

ABSTRACT
Process Economics Program Report No. 11D
METHACRYLIC ACID AND ESTERS
(January 1993)

Methacrylate esters and methacrylic acid (MAA) are widely used in clear polyacrylate plastics and in surface coatings such as acrylic latex paints. This report concentrates on the most important ester, methyl methacrylate (MMA). For many years, MMA has been made almost exclusively by a three-step process from acetone and HCN, via acetone cyanohydrin (ACH). In the ACH process, large proportions of sulfuric acid are used, and disposal of the acidic sludge by-product is expensive. Alternative processes and other raw materials are under development, and several plants based on a new C₄ process have been built in Japan. The C₄ process is based on two-stage vapor-phase oxidation of isobutylene or t-butanol to make methacrylic acid.

This report contains updated evaluations of the ACH process, the C₄ process, and processes that start with propionaldehyde or isobutyric acid. Also included is a new evaluation of a commercial variation of the C₄ process (10¢/lb lower product value) and an update of an evaluation of a variation of the ACH process (soon to be commercial) in which sulfuric acid is not used and capital is lower (7¢/lb lower product value).

In addition, this report includes new evaluations of noncommercial processes that start with propionic acid or propyne. The propyne process is especially attractive, because it produces MMA by a single-step carbonylation at very high yields. It has a lower product value than any of the other processes in this report.

This report is of special interest to current and potential producers of MMA, and to companies that produce the raw materials or intermediates. Purchasers of MMA will also be interested. Process engineers will find that the many different processing steps described here in detail can be adapted to the large-scale production of numerous other chemicals.

CONTENTS

1 INTRODUCTION	1-1
2 SUMMARY	2-1
TECHNICAL ASPECTS	2-1
MMA from ACH via Methacrylamide Sulfate (MAS)	2-1
MMA from ACH via AHIBA and MAHIB	2-1
MMA from TBA with Intermediate MA Separation	2-2
MMA from TBA by Tandem Oxidation	2-2
MMA from Propionaldehyde via MA and MAA	2-3
MMA from Propionic Acid via MAA	2-3
MMA from Ethylene via Methyl Propionate	2-3
MMA from Propyne	2-4
MMA from Propylene via Isobutyric Acid	2-4
ECONOMIC ASPECTS	2-4
3 INDUSTRY STATUS	3-1
MARKETS	3-1
PRICES	3-2
PRODUCING PLANTS	3-2
4 ROUTES TO METHYL METHACRYLATE AND METHACRYLIC ACID	4-1
MMA FROM ACETONE AND HCN	4-1
MMA FROM BRANCHED C ₄ COMPOUNDS	4-1
MMA FROM C ₃ COMPOUNDS	4-1
ROUTES TREATED IN THIS REPORT	4-4
OTHER ROUTES	4-4
5 MMA FROM t-BUTANOL (OR ISOBUTYLENE) VIA METHACROLEIN AND METHACRYLIC ACID	5-1
CHEMISTRY	5-1
PROCESS REVIEW	5-2
Methacrolein Production	5-2
Methacrolein Oxidation to MAA	5-3

CONTENTS (Continued)

5 MMA FROM t-BUTANOL (OR ISOBUTYLENE) VIA METHACROLEIN AND METHACRYLIC ACID (Continued)	
Methacrylic Acid Recovery and Purification	5-3
Methacrylic Acid Esterification	5-4
MMA Purification	5-4
Combination Processes	5-5
MAA from Isobutylene or t-Butanol (Tandem Oxidation)	5-5
MMA Directly from MA	5-5
Sources of Feedstock	5-6
t-Butanol	5-6
Oxidation of Isobutane to t-Butanol via TBHP	5-6
Oxidation of Isobutane to t-Butanol	5-6
Isobutane from n-Butane	5-6
Isobutylene	5-7
Isobutylene by Isobutane Dehydrogenation	5-7
Isobutylene from MTBE	5-7
Isobutylene from Mixed Butenes	5-8
Isobutylene from n-Butylenes	5-8
MA Production from Other Feedstocks	5-8
Oxidation of Isobutane directly to MA	5-8
Oxidation of MTBE directly to MA	5-8
MMA FROM TBA WITH INTERMEDIATE MA SEPARATION	5-9
Process Description	5-9
Oxidation of t-Butanol to Methacrolein (Section 100)	5-11
Oxidation of Methacrolein to Methacrylic Acid (Section 200)	5-11
Esterification of Methacrylic Acid with Methanol (Section 300)	5-12
Process Discussion	5-22
Oxidation of t-Butanol to Methacrolein	5-22
Recovery of Methacrolein	5-23
Oxidation of Methacrolein to Methacrylic Acid	5-23
Recovery of Methacrylic Acid	5-24
Esterification	5-24
Waste Streams	5-25
Materials of Construction	5-28
Cost Estimates	5-28
Capital Investment	5-28

