

**Abstract**  
**Process Economics Program Report 37B**  
**ACETIC ACID AND ACETIC ANHYDRIDE**  
**(November 1994)**

This Report presents preliminary process designs and estimated economics for the manufacture of acetic acid and acetic anhydride by carbonylation technology. The three processes evaluated in this report include Monsanto's low pressure carbonylation of methanol process (BP Chemical acquired licensing rights to this process in 1985), Eastman's process for carbonylation of methyl acetate to produce acetic anhydride (methanol added to the reaction mixture results in the coproduction of acetic acid in this process), and a process based on BP Chemical patents that coproduces acetic acid and acetic anhydride via carbonylation of methyl acetate in the presence of water. Both the Eastman and BP Chemical processes are back-integrated into the manufacture of the methyl acetate feedstock from methanol and acetic acid.

We have included a discussion of other commercialized acetic acid and acetic anhydride processes as well as potential new processes. A list of the world's acetic acid and acetic anhydride producers along with their estimated plant capacities and a description of the major acetic acid and acetic anhydride markets are also included in this Report. This Report will be useful to producers of acetic acid and acetic anhydride, as well as to producers of methanol and downstream products such as vinyl acetate monomer.

## CONTENTS

<b>1 INTRODUCTION</b>	1-1
<b>2 SUMMARY</b>	2-1
GENERAL ASPECTS	2-1
ECONOMIC ASPECTS	2-1
TECHNICAL ASPECTS	2-3
Low Pressure Carbonylation of Methanol	2-3
Acetic Acid and Acetic Anhydride (Eastman Process)	2-3
Coproduct of Acetic Acid and Acetic Anhydride (BP Process)	2-4
<b>3 INDUSTRY STATUS</b>	3-1
ACETIC ACID	3-1
Manufacturing Processes	3-1
Acetic Acid Supply and Demand	3-2
Acetic Acid Markets	3-3
Vinyl Acetate Monomer	3-4
Acetic Anhydride	3-4
Acetate Esters	3-4
Dimethyl Terephthalate and Terephthalic Acid	3-5
Monochloroacetic Acid	3-5
Other Uses	3-5
ACETIC ANHYDRIDE	3-5
Manufacturing Processes	3-6
Acetic Anhydride Supply and Demand	3-6
Acetic Anhydride Markets	3-6
Cellulose Acetate Esters	3-6
Other Uses	3-8
<b>4 ACETIC ACID BY LOW PRESSURE CARBONYLATION OF METHANOL</b>	4-1
REVIEW OF PROCESSES	4-1
PROCESS DESCRIPTION	4-3
Catalyst Preparation and Regeneration	4-4
Carbonylation	4-5
Purification	4-6

## CONTENTS (Continued)

<b>4 ACETIC ACID BY LOW PRESSURE CARBONYLATION OF METHANOL (Concluded)</b>	
PROCESS DISCUSSION	4-12
Reactor Conditions	4-12
Catalyst Components	4-12
Vent Gas Scrubbing	4-12
Product Purification	4-13
Materials of Construction	4-13
Waste Streams	4-14
Raw Materials and Product Storage	4-14
COST ESTIMATES	4-14
<b>5 ACETIC ACID AND ACETIC ANHYDRIDE (EASTMAN PROCESS)</b>	5-1
REVIEW OF PROCESSES	5-1
Methyl Acetate Production	5-1
Methyl Acetate Carbonylation	5-2
PROCESS DESCRIPTION	5-4
Methyl Acetate Production	5-4
Methyl Acetate Carbonylation	5-7
Tar Removal Section	5-8
PROCESS DISCUSSION	5-19
Methyl Acetate Production	5-19
Acetic Anhydride Production	5-19
Methyl Acetate Conversion	5-19
Acetic Acid Coproduction	5-20
Carbon Monoxide	5-20
Catalyst Components	5-20
By-Products	5-20
Methyl Iodide Scrubber	5-21
Iodide Removal	5-21
Tar Removal Section	5-21
Materials of Construction	5-22
Waste Streams	5-23
Heat Integration	5-23
Raw Materials and Product Storage	5-23
COST ESTIMATES	5-24

## CONTENTS (Continued)

<b>6 COPRODUCTION OF ACETIC ACID AND ACETIC ANHYDRIDE (BP CHEMICALS PROCESS)</b>	<b>6-1</b>
REVIEW OF PROCESSES	6-1
PROCESS DESCRIPTION	6-2
Methyl Acetate Production	6-4
Acetic Acid and Acetic Anhydride Production	6-4
PROCESS DISCUSSION	6-13
Methyl Acetate Production	6-13
Catalyst	6-13
Entrainer	6-13
Acetic Acid and Acetic Anhydride Production	6-14
Carbon Monoxide/Hydrogen Feed	6-14
Water	6-14
High Boiling Solvent	6-14
Catalyst Components	6-15
Product Separation and Purification	6-15
Waste Streams	6-16
Materials of Construction	6-16
COST ESTIMATES	6-16
<b>7 OTHER PROCESSES</b>	<b>7-1</b>
ACETIC ACID	7-1
Methanol Carbonylation Processes	7-1
Low-Water Methanol Carbonylation Process	7-1
Non-Rhodium Catalysts	7-1
Other Acetic Acid Processes	7-2
Acetic Acid from Synthesis Gas	7-2
Acetic Acid by Methyl Formate Rearrangement	7-2
Acetic Acid by Acetaldehyde Oxidation	7-2
Acetic Acid by Oxidation of n-Butane or Naphtha	7-3
Acetic Acid by Olefin Oxidation	7-3
Acetic Acid from Methane	7-3
ACETIC ANHYDRIDE	7-4
From Ketene via Acetic Acid	7-4
From Ketene via Acetone	7-4
Acetaldehyde Oxidation Process	7-4

