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Linear alpha-Olefins
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SUMMARY

This report covers supply and demand for linear alpha-olefins (LAOs) with carbon chain-lengths of four (butene-1) and higher that are produced in facilities that generate an entire range of LAOs. Most of the current commercial LAO plants produce even-numbered alpha-olefins based on ethylene oligomerization. The exceptions are the coal-based synthetic fuel plant of Sasol Chemical Industries in South Africa, which currently produces hexene-1, octene-1 and small quantities of pentene-1; Q-Chem and Sinopec Beijing Yanhua Petrochemical, which produce hexene-1 from ethylene; and Dow, which produces octene-1 from butadiene in Tarragona, Spain. Butene-1 that is produced from refinery and steam cracker C₄ hydrocarbon streams is not included in this discussion.

The following table presents world supply/demand for linear alpha-olefins:

World Supply/Demand for Linear alpha-Olefins by LAO-Producing Region—2009^a
(thousands of metric tons)

	Annual Capacity (year-end)		Production	Imports	Exports	Apparent Consumption		Average Annual Consumption Growth Rate, 2009-2014 (percent)
	2009	2014				2009	2014	
North America	1,889	2,189	1,575	200	269	1,506	1,649	1.8
Central and South America	--	--	--	61	--	61	74	3.9
Western Europe	730	730	551	229	135	645	711	2.0
Central and Eastern Europe	90	120	15	5	7	13	16	4.2
South Africa	420	460	340	--	270	70	90	5.2
Middle East	197 ^b	860	55	25	10	70	113	10.1
Japan	58 ^c	88	90	28	30	88	90	0.5
Other Asia	50	85	40	168	--	208	335	10.0
Oceania	--	--	--	5	--	5	6	3.7
Total	3,434	4,532	2,666	721	721	2,666	3,084	3.0%

a. Data include C₄ produced in alpha-olefin plants for all regions, except Western Europe.

b. Jubail United Petrochemicals' 150 thousand metric ton-per-year plant came on stream in December 2009.

c. Mitsubishi Chemical discontinued LAO production in Mizushima, Japan (annual capacity of 60 thousand metric tons) in May 2009.

SOURCE: CEH estimates.

In 2009, world alpha-olefins production was 2.7 million metric tons (reflecting a global capacity utilization rate of 82%—based on an effective capacity of approximately 3,250 thousand metric tons) valued at approximately \$3.7 billion. North America accounted for 59% of world production during 2009, followed by Western Europe (21%), South Africa (13%) and Japan (3%), with Russia, the Middle East and Other Asia accounting for the remainder.

World linear alpha-olefins capacity (excluding butene-1 from refinery streams) amounted to approximately 3.4 million metric tons by year-end 2009. There are currently (as of mid-2010) ten producers of alpha-olefins operating twelve plants internationally. The following table presents world producers of LAOs:

World Producers of Linear alpha-Olefins

Company and Plant Location	Annual Capacity as of Mid-2010 (thousands of metric tons)	Process	Remarks
Chevron Phillips Chemical Company LP (CPChem) Cedar Bayou, TX, United States	703	CPChem	
Dow Chemical Tarragona, Spain	100	Telomerization of butadiene	Plant came on stream in 2007. Produces octene from butadiene.
Idemitsu Petrochemical Company, Ltd. Ichihara, Chiba Prefecture, Japan	58	Idemitsu	Plant came on stream in 1989.
INEOS Joffre, Alberta, Canada	265	Ethyl	Plant came on stream in late 2001.
Feluy, Belgium	300	Ethyl	Plant came on stream in July 1992.
Jubail United Petrochemical Company (JUPC) Al Jubail, Saudi Arabia	150	alpha-SABLIN™	Plant came on stream in December 2009.
Nizhnekamskneftekhim Nizhnekamsk, Russia	90	Ethyl	Original plant capacity was 180 thousand metric tons.
Qatar Chemical Company (Q-Chem) Mesaieed, Qatar	47	CPChem	Single-fraction 1-hexene plant (hexene-1 is produced from ethylene). Operational since February 2003.
Sasol Chemical Industries Secunda, South Africa	420	Separation and distillation of the Fischer Tropsch stream from the Secunda coal-to-fuels process	High purity hexene-1, octene-1 and pentene-1 are isolated, primarily for comonomers applications. C ₁₁ and higher LAOs are extracted for the local production of detergent alcohols. The first hexene unit came on stream in 1994. Hexene-1 capacity is 188 thousand metric tons. Octene-1 capacity is 186 thousand metric tons, including the 90 thousand metric ton unit that became operational in June 2008.
Shell Chemical Company Geismar, LA, United States	921	Shell (SHOP)	
Ellesmere Port, United Kingdom	330	Shell (SHOP)	
Sinopec Beijing Yanhua Petrochemical Co., Ltd. Beijing, China	50	Ethylene trimerization	Came on stream in May 2007. Produces hexene-1 from ethylene.
Total	3,434		

SOURCE: CEH estimates.

The following table presents the largest world producers of LAOs by capacity:

Major World Producers of Linear alpha-Olefins		
	Annual Capacity as of September 1, 2010 (thousands of metric tons)	Percent of World Capacity
Shell	1,251	36.4
CPChem	703	20.5
INEOS	565	16.5
Sasol	420	12.2
Other	495	14.4
Total	3,434	100.0%

SOURCE: CEH estimates.

The following table presents planned world capacity additions for LAOs:

Planned World Capacity Additions for Linear alpha-Olefins		
Company and Plant Location	Annual Capacity Addition (thousands of metric tons)	Estimated On-Stream Date/Remarks
CPCC Jubail Jubail Industrial City, Saudi Arabia	100	2012. Hexene-1.
CPChem Cedar Bayou, Texas	200	First-quarter 2014. Hexene-1.
Dow Thailand	na	2012. Octene-1. Dow is starting a polyethylene plant in Thailand in 2010.
Gurevesky Karabatan, Kazakhstan	20-40	2011. Butene-1.
Jam Petrochemical Company Asulayeh, Iran	168	2011. LAOs. It is not likely that this plant will be built. Butene-1 (100 thousand metric tons capacity).
Mitsui Chiba, Japan	30	2010. Hexene-1.
ONGC Petroadditions Ltd. (OPaL) Dahej, Gujarat, India	35	Fourth-quarter 2012. Butene-1.
PetroRabigh Rabigh, Saudi Arabia	50	Butene-1. On stream date for C ₄ is unknown.
Qatar Chemical Company II Ltd. (Q-Chem II) Ras Laffan, Qatar	345	Fourth-quarter 2010. Broad range of LAOs. Capacity for C ₄ is 58 thousand metric tons. Capacity for C ₆ is 60 thousand metric tons.
Sasol Lake Charles, Louisiana	100	2013. Hexene-1 and octene-1. Sasol tetramerization technology. Construction to commence in 2011.
Total	1,058	

SOURCE: CEH estimates.

The largest uses for linear alpha-olefins are as comonomers for polyethylene production, for the production of alcohols (used largely in detergents and plasticizers) and for making polyalphaolefins (used in synthetic lubricants). The following table presents a comparison of end-use patterns for the major producing regions during 2009:

Consumption of Linear alpha-Olefins by Major Region—2009
(percent)

	North America	Western Europe	Japan
Polyethylene Comonomer	51	35	59
Oxo Alcohols	15	25	7
Polyalphaolefins	13	30	.. ^a
Other	21	10	34
Total	100%	100%	100%

a. Japanese consumption of LAO for polyalphaolefins is small and included in OTHER.

SOURCE: CEH estimates.