CONTENTS (Continued)

5 MMA FROM t-BUTANOL (OR ISOBUTYLENE) VIA METHACROLEIN AND METHACRYLIC ACID (Concluded)	
Operating Costs	5-29
MMA FROM TBA BY TANDEM OXIDATION	5-35
Process Description	5-35
Methacrolein From t-Butanol (Section 100)	5-35
Methacrolein to Methacrylic Acid (Section 200)	5-36
Esterification and MMA Refining (Section 300)	5-36
Process Discussion	5-40
Yield	5-40
Wastes	5-40
Cost Estimates	5-40
Capital Investment	5-40
Operating Costs	5-41
6 MMA FROM PROPYLENE VIA ISOBUTYRIC ACID	6-1
PROCESS REVIEW	6-2
Carboxylation of Propylene to IBF	6-2
Hydrolysis of IBF to IBA and HF	6-2
Other Feedstocks	6-2
Purification of Crude IBA	6-3
IBA Dehydrogenation to Methacrylic Acid	6-3
Recovery, Purification, and Esterification of MAA	6-4
PROCESS DESCRIPTION	6-4
Hydrocarboxylation of Propylene to IBA (Section 100)	6-4
Dehydrogenation of IBA to MAA (Section 200)	6-6
Esterification of MAA to MMA (Section 300)	6-6
PROCESS DISCUSSION	6-7
Hydrocarboxylation of Propylene to IBA	6-7
Dehydrogenation of IBA to MAA	6-7
Esterification of MAA to MMA	6-8
COST ESTIMATES	6-8
Capital Investment	6-8
Operating Costs	6-8

CONTENTS (Continued)

7 MMA VIA ACETONE CYANOHYDRIN	7-1
MMA FROM ACH VIA METHACRYLAMIDE SULFATE (MAS)	7-1
Process Review	7-3
One-Step Conversion of ACH to MMA	7-3
Waste Treatment	7-3
SO ₂ Recovery	7-4
Process Description	7-4
Preparation of Acetone Cyanohydrin (ACH)	7-4
Hydrolysis of Acetone Cyanohydrin (ACH)	7-6
Esterification of Methacrylamide Sulfate	7-6
Recovery and Purification of Methyl Methacrylate	7-6
Cost Estimates	7-6
Capital Investment	7-6
Operating Costs	7-6
MMA FROM ACH VIA AHIBA AND MAHIB	7-12
Process Review	7-12
Formation of Acetone Cyanohydrin	7-13
Partial Hydrolysis of Acetone Cyanohydrin to AHIBA	7-13
Transesterification of AHIBA to MAHIB with Methyl Formate	7-13
Dehydration of MAHIB to MMA	7-14
Related Process	7-14
Variation	7-14
Dehydration of Formamide to HCN	7-15
Production of Methyl Formate	7-15
Methyl Formate by Methanol Dehydrogenation	7-15
Methyl Formate by Methanol Oxydehydrogenation	7-16
Methyl Formate by Methanol Carbonylation	7-16
Transesterification of AHIBA to MAHIB via in situ Production of Methyl Formate	7-16
Process Description	7-17
Process Discussion	7-23
Sources of Makeup HCN	7-23
Sources of Formamide	7-23
Sales of Formamide	7-23
Additional Alternatives	7-23
Cost Estimates	7-24

CONTENTS (Continued)

