total Capital Investment ........................................................................................................... 5-18
5.3 Ethylene Dichloride by Direct Chlorination of Ethylene — Liquid Phase Production Costs ..................................................................................................................... 5-19
5.4 Ethylene Dichloride by Oxochlorination of Ethylene Production Costs .................. 5-20
5.5 Vinyl Chloride from Ethylene Dichloride by Noncatalytic Pyrolysis Total Capital Investment ........................................................................................................... 5-21
5.6 Vinyl Chloride from Ethylene Dichloride by Noncatalytic Pyrolysis Production Costs ..................................................................................................................... 5-22
5.7 Vinyl Chloride from Ethane Total Capital Investment ........................................... 5-28
5.8 Vinyl Chloride from Ethane Production Costs ....................................................... 5-29
5.9 Vinyl Chloride by Dow Ethane Oxydehydrochlorination Process Design Bases ................................................................. 5-33
5.10 Vinyl Chloride by Dow Ethane Oxydehydrochlorination Process Stream Flows ................................................................. 5-34
5.11 Vinyl Chloride by Dow Ethane Oxydehydrochlorination Process Major Equipment ......................................................................................... 5-39
5.12 Vinyl Chloride by Dow Ethane Oxydehydrochlorination Process Total Capital Investment ................................................................. 5-43

TABLES (Continued)

5.13 Vinyl Chloride by Dow Ethane Oxydehydrochlorination Process Capital Investment by Section ................................................................. 5-44
5.14 Vinyl Chloride by Dow Ethane Oxydehydrochlorination Process Production Costs ......................................................................................... 5-45
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.4</td>
<td>Polyvinyl Chloride by Emulsion Polymerization Process</td>
<td>8-13</td>
</tr>
<tr>
<td></td>
<td>Utilities Summary</td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>Polyvinyl Chloride by Emulsion Polymerization Process</td>
<td>8-17</td>
</tr>
<tr>
<td></td>
<td>Total Capital Investment</td>
<td></td>
</tr>
<tr>
<td>8.6</td>
<td>Polyvinyl Chloride by Emulsion Polymerization Process</td>
<td>8-18</td>
</tr>
<tr>
<td></td>
<td>Capital Investment by Section</td>
<td></td>
</tr>
<tr>
<td>8.7</td>
<td>Polyvinyl Chloride by Emulsion Polymerization Process</td>
<td>8-20</td>
</tr>
<tr>
<td></td>
<td>Production Costs</td>
<td></td>
</tr>
</tbody>
</table>