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CR002

On Purpose Linear Alpha Olefin
Processes

By Marianna Asaro

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PEP Report CR002

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Abstract

This report consolidates and updates the Process Economics Program's technical and economic analyses of on-purpose linear alpha olefin (LAO) manufacturing technologies published through 2013. LAO are used as comonomers in polyethylene production and in the plasticizer, detergent, and lubricant markets. Almost half of the LAO produced worldwide today come from large-scale processes that make a wide range of LAO, with carbon numbers in the range C_4 - C_{20+} . Recent entrants into the market include on-purpose processes, focused predominantly on one LAO product: 1-butene, 1-hexene, or 1-octene. Major producers of on-purpose C_6 or C_8 LAO from ethylene include Chevron Phillips, Sasol, and Saudi Polymers. Smaller-scale producers of on-purpose 1-hexene include Q-Chem, Mitsui, and Yanshan PC. Numerous companies have licensed the selective ethylene dimerization technology of IFP for production of 1-butene, typically operating at very small scale.

The majority of 1-butene is produced by on-purpose isolation from mixed C_4 streams, particularly steam cracker raffinate. The C_4 components of raffinate boil too closely to separate economically by simple distillation. The dominant raffinate-based process involves upfront removal of butadiene by reactive distillation, followed by conversion of isobutylene to MTBE, and then distillative separation of the 1-butene. The MTBE may be sold or cracked in-house to give isobutylene of very high purity (HPIB). 1-Butene also can be isolated from raffinate by selective adsorption, as developed by UOP and by Union Carbide. Selective adsorption processes do not appear to be in current use, likely because the HPIB produced via MTBE is of relatively high current market value. Alternatively, raffinate streams may be significantly enriched in 1-butene prior to downstream isolation of the C_4 LAO by selectively hydrogenating the butadiene content of crude raffinate.

On-purpose LAO are also produced from Fischer-Tropsch effluents, as practiced commercially by Sasol. Dow Iberica selectively produces 1-octene in a small-scale process using 1-butene as feed. Additional on-purpose LAO processes are commercialization-ready or under development, including metathesis of 1-butene from raffinate to give hexene and ethylene as commercialized at demonstration scale by Lummus/CB&I.

Technical descriptions and economic analysis are provided herein for the following technologies:

- 1-Octene and 1-hexene by the Sasol ethylene tetramerization process
- 1-Hexene by the Chevron Phillips ethylene trimerization process
- 1-Hexene by the Axens ethylene trimerization process
- 1-Hexene by the Lummus C_4 metathesis process
- 1-Butene by the Axens-IFP-SABIC ethylene dimerization process
- 1-Butene by distillation of raffinate-2 from MTBE production
- 1-Butene from raffinate-1 by the UOP adsorption process
- 1-Butene and isobutylene from raffinate-1 by the UCC adsorption process
- 1-Butene-enriched C_4 by selective hydrogenation of butadiene

These and other technologies past, present, and emerging for on-purpose LAO are reviewed, with bibliography and abstracts for relevant patents since the 1980s. The industry status is updated, and a summary is provided of all commercial or commercial-ready intermediate- to large-scale on-purpose LAO processes in terms of comparative economics and the key process indicators (KPI) of carbon efficiency, energy intensity, carbon intensity, and capital intensity. Lastly an interactive module is included, the iPEP Navigator OPLAO tool, which provides a snapshot of economics for each process and allows the user to select the process, units, and region of interest.

