

Abstract
Process Economics Program Report 31B
HEXAMETHYLENEDIAMINE
(March 1997)

This report, Supplement B to PEP Report 31, *Hexamethylene Diamine* (September 1972), reviews the technology for producing hexamethylenediamine (HMDA), one of the two precursors for the production of nylon 6,6. We also present the economics for the following alternative routes to HMDA:

- HMDA from butadiene via adiponitrile (ADN) by hydrocyanation
- HMDA from acrylonitrile via ADN by electrohydrodimerization
- HMDA from adipic acid via ADN by ammoniation and hydrogenation.

World production of HMDA in 1995 was estimated at 1.19 million tons (2.62 billion pounds), of which 90% was accounted for by demand in the United States, Western Europe, Japan, and Canada. The average growth in HMDA demand through 2001, is estimated at 2.2%/yr in the United States, 2.5% in Western Europe, 2.4% in Japan, and 2.3% in Canada. As of January 1996, world HMDA production capacity was estimated at 1.33 million t/yr (2.93 billion lb/yr).

In addition to its use in the production of nylon 66 fibers and resins, HDMA is reacted with other dicarboxylic acids to make nylon 69, nylon 610, and nylon 612. In addition, HMDA can be used as a hardener for epoxy resins, in the production of hexamethylene diisocyanate for weather-resistant polyurethane, and of HDMA carbamate as an accelerator in fluorinated and polyacrylate elastomer vulcanization.

This report will be of interest to those involved with the production of nylon fiber and resins, and the hardener business in epoxy resin production. The report provides both a technology review and the economics for HMDA production.

CONTENTS

| | |
|---|------|
| GLOSSARY | xi |
| 1 INTRODUCTION..... | 1-1 |
| 2 SUMMARY | 2-1 |
| GENERAL ASPECTS..... | 2-1 |
| TECHNICAL ASPECTS | 2-1 |
| HMDA from BD | 2-9 |
| HMDA from ACN..... | 2-9 |
| HMDA from ADA..... | 2-9 |
| 3 INDUSTRY STATUS | 3-1 |
| DEMAND FOR HMDA | 3-1 |
| PRODUCTION CAPACITY OF HMDA | 3-2 |
| 4 REVIEW OF TECHNOLOGY | 4-1 |
| ADN FROM BD BY HYDROCYANATION..... | 4-1 |
| BD Hydrocyanation | 4-3 |
| 2PN Removal | 4-4 |
| Isomerization of 2M3BN to 3PN | 4-4 |
| PN Hydrocyanation | 4-4 |
| Catalyst and Product Recovery | 4-6 |
| ADN FROM ADA BY AMMONIATION AND DEHYDRATION..... | 4-6 |
| ADN FROM ACN BY ELECTROHYDRODIMERIZATION | 4-7 |
| ADN FROM ACN BY CATALYTIC DIMERIZATION..... | 4-9 |
| HMDA FROM ADN BY HYDROGENATION | 4-10 |
| ADN Hydrogenation | 4-11 |
| HMDA Purification | 4-12 |
| 5 HEXAMETHYLENEDIAMINE FROM BUTADIENE VIA ADIPONITRILE BY HYDROCYANATION | 5-1 |
| PROCESS DESCRIPTION..... | 5-1 |

CONTENTS (Continued)

| | | |
|----------|---|------------|
| 5 | HEXAMETHYLENEDIAMINE FROM BUTADIENE VIA ADIPONITRILE BY HYDROCYANATION (concluded) | |
| | BD Hydrocyanation | 5-1 |
| | 2M3BN Isomerization | 5-4 |
| | PN Hydrocyanation | 5-4 |
| | ADN Purification | 5-5 |
| | Catalyst Regeneration..... | 5-5 |
| | ADN Hydrogenation | 5-5 |
| | PROCESS DISCUSSION..... | 5-13 |
| | COST ESTIMATES | 5-13 |
| 6 | HEXAMETHYLENEDIAMINE FROM ACRYLONITRILE BY ELECTROHYDRODIMERIZATION | 6-1 |
| | PROCESS DESCRIPTION..... | 6-1 |
| | ACN Electrolysis..... | 6-3 |
| | ADN Purification | 6-4 |
| | ADN Hydrogenation | 6-4 |
| | Purge Stream Treatment | 6-4 |
| | PROCESS DISCUSSION..... | 6-15 |
| | COST ESTIMATES | 6-15 |
| 7 | HMDA FROM ADIPIC ACID VIA ADIPONITRILE BY AMMONIATION AND HYDROGENATION | 7-1 |
| | PROCESS DESCRIPTION..... | 7-1 |
| | ADA Ammoniation/Dehydration..... | 7-1 |
| | Purification of ADN..... | 7-3 |
| | Hydrogenation of ADN..... | 7-4 |
| | PROCESS DISCUSSION..... | 7-9 |
| | COST ESTIMATES | 7-9 |
| | ECONOMIC COMPARISON..... | 7-9 |

