

Abstract
Process Economics Program Report 35D
BUTADIENE AS A CHEMICAL RAW MATERIAL
(September 1998)

The dominant technology for producing butadiene (BD) is the cracking of naphtha to produce ethylene. BD is obtained as a coproduct. As the growth of ethylene production outpaced the growth of BD demand, an oversupply of BD has been created. This situation provides the incentive for developing technologies with BD as the starting material. The objective of this report is to evaluate the economics of BD-based routes and to compare the economics with those of currently commercial technologies. In addition, this report addresses commercial aspects of the butadiene industry such as supply/demand, BD surplus, price projections, pricing history, and BD value in nonchemical applications.

We present process economics for two technologies:

- Cyclodimerization of BD leading to ethylbenzene (DSM-Chiyoda)
- Hydrocyanation of BD leading to caprolactam (BASF).

Furthermore, we present updated economics for technologies evaluated earlier by PEP:

- Cyclodimerization of BD leading to styrene (Dow)
- Carboalkoxylation of BD leading to caprolactam and to adipic acid
- Hydrocyanation of BD leading to hexamethylenediamine.

We also present a comparison of the DSM-Chiyoda and Dow technologies for producing styrene. The Dow technology produces styrene directly and is limited in terms of capacity by the BD available from a world-scale naphtha cracker. The 250 million lb/yr (113,000 t/yr) capacity selected for the Dow technology requires the BD output of two world-scale naphtha crackers. The DSM-Chiyoda technology produces ethylbenzene. In our evaluations, we assumed a scheme whereby ethylbenzene from a 266 million lb/yr (121,000 t/yr) DSM-Chiyoda unit is combined with 798 million lb/yr (362,000 t/yr) of ethylbenzene produced by conventional alkylation of benzene with ethylene. The combined ethylbenzene stream is then dehydrogenated to styrene in a Fina/Badger unit of 1,000 million lb/yr (454,000 t/yr) capacity.

GLOSSARY

Symbol or Term	Definition
ABS	Acrylonitrile-butadiene-styrene
ACN	6-Aminocapronitrile
ADA	Adipic acid
ADN	Adiponitrile
BD	Butadiene
BDO	Butanediol
BLI	Battery limits
CAPM	Caprolactam
COD	1,5-Cyclooctadiene
DMF	Dimethyl formamide
DMN	Dimethyl naphthalene
DMT	Dimethyl terephthalate
EB	Ethylbenzene
ECH	Ethylcyclohexane
EPB	3,4-Epoxy-1-butene
HCN	Hydrocyanic acid
HMDA	Hexamethylenediamine
HMI	Hexamethyleneimine
2M2BN	2-Methyl-2-butenenitrile
2M3BN	2-Methyl-3-butenenitrile
M2P	Methyl-2-pentenoate
M3P	Methyl-3-pentenoate
M4P	Methyl-4-pentenoate
M5FV	Methyl 5-formylvalerate
M6AC	Methyl 6-aminocaproate
MBN	Methyl butenenitrile
NDA	Naphthalenedicarboxylic acid

GLOSSARY (Concluded)

Symbol or Term	Definition
PBR	Polybutadiene rubber
PEN	Polyethylene naphthalate
PN	Pentenenitrile
Ra-Co	Raney cobalt
Ra-Ni	Raney nickel
ROI	Return on investment
SB	Styrene-butadiene
SBR	Styrene-butadiene rubber
TFC	Total fixed capital
THA	Tetrahydroazepine
THF	Tetrahydrofuran
TPB	Triphenylborane
VCH	Vinylcyclohexene

CONTENTS

GLOSSARY.....	xiii
1 INTRODUCTION.....	1-1
2 SUMMARY.....	2-1
INDUSTRY ASPECTS.....	2-1
Butadiene demand.....	2-1
Butadiene Supply.....	2-4
Supply/Demand Balance.....	2-5
Pricing History.....	2-7
Projected Butadiene Prices and Values.....	2-10
Future Butadiene Prices in the United States.....	2-11
Ethylene-Based Price Projections.....	2-11
Value-Based Price Projections.....	2-12
TECHNICAL ASPECTS.....	2-15
Ethylbenzene and Styrene.....	2-15
Caprolactam.....	2-17
Hexamethylenediamine.....	2-20
Adipic Acid.....	2-21
3 BUTADIENE SUPPLY/DEMAND.....	3-1
BUTADIENE SOURCES.....	3-1
GLOBAL BUTADIENE DEMAND.....	3-2
REGIONAL BUTADIENE DEMAND.....	3-5
BUTADIENE SUPPLY.....	3-7
SUPPLY/DEMAND CONSIDERATIONS.....	3-10
4 BUTADIENE PRICING HISTORY.....	4-1