7 MMA VIA ACETONE CYANOHYDRIN (Concluded)	
Capital Investment	7-24
Operating Costs	7-26
8 MMA FROM ETHYLENE VIA PROPIONIC ACID, PROPIONALDEHYDE, OR METHYL PROPIONATE	8-1
PROCESS REVIEW	8-1
MAA from Propionic Acid	8-1
MAA from Propionaldehyde via MA	8-4
MMA from Methyl Propionate	8-4
MMA from Propionic Acid and Methylal	8-5
General Comparison	8-5
Production of Intermediates	8-6
Propionaldehyde from Ethylene	8-6
Propionic Acid from Propionaldehyde	8-6
Propionic Acid from Ethylene	8-6
Propionic Acid from Syn Gas via Methyl Acetate	8-7
Methyl Propionate from Ethylene	8-7
Methyl Propionate from Propionic Acid	8-8
Methyl Propionate from Propionaldehyde	8-8
MMA FROM PROPIONIC ACID VIA MAA	8-9
Process Description	8-9
Propionic Acid Reaction (Section 100)	8-9
Methacrylic Acid Recovery (Section 200)	8-9
Esterification and MMA Recovery (Section 300)	8-10
Process Discussion	8-17
Purification of Propionic Acid Feed	8-17
Reaction of Propionic Acid and Formaldehyde	8-17
Removal of Water from Recycle and Fresh Formaldehyde	8-17
Recovery of Unreacted Propionic Acid	8-17
MAA Esterification	8-18
Materials of Construction	8-19
Waste Streams	8-19
Cost Estimates	8-19
Capital Investment	8-19
Operating Costs	8-20

CONTENTS (Continued))

8 MMA FROM ETHYLENE VIA PROPIONIC ACID, PROPIONALDEHYDE, OR METHYL PROPIONATE (Concluded)	
MMA FROM PROPIONALDEHYDE VIA MA AND MAA	8-28
Process Description	8-28
Process Discussion	8-33
Materials of Construction	8-33
Waste Streams	8-33
Cost Estimates	8-33
Capital Investment	8-33
Operating Costs	8-34
PROCESS COMPARISON	8-42
MMA FROM ETHYLENE VIA METHYL PROPIONATE	8-43
9 MMA FROM PROPYNE	9-1
SOURCES OF PROPYNE	9-1
PROCESS REVIEW	9-2
Propyne Carbonylation	9-2
Propyne Feed from C ₃ Streams	9-3
Propadiene Isomerization	9-4
PROCESS DESCRIPTION	9-4
PROCESS DISCUSSION	9-13
Catalyst Recovery and Reuse	9-13
Materials of Construction	9-13
Safety	9-14
Waste Streams	9-14
COST ESTIMATES	9-14
Capital Investment	9-14
Operating Costs	9-14
Discussion	9-15

CONTENTS (Concluded)

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

4.1	ROUTES TO METHYL METHACRYLATE AND METHACRYLIC ACID FROM C ₄ COMPOUNDS	4-2
4.2	ROUTES TO METHYL METHACRYLATE AND METHACRYLIC ACID FROM C ₃ COMPOUNDS	4-3
5.1	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION PROCESS FLOW DIAGRAM	E-3
5.2	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	5-34
5.3	MMA FROM TBA BY TANDEM OXIDATION PROCESS FLOW DIAGRAM	E-9
5.4	MMA FROM TBA BY TANDEM OXIDATION EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	5-46
6.1	MMA FROM PROPYLENE VIA ISOBUTYRIC ACID PROCESS FLOW DIAGRAM	E-11
6.2	MMA FROM PROPYLENE VIA ISOBUTYRIC ACID EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	6-11
7.1	MMA FROM ACH VIA MAS PROCESS FLOW DIAGRAM	E-17
7.2	MMA FROM ACH VIA MAS EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	7-10
7.3	MMA FROM ACH VIA MAS EFFECT OF ACETONE AND HCN PRICES	7-11
7.4	MMA FROM ACH VIA AHIBA AND MAHIB PROCESS FLOW DIAGRAM	E-19
7.5	MMA FROM ACH VIA AHIBA AND MAHIB VAPOR PRESSURE OF INTERMEDIATES	7-25
7.6	MMA FROM ACH VIA AHIBA AND MAHIB EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	7-30

ILLUSTRATIONS (Concluded)

