

IHS CHEMICAL

PEP Report 293

Iso-C₄ Processes

December 2015

ihc.com

PEP Report

Process Economics Program

Richard Nielsen
Sr. Principal Analyst

Anshuman Agrawal
Principal Analyst



PEP Report 293

Iso-C₄ Processes

Richard Nielsen, Sr. Principal Analyst

Anshuman Agrawal, Principal Analyst

Abstract

An oversupply of n-butane is anticipated in North America due to three primary trends: (1) increased natural gas liquids (NGL) production, (2) a lower percentage of n-butane being blended into gasoline, and (3) displacement of n-butane by ethane as steam cracking feedstock for ethylene production. Direct blending of butanes and butylenes into gasoline is limited by vapor pressure and olefin specifications. The surge in production of NGL from tight (shale) oil and gas formations due to the rapid growth of fracking technology for oil and gas production is producing considerably more associated ethane as well as butane. Where possible in North America, inexpensive ethane is already displacing n-butane and naphtha from the feedstock slate of existing ethylene steam crackers. New ethane cracking capacity is planned. US exports of ethane to Western Europe are starting to impact steam cracking there, too. Steam cracking ethane produces only a small amount of butylenes compared to cracking butanes and heavier feedstocks. Although tight oil production may well decline over the next one to two years or so, production is forecasted to then resume increasing.

These trends provide incentives to convert butanes (and n-butenes), mostly consumed indirectly or directly as fuel components, to more valuable products such as iso-C₄s (isobutane and isobutylene) that are intermediates for producing gasoline blending stocks and chemicals. n-Butane is isomerized to isobutane in petroleum refineries when additional isobutane is needed for alkylation. Isobutene is a polymerization feedstock for butyl rubber and polybutenes. It is also a feedstock for methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), isoprene, methacrylic acid, methacrylonitrile, and t-butyl alcohol.

In this PEP Report, we first review the developments in three processes producing on-purpose iso-C₄s— isomerization of n-butane to isobutane, dehydrogenation of isobutane to isobutylene, and isomerization of n-butenes to isobutylene. Process economics are then developed for producing iso-C₄s based on three successful commercial processes—the Butamer™ process for n-butane isomerization, the Catofin® isobutane dehydrogenation process, and the ISOMPLUS® n-butenes skeletal isomerization process.

Contents

1	Introduction	8
2	Conclusions	10
3	Summary	12
	Commercial aspects	12
	Uses	12
	Supply	13
	Demand	14
	Fuel demand	14
	Butylenes	14
	Butanes	14
	Prices	15
	Technology	15
	n-Butane isomerization	15
	Isobutane dehydrogenation	16
	N-Butenes isomerization	17
	Process economics	18
4	Industry status	21
	Uses	21
	Fuel uses	21
	Chemical uses	22
	Supply	22
	Butylenes	23
	Butanes	24
	Demand	29
	Fuel	31
	Chemical	34
	Butylenes	34
	Butanes	36
	Specifications	36
	C ₄ stream	36
	Butenes	38
	Butanes	39
	Prices	41
	Mixed C ₄ s	41
	Butanes	44
	Butenes	46
	Capacity	46
5	Chemistry	51
	Isomerization of n-butane	51
	Mechanisms	52
	Bi- and monomolecular mechanisms	53
	Dual-nature mechanism	56
	Kinetics	59
	Catalysts	59
	Catalyst deactivation	61
	Molecular sieves	61
	Mordenite	61
	ZSM-5	62
	MCM-41	62
	SAPO	63
	Sulfated zirconia	63
	Preparation	66

Water content	67
Pretreatment	67
Pt	67
Al/Ga	68
Fe/Mn	68
Hafnia	69
MCM-41 supported	69
Nanocatalyst	69
Pretreatment	70
WO _x /zirconia	70
Heteropolyacids	71
Other catalysts	72
Supercritical isomerization	72
Dehydrogenation of isobutane	73
Equilibrium	73
Mechanism	74
Catalysts	76
Chromium catalysts	76
Characterization	78
Other supports	79
Platinum catalysts	80
Deactivation	82
Other catalysts	83
Oxidative dehydrogenation	83
CO ₂ oxidative dehydrogenation	86
Kinetics	87
Coke formation kinetics	92
Oxidative dehydrogenation	92
Isomerization of n-butenes	92
Mechanism	93
Monomolecular mechanism	94
Bimolecular mechanism	95
By-products	96
Coking	96
Kinetics	97
Catalysts	98
Ferrierte	99
Tungsten oxide	103
Clays	103
Dehydroisomerization	103
6 Process review	105
Butane isomerization	105
Butamer process	105
Lummus Global process	108
Isomalk-3 SM process	108
Phillips Petroleum process	109
Shell	109
BP	109
Developmental processes	110
Dehydrogenation	110
C ₃ -C ₄ mixture	112
Catofin [®] process	112
Oleflex [™] process	113
STAR process	114
NIIMSK process	115