CONTENTS (Continued)

5	BUTADIENE VALUES AND FUTURE PRICES.....	5-1
	BUTADIENE VALUES.....	5-1
	FUTURE BUTADIENE PRICES IN THE UNITED STATES.....	5-6
	Option 1: Ethylene-Based Price Projections.....	5-6
	Option 2: Value-Based Price Projections.....	5-8
6	CHEMISTRY.....	6-1
	CYCLODIMERIZATION OF BUTADIENE TO ETHYLBENZENE OR STYRENE.....	6-1
	ACETOXYLATION OF BUTADIENE TO BUTANEDIOL AND TETRAHYDROFURAN.....	6-3
	HYDROCYANATION OF BUTADIENE TO CAPROLACTAM AND/OR HEXAMETHYLENEDIAMINE.....	6-4
	Hydrocyanation to Pentene- and Butenenitriles.....	6-4
	Hydrocyanation of 4-Pentenenitrile to Adiponitrile.....	6-5
	Hydrogenation of Adiponitrile to HMDA.....	6-6
	Partial Hydrogenation of Adiponitrile to HMDA and 6-Aminocapronitrile.....	6-6
	Cyclization of 6-Aminocapronitrile to Caprolactam.....	6-6
	CARBOALKOXYLATION OF BUTADIENE TO EITHER CAPROLACTAM OR ADIPIIC ACID.....	6-7
	Carboalkoxylation of Butadiene.....	6-7
	Isomerization of Methyl 3-Pentenoate.....	6-8
	Carobalkoxylation of Methyl 3-Pentenoate.....	6-8
	Hydrolysis of Dimethyl Adipate to Adipic Acid.....	6-8
	Hydroformylation of Methyl 4-Pentenoate to Formylvalerate.....	6-9
	Reductive Amination of M5FV to Methyl 6-Aminocaproate.....	6-9
	Cyclization of Methyl 6-Aminocaproate to Caprolactam.....	6-9
	ALKENYLATION OF o-XYLENE WITH BUTADIENE LEADING TO DIMETHYL NAPHTHALENE.....	6-9

CONTENTS (Continued)

7	STYRENE FROM BUTADIENE.....	7-1
	PROCESS REVIEW.....	7-1
	Cyclodimerization of 1,3-Butadiene.....	7-2
	DSM-Chiyoda Butadiene Dimerization Process.....	7-2
	Dow Chemical Butadiene Dimerization Process.....	7-3
	Dehydrogenation of 4-Vinylcyclohexene to Ethylbenzene.....	7-3
	Oxidative Dehydrogenation of 4-Vinylcyclohexene to Ethylbenzene.....	7-5
	PROCESS DESCRIPTION.....	7-5
	BD Dimerization (Section 100).....	7-8
	VCH Dehydrogenation (Section 200).....	7-8
	PROCESS DISCUSSION.....	7-15
	Design Basis.....	7-15
	BD Dimerization (Section 100).....	7-15
	VCH Dehydrogenation (Section 200).....	7-16
	Materials of Construction.....	7-18
	Waste Streams.....	7-18
	COST ESTIMATES.....	7-19
	COMPARISON OF STYRENE ECONOMICS.....	7-19
8	CAPROLACTAM BY HYDROCYANATION OF BUTADIENE.....	8-1
	PROCESS REVIEW.....	8-1
	Selective Partial Hydrogenation of Adiponitrile.....	8-2
	Raney Nickel and Raney Cobalt Catalysts.....	8-2
	Ruthenium Complex Catalysts.....	8-3
	BASF Gas-Phase Processes.....	8-3
	BASF Liquid-Phase Processes.....	8-4
	Recovery of ACN, HMDA, and ADN.....	8-4

CONTENTS (Continued)

