



PROCESS ECONOMICS PROGRAM

SRI INTERNATIONAL
Menlo Park, California
94025

Abstract

Process Economics Program Report No. 41B

CAPROLACTAM AND NYLON 6

(March 1988)

This report reviews the technology for the production of caprolactam and its polymer, nylon 6. A total of three major caprolactam manufacturing and one nylon 6 manufacturing routes are evaluated in detail:

- Caprolactam from cyclohexane via cyclohexanone by oxidation, oximation, and Beckmann rearrangement
- Caprolactam from phenol via cyclohexanone by hydrogenation, oximation, and Beckmann rearrangement
- Caprolactam from toluene via cyclohexanone carboxylic acid by oxidation, hydrogenation, nitrosation, and rearrangement
- Nylon 6 from caprolactam by hydrolysis, poly addition, and polycondensation.

Economics for three alternative processes using the first route, one process each using the second and third routes, and two alternative processes using the forth route are presented.

As of January 1987, the world production capacity for caprolactam was about 7,000 million lb/yr (3,157 thousand metric tons/yr), and that for nylon 6 is more than 4,786 million lb/yr (2,173 thousand metric tons/yr).

SRI International

Report No. 41B

NYLON 6 AND CAPROLACTAM

SUPPLEMENT B

by YU-REN CHIN

with contributions by KUEN-TIAN CHANG
REN-BEN CHEN
KUN-HO LIU

February 1988

A private report by the
PROCESS ECONOMICS PROGRAM

Menlo Park, California 94025



For detailed marketing data and information, the reader is referred to one of the SRI 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 SRI DIRECTORY OF CHEMICAL PRODUCERS services provide detailed lists of chemical producers by company, product, and plant for the United States and Western Europe.

CONTENTS

| | | |
|----------|--|-----------|
| 1 | INTRODUCTION | 1 |
| 2 | SUMMARY | 3 |
| | Technical Aspects | 5 |
| | Caprolactam | 5 |
| | Nylon 6 | 7 |
| | Economics and Process Comparison | 8 |
| | Caprolactam Production | 8 |
| | Nylon 6 Production | 13 |
| 3 | INDUSTRY STATUS | 17 |
| | World Overview | 17 |
| | Supply and Demand—Caprolactam | 22 |
| | United States | 22 |
| | Western Europe | 28 |
| | Japan | 30 |
| | Supply and Demand—Nylon 6 | 30 |
| | United States | 41 |
| | Western Europe | 43 |
| | Japan | 43 |
| 4 | TECHNOLOGIES FOR MANUFACTURING CAPROLACTAM | 47 |
| | General | 47 |
| | Review of Processes | 49 |
| | Oxidation of Cyclohexane | 49 |
| | Hydrogenation of Phenol | 54 |
| | Hydroxylamine Production—General | 57 |
| | Hydroxylamine Production—The Raschig Process | 57 |
| | Hydroxylamine Production—The HPO Process | 58 |
| | Hydroxylamine Production—The Nitric Oxide Reduction Process | 60 |
| | Oximation of Cyclohexanone | 62 |
| | Rearrangement of Cyclohexanone Oxime | 66 |
| | Caprolactam Recovery and Purification | 69 |
| | Ammonium Sulfate Recovery | 75 |
| 5 | TECHNOLOGIES FOR MANUFACTURING NYLON 6 | 77 |
| | Hydrolytic Polymerization | 77 |
| | Anionic Polymerization | 80 |
| | Recovery of Caprolactam from Oligomers or Nylon 6 Scrap | 83 |

CONTENTS

| | | |
|----------|---|------------|
| 6 | CAPROLACTAM FROM CYCLOHEXANE, NITRIC OXIDE HYDROGENATION | 87 |
| | Process Description | 87 |
| | Cyclohexane Oxidation | 88 |
| | Nitric Oxide Hydrogenation | 92 |
| | Cyclohexanone Oximation | 93 |
| | Rearrangement and Purification | 94 |
| | Ammonium Sulfate Recovery | 96 |
| | Process Discussion | 114 |
| | Cost Estimates | 115 |
| 7 | CAPROLACTAM FROM PHENOL BY THE HYDROXYLAMINE PHOSPHATE OXIME PROCESS | 127 |
| | Process Description | 127 |
| | Phenol Hydrogenation | 128 |
| | Nitrate Hydrogenation and Cyclohexanone Oximation | 130 |
| | Oxime Rearrangement | 132 |
| | Caprolactam Extraction | 134 |
| | Caprolactam Purification | 135 |
| | Ammonium Sulfate Recovery | 135 |
| | Process Discussion | 151 |
| | Cost Estimates | 152 |
| 8 | CAPROLACTAM FROM TOLUENE VIA CYCLOHEXANE CARBOXYLIC ACID | 165 |
| | Process Description | 165 |
| | Toluene Oxidation | 165 |
| | Benzoic Acid Hydrogenation | 167 |
| | Nitrosyl Sulfuric Acid Preparation | 168 |
| | CHCA Nitrosation | 169 |
| | Sulfate Crystallization and Caprolactam Extraction | 169 |
| | Caprolactam Purification | 170 |
| | Process Discussion | 183 |
| | Cost Estimates | 184 |
| 9 | PRODUCTION OF NYLON 6 | 193 |
| | Continuous Production of Nylon 6 Melt | 193 |
| | Process Description | 193 |
| | Process Discussion | 201 |
| | Cost Estimates | 202 |
| | Continuous Production of Nylon 6 Chips | 209 |
| | Process Description | 209 |
| | Process Discussion | 218 |
| | Cost Estimates | 219 |