FBD-4 process	116
Coastal process	117
Comparison of processes	117
Catalyst regeneration	118
Developmental processes	119
Circulating fluidized bed process	120
Bimodal fluid bed process	120
Oxidative dehydrogenation	120
Membrane reactors	121
Selective hydrogen combustion	122
Combination of dehydrogenation with exothermic reaction	123
n-Butene isomerization	124
ISOMPLUS [®] process	124
UOP Butesom [™] process	125
Isofin [™]	125
IsoTex	125
ISO-4	125
7 n-Butane isomerization process economics	127
Process description	127
Process discussion	133
Cost estimates	135
Capital cost	135
Production cost	136
Profitability	140
8 Isobutane dehydrogenation process economics	141
Process description	141
Process discussion	150
Capacity	150
Feedstock	150
Reactors	150
Catalyst	152
Product	153
Regeneration	153
Environment	153
Cost estimates	153
Capital cost	154
Production costs	156
Profitability	160
9 n-Butene skeletal isomerization process economics	161
Process description	161
Process discussion	165
Cost estimates	166
Capital cost	166
Production costs	167
Profitability	171
Appendix A—Patent summary	172
Appendix B—Design and cost bases	205
Design conditions	206
Cost bases	206
Capital investment	206
Production costs	208
Effect of operating level on production costs	209
Overall estimate confidence rating	209
Appendix C—Cited references	211
Literature	212

Patents	224
IHS Publications	234
PEP Publications	234
Reports	234
Reviews	234
Yearbook	235
Appendix D—Patent references by company	236
Appendix E—Process flow diagrams	243

Figures

Figure 4.1 Butylenes production by region	23
Figure 4.2 US production of butylenes from steam cracking	24
Figure 4.3 2011 Butanes production by region and source	25
Figure 4.4 US NGL from shale gas/oil	26
Figure 4.5 US NGL production by source	27
Figure 4.6 US isobutane production	27
Figure 4.7 US n-butane production	28
Figure 4.8 US production of n-butane and isobutane purity products	29
Figure 4.9 2013 butylenes consumption by region	30
Figure 4.10 2014 butanes consumption by region	31
Figure 4.11 2013 World butylenes consumption as fuel by region, %	32
Figure 4.12 2013 World butylenes reacted to alkylate	33
Figure 4.13 Global MTBE production by region and feedstock source in 2013	34
Figure 4.14 2013 chemical demand for n-butenes	35
Figure 4.15 2013 chemical demand for isobutylene	35
Figure 4.16 Regional crude C ₄ price, 2013–14, US\$ per metric ton	42
Figure 4.17 Price history of raffinate-1 by region	42
Figure 4.18 Price history of raffinate-2 by region	43
Figure 4.19 North American price spread between raffinate-1 and raffinate-2 history	43
Figure 4.20 Isobutane—n-Butane price spread history	45
Figure 4.21 North American high-purity isobutylene price history	46
Figure 5.1 Isomerization of n-butane	51
Figure 5.2 Bimolecular pathway for n-butane isomerization	53
Figure 5.3 Monomolecular pathway for n-butane isomerization	54
Figure 5.4 Alkylation/dealkylation/rearrangement mechanism for isobutane formation	55
Figure 5.5 Dual-nature mechanism for n-butane isomerization	57
Figure 5.6 Equilibrium of isobutane dehydrogenation at one atm. total pressure	73
Figure 5.7 Possible mechanism for isobutane dehydrogenation over Cr ₂ O ₃ /Al ₂ O ₃ catalysts	75
Figure 5.8 Equilibrium among C ₄ olefins	93
Figure 5.9 Reaction pathway for skeletal isomerization of n-butenes including by-product formation	94
Figure 6.1 Original Butamer process simplified flowsheet	107
Figure 6.2 Butamer HOT process flow diagram	108
Figure 6.3 Catofin process [®]	113
Figure 6.4 Oleflex process	114
Figure 6.5 NIIMSK isobutane dehydrogenation process simplified flow diagram	116
Figure 6.6 Theoretical isobutane conversion as a function of the number of SHC stages	123
Figure 6.7 ISOMPLUS [®] process	124
Figure 8.2 Isobutane dehydrogenation equilibria as a function of pressure (no added hydrogen)	151