PROCESS REVIEW (Concluded)	
Cyclization of ACN.....	8-4
Purification of Caprolactam.....	8-5
PROCESS DESCRIPTION.....	8-5
ACN Production (Section 100).....	8-9
Caprolactam Production (Section 200).....	8-9
PROCESS DISCUSSION.....	8-22
Design Basis.....	8-22
ACN Production (Section 100).....	8-22
Caprolactam Production (Section 200).....	8-22
Waste Streams.....	8-22
COST ESTIMATES.....	8-24
COMPARISON OF CAPROLACTAM ECONOMICS.....	8-25
9 CAPROLACTAM BY CARBOALKOXYLATION OF BUTADIENE.....	9-1
PROCESS REVIEW.....	9-1
Carboalkoxylation and Isomerization.....	9-1
Hydroformylation.....	9-2
Reductive Amination and Cyclization.....	9-2
PROCESS DESCRIPTION.....	9-3
Carboalkoxylation (Section 100).....	9-7
Isomerization and Hydroformylation (Section 200).....	9-7
Reductive Amination (Section 300).....	9-8
Cyclization (Section 400).....	9-8
PROCESS ECONOMICS.....	9-8

CONTENTS (Concluded)

10	HEXAMETHYLENEDIAMINE FROM BUTADIENE VIA ADIPONITRILE BY HYDROCYANATION.....	10-1
	PROCESS DESCRIPTION.....	10-1
	Butadiene Hydrocyanation to Pentenenitrile (Section 100).....	10-1
	2M3BN Isomerization to Pentenenitrile (Section 200).....	10-1
	Pentenenitrile Hydrocyanation to Adiponitrile (Section 300).....	10-3
	Adiponitrile Purification (Section 400).....	10-4
	Catalyst Regeneration (Section 500).....	10-4
	Adiponitrile Hydrogenation (Section 600).....	10-4
	PROCESS ECONOMICS.....	10-5
11	ADIPIIC ACID FROM BUTADIENE BY CARBOALKOXYLATION.....	11-1
	PROCESS DESCRIPTION.....	11-1
	Catalyst Reduction (Section 100).....	11-1
	Carboalkoxylation (Section 200).....	11-1
	Catalyst Oxidation (Section 300).....	11-3
	Dimethyl Adipate Recovery (Section 400).....	11-4
	Hydrolysis and Crystallization (Section 500).....	11-4
	PROCESS ECONOMICS.....	11-5
	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

2.1	Regional Butadiene Demand.....	2-3
2.2	Growth Rates for Regional Butadiene Demand.....	2-4
2.3	Global Butadiene Surplus.....	2-6
2.4	Butadiene Surplus By Region.....	2-7
2.5	U.S. Butadiene/Ethylene Price Ratio History, 1970–1995.....	2-8
2.6	U.S. Butadiene and Ethylene Prices, 1994–1997.....	2-9
2.7	U.S. Butadiene/Ethylene Price Ratio History, 1994–1997.....	2-10
2.8	Butadiene Prices in the United States—Ethylene-Based Projections.....	2-12
2.9	Butadiene Prices Based on Butane Values.....	2-13
2.10	Butadiene Prices Based on Butene Values.....	2-14
2.11	Summary of Projected BD Prices.....	2-15
2.12	Styrene from Butadiene—Process Comparisons.....	2-16
3.1	Regional Butadiene Demand.....	3-6
3.2	Growth Rates for Regional Butadiene Demand.....	3-7
3.3	Regional Butadiene Supply.....	3-9
3.4	Increases in Butadiene Supply, 1996–2000.....	3-10
3.5	Global Butadiene Surplus.....	3-11
3.6	Global Butadiene Capacity Utilization.....	3-12
3.7	Butadiene Surplus by Region.....	3-13
4.1	U.S. Butadiene and Ethylene Prices, 1970–1995.....	4-2
4.2	U.S. Butadiene/Ethylene Price Ratio History, 1970–1995.....	4-3
4.3	U.S. Butadiene and Ethylene Prices, 1994–1997.....	4-4
4.4	U.S. Butadiene/Ethylene Price Ratio History, 1994–1997.....	4-5
4.5	U.S. and European Butadiene Prices, 1994–1997.....	4-6
4.6	U.S./European Butadiene Price Ratios, 1994–1997.....	4-7
4.7	U.S. and Korean Butadiene Prices, 1994–1997.....	4-8
4.8	Butadiene Price Deltas Relative to U.S. Prices.....	4-9
5.1	Valuation Scheme for Butadiene as Alkylation Feed.....	5-2
5.2	Value of Butadiene in Alkylate.....	5-5
5.3	Butadiene Prices in the United States—Ethylene-Based Projections.....	5-8
5.4	Value-Based Projection Scheme.....	5-9
5.5	Butadiene Prices Based on Butane Values.....	5-9