Forecasts of growth rates vary significantly by region. Annual growth during 2009-2014 is expected to average 2% in North America, 2% in Western Europe and 0.5% in Japan. However, growth for comonomer-grade LAOs is expected to be considerably higher, or 5-6% globally. On a global scale, total LAO consumption should average 3% annually through 2014.

Key findings in the overall LAO market include the following:

- Mitsubishi Chemical discontinued production of linear alpha-olefins in May 2009.
- Jubail United Petrochemicals started its 150 thousand metric ton-per-year LAO plant in Al Jubail, Saudi Arabia in December 2009.
- The LAO market was relatively balanced in most of 2008. However, by the end of the year weak demand brought about by the global economic crisis saw LAO consumption decrease significantly, especially for polyethylene.
- Continued weak demand in the major LAO-consuming markets in 2009 resulted in lower LAO consumption and therefore production. By late 2009 and early 2010, when demand started to pick back up for polyethylene and polyalphaolefins, supplies were tight, especially for hexene-1 and decene-1.
- As of September 2010, the LAO market was relatively balanced as a result of additional capacity that came on stream in late 2009 and the overall ramp-up in production due to stronger demand from most sectors.
- Most of the announced capacity additions (for 2011-2013 commencement) are for C₄, C₆ and C₈ for the polyethylene market.
- Supplies of C₁₀₊ cuts will become tighter with capacity expansions focused on C₄-C₈. However, some producers in markets that have historically consumed some of the higher cuts (e.g. detergent alcohols and alkyldimethylamines) have switched to using “natural” feedstocks.

The following table presents key findings and future concerns and implications for the LAO market by major consuming market:

Key Findings and Future Concerns and Implications for the Linear alpha-Olefin Market

Major Linear alpha-Olefin Consuming Market	World Average Annual Growth Rate, 2009-2014 (percent)
<p>Polyethylene (PE) Comonomer</p> <ul style="list-style-type: none"> As of mid-2010, hexene-1 supply was relatively balanced after being tight in the beginning of the year. The market for octene-1, long in early to mid-2010, is being driven by high demand for elastomers (Dow announced plans to increase its specialty elastomers capacity in Texas and Spain in August 2010). The short-term outlook for PE indicates that from the middle of 2010, HDPE has been in larger supply. LLDPE has been tight and shows the best supply/demand balance of the two. In the long term it is expected that the new volumes from the Middle East will refocus trade flows in Asia and Western Europe. North America may become a more regional net importing market. However, developments leading to low/competitively priced U.S. ethane and ethylene feedstocks (namely natural gas in shale) are likely to be very positive for U.S.-based PE producers. Oversupply of PE in the market in the future will drive differentiation toward the high performance PE (from C₄ to C₆, C₈). 	5-6%
<p>Polyalphaolefins</p> <ul style="list-style-type: none"> Global PAO capacity utilization in 2009 was approximately 85% due to weak demand worldwide brought about by the global economic crisis (compared to typical operating rates exceeding 90% in recent years). PAO demand, and thus production, has rebounded strongly in 2010, with most producers running at or near effective capacity. If the global economy continues strong in the latter part of 2010, utilization rates could reach higher than 90% for the year. Growth for PAOs will not necessarily be limited by the expansion of Group III lubricants or gas-to-liquid base stocks, as the high performance of PAOs versus Group III base oils has allowed them to retain market share in those sectors that require this performance. PAO demand will be driven by tightening emissions standards in the transportation industry (passenger vehicles and heavy-duty diesel). It is difficult to predict the growth of PAO for gear boxes in wind turbines. Although an important market, there are regulatory issues, among others, that come into play, making it a challenge to estimate consumption in the next five years. 	5%
<p>Oxo Alcohols</p> <p>Detergent Alcohols</p> <ul style="list-style-type: none"> LAOs compete with natural fats and oils as raw materials in the production of detergent alcohols. LAO consumption for detergent alcohols saw a decrease from 2006 to 2009 with increasing imports of detergent alcohols from natural alcohol plants that came on line in Southeast Asia and Brazil. Natural alcohol plants planned in Southeast Asia will increase detergent alcohol supplies and Asian exports will likely continue to increase. 	2%
<p>Oxo Alcohols</p> <p>Plasticizer Alcohols</p> <ul style="list-style-type: none"> Competition from branched plasticizers contributed to decreased LAO consumption in this application. The global average annual growth rate for LAOs used in the production of plasticizer alcohols during 2009-2014 is estimated to be approximately 0.5%. 	0-1%

SOURCE: CEH estimates.