8.1	ROUTES TO METHYL METHACRYLATE AND METHACRYLIC ACID FROM ETHYLENE	8-2
8.2	MMA FROM PROPIONIC ACID VIA MAA PROCESS FLOW DIAGRAM	E-21
8.3	MMA FROM PROPIONIC ACID VIA MAA EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	8-26
8.4	MMA FROM PROPIONIC ACID VIA MAA EFFECT OF PROPIONIC ACID PRICE ON PRODUCT VALUE	8-27
8.5	MMA FROM PROPIONALDEHYDE VIA MA AND MAA PROCESS FLOW DIAGRAM	E-23
8.6	MMA FROM PROPIONALDEHYDE VIA MA AND MAA EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	8-40
8.7	MMA FROM PROPIONALDEHYDE VIA MA AND MAA EFFECT OF PROPIONALDEHYDE PRICE ON PRODUCT VALUE	8-41
9.1	MMA FROM PROPYNE PROCESS FLOW DIAGRAM	E-25
9.2	MMA FROM PROPYNE EFFECT OF OPERATING LEVEL AND PLANT CAPACITY ON PRODUCT VALUE	9-21

TABLES

2.1	SUMMARY OF ECONOMICS OF MMA PROCESSES	2-7
3.1	MMA PRODUCERS IN THE UNITED STATES	3-3
3.2	MMA PRODUCERS IN EUROPE	3-4
3.3	MMA PRODUCERS IN JAPAN	3-5
3.4	MMA PRODUCERS IN OTHER COUNTRIES	3-6
5.1	METHACROLEIN BY OXIDATION OF T-BUTANOL OR ISOBUTYLENE PATENT SUMMARY	A-4
5.2	METHACRYLIC ACID BY OXIDATION OF METHACROLEIN PATENT SUMMARY	A-6
5.3	MAA RECOVERY AND PURIFICATION PATENT SUMMARY	A-8
5.4	ESTERIFICATION PATENT SUMMARY	A-13
5.5	MMA PURIFICATION PATENT SUMMARY	A-15
5.6	TANDEM MAA PROCESSES PATENT SUMMARY	A-18
5.7	OXIDATION OF ISOBUTANE TO TBA PATENT SUMMARY	A-20
5.8	MA AND MAA FROM ISOBUTANE PATENT SUMMARY	A-28
5.9	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION DESIGN BASES AND ASSUMPTIONS	5-10
5.10	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION STREAM FLOWS	5-14
5.11	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION MAJOR EQUIPMENT	5-18
5.12	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION UTILITIES SUMMARY	5-21

TABLES (Continued)

5.13	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION WASTE STREAMS	5-26
5.14	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION TOTAL CAPITAL INVESTMENT	5-30
5.15	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION CAPITAL INVESTMENT BY SECTION	5-31
5.16	MMA FROM TBA WITH INTERMEDIATE MA SEPARATION PRODUCTION COSTS	5-32
5.17	MMA FROM TBA COMPARISON OF TBA-BASED MMA PROCESSES	5-38
5.18	MMA FROM TBA DESIGN CHANGES FOR TANDEM OXIDATION	5-39
5.19	MMA FROM TBA BY TANDEM OXIDATION TOTAL CAPITAL INVESTMENT	5-42
5.20	MMA FROM TBA BY TANDEM OXIDATION CAPITAL INVESTMENT BY SECTION	5-43
5.21	MMA FROM TBA BY TANDEM OXIDATION PRODUCTION COSTS	5-44
6.1	ISOBUTYRIC ACID BY HYDROCARBOXYLATION OF PROPYLENE PATENT SUMMARY	A-30
6.2	METHACRYLIC ACID BY DEHYDROGENATION OF ISOBUTYRIC ACID PATENT SUMMARY	A-36
6.3	MMA FROM PROPYLENE VIA ISOBUTYRIC ACID DESIGN BASES AND ASSUMPTIONS	6-5
6.4	MMA FROM PROPYLENE VIA ISOBUTYRIC ACID PRODUCTION COST	6-9
7.1	MANUFACTURE OF ACETONE CYANOHYDRIN PATENT SUMMARY	A-38
7.2	CONVERSION OF ACH TO METHACRYLAMIDE SULFATE PATENT SUMMARY	A-39
7.3	CONVERSION OF METHACRYLAMIDE SULFATE TO MMA PATENT SUMMARY	A-42

TABLES (Continued)