ILLUSTRATIONS (Concluded)

5.6	Butadiene Prices Based on Butene Values.....	5-10
5.7	Projected U.S. Butadiene Prices.....	5-11
5.8	Value of Extracted Butadiene in Korea.....	5-12
6.1	Cyclodimerization of Butadiene.....	6-2
6.2	Acetoxylation of Butadiene.....	6-3
6.3	Hydrocyanation of Butadiene.....	6-4
6.4	Carboxylation of Butadiene.....	6-8
6.5	Alkenylation of o-Xylene with Butadiene.....	6-11
7.1	Styrene from Butadiene—Process Comparisons.....	7-1
7.2	Ethylbenzene from Butadiene by DSM-Chiyoda Process.....	E-3
7.3	Ethylbenzene from Butadiene by DSM-Chiyoda Process Net Production Cost or Product Value as a Function of Butadiene Price.....	7-34
8.1	Caprolactam by Hydrocyanation of Butadiene—Process Flow.....	8-1
8.2	Caprolactam from Adiponitrile by Partial Hydrogenation and 6-Aminocapronitrile Cyclization.....	E-5
8.3	Caprolactam by Hydrocyanation of Butadiene Effect of Operating Level and Plant Capacity on Product Value.....	8-37
8.4	Caprolactam by Hydrocyanation of Butadiene Net Production Cost or Product Value as a Function of Butadiene Price.....	8-38
9.1	Caprolactam by Carboalkoxylation of Butadiene.....	E-7
9.2	Caprolactam by Carboalkoxylation of Butadiene Net Production Cost or Product Value as a Function of Butadiene Price.....	9-12
10.1	HMDA from Butadiene via Adiponitrile by Hydrocyanation.....	E-11
10.2	HMDA from Butadiene via Adiponitrile by Hydrocyanation Net Production Cost or Product Value as a Function of Butadiene Price.....	10-8
11-1	Adipic Acid from Butadiene by Carboalkoxylation.....	E-15
11-2	Adipic Acid from Butadiene by Carboalkoxylation Net Production Cost or Product Value as a Function of Butadiene Price.....	11-9

TABLES

2.1	Regional Butadiene Demand.....	2-2
2.2	Regional Butadiene Supply.....	2-5
2.3	Projected Values for Butadiene.....	2-11
2.4	Ethylbenzene from Butadiene or from Benzene and Ethylene Summary of Economics.....	2-18
2.5	Styrene from Butadiene or from Benzene and Ethylene Summary of Economics.....	2-19
2.6	Caprolactam from Cyclohexane or from Butadiene Summary of Economics.....	2-20
2.7	HMDA from Butadiene via Adiponitrile by Hydrocyanation Summary of Economics.....	2-22
2.8	Adipic Acid from Cyclohexane or from Butadiene Summary of Economics.....	2-23
3.1	Yields of Butadiene in Ethylene Plants.....	3-1
3.2	Global Butadiene Demand by End Use.....	3-2
3.3	Share of Butadiene Demand by Major End Use.....	3-3
3.4	Butadiene-Based Adiponitrile Plants.....	3-4
3.5	Butadiene-Based Butanediol Plants.....	3-4
3.6	Regional Butadiene Demand.....	3-5
3.7	Regional Butadiene Supply.....	3-8
5.1	Input Values for Butadiene Valuation.....	5-3
5.2	Value of Butadiene in Alkylate.....	5-4
5.3	Value of Butadiene as Butane.....	5-6
5.4	Butadiene Prices in the United States—Ethylene-Based Projections.....	5-7
7.1	Cyclodimerization of Butadiene to 4-Vinylcyclohexene Patent Summary.....	A-3
7.2	Dehydrogenation of 4-Vinylcyclohexene to Ethylbenzene Patent Summary.....	A-9
7.3	Oxidative Dehydrogenation of 4-Vinylcyclohexene to Styrene Patent Summary.....	A-13
7.4	Ethylbenzene from Butadiene by DSM-Chiyoda Process Design Basis and Assumptions.....	7-6
7.5	Ethylbenzene from Butadiene by DSM-Chiyoda Process Stream Flows.....	7-10
7.6	Ethylbenzene from Butadiene by DSM-Chiyoda Process Major Equipment.....	7-12