The use of linear alpha-olefins in the production of polyethylene, for polyalphaolefins and for use in oil field drilling applications will be the fastest growing segments in North America. Globally, comonomer-grade LAO consumption will also be the fastest growing application, particularly LAO consumption for the production of linear low-density polyethylene resins.

INTRODUCTION

alpha-Olefins are straight-chain hydrocarbons characterized by a double bond in the terminal or alpha position. Production of linear alpha-olefins (LAOs) based on ethylene oligomerization yields an entire range of even-numbered carbon chain-length LAOs rather than a single product. Chain lengths vary from four carbons (butene-1) to more than thirty carbons (expressed as C₃₀₊). Since 1994, Sasol Chemical Industries has recovered C₅ and C₆ alpha-olefins contained in product streams for its coal-based synthetic fuel plant in Secunda, South Africa. It is the only producer of pentene-1 (C₅) in commercial quantities and has the potential to recover other LAOs. The following table lists the chemical names and chemical formulas for C₄ through C₃₀ LAOs:

Linear alpha-Olefin Nomenclature

Carbon Chain Length	Chemical Name	Chemical Formula
4	Butene-1	CH ₂ =CH-(CH ₂)-CH ₃
5	Pentene-1	CH ₂ =CH-(CH ₂) ₂ -CH ₃
6	Hexene-1	CH ₂ =CH-(CH ₂) ₃ -CH ₃
8	Octene-1	CH ₂ =CH-(CH ₂) ₅ -CH ₃
10	Decene-1	CH ₂ =CH-(CH ₂) ₇ -CH ₃
12	Dodecene-1	CH ₂ =CH-(CH ₂) ₉ -CH ₃
14	Tetradecene-1	CH ₂ =CH-(CH ₂) ₁₁ -CH ₃
16	Hexadecene-1	CH ₂ =CH-(CH ₂) ₁₃ -CH ₃
18	Octadecene-1	CH ₂ =CH-(CH ₂) ₁₅ -CH ₃
20	Eicosene-1	CH ₂ =CH-(CH ₂) ₁₇ -CH ₃
22	Docosene-1	CH ₂ =CH-(CH ₂) ₁₉ -CH ₃
24	Tetracosene-1	CH ₂ =CH-(CH ₂) ₂₁ -CH ₃
26	Hexacosene-1	CH ₂ =CH-(CH ₂) ₂₃ -CH ₃
28	Octacosene-1	CH ₂ =CH-(CH ₂) ₂₅ -CH ₃
30	Triacosene-1	CH ₂ =CH-(CH ₂) ₂₇ -CH ₃

SOURCE: G. R. Lappin and J. D. Sauer, *alpha-Olefins Applications Handbook*, Marcel Dekker, Inc., New York, 1989.

Physical properties, and, therefore, commercial applications, vary depending on the chain length. Butene-1 is a gas at room temperature and C₆-C₁₈ LAOs are clear, colorless liquids, whereas C₂₀₊ LAOs are waxy solids. The utility of LAOs is usually because of the reactivity of the double bond. The most common commercial reactions involving LAOs include oxo reactions (hydroformylations), oligomerization/polymerization, simple addition reactions, alkylation reactions, sulfations/sulfonations and oxidations. Even-numbered alpha-olefins below C₂₀ are available individually or in narrow carbon ranges. C₂₀₊ alpha-olefins are generally consumed in a broad range of chain lengths and some of these products contain high levels of other impurities. The following table summarizes major applications for LAOs by carbon chain length:

Linear alpha-Olefin Applications by Chain Length

C ₄ -C ₈	Polymers and polyethylene comonomer
C ₆ -C ₈	Low-molecular-weight fatty acids and mercaptans
C ₆ -C ₁₀	Plasticizer alcohols
C ₁₀ -C ₁₂	Polyalphaolefins and other additives for lubricants, amine oxides and amines
C ₁₀ -C ₁₆	Detergent alcohols, nonionics and oil field chemicals
C ₁₆ -C ₁₈ ^a	Oil field chemicals, lube oil additives and surfactants
C ₂₀ -C ₃₀ ⁺	Oil field chemicals and wax replacement

a. Includes some C₁₄ for oil field chemicals.

SOURCES: (A) D. L. Burdick and W. L. Leffler, *Petrochemicals in Nontechnical Language*, Pennwell Publishing Company, Tulsa, Oklahoma, 1990.

(B) CEH estimates.

MANUFACTURING PROCESSES

Most linear alpha-olefins are currently commercially produced by ethylene oligomerization. The products of the oligomerization consist of even-numbered carbon chains ranging from C₄ to C₃₀⁺.^{*} They have relatively small amounts of branched and internal olefin isomers and paraffin impurities. Sasol operates a purification facility in South Africa that recovers alpha-olefins contained in streams from coal-based synthetic fuel plants. This plant can recover odd-numbered alpha-olefins in addition to even-numbered products.

ETHYLENE OLIGOMERIZATION

The first commercial production of linear alpha-olefins by ethylene oligomerization was in 1966. All but one LAO producer worldwide currently use an oligomerization process, and the catalyzed chain-growth chemistry is similar in all of the methods. However, modifications by some producers at different stages of the reaction sequence lead to different product and chain-length distributions.

There are three main processes currently in use—Chevron Phillips Chemical (CPChem), Ethyl and Shell. The CPChem route uses a single stage for chain growth and displacement reactions, but is the least flexible of these processes in product distribution. The Ethyl process, which uses two separate steps for chain growth and displacement, gives greater flexibility in product distribution at the expense of increased process complexity and increased branching of heavier fractions. Shell's process is the most complex process of these three routes. It feeds selected alpha-olefins to an isomerization-disproportionation unit that can produce internal olefins for subsequent internal consumption or merchant sale at generally higher market values than the feed materials. The SHOP (Shell Higher Olefins Process) process is the most flexible with regard to product distribution. The isomerization-disproportionation part of the SHOP process converts alpha-olefins to internal olefins.

^{*} Butene-1 is also commercially produced by separation from various refinery and steam cracker C₄ hydrocarbon streams. In fact, butene-1 is most commonly classified as belonging to the C₄ hydrocarbon group of products, regardless of its source. For additional information on butene-1 see the CEH *Butylenes* marketing research report.

The chemical composition and quality of the alpha-olefin products vary somewhat from process to process. The CPChem and Shell processes result in a higher alpha-olefin content in C₁₂₊ cuts compared with the Ethyl process. Higher linearity in alpha-olefins is desired in some end-use applications, while the higher branching in C₁₄-C₁₈ olefins produced by the Ethyl process is preferred in some other applications.

The different processes also yield different chain-length distributions. The Ethyl process (owned by INEOS) results in a Poisson distribution. The CPChem and Shell alpha-olefin processes produce a Schulz-Flory distribution. The following table presents typical product distributions for each of these processes, although each has some flexibility in chain-length distributions:

**Typical Chain-Length Distributions of
Linear alpha-Olefins by Process^a
(percent by weight)**

	CPChem	Ethyl ^b (Canada/ Western Europe)	Shell
C ₄	14	0	7-14
C ₆ -C ₁₀	41	70-77	25-41
C ₁₂ -C ₁₄	19	21-28	15-18
C ₁₆ -C ₁₈	12	0	11-15
C ₂₀₊	14	2	14-42

a. See the following sections for more information on product distributions.

b. The Ethyl process (owned by INEOS) in Canada and Western Europe recycles C₄ to produce higher olefins.

