

Abstract
Process Economics Program Report 35E
ON-PURPOSE BUTADIENE PRODUCTION
(December 2012)

1,3-Butadiene is currently almost entirely produced as a by-product of ethylene steam cracking of naphtha or gas oil feedstocks. A switch to lighter feedstocks has reduced the amount of butadiene available from ethylene cracking and presented a foreseeable market demand for on-purpose butadiene. The small amount of butadiene produced during steam cracking of light feedstocks is not economically recoverable.

The demand for 1,3-butadiene continues to grow driven primarily by the development of demand in the emerging markets, especially for motor vehicle tires. As a result of the decreasing trend in supply and the growth trend in demand, the price of butadiene has risen significantly and been volatile. Today there is growing interest in producing butadiene from renewable resources. These conditions have renewed interest in on-purpose butadiene production.

In this PEP Report, we first extensively review proven or potential technologies for producing 1,3-butadiene, whether commercial or in the research or development stage such as processing renewable feedstocks. Emphasis is on developments since 1990 for n-butane and mixed butenes feedstocks.

The process economics are then developed in this PEP Report for producing 100,000 mt/year of 1,3-butadiene by two currently commercially successful processes: n-butane dehydrogenation and mixed butenes oxidative dehydrogenation. We also develop the process economics for our version of the American Process, a two-stage ethanol to butadiene process developed by Carbide and Carbon Chemicals Corporation in the 1940s. These three processes have demonstrated the most commercial success.



A private report by the
**Process Economics
Program**

Report No. 35E

ON-PURPOSE BUTADIENE PRODUCTION

by Richard H. Nielsen

December 2012

Santa Clara, California 95054



IHS Chemical agrees to assign professionally qualified personnel to the preparation of the Process Economics Program's reports and will perform the work in conformance with generally accepted professional standards. No other warranties expressed or implied are made. Because the reports are of an advisory nature, neither IHS Chemical nor its employees will assume any liability for the special or consequential damages arising from the Client's use of the results contained in the reports. The Client agrees to indemnify, defend, and hold IHS Chemical, its officers, and employees harmless from any liability to any third party resulting directly or indirectly from the Client's use of the reports or other deliverables produced by IHS Chemical pursuant to this agreement.

For detailed marketing data and information, the reader is referred to one of the IHS Chemical programs specializing in marketing research. THE IHS CHEMICAL ECONOMICS HANDBOOK Program covers most major chemicals and chemical products produced throughout the world. In addition the IHS DIRECTORY OF CHEMICAL PRODUCERS services provide detailed lists of chemical producers by company, product, and plant for the United States, Europe, East Asia, China, India, South & Central America, the Middle East & Africa, Canada, and Mexico.

CONTENTS

1	INTRODUCTION	1-1
2	CONCLUSION	2-1
3	SUMMARY	3-1
	COMMERCIAL ASPECTS	3-1
	TECHNOLOGY	3-2
	PROCESS ECONOMICS.....	3-4
4	INDUSTRY STATUS	4-1
	USES	4-2
	DEMAND	4-3
	SUPPLY.....	4-8
	Northeast Asia	4-13
	North America.....	4-13
	Europe	4-14
	Commonwealth of Independent States and Baltic States	4-14
	Southeast Asia	4-15
	Middle East.....	4-15
	South America	4-15
	Indian Subcontinent.....	4-15
	Africa.....	4-15
	On-Purpose Production	4-15
	PRICES	4-16
	Feedstock	4-16
	Butadiene.....	4-18
	HANDLING	4-21
	SPECIFICATIONS.....	4-21
	Mixed C ₄ Streams.....	4-21
	1,3-Butadiene	4-22
	PLANT CAPACITY	4-24
	NEW CAPACITY	4-31

CONTENTS (Continued)