TABLES (Continued)

7.7	Ethylbenzene from Butadiene by DSM-Chiyoda Process Utilities Summary.....	7-14
7.8	Ethylbenzene from Butadiene by DSM-Chiyoda Process Comparison of Dow and DSM-Chiyoda BD Dimerization Processes.....	7-16
7.9	Ethylbenzene from Butadiene by DSM-Chiyoda Process Comparison of DSM-Chiyoda VCH Dehydrogenation and Dow VCH Oxi-Dehydrogenation Processes.....	7-17
7.10	Ethylbenzene from Butadiene by DSM-Chiyoda Process Waste Streams Summary.....	7-18
7.11	Ethylbenzene from Butadiene by DSM-Chiyoda Process Total Capital Investment.....	7-21
7.12	Ethylbenzene from Butadiene by DSM-Chiyoda Process Capital Investment by Section.....	7-22
7.13	Ethylbenzene from Butadiene by DSM-Chiyoda Process Production Costs.....	7-23
7.14	Ethylbenzene from Butadiene by DSM-Chiyoda Process Direct Costs by Section.....	7-25
7.15	Ethylbenzene from Benzene and Ethylene by Vapor-Phase Alkylation: Third Generation Production Costs.....	7-26
7.16	Ethylbenzene from Butadiene or from Benzene and Ethylene Comparison of Economics.....	7-28
7.17	Styrene from Butadiene via 4-Vinylcyclohexane by the Dow Process Production Costs.....	7-29
7.18	Styrene from Ethylbenzene by Adiabatic Dehydrogenation: Two Reactors with Interstage Reheat Production Costs.....	7-31
7.19	Styrene from Butadiene or from Benzene and Ethylene Comparison of Economics.....	7-33
8.1	6-Aminocapronitrile by Selective Partial Hydrogenation of Adiponitrile Patent Summary.....	A-16
8.2	Caprolactam by Cyclization of 6-Aminocapronitrile Patent Summary.....	A-19
8.3	Caprolactam from Adiponitrile by Partial Hydrogenation and 6-Aminocapronitrile Cyclization Design Bases and Assumptions.....	8-7
8.4	Caprolactam from Adiponitrile by Partial Hydrogenation and 6-Aminocapronitrile Cyclization Stream Flows.....	8-11

TABLES (Concluded)

8.5	Caprolactam from Adiponitrile by Partial Hydrogenation and 6-Aminocapronitrile Cyclization Major Equipment.....	8-17
8.6	Caprolactam from Adiponitrile By Partial Hydrogenation and 6-Aminocapronitrile Cyclization Utilities Summary.....	8-21
8.7	Caprolactam from Adiponitrile by Partialhydrogenation and 6-Aminocapronitrile Cyclization Waste Streams Summary.....	8-23
8.8	Caprolactam from Adiponitrile by Partial Hydrogenation and 6-Aminocapronitrile Cyclization Total Capital Investment.....	8-26
8.9	Caprolactam from Adiponitrile by Partial Hydrogenation and 6-Aminocapronitrile Cyclization Capital Investment by Section.....	8-27
8.10	Caprolactam from Adiponitrile by Partial Hydrogenation and 6-Aminocapronitrile Cyclization Production Costs.....	8-28
8.11	Adiponitrile from Butadiene by Hydrocyanation Production Costs.....	8-30
8.12	Caprolactam from Butadiene in an Integrated Facility Production Costs.....	8-32
8.13	Caprolactam from Cyclohexane with Nitric Oxide Hydrogenation Production Costs.....	8-34
8.14	Caprolactam from Cyclohexane or from Butadiene Summary of Economics.....	8-36
9.1	Caprolactam by Carboalkoxylation of Butadiene Design Bases and Assumptions.....	9-4
9.2	Caprolactam by Carboalkoxylation of Butadiene Production Costs.....	9-10
10.1	HMDA from Butadiene via Adiponitrile by Hydrocyanation Design Bases and Assumptions.....	10-2
10.2	HMDA from Butadiene via Adiponitrile by Hydrocyanation Production Costs.....	10-6
11.1	Adipic Acid from Butadiene by Carboalkoxylation Design Bases and Assumptions.....	11-2
11.2	Adipic Acid from Butadiene by Carboalkoxylation Production Costs.....	11-6
11.3	Adipic Acid from Cyclohexane or from Butadiene Summary of Economics.....	11-8