SOURCES: (A) G. R. Lappin and J. D. Sauer, *alpha-Olefins Applications Handbook*, Marcel Dekker, Inc., New York, 1989 (data for ETHYL [now INEOS]).

(B) CEH estimates (all other data).

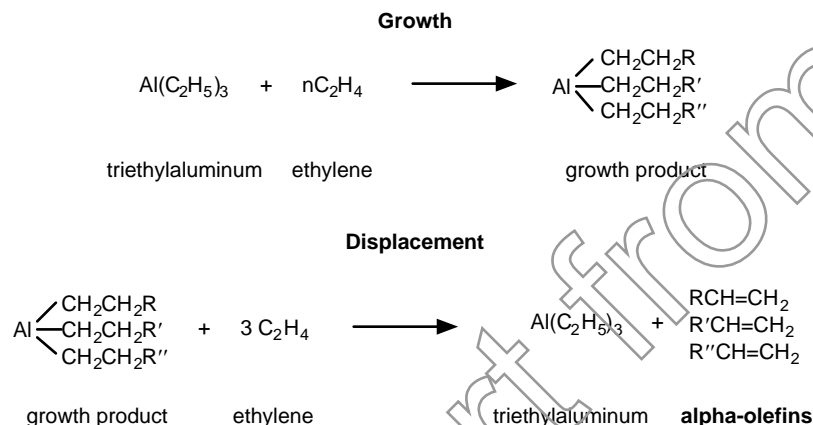
The processes used by INEOS and CPChem are based on Ziegler chemistry using ethylene and a triethyl-aluminum catalyst to promote chain growth of even-carbon-number alpha-olefin molecules. In both of these methods, the chain-length distribution of the linear alpha-olefin product can be changed to a limited extent by altering operating conditions. Notable differences in the two routes include the following: (1) olefins can be recycled for further growth in the Ethyl process, thus maximizing yields of the C₆-C₁₄ olefins, and (2) INEOS' product contains a slightly higher percentage of branched material, particularly in the detergent range, than the product obtained via the CPChem process.

Shell's SHOP ethylene oligomerization route to alpha-olefins differs from the others in that it uses a proprietary nickel complex catalyst in the initial chain-growth step and it can convert alpha-olefins to internal olefins of a desired carbon number by isomerization and disproportionation.

The major commercial processes, in addition to other processes available for commercialization, are described in the following sections. For more detailed information on manufacturing processes for the production of linear alpha-olefins, see the Process Economics Program *Linear alpha-Olefins* report.

CHEVRON PHILLIPS CHEMICALS' ETHYLENE OLIGOMERIZATION (ZIEGLER PROCESS)

Chevron Phillips' process uses a technology developed by Gulf Oil Chemicals Company, which Chevron (now Chevron Phillips Chemical Company LP [CPCChem]) acquired in 1985. This one-step conventional Ziegler process combines high-temperature addition of ethylene and displacement of the generated aluminum alkyls to produce linear alpha-olefins. Ethylene reacts with the triethylaluminum growth products to yield even-numbered carbon olefins by displacement. Typical reaction conditions are 175-290°C at pressures of 2,000-4,000 psi. The resulting carbon number range for this process is C₄-C₃₀₊, with distribution skewed toward the lower-carbon-number olefins in the C₄-C₁₀ range. The basic reactions occurring in this process can be represented as follows:



The linear alpha-olefin reaction product is a mixture of olefins that are subsequently purified and can also be fractionated into specific carbon chain-length fractions. The metal alkyl catalyst is deactivated and removed before the products are separated to avoid further isomerization.