5	CHEMISTRY REVIEW	5-1
	BUTADIENE REACTIVITY AND INSTABILITY	5-1
	Inhibitors	5-1
	Polymerization	5-2
	Material of Construction.....	5-3
	DEHYDROGENATION REACTION	5-4
	n-Butane Dehydrogenation Mechanism with Ga-ZSM-5.....	5-6
	t-2-Butene Dehydrogenation Mechanism on Pd(110).....	5-10
	Oxidative Dehydrogenation	5-11
	DEHYDROGENATION REACTION EQUILIBRIUM AND KINETICS	5-12
	DEHYDROGENATION CATALYSIS	5-17
	Adsorption on Pt(111).....	5-17
	Catalysts	5-17
	Bismuth Molybdenum Catalysts	5-23
	Ferrite Catalysts	5-24
	Pyrophosphate Catalysts.....	5-25
	Vanadium Catalysts.....	5-25
	Precious Metal Catalysts	5-27
	Carbon	5-28
	Other Catalysts.....	5-28
	CRUDE BUTADIENE COMPOSITION	5-29
	BIO-ETHANOL COMPOSITION.....	5-30
	ETHANOL TO BUTADIENE	5-31
6	PROCESS REVIEW.....	6-1
	BUTANE OR BUTENE-BASED PROCESSES	6-2
	Dehydrogenation to Butadiene	6-2
	Houdry (Catadiene)	6-3
	Dow.....	6-5
	Shell.....	6-6
	Phillips Butane Dehydrogenation	6-6
	Phillips Butene Dehydrogenation	6-7
	Dehydrogenation to n-Butenes.....	6-8

CONTENTS (Continued)

Snamprogetti-Yarsintez	6-8
Snamprogetti	6-9
Linde-BASF	6-9
Uhde STAR.....	6-10
UOP Oleflex.....	6-11
Selective Hydrogen Combustion	6-12
Uhde	6-13
Sunoco, Inc. (R&M)	6-13
Oxidative Dehydrogenation	6-13
Petro-Tex Oxo-D	6-14
Phillips O-X-D	6-15
SK Energy.....	6-16
Mitsubishi.....	6-18
Catalysts	6-18
Process	6-19
Plate Reactor	6-19
Start-up	6-19
Suppression of Polymerization	6-19
BP	6-20
Nippon Zeon	6-20
Saipem, S.p.A.....	6-20
Oxidative-Halo-Dehydrogenation	6-20
Comparison of Dehydrogenation Processes.....	6-21
RENEWABLE FEEDSTOCK-BASED	6-25
Ethanol-Based	6-26
American Process	6-26
Lebedev Process.....	6-29
Bifunctional Catalyst Processes	6-30
Butanol-Based	6-30
Acetylene-Based	6-31
Four-Step (Aldol) Process	6-31
Reppe Process	6-31
OTHER R&D STAGE PROCESSES.....	6-31
Membrane Processes.....	6-31
Monolith Catalyst Process.....	6-32

CONTENTS (Continued)

Rapid Pressure Swing Reaction Process.....	6-32
Radiation Assisted.....	6-32
PROCESS PATENTS	6-32
7 BUTANE DEHYDROGENATION PROCESS ECONOMICS	7-1
PROCESS DESCRIPTION	7-1
PROCESS DISCUSSION.....	7-11
Feed Composition	7-11
Reactors	7-11
Downstream	7-12
Emissions	7-13
COST ESTIMATES	7-13
Capital Cost	7-13
Production Costs	7-17
8 OXIDATIVE DEHYDROGENATION PROCESS	8-1
PROCESS DESCRIPTION	8-1
PROCESS DISCUSSION.....	8-13
Feedstock	8-13
Reactor	8-14
Downstream	8-14
Product	8-14
Emissions	8-15
COST ESTIMATES	8-15
Capital Cost	8-15
Production Costs	8-18
9 BUTADIENE EXTRACTION	9-1
DESCRIPTION	9-1
DISCUSSION	9-10
COST ESTIMATES	9-10
Capital Cost	9-10
Production Costs	9-14

CONTENTS (Concluded)

10 ETHANOL TO BUTADIENE PROCESS	10-1
DESCRIPTION	10-1
Section 100.....	10-11
Section 200.....	10-11
DISCUSSION	10-12
COST ESTIMATES	10-13
Capital Cost.....	10-13
Production Costs	10-17
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