CONTENTS

| | |
|---|------------|
| APPENDIX A DESIGN AND COST BASES | 227 |
| PATENT SUMMARY TABLES | 231 |
| CITED REFERENCES | 261 |
| PATENT REFERENCES BY COMPANY | 277 |

ILLUSTRATIONS

| | | |
|-----|--|-----|
| 2.1 | Effect of Feedstock Prices on Caprolactam Product Value Half Ammonium Sulfate Credit | 14 |
| 2.2 | Effect of Feedstock Prices on Caprolactam Product Value No Ammonium Sulfate Credit | 15 |
| 4.1 | Commercial Caprolactam Processes | 48 |
| 6.1 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation Flow Sheet | 287 |
| 6.2 | Caprolactam from Cyclohexane Using Nitric Oxide Hydrogenation Effect of Operating Level and Plant Capacity on Product Value | 122 |
| 7.1 | Caprolactam from Phenol by Hydroxylamine Oxime Phosphate Process Flow Sheet | 295 |
| 7.2 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process Sketch of Rotation Chamber of Rearrangement Reactor | 133 |
| 7.3 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process Effect of Operating Level and Plant Capacity on Product Value | 162 |
| 7.4 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process Effect of Phenol on Product Value | 163 |
| 8.1 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Flow Sheet | 303 |
| 8.2 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Effect of Operating Level and Plant Capacity on Product Value | 190 |
| 8.3 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Effect of Costs of Oleum and Toluene on the Product Value | 191 |
| 8.4 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Effect of Ammonium Sulfate Credit on the Product Value | 192 |
| 9.1 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Flow Sheet | 311 |
| 9.2 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Effect of Operating Level and Plant Capacity on Product Value | 207 |
| 9.3 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Effect of Monomer Cost on Product Value | 208 |
| 9.4 | Continuous Production of Nylon 6 Chip | 313 |

ILLUSTRATIONS

| | | |
|------------|--|------------|
| 9.5 | Continuous Production of Nylon 6 Chip | |
| | Effect of Operating Level and Plant Capacity on Product Value | 224 |
| 9.6 | Continuous Production of Nylon 6 Chip | |
| | Effect of Monomer Cost on Product Value | 225 |

TABLES

| | | |
|-------------|---|------------|
| 2.1 | Processes for Caprolactam | |
| | Summary of Economics | 9 |
| 2.2 | Processes for Nylon 6 | |
| | Summary of Economics | 10 |
| 3.1 | World Capacity for Caprolactam | 18 |
| 3.2 | World Production and Consumption of Caprolactam – 1985 | 19 |
| 3.3 | World Capacity for Nylon 6 Fibers | 20 |
| 3.4 | World Production and Consumption of Nylon Fibers – 1985 | 21 |
| 3.5 | World Producers of Caprolactam | 23 |
| 3.6 | Largest Producers of Caprolactam | 25 |
| 3.7 | Largest Consumers of Caprolactam | 26 |
| 3.8 | Breakdown of Capacity for Caprolactam by Raw Material – 1987 | 27 |
| 3.9 | United States Salient Statistics for Caprolactam – 1985 and 1986 | 29 |
| 3.10 | Western European Salient Statistics for Caprolactam – 1985 | 31 |
| 3.11 | Japanese Salient Statistics for Caprolactam – 1985 | 32 |
| 3.12 | World Producers of Nylon 6 Fibers | 33 |
| 3.13 | Largest Producers of Nylon 6 Fibers | 37 |
| 3.14 | World Producers of Nylon 6 Resin | 38 |
| 3.15 | United States | |
| | Salient Statistics for Nylon Fibers – 1985 | 42 |
| 3.16 | Western Europe | |
| | Salient Statistics for Nylon Fibers – 1985 | 44 |
| 3.17 | Japan | |
| | Salient Statistics for Nylon Fibers – 1985 | 45 |
| 4.1 | Characteristics of Commercial Caprolactam Processes | 50 |
| 4.2a | Oxidation of Cyclohexane | |
| | Patent Summary | 223 |
| 4.2b | Dehydrogenation of Cyclohexanol | |
| | Patent Summary | 236 |
| 4.3 | Hydrogenation of Phenol | |
| | Patent Summary | 237 |