Contents

1. Introduction	1-1
2. Summary	2-1
Commercial status	2-1
Industrial producers/licensors.....	2-1
Linear alpha olefins technologies.....	2-2
1-Octene and 1-hexene by the Sasol ethylene tetramerization process	2-5
1-Hexene by the Chevron Phillips ethylene trimerization process.....	2-9
1-Hexene by the Axens ethylene trimerization process.....	2-10
1-Hexene by the Lummus C ₄ metathesis process	2-10
1-Butene by the Axens-IFP-SABIC ethylene dimerization process.....	2-11
1-Butene by distillation of raffinate-2 from MTBE production	2-11
1-Butene from raffinate-1 by the UOP adsorption process	2-12
1-Butene and isobutylene from raffinate-1 by the UCC adsorption process	2-13
1-Butene-enriched C ₄ by selective hydrogenation of butadiene	2-13
Process economics.....	2-14
3. Industry status	3-1
Demand and market drivers	3-2
Current producers and plant capacity	3-3
Recent and planned capacity additions	3-10
Transaction prices	3-11
4. Technology review.....	4-1
Historical process development.....	4-1
Ethylene oligomerization to produce C ₄ , C ₆ , and C ₈ LAO.....	4-2
I. Ethylene tetramerization: 1-octene.....	4-3
II. Ethylene trimerization: 1-hexene	4-17
III. Ethylene dimerization: 1-butene.....	4-33
Production of LAO from raffinate streams	4-42
I. Isolation of 1-butene from raffinate streams	4-42
II. Partial hydrogenation of butadiene to produce 1-butene from raffinate-1	4-56
III. Telomerization of butadiene to produce 1-octene	4-63
IV. Dimerization of 1-butene to produce 1-octene	4-65
V. Butene metathesis to produce 1-hexene from raffinate-1	4-65
Production of LAO from Fischer-Tropsch synthesis via hydroformylation	4-68
Hydroformylation	4-69
Hydrogenation	4-72
Dehydration	4-74
5. Octene and 1-hexene by the Sasol ethylene tetramerization process	5-1

Process review.....	5-1
Chemistry and reaction conditions	5-1
Reactor.....	5-2
Catalyst and product distribution.....	5-3
Product separation	5-3
Process description.....	5-3
Section 100—Ethylene tetramerization.....	5-4
Section 200—Product recovery.....	5-5
Materials of construction.....	5-13
Process waste effluents.....	5-14
Cost estimates.....	5-14
Fixed capital costs.....	5-14
Production costs.....	5-15
6. 1-Hexene by the Chevron Phillips ethylene trimerization process.....	6-1
Process review.....	6-1
Chemistry and reaction conditions	6-1
Reactor.....	6-2
Catalyst and product distribution.....	6-2
Product separation	6-2
Process description.....	6-2
Section 100— Ethylene trimerization.....	6-3
Section 200—Product separation	6-4
Process discussion.....	6-10
Materials of construction.....	6-11
Process waste effluents.....	6-11
Cost estimates.....	6-11
Fixed capital costs.....	6-12
Production costs.....	6-12
7. 1-Hexene by the Axens ethylene trimerization process.....	7-1
Process review.....	7-1
Chemistry and reaction conditions	7-1
Reactor.....	7-2
Catalyst and product distribution.....	7-2
Product separation	7-2
Process description.....	7-3
Section 100— Ethylene trimerization.....	7-4
Section 200—Product separation	7-4
Process discussion.....	7-10
Materials of construction.....	7-10
Process waste effluents.....	7-10
Cost estimates.....	7-11

Fixed capital costs.....	7-11
Production costs.....	7-11
8. 1-Hexene by the Lummus C ₄ metathesis process.....	8-1
Process review.....	8-2
Chemistry and reaction conditions	8-2
Reactors	8-4
Catalyst and product distribution.....	8-4
Product separation	8-5
Process description.....	8-5
Section 100—Butene hydroisomerization.....	8-6
Section 200—Butene distillation.....	8-6
Section 300—Autometathesis and purification.....	8-6
Section 400—Hexene isomerization and product recovery.....	8-7
Process discussion.....	8-12
Materials of construction.....	8-13
Process waste effluents.....	8-13
Cost estimates.....	8-13
Fixed capital costs.....	8-13
Production costs.....	8-14
9. 1-Butene by the Axens-IFP-Sabir ethylene dimerization process	9-1
Process review.....	9-1
Chemistry and reaction conditions	9-1
Reactor.....	9-2
Catalyst and product distribution.....	9-2
Product separation	9-2
Process description.....	9-3
Section 100—Ethylene dimerization.....	9-4
Section 200—Product recovery.....	9-4
Process discussion.....	9-9
Materials of construction.....	9-9
Process waste effluents.....	9-10
Cost estimates.....	9-10
Fixed capital costs.....	9-10
Production costs.....	9-11
10. 1-Butene by distillation of raffinate-2 from MTBE production.....	10-1
Process review.....	10-2
Chemistry and reaction conditions	10-2
Reactors	10-3
Catalyst	10-3