Tables

Table 3.1 Summary of process economics of iso-C ₄ processes	20
Table 4.1 US butanes production from shale oil and gas trends, B/D	25
Table 4.2 US production of NGLs by source (millions of barrels)	26
Table 4.3 World demand for butylenes and butanes in 2013, MMt	30
Table 4.4 Typical composition ranges for low 1,3-butadiene C ₄ streams	37
Table 4.5 Raffinate-3 sales specification	38
Table 4.6 High-purity commercial butene product specifications	38
Table 4.7 Typical chemically pure isobutylene specifications of one supplier	39
Table 4.8 Specifications for refinery grade n-butane	40
Table 4.9 Isobutane specifications of one major supplier	40
Table 4.10 Composition range of refinery mixed butane-butylene streams	41
Table 4.11 Regional spot prices for n-butane, \$/metric ton	44
Table 4.12 US NGL price history, \$/metric ton	45
Table 4.13 Isobutane producers	47
Table 4.14 High-purity isobutylene producers	48
Table 4.15 High-purity isobutylene capacity by region, MMt	50
Table 5.1 Catalysts evaluated for n-butane skeletal isomerization	60
Table 5.2 Sulfated zirconia catalysts evaluated for n-butane isomerization	64
Table 5.3 Isobutane oxidative dehydrogenation catalysts	84
Table 5.4 Catalysts for CO ₂ oxidative dehydrogenation of isobutane	86
Table 5.5 Average intrinsic rate parameters for isobutane dehydrogenation to isobutene	91
Table 5.6 High selectivity, high stability n-butene skeletal isomerization catalysts	98
Table 5.7 Feedstock properties	100
Table 5.8 Skeletal isomerization product over ferrierite catalyst	100
Table 6.1 BIC and butamer processes operating conditions	110
Table 6.2 Comparison of major commercial isobutane dehydrogenation processes	118
Table 7.1 n-Butane isomerization process—Design basis and assumptions	128
Table 7.2 Feed and product compositions	129
Table 7.3 n-Butane isomerization process—Stream flows	130
Table 7.4 n-Butane isomerization process—Major equipment	132
Table 7.5 n-Butane isomerization process—Utilities summary	133
Table 7.6 n-Butane isomerization process—Total capital investment	136
Table 7.7 n-Butane isomerization process—Production costs	138
Table 7.8 Effect of feedstock cost on n-butane isomerization product value	140
Table 8.1 Isobutane dehydrogenation process—Design basis and assumptions	142
Table 8.2 Isobutane dehydrogenation process—Feed and product compositions	143
Table 8.3 Isobutane dehydrogenation process—Stream flows	144
Table 8.4 Isobutane dehydrogenation process—Major equipment	147
Table 8.5 Isobutane dehydrogenation process—Utilities summary	149
Table 8.6 Distribution of sources of reactor heat	152
Table 8.7 Isobutane dehydrogenation process—Total capital investment	155
Table 8.8 Isobutane dehydrogenation process—Total capital investment by section	156
Table 8.9 Isobutane dehydrogenation process—Production costs	158
Table 8.10 Effect of feedstock cost on isobutane dehydrogenation product value	160
Table 9.1 n-Butene isomerization process—Design basis and assumptions	162
Table 9.2 Feed and product compositions	163
Table 9.3 n-Butene skeletal isomerization process—Stream flows	163
Table 9.4 n-Butene skeletal isomerization process—Major equipment	164
Table 9.5 n-Butene skeletal isomerization process—Utilities summary	165
Table 9.6 n-Butene skeletal isomerization process—Total capital investment	167
Table 9.7 n-Butenes skeletal isomerization to isobutylene—Production costs	169
Table 9.8 Effect of feedstock cost on n-butene skeletal isomerization product value	171

Appendix tables and figures

Appendix A: Table A.1 n-Butane isomerization patent summary	173
Appendix A: Table A.2 Isobutane dehydrogenation patent summary	176
Appendix A: Table A.3 Isobutane oxidative dehydrogenation patent summary	195
Appendix A: Table A.4 n-Butene skeletal isomerization patent summary	199
Appendix E: Figure 7.1 n-Butane isomerization process flow diagram	244
Appendix E: Figure 8.1 Isobutane dehydrogenation process flow diagram	245
Appendix E: Figure 9.1 n-Butene skeletal isomerization process flow diagram	246

IHS Customer Care:

Americas: +1 800 IHS CARE (+1 800 447 2273); CustomerCare@ihs.com
Europe, Middle East, and Africa: +44 (0) 1344 328 300; Customer.Support@ihs.com
Asia and the Pacific Rim: +604 291 3600; SupportAPAC@ihs.com