FIGURES

1.1	Typical Steam Cracker C ₄ Flow to Produce Crude Butadiene	1-1
1.2	Typical Extractive Distillation Butadiene Recovery from Crude C ₄ s and Purification	1-2
4.1	2011 Worldwide Butadiene Uses	4-2
4.2	2011 North American Butadiene Uses	4-3
4.3	Butadiene Demand by Region.....	4-4
4.4	US Butadiene Supply and Demand.....	4-6
4.5	Global Consumption Growth 2010–2025 Allocated by End Use.....	4-7
4.6	Butadiene Extraction Capacity Utilization by Region	4-9
4.7	Butadiene Supply by Region	4-12
4.8	US Butadiene Production and Forecast by Feedstock	4-13
4.9	On-Purpose Butadiene Production.....	4-16
4.10	Crude C ₄ Price History by Region	4-17
4.11	Butadiene Spot Price History by Region	4-19
4.12	US Gulf Coast Butadiene and Butane Price History	4-20
4.13	Distribution of Worldwide Butadiene Extraction Plant Capacity	4-30
5.1	Reaction Network for Non-Oxidative Dehydrogenation of n-Butane.....	5-5
5.2	Equilibrium Conversion of Light Alkanes at 1 Atmosphere	5-5
5.3	Three-Step Mechanism for Dehydrogenation of n-Butane to 1-Butene.....	5-7
5.4	Reaction Energy Profile for Dehydrogenation of n-Butane by the Three-Step Mechanism (Channel 1 = 1-Butene, Channel 2 = 2-Butene)	5-8
5.5	Three-Step Mechanism for Dehydrogenation of n-Butane to 2-Butene.....	5-9
5.6	Energy Profile of t-2-Butene Dehydrogenation on the Pd(110) Surface	5-11
5.7	Oxidative Dehydrogenation of n-Butane Reaction Scheme.....	5-12
6.1	Simplified Houdry Process	6-4
6.2	Lummus Catadiene Process Schematic	6-5
6.3	Phillips Two-Stage Butane Dehydrogenation Process.....	6-7
6.4	Snamprogetti Fluid Bed Process.....	6-9
6.5	Phillips Star Process.....	6-10
6.6	UOP Oleflex Process.....	6-11
6.7	UOP Oleflex Catalyst Regeneration.....	6-12
6.8	Petro-Tex (TPC) Oxo-D Simplified Process	6-15
6.9	Phillips O-X-D Simplified Flowsheet.....	6-16

FIGURES (Concluded)

6.10	American Process for Butadiene from Ethanol	6-27
7.1	Butane Dehydrogenation Process Process Flow Diagram	E-3
8.1	Oxidative Dehydrogenation of Butenes by Petro-Tex Oxo-D Process Process Flow Diagram	E-7
9.1	Butadiene Extraction by BASF NMP Process Process Flow Diagram	E-9
10.1	Ethanol to 1,3-Butadiene by Two-Stage American Process Process Flow Diagram	E-11

TABLES

1.1	Butadiene Content from Steam Cracking Various Feedstocks	1-2
3.1	Comparison of Oxidative and Non-Oxidative Dehydrogenation.....	3-3
3.2	Summary of Process Economics for Making 100,000 MT/Year 1,3-Butadiene	3-6
4.1	Total Global Butadiene Demand Summary by Region, 2006–2016	4-5
4.2	Regional Forecast Consumption Growth Rates of 1,3-Butadiene, 2010–2025	4-8
4.3	US Ethylene Fresh Feed Slate—Second Half 2011	4-9
4.4	Distribution of Butadiene Plant Capacity	4-10
4.5	Expansion of Butadiene Capacity from 2009 to 2019	4-11
4.6	Total Global Butadiene Supply Summary by Region, 2006–2016	4-12
4.7	Fuel Ethanol Quarterly Average Price since 2000	4-18
4.8	Typical Composition Ranges for Low 1,3-Butadiene C ₄ Streams	4-22
4.9	Raffinate-3 Sales Specification.....	4-22
4.10	Example of a 1,3-Butadiene Product Specification	4-23
4.11	Typical Specifications of Butadiene.....	4-24
4.12	World Capacity of Butadiene C ₄ Extraction Plants	4-25
4.13	World Capacity of on-Purpose Butadiene Plants	4-31
4.14	Announced Butadiene Plant Capacity Additions	4-32
5.1	Butadiene Dimerization Rate as a Function of Temperature	5-2
5.2	Some Chemical Incompatibilities with Butadiene and Potential Outcome	5-4
5.3	Conversion of n-Butene Isomers Depends upon the Catalyst	5-12
5.4	Reaction Equilibrium of n-Butane, Butenes, and Butadiene	5-13
5.5	Chemical Reactions and Rate Constants for the Oxidative Dehydrogenation of n-Butane to Butene and Butadiene	5-15
5.6	Rates of Formation Equations	5-16
5.7	Non-Oxidative Dehydrogenation Catalysts	5-18
5.8	Oxidative Dehydrogenation Catalysts	5-19
5.9	Patents on Catalysts for Production of Butenes.....	5-22
5.10	Oxydehydrogenation Catalyst Patents	5-22
5.11	Dehydrogenation/Other Catalyst Patents.....	5-23
5.12	Example Crude Butadiene Stream Analysis	5-29
5.13	Normal Boiling Points of C ₄ Hydrocarbons.....	5-30
5.14	Binary Azeotropes of 1,3-Butadiene and of Other C ₄ Hydrocarbons	5-30