Product separation	10-4
Process description.....	10-4
Section 100—MTBE preparation	10-5
Section 200—Raffinate partial hydrogenation	10-6
Section 300—Distillation	10-6
Process discussion.....	10-16
Materials of construction	10-17
Process waste effluents.....	10-17
Cost estimates.....	10-18
Fixed capital costs.....	10-18
Production costs.....	10-19
11. 1-Butene from raffinate-1 by the UOP adsorption process.....	11-1
Process review.....	11-2
Adsorbent and adsorption conditions	11-2
Adsorber	11-2
Process description.....	11-3
Section 100—Feed preparation	11-4
Section 200—Adsorption	11-4
Process discussion.....	11-10
Materials of construction.....	11-10
Process waste effluents.....	11-11
Cost estimates.....	11-11
Fixed capital costs.....	11-11
Production costs.....	11-12
12. 1-Butene and isobutylene from raffinate-1 by the UCC adsorption process	12-1
Process review.....	12-2
Adsorbent and adsorption conditions	12-2
Adsorber	12-2
Process description.....	12-3
Section 100—Feed preparation	12-4
Section 200—Adsorption	12-4
Section 300—Post fractionation.....	12-5
Process discussion.....	12-15
Materials of construction.....	12-16
Process waste effluents.....	12-17
Cost estimates.....	12-17
Fixed capital costs—Case A.....	12-17
Fixed capital costs—Case B.....	12-18
Production costs.....	12-18

13. 1-Butadiene-enriched C ₄ by selective hydrogenation of butadiene.....	13-1
Process review.....	13-3
Chemistry and reaction conditions	13-3
Reactor.....	13-4
Catalyst and product distribution.....	13-5
Process description.....	13-6
Section 100A— Single-reactor hydrogenation.....	13-7
Section 100—hydrogenation, case B.....	13-8
Process discussion.....	13-14
Reactor system.....	13-14
Temperature control.....	13-15
Butene isomerization	13-15
Materials of construction.....	13-16
Process waste effluents.....	13-16
Cost estimates.....	13-16
Fixed capital costs.....	13-16
Production costs.....	13-17
 Appendix A: Design and cost bases.....	 A-1
 Appendix B: Patents by company.....	 B-1
 Appendix C: Cited references.....	 C-1
 Appendix D: Selected patent summaries by assignee.....	 D-1
 Appendix E: Process flow diagrams	 E-1
 Appendix F: iPEP Navigator for on purpose LAO.....	 F-1

Tables

Table 1.1: Technologies for production of linear alpha olefins	1-2
Table 2.1: Major world producers of linear alpha olefins	2-2
Table 2.2: Summary of on purpose 1-octene and 1-hexene process technologies	2-6
Table 2.3: Summary of on purpose 1-butene process technologies	2-7
Table 2.4: C ₄ components in crude raffinate streams.....	2-9
Table 2.5: On purpose 1-octene and 1-hexene technologies Total capital investment	2-18
Table 2.6: On purpose 1-butene technologies Total capital investment.....	2-19
Table 2.7: On purpose 1-octene and 1-hexene technologies Production costs.....	2-21
Table 2.8: On purpose 1-butene technologies Production costs.....	2-22
Table 2.9: Estimated average price for LAO product by process	2-24