7.4	TREATMENT OF ACIDIC WASTES PATENT SUMMARY	A-46
7.5	MMA FROM ACH VIA MAS DESIGN BASES AND ASSUMPTIONS	7-5
7.6	MMA FROM ACH VIA MAS PRODUCTION COST SUMMARY	7-8
7.7	HYDRATION OF ACH TO AHIBA PATENT SUMMARY	A-47
7.8	CONVERSION OF AHIBA TO MAHIB PATENT SUMMARY	A-49
7.9	DEHYDRATION OF MAHIB TO MMA PATENT SUMMARY	A-51
7.10	DECOMPOSITION OF FORMAMIDE TO HCN PATENT SUMMARY	A-53
7.11	MMA FROM ACH VIA AHIBA AND MAHIB DESIGN BASES AND ASSUMPTIONS	7-20
7.12	MMA FROM ACH VIA AHIBA AND MAHIB STREAM FLOWS FOR SECTION 100	7-22
7.13	MMA FROM ACH VIA AHIBA AND MAHIB CAPITAL COST ESTIMATE	7-27
7.14	MMA FROM ACH VIA AHIBA AND MAHIB PRODUCTION COSTS	7-28
8.1	MAA FROM PROPIONIC ACID PATENT SUMMARY	A-54
8.2	MA FROM PROPIONALDEHYDE PATENT SUMMARY	A-59
8.3	MMA FROM METHYL PROPIONATE PATENT SUMMARY	A-60
8.4	MMA FROM PROPIONIC ACID AND METHYLAL PATENT SUMMARY	A-64

TABLES (Continued)

8.5	METHYL PROPIONATE PRODUCTION PATENT SUMMARY	A-65
8.6	MMA FROM PROPIONIC ACID VIA MAA DESIGN BASES AND ASSUMPTIONS	8-11
8.7	MMA FROM PROPIONIC ACID VIA MAA STREAM FLOWS	8-12
8.8	MMA FROM PROPIONIC ACID VIA MAA MAJOR EQUIPMENT	8-14
8.9	MMA FROM PROPIONIC ACID VIA MAA UTILITIES SUMMARY	8-16
8.10	MMA FROM PROPIONIC ACID VIA MAA TOTAL CAPITAL INVESTMENT	8-21
8.11	MMA FROM PROPIONIC ACID VIA MAA CAPITAL INVESTMENT BY SECTION	8-22
8.12	MMA FROM PROPIONIC ACID VIA MAA PRODUCTION COSTS	8-23
8.13	MMA FROM PROPIONIC ACID VIA MAA DIRECT COSTS BY SECTION	8-25
8.14	MMA FROM PROPIONALDEHYDE VIA MA AND MAA DESIGN BASES AND ASSUMPTIONS	8-29
8.15	MMA FROM PROPIONALDEHYDE VIA MA AND MAA STREAM FLOWS FOR SECTION 100	8-30
8.16	MMA FROM PROPIONALDEHYDE VIA MA AND MAA MAJOR EQUIPMENT FOR SECTION 100	8-31
8.17	MMA FROM PROPIONALDEHYDE VIA MA AND MAA UTILITIES SUMMARY FOR SECTION 100	8-32
8.18	MMA FROM PROPIONALDEHYDE VIA MA AND MAA TOTAL CAPITAL INVESTMENT	8-35
8.19	MMA FROM PROPIONALDEHYDE VIA MA AND MAA CAPITAL INVESTMENT BY SECTION	8-36
8.20	MMA FROM PROPIONALDEHYDE VIA MA AND MAA PRODUCTION COSTS	8-37

TABLES (Concluded)

8.21	MMA FROM PROPIONALDEHYDE VIA MA AND MAA DIRECT COSTS BY SECTIONS	8-39
8.22	SUMMARY OF ECONOMICS OF ETHYLENE-BASED MMA PROCESS	8-42
9.1	MMA BY PROPYNE CARBONYLATION PATENT SUMMARY	A-70
9.2	MMA FROM PROPYNE DESIGN BASES AND ASSUMPTIONS	9-6
9.3	MMA FROM PROPYNE STREAM FLOWS	9-8
9.4	MMA FROM PROPYNE MAJOR EQUIPMENT	9-10
9.5	MMA FROM PROPYNE UTILITIES SUMMARY	9-12
9.6	MMA FROM PROPYNE TOTAL CAPITAL INVESTMENT	9-16
9.7	MMA FROM PROPYNE CAPITAL INVESTMENT BY SECTION	9-17
9.8	MMA FROM PROPYNE PRODUCTION COSTS	9-18
9.9	MMA FROM PROPYNE DIRECT COSTS BY SECTION	9-20