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 | Four Major Routes for HDMA Manufacture | 4-2 |
| 4.2 | Structural Formulas for the Major Reaction Products of Du Pont's ADN from BD Process | 4-35.1 |
| |HMDA from BD via ADN by Hydrocyanation | E-3 |
| 5.2 | HMDA from BD via ADN by Hydrocyanation Effect of Operating Level and Plant Capacity on Product Value..... | 5-19 |
| 5.3 | HMDA from BD via ADN by Hydrocyanation Effect of Raw Material Costs on HMDA Product Value..... | 5-20 |
| 6.1 | HMDA from ACN via ADN by Undivided Cells Electrohydrodimerization..... | E-7 |
| 6.2 | HMDA from ACN via ADN by EHD and Hydrogenation Effect of Operating Level and Plant Capacity on Product Value..... | 6-21 |
| 6.3 | HMDA from ACN via ADN by EHD and Hydrogenation Effect of ACN Unit Price on HMDA Product Value | 6-22 |
| 7.1 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Effect of Operating Level and Plant Capacity on Product Value..... | 7-15 |
| 7.2 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Effect of ADA Unit Price on HMDA Product Value | 7-15 |

TABLES

| | | |
|-----|---|------|
| 2.1 | HMDA from BD via ADN by Hydrocyanation Design Bases and Assumptions | 2-2 |
| 2.2 | HMDA from ACN via ADN by Electrohydrodimerization and Hydrogenation Design Bases and Assumptions | 2-4 |
| 2.3 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Design Bases and Assumptions | 2-6 |
| 2.4 | Economic Comparison of Three HMDA Processes | 2-8 |
| 3.1 | HMDA Consumption by Major World Region..... | 3-1 |
| 3.2 | Regional HMDA Consumption by Major End Use..... | 3-2 |
| 3.3 | HMDA Producers Worldwide | 3-4 |
| 4.1 | ADN Production Patent Summary..... | A-3 |
| 4.2 | Dimerization of ACN with Isopropyl Diphenylphosphinite Catalyst..... | 4-11 |
| 4.3 | HMDA from ADN by Hydrogenation Patent Summary..... | A-18 |
| 4.4 | By-Products in Crude HMDA from ADN Hydrogenation..... | 4-13 |
| 5.1 | HMDA from BD via ADN by Hydrocyanation Design Bases and Assumptions | 5-2 |
| 5.2 | HMDA from BD via ADN by Hydrocyanation Major Equipment..... | 5-7 |
| 5.3 | HMDA from BD via ADN by Hydrocyanation Utilities Summary | 5-12 |
| 5.4 | HMDA from BD via ADN by Hydrocyanation Total Capital Investment..... | 5-14 |
| 5.5 | HMDA from BD via ADN by Hydrocyanation Capital Investment by Section | 5-15 |
| 5.6 | HMDA from BD via ADN by Hydrocyanation Production Costs | 5-17 |
| 6.1 | HMDA from ACN via ADN by EHD and Hydrogenation Design Bases and Assumptions | 6-2 |
| 6.2 | HMDA from ACN via ADN by EHD and Hydrogenation Stream Flows | 6-6 |
| 6.3 | HMDA from ACN via ADN by EHD and Hydrogenation Major Equipment..... | 6-11 |

TABLES (Concluded)

| | | |
|-----|---|------|
| 6.4 | HMDA from ACN via ADN by EHD and Hydrogenation Utilities Summary | 6-14 |
|-----|---|------|

| | | |
|-----|---|------|
| 6.5 | HMDA from ACN via ADN by EHD and Hydrogenation Total Capital Investment..... | 6-16 |
| 6.6 | HMDA from ACN via ADN by EHD and Hydrogenation Capital Investment by Section | 6-17 |
| 6.7 | HMDA from ACN via ADN by EHD and Hydrogenation Production Costs | 6-19 |
| 7.1 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Design Bases and Assumptions | 7-2 |
| 7.2 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Major Equipment..... | 7-5 |
| 7.3 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Utilities Summary | 7-8 |
| 7.4 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Total Capital Investment..... | 7-10 |
| 7.5 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Capital Investment by Section | 7-11 |
| 7.6 | HMDA from ADA via ADN by Ammoniation and Hydrogenation Production Costs | 7-12 |
| 7.7 | Economic Comparison of Three HMDA Processes | 7-14 |