Table 2.10:	Definitions of key process indicators	2-25
Table 3.1:	Technologies for production of linear alpha olefins	3-1
Table 3.2:	World consumption of linear alpha olefins by region and end use	3-2
Table 3.3:	World supply/demand for linear alpha olefins by region.....	3-4
Table 3.4:	Producers of linear alpha olefins.....	3-5
Table 3.5:	Recent and planned capacity additions	3-10
Table 3.6:	Average transaction prices of LAO products	3-11
Table 4.1:	Performance of SK catalysts containing a bridging cyclohexyl group	4-8
Table 4.2:	Performance of Nova catalysts containing ortho-fluorinated aryl groups on phosphorus	4-9
Table 4.3:	Effect of temperature on catalyst activity, ethylene conversion, and product selectivity for Sasol's catalyst system.....	4-14
Table 4.4:	Effects of ethylene feed rate variation on conversion and product selectivity.....	4-14
Table 4.5:	Early catalyst systems for ethylene trimerization	4-20
Table 4.6:	Performance of IFP/Axens ethylene trimerization catalysts using phenoxide ligands	4-25
Table 4.7:	Conditions and performance of Tosoh trimerization catalyst system	4-26
Table 4.8:	Effects of various halides on ethylene trimerization.....	4-31
Table 4.9:	Effects of HCE/Cr molar ratio on ethylene trimerization	4-31
Table 4.10:	Effects of ligand/Cr molar ratio on ethylene trimerization	4-32
Table 4.11:	Performance of selected Group IVB transition metal complexes as catalysts for ethylene dimerization.....	4-34
Table 4.12:	Hydrocarbon product composition of ethylene dimerization over $Ti(OBu)_4-AlEt_3$	4-35
Table 4.13:	Impact of pretreating $Ti(OBu)_4-AlEt_3$ catalyst with ethylene and hydrogen	4-37
Table 4.14:	Temperature variation effects on conversion and selectivity in Ti-catalyzed ethylene dimerization.....	4-38
Table 4.15:	Effects of process pressure on catalyst activity and product selectivity in Ti- catalyzed ethylene dimerization.....	4-38
Table 4.16:	Specific surface area, acidity, and activity of $NiSO_4/ZrO_2$ catalysts for butene dimerization	4-39
Table 4.17:	Examples of organonickel complexes having N-donor ligands for ethylene dimerization	4-41
Table 4.18:	C_4 component compositional ranges of crude raffinates.....	4-43
Table 4.19:	Relative volatilities of C_4 hydrocarbons in crude raffinate	4-44
Table 4.20:	Specifications of 1-butene sold as comonomer/polymer grade.....	4-55
Table 4.21:	Hydrogenation reactions of unsaturated compounds in raffinate.....	4-56
Table 4.22:	Equilibrium distribution of normal butenes	4-60
Table 4.23:	Typical conditions for selective hydrogenation of butadiene	4-61
Table 4.24:	Hydroformylation of LAO with a bisphosphite Rh catalyst	4-71
Table 5.1:	1-Octene and 1-hexene by the Sasol ethylene tetramerization process Design basis	5-6
Table 5.2:	1-Octene and 1-hexene by the Sasol ethylene tetramerization process Stream flows	5-8
Table 5.3:	1-Octene and 1-hexene by the Sasol ethylene tetramerization process Major equipment.....	5-11
Table 5.4:	1-Octene and 1-hexene by the Sasol ethylene tetramerization process Utilities summary.....	5-13

Table 5.5:	1-Octene and 1-hexene by the Sasol ethylene tetramerization process Total capital investment.....	5-16
Table 5.6:	1-Octene and 1-hexene by the Sasol ethylene tetramerization process Capital investment by section.....	5-17
Table 5.7:	1-Octene and 1-hexene by the Sasol ethylene tetramerization process Production costs	5-18
Table 6.1:	1-Hexene by the Chevron Phillips ethylene trimerization process Design basis	6-5
Table 6.2:	1-Hexene by the Chevron Phillips ethylene trimerization process Stream flows	6-6
Table 6.3:	1-Hexene by the Chevron Phillips ethylene trimerization process Major equipment.....	6-9
Table 6.4:	1-Hexene by the Chevron Phillips ethylene trimerization process Utilities summary.....	6-10
Table 6.5:	1-Hexene by the Chevron Phillips ethylene trimerization process Total capital investment.....	6-13
Table 6.6:	1-Hexene by the Chevron Phillips ethylene trimerization process Capital investment by section.....	6-14
Table 6.7:	1-Hexene by the Chevron Phillips ethylene trimerization process Production costs	6-15
Table 7.1:	1-Hexene by the Axens ethylene trimerization process Design basis.....	7-5
Table 7.2:	1-Hexene by the Axens ethylene trimerization process Stream flows	7-6
Table 7.3:	1-Hexene by the Axens ethylene tetramerization process Major equipment	7-9
Table 7.4:	1-Hexene by the Axens ethylene trimerization process Utilities summary	7-10
Table 7.5:	1-Hexene by the Axens ethylene trimerization process Total capital investment.....	7-13
Table 7.6:	1-Hexene by the Axens ethylene trimerization process Production costs.....	7-14
Table 8.1:	1-Hexene by the Lummus-CB&I C ₄ metathesis process Design basis	8-8
Table 8.2:	1-Hexene by the Lummus-CB&I C ₄ metathesis process Stream flows	8-9
Table 8.3:	1-Hexene by the Lummus-CB&I C ₄ metathesis process Major equipment	8-10
Table 8.4:	1-Hexene by the Lummus-CB&I C ₄ metathesis process Utilities summary	8-12
Table 8.5:	1-Hexene by the Lummus-CB&I C ₄ metathesis process Total capital investment.....	8-15
Table 8.6:	1-Hexene by the Lummus-CB&I C ₄ metathesis process Production costs	8-16
Table 9.1:	1-Butene by the Axens-IFP-Sabic ethylene dimerization process Design basis.....	9-5
Table 9.2:	1-Butene by the Axens-IFP-SABIC ethylene dimerization process Stream flows	9-6
Table 9.3:	1-Butene by the Axens-IFP-Sabic ethylene dimerization process Major equipment.....	9-8
Table 9.4:	1-Butene by the Axens-IFP-Sabic ethylene dimerization process Utilities summary.....	9-9
Table 9.5:	1-Butene by the Axens-IFP-Sabic ethylene dimerization process Total capital investment.....	9-12
Table 9.6:	1-Butene by the Axens-IFP-Sabic ethylene dimerization process Capital investment by section	9-13
Table 9.7:	1-Butene by the Axens-IFP-Sabic ethylene dimerization process Production costs.....	9-14
Table 10.1:	1-Butene by distillation of raffinate-2 from MTBE production Design basis.....	10-7
Table 10.2:	1-Butene by distillation of raffinate-2 from MTBE production Stream flows.....	10-9
Table 10.3:	1-Butene by distillation of raffinate-2 from MTBE production Major equipment	10-13
Table 10.4:	1-Butene by distillation of raffinate-2 from MTBE production Utilities summary	10-16
Table 10.5:	1-Butene by distillation of raffinate-2 from MTBE production Total capital investment.....	10-20
Table 10.6:	1-Butene by distillation of raffinate-2 from MTBE production Capital investment by section	10-21