TABLES (Continued)

5.15	Composition of Corn Derived Fuel Ethanol	5-31
6.1	Typical Raw C ₄ Refinery Fraction Composition	6-2
6.2	Butene Dehydrogenation Catalyst Performance	6-8
6.3	Dual-Bed Technology Improves Conversion of n-Butene Isomers	6-17
6.4	Characterization of an Early Mobifesi Composite Catalyst	6-18
6.5	Comparison of Non-Oxidative Dehydrogenation Processes	6-21
6.6	Comparison of Oxidative and Non-Oxidative Dehydrogenation Processes	6-22
6.7	Comparison of Oxidative Dehydrogenation Processes	6-23
6.8	Comparison of n-Butene Processes	6-24
6.9	American Process Plant Product Selectivities	6-29
6.10	Process Patents	6-33
6.11	Separation/Purification Patents	6-34
7.1	Design Basis and Assumptions	7-2
7.2	1,3-Butadiene by Butane Dehydrogenation Process Stream Flows	7-4
7.3	1,3-Butadiene by Butane Dehydrogenation Process Major Equipment	7-7
7.4	1,3-Butadiene by Butane Dehydrogenation Process Utilities Summary	7-9
7.5	Chrome-Alumina Catalyst Typical Properties	7-12
7.6	1,3-Butadiene by Butane Dehydrogenation Process Total Capital Investment	7-14
7.7	1,3-Butadiene by Butane Dehydrogenation Process Capital Investment by Section	7-16
7.8	1,3-Butadiene by Butane Dehydrogenation Process Production Costs	7-18
7.9	Effect of Feedstock Cost on Product Value	7-20
8.1	Design basis and assumptions	8-2
8.2	Fresh C ₄ Feedstock Composition	8-3
8.3	1,3-Butadiene by Oxidative Dehydrogenation Stream Flows	8-4
8.4	1,3-Butadiene by Oxidative Dehydrogenation Major Equipment	8-9
8.5	1,3-Butadiene by Oxidative Dehydrogenation Utilities Summary	8-12

TABLES (Continued)

8.6	Maximum Fresh Feed Impurities	8-14
8.7	Crude Butadiene Composition.....	8-15
8.8	1,3-Butadiene by Oxidative Dehydrogenation Total Capital Investment.....	8-17
8.9	1,3-Butadiene by Oxidative Dehydrogenation Production Costs	8-19
8.10	Effect of Feedstock Cost on Product Value.....	8-21
9.1	Design Basis and Assumptions	9-2
9.2	Feedstock Composition	9-2
9.3	Butadiene Extraction by NMP Process Stream Flows.....	9-3
9.4	Butadiene Extraction by NMP Process Major Equipment	9-6
9.5	Butadiene Extraction by NMP Process—Oxidative Dehydrogenation Utilities Summary.....	9-8
9.6	Butadiene Extraction by NMP Process—Oxidative Dehydrogenation Total Capital Investment.....	9-11
9.7	Butadiene Extraction by NMP Process—Oxidative Dehydrogenation—Surge Tanks Total Capital Investment.....	9-13
9.8	Butadiene Extraction by NMP Process—Oxidative Dehydrogenation Production Costs	9-15
9.9	1,3-Butadiene Price Sensitivity.....	9-18
9.10	Butadiene Extraction by NMP Process—Oxidative Dehydrogenation—Surge tanks Production Costs	9-19
10.1	Design Basis and Assumptions	10-2
10.2	Ethanol to 1,3-Butadiene by Two-Stage American Process Stream Flows.....	10-3
10.3	Ethanol to 1,3-Butadiene by Two-Stage American Process Major Equipment	10-8
10.4	Ethanol to 1,3-Butadiene by Two-Stage American Process Utilities Summary.....	10-10
10.5	Ethanol to 1,3-Butadiene by Two-Stage American Process Total Capital Investment.....	10-14
10.6	Ethanol to 1,3-Butadiene by Two-Stage American Process Capital Investment by Section	10-16

TABLES (Concluded)

10.7	Ethanol to 1,3-Butadiene by Two-Stage American Process Production Costs	10-18
10.8	Ethanol to 1,3-Butadiene by Two-Stage American Process—Petrochemical Ethanol Production Costs	10-21