TABLES

| | | |
|-------------|--|-----|
| 4.4 | Hydroxylamine Production | |
| | Patent Summary | 238 |
| 4.5a | Oximation of Cyclohexanone | |
| | Patent Summary | 241 |
| 4.5b | Vapor Phase Oximation of Cyclohexanone | |
| | Patent Summary | 242 |
| 4.6a | Vapor Phase Rearrangement of Cyclohexanone Oxime | |
| | Patent Summary | 243 |
| 4.6b | Liquid Phase Rearrangement of Cyclohexanone Oxime | |
| | Patent Summary | 245 |
| 4.7 | Recovery and Purification of Caprolactam Formed in Liquid Phase | |
| | Patent Summary | 247 |
| 4.8 | Recovery and Purification of Caprolactam Formed in Vapor Phase | |
| | Patent Summary | 250 |
| 4.9 | Ammonium Sulfate Recovery | |
| | Patent Summary | 251 |
| 5.1 | Nylon 6 by Hydrolytic Polymerization | |
| | Patent Summary | 252 |
| 5.2 | Nylon 6 by Anionic Polymerization | |
| | Patent Summary | 255 |
| 5.3 | Recovery of Caprolactam | |
| | Patent Summary | 258 |
| 6.1 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Design References | 88 |
| 6.2 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Design Bases and Assumptions | 89 |
| 6.3 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Stream Flows | 97 |
| 6.4 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Major Equipment | 108 |
| 6.5 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Utilities Summary | 113 |

TABLES

| | | |
|-------------|--|-----|
| 6.6 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Total Capital Investment | 117 |
| 6.7 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Capital Investment by Section | 118 |
| 6.8 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation | |
| | Production Costs | 120 |
| 6.9 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation (Conventional) | |
| | Total Capital Investment | 123 |
| 6.10 | Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation (Conventional) | |
| | Production Costs | 124 |
| 7.1 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process | |
| | Design References | 128 |
| 7.2 | Caprolactam by Hydroxylamine Phosphate Oxime Process | |
| | Design Bases and Assumptions | 129 |
| 7.3 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process | |
| | Stream Flows | 137 |
| 7.4 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process | |
| | Major Equipment | 145 |
| 7.5 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process | |
| | Utilities Summary | 150 |
| 7.6 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process | |
| | Total Capital Investment | 154 |
| 7.7 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process | |
| | Capital Investment by Section | 155 |
| 7.8 | Caprolactam from Phenol by Hydroxylamine Phosphate Oxime Process | |
| | Production Costs | 157 |
| 7.9 | Caprolactam from Cyclohexane by Hydroxylamine Phosphate Oxime Process | |
| | Total Capital Investment | 159 |
| 7.10 | Caprolactam from Cyclohexane by Hydroxylamine Phosphate Oxime Process | |
| | Production Costs | 160 |

TABLES

| | | |
|------|--|-----|
| 8.1 | Caprolactam from Toluene Via Cyclohexane Carboxylic Acid Design Bases and Assumptions | 166 |
| 8.2 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Stream Flows | 171 |
| 8.3 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Major Equipment | 176 |
| 8.4 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Utilities Summary | 182 |
| 8.5 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Total Capital Investment | 185 |
| 8.6 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Capital Investment by Section | 186 |
| 8.7 | Caprolactam from Toluene via Cyclohexane Carboxylic Acid Production Costs | 188 |
| 9.1 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Design Bases and Assumptions | 194 |
| 9.2 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Stream Flows | 197 |
| 9.3 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Major Equipment | 198 |
| 9.4 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Utilities Summary | 200 |
| 9.5 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Total Capital Investment | 203 |
| 9.6 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Capital Investment by Section | 204 |
| 9.7 | Continuous Production of Nylon 6 Polymer Melt for Direct Spinning Production Costs | 205 |
| 9.8 | Continuous Production of Nylon 6 Polymer Chips Design Bases and Assumptions | 210 |
| 9.9 | Continuous Production of Nylon 6 Chip Stream Flows | 212 |
| 9.10 | Continuous Production of Nylon 6 Chip Major Equipment | 214 |

TABLES

| | | |
|-------------|--|------------|
| 9.11 | Continuous Production of Nylon 6 Chip | |
| | Utilities Summary | 217 |
| 9.12 | Continuous Production of Nylon 6 Chip | |
| | Total Capital Investment | 220 |
| 9.13 | Continuous Production of Nylon 6 Chip | |
| | Capital Investment by Section | 221 |
| 9.14 | Continuous Production of Nylon 6 Chip | |
| | Production Costs | 222 |