## CONTENTS (Concluded)

<b>APPENDIX A: PATENT SUMMARY TABLES</b>	<b>A-1</b>
<b>APPENDIX B: DESIGN AND COST BASES</b>	<b>B-1</b>
<b>APPENDIX C: CITED REFERENCES</b>	<b>C-1</b>
<b>APPENDIX D: PATENT REFERENCES BY COMPANY</b>	<b>D-1</b>
<b>APPENDIX E: PROCESS FLOW DIAGRAMS</b>	<b>E-1</b>

## ILLUSTRATIONS

4.1	Acetic Acid by Low Pressure Carbonylation of Methanol Process Flow Diagram	E-3
5.1	Acetic Acid and Acetic Anhydride (Eastman Process) Process Flow Diagram	E-5
5.2	Methyl Acetate Reactor	5-6
6.1	Coproduction of Acetic Acid and Acetic Anhydride (BP Process) Process Flow Diagram	E-11



## TABLES

2.1	Acetic Acid and Acetic Anhydride Estimated Production Costs	2-2
3.2	Supply/Demand for Acetic Acid by Major Region in 1993	3-3
3.3	Consumption of Acetic Acid by End Use in 1993	3-3
3.5	Supply/Demand for Acetic Anhydride by Major Region in 1992	3-7
3.6	Consumption of Acetic Anhydride by End Use in 1991	3-7
3.1	Worldwide Producers of Acetic Acid	3-9
3.4	Worldwide Producers of Acetic Anhydride	3-17
4.1	Acetic Acid by the Low Pressure Carbonylation of Methanol (Catalyst System Patents) Patent Summaries	A-3
4.2	Acetic Acid By Low Pressure Carbonylation of Methanol (Acetic Acid Purification/Catalyst Recovery) Patent Summary	A-12
4.3	Acetic Acid by Low Pressure Carbonylation of Methanol Design Bases and Assumptions	4-4
4.4	Acetic Acid by Low Pressure Carbonylation of Methanol Stream Flows	4-7
4.5	Acetic Acid by Low Pressure Carbonylation of Methanol Major Equipment	4-9
4.6	Acetic Acid by Low Pressure Carbonylation of Methanol Utilities Summary	4-11
4.7	Acetic Acid by Low Pressure Carbonylation of Methanol Total Capital Investment	4-16
4.8	Acetic Acid by Low Pressure Carbonylation of Methanol Capital Investment by Section	4-17
4.9	Acetic Acid by Low Pressure Carbonylation of Methanol Production Costs	4-18
5.1	Carbonylation of Methyl Acetate and/or Dimethyl Ether (Eastman/Halcon Patents) Patent Summaries	A-18



## TABLES (Continued)

5.2	Carbonylation of Methyl Acetate and/or Dimethyl Ether (Catalyst System Patents) Patent Summaries	A-24
5.3	Carbonylation of Methyl Acetate and/or Dimethyl Ether (Acetic Anhydride Purification/Catalyst Recovery) Patent Summaries	A-32
5.4	Acetic Acid And Acetic Anhydride (Eastman Process) Design Bases And Assumptions	5-5
5.5	Acetic Acid And Acetic Anhydride (Eastman Process) Stream Flows	5-10
5.6	Acetic Acid And Acetic Anhydride (Eastman Process) Major Equipment	5-14
5.7	Acetic Acid And Acetic Anhydride (Eastman Process) Utilities Summary	5-18
5.8	Acetic Acid And Acetic Anhydride (Eastman Process) Total Capital Investment	5-25
5.9	Acetic Acid And Acetic Anhydride (Eastman Process) Capital Investment by Section	5-26
5.10	Acetic Acid And Acetic Anhydride (Eastman Process) Production Costs	5-27
6.1	Coproduction of Acetic Acid and Acetic Anhydride Patent Summaries	A-34
6.2	Production of Methyl Acetate Patent Summaries	A-37
6.3	Coproduction of Acetic Acid and Acetic Anhydride (BP Chemicals Process) Design Bases and Assumptions	6-3
6.4	Coproduction of Acetic Acid and Acetic Anhydride (BP Chemicals Process) Stream Flows	6-6
6.5	Coproduction of Acetic Acid and Acetic Anhydride (BP Chemicals Process) Major Equipment	6-9

## TABLES (Concluded)

6.6	Coproduction of Acetic Acid and Acetic Anhydride (BP Chemicals Process) Utilities Summary	6-12
6.7	Coproduction of Acetic Acid and Acetic Anhydride (BP Chemicals Process) Total Capital Investment	6-18
6.8	Coproduction of Acetic Acid and Acetic Anhydride (BP Chemicals Process) Capital Investment by Section	6-19
6.9	Coproduction of Acetic Acid and Acetic Anhydride (BP Chemicals Process) Production Costs	6-20