Table 10.7:	1-Butene by distillation of raffinate-2 from MTBE production Production costs	10-22
Table 11.1:	1-Butene from raffinate-1 by the UOP adsorption process Design basis.....	11-6
Table 11.2:	1-Butene from raffinate-1 by the UOP adsorption process Stream flows.....	11-7
Table 11.3:	1-Butene from raffinate-1 by the UOP adsorption process Major equipment	11-8
Table 11.4:	1-Butene from raffinate-1 by the UOP adsorption process Utilities summary	11-9
Table 11.5:	1-Butene from raffinate-1 by the UOP adsorption process Total capital investment	11-13
Table 11.6:	1-Butene from raffinate-1 by the UOP adsorption process Capital investment by section	11-14
Table 12.1:	1-Butene-and isobutylene from raffinate-1 by the UCC adsorption process–Cases A and B Design basis.....	12-6
Table 12.2A:	1-Butene and 97.9% isobutylene from raffinate-1 by the UCC adsorption process–Case A Stream flows.....	12-8
Table 12.2B:	1-Butene and 94.8% isobutylene from raffinate-1 by the UCC adsorption process–Case B Stream flows.....	12-9
Table 12.3A:	1-Butene and 97.9% isobutylene from raffinate-1 by the UCC adsorption process–Case A Major equipment	12-10
Table 12.3B:	1-Butene and 94.8% isobutylene from raffinate-1 by the UCC adsorption process–Case B Major equipment	12-12
Table 12.4A:	1-Butene and 97.9% isobutylene from raffinate-1 by the UCC adsorption process–Case A Utilities summary	12-14
Table 12.4B:	1-Butene and 94.8% isobutylene from raffinate-1 by the UCC adsorption process–Case B Utilities summary	12-15
Table 12.5A:	1-Butene and 97.9% isobutylene from raffinate-1 by the UCC adsorption process–Case A Total capital investment	12-21
Table 12.6A:	1-Butene and 97.9% isobutylene from raffinate-1 by the UCC adsorption process–Case A Capital investment by section	12-22
Table 12.7A:	1-Butene and 97.9% isobutylene from raffinate-1 by the UCC adsorption process–Case A Production costs	12-23
Table 12.5B:	1-Butene and 94.8% isobutylene from raffinate-1 by the UCC adsorption process–Case B Total capital investment.....	12-25
Table 12.6B:	1-Butene and 94.8% isobutylene from raffinate-1 by the UCC adsorption process–Case B Capital investment by section.....	12-26
Table 12.7B:	1-Butene and 94.8% isobutylene from raffinate-1 by the UCC adsorption process–Case B Production costs.....	12-27
Table 13.1:	Technology licensors for selective hydrogenation of butadiene to 1-butene	13-2
Table 13.2:	Typical conditions for selective hydrogenation of butadiene	13-4
Table 13.3:	1-Butene-enriched C ₄ by selective hydrogenation Design basis.....	13-9
Table 13.4A:	1-Butene-enriched C ₄ by selective hydrogenation, 2000 ppm butadiene–Case A Stream flows	13-10
Table 13.4B:	1-Butene-enriched C ₄ by selective hydrogenation, 500 ppm butadiene–Case B Stream flows	13-11
Table 13.5A:	1-Butene-enriched C ₄ by selective hydrogenation, 2000 ppm butadiene–Case A Major equipment.....	13-12
Table 13.5B:	1-Butene-enriched C ₄ by selective hydrogenation, 500 ppm butadiene–Case B Major equipment.....	13-13

Table 13.6A: 1-Butene-enriched C ₄ by selective hydrogenation of butadiene, 2000 ppm butadiene in product–Case A Utilities summary	13-14
Table 13.6B: 1-Butene-enriched C ₄ by selective hydrogenation of butadiene, 500 ppm butadiene in product–Case B Utilities summary	13-14
Table 13.7A: 1-Butene-enriched C ₄ by selective hydrogenation, 2000 ppm butadiene–Case A Total capital investment.....	13-19
Table 13.7B: 1-Butene-enriched C ₄ by selective hydrogenation, 500 ppm butadiene–Case B Total capital investment.....	13-20
Table 13.8A: 1-Butene-enriched C ₄ by selective hydrogenation, 2000 ppm butadiene–Case A Production costs.....	13-21
Table 13.8B: 1-Butene-enriched C ₄ by selective hydrogenation, 500 ppm butadiene–Case B	13-23

Figures

Figure 2.1: Process steps for on purpose LAO production.....	2-3
Figure 2.2: Factors of production for on purpose LAO processes.....	2-24
Figure 2.3: Factors of production for 1-butene-enriched C ₄ process.....	2-25
Figure 2.4: Key process indicators	2-27
Figure 2.5: CO ₂ footprint breakdown	2-28
Figure 3.1: World capacity for all C ₄ –C ₈ LAO by process type.....	3-1
Figure 3.2: Performance of LLDPE with and without inclusion of LAO	3-3
Figure 4.1: P–N–P backbone and example of Sasol’s ethylene tetramerization catalyst	4-4
Figure 4.2: Selectivity and productivity effects in representative Sasol ethylene tetramerization catalyst systems.....	4-5
Figure 4.3: Ligand for Chevron Phillips catalyst that gives majority 1-octene as product	4-7
Figure 4.4: P–C–C–P backbone of SK’s ethylene tetramerization catalyst.....	4-7
Figure 4.5: Structure of ligand providing majority 1-octene in ExxonMobil’s ethylene trimerization/tetramerization system	4-12
Figure 4.6: Feed and reactor system described by PetroChina.....	4-15
Figure 4.7: Catalyst productivity with decreasing Cr concentration	4-16
Figure 4.8: Selectivity as a function of ethylene conversion and catalyst concentration	4-17
Figure 4.9: Ratio of 1-octene to 1-hexene as a function of ethylene conversion.....	4-17
Figure 4.10: Chevron Phillips polydentate ligand with bridged pyrrole groups.....	4-22
Figure 4.11: Chevron Phillips catalyst containing an N-phosphinoamidinyl, N–C–N–P, ligand	4-24
Figure 4.12: Tosoh pyrazolyl ligand used for ethylene trimerization.....	4-26
Figure 4.13: ExxonMobil N–C–C–N, pyridyl amine chromium complex used for ethylene trimerization.....	4-27
Figure 4.14: Representative Mitsui ethylene trimerization catalyst	4-29
Figure 4.15: Framework of proposed catalytically active intermediate in ethylene dimerization.....	4-36
Figure 4.16: Separation processes for 1-butene from mixed butylene streams	4-45
Figure 4.17: Schematic of a representative process for removal of isobutylene from raffinate in two stages via MTBE.....	4-48
Figure 4.18: Flow diagram of isobutylene removal from raffinate with one reactor stage plus catalytic distillation.....	4-49
Figure 4.19: Block flow diagram of the UCC 1-butene adsorption process.....	4-52