The distribution of chain lengths may be varied to some extent by altering process conditions in order to meet merchant market demands. The curve typically is a geometric distribution with ranges as follows:

Percent by Weight	
C ₄	14
C ₆ -C ₁₀	41
C ₁₂ -C ₁₄	19
C ₁₆ -C ₁₈	12
C ₂₀₊	14

Typical linear alpha-olefin content ranges from 90.5% to 98.3% for C₄-C₁₈, with the butene-1 fraction being the most pure. Impurities include internal olefins, paraffins and branched olefins. Typical alpha-olefin content for C₂₀-C₂₄ is 88.3% and 33.0-48.0% for C₂₄-C₃₀₊.

CPCChem currently uses this technology in the United States at its plant in Cedar Bayou, Texas. Mitsubishi Chemical Corporation licenses the CPCChem technology for its plant in Mizushima, Okayama Prefecture, Japan, but Mitsubishi Chemical discontinued its production in May 2009. Another plant using this technology started up in September 1992 at Chemopetrol's SPOLANA chemical complex in Neratovice, the Czech Republic (but this plant closed in 2003). CPCChem has expanded its U.S. production site several times.

CPChem (formed from the chemical businesses of Chevron and Phillips) acquired the Phillips hexene-1 technology. Q-Chem, a joint venture between CPChem and Qatar Petroleum, has a hexene-1 plant in Qatar based on Phillips' technology. However, Q-Chem's hexene-1 is produced from ethylene.

INEOS' ETHYLENE OLIGOMERIZATION (MODIFIED ZIEGLER PROCESS)

A second oligomerization process was developed and first used by Ethyl Corporation. Ethyl's LAO business became part of Albemarle Corporation in 1994, when the former split out its chemical activities that were not related to lubricants and fuel oil additives. Subsequently, Albemarle sold its LAO, polyalpha-olefin and detergent alcohol businesses to Amoco Corp. in 1996. The latter then merged with British Petroleum plc (BP) to form BP Amoco Corp. within North America. The company later changed its name to BP. BP's refining, olefins and derivatives business (Innovene) was fully acquired by INEOS in 2005.

In the first stage, ethylene is oligomerized by trialkylaluminum growth promotion in a process similar to the one-step process. Typical reaction conditions are temperatures of 116-132°C and pressures of 2,700-3,000 psi.

In the displacement step, the trialkylaluminum compounds formed in the first stage are displaced with ethylene to yield linear alpha-olefins in the C₄-C₁₈ range and to regenerate the triethylaluminum for recycle. Reaction conditions range from temperatures of 260-316°C and pressures of 230-250 psi.

The product separation step processes unconverted ethylene from the growth and displacement reactor stages for recycle and separates the individual C₄-C₁₈ olefins. The linear alpha-olefins are distilled at 90-125°C.

Typical linear alpha-olefin content ranges from 93.7% to 99.7% for C₄-C₁₂, with the butene-1 fraction being the most pure. Impurities include paraffins, internal olefins and branched olefins. This process yields higher amounts of the branched oligomers than the one-step reaction because of the continued reaction of alpha-olefin product in the recycle step. These branched products are concentrated in the higher-carbon-number C₁₄-C₁₈ ranges, whereas the shorter-chain-length linear alpha-olefins have lower concentrations of the branched impurities. Typical alpha-olefin content for C₁₄ is 81.0% and 62.7% for C₁₆₋₁₈.

To satisfy changing market demands, distribution of chain lengths can be altered by changing reaction conditions. Automated computer control allows for shifting the production of chain-length distributions. Current production emphasis is on the lower-carbon-number olefins, to supply the comonomer, plasticizer and polyalphaolefin markets. The typical product distribution by chain-length range exhibits a Poisson distribution, as follows:

	Percent by Weight
C ₄	12
C ₆ -C ₁₀	54-60
C ₁₂ -C ₁₄	20-25
C ₁₆ -C ₁₈	5-7
C ₂₀₊	2

BP used this process in its plant at Pasadena, Texas (which closed in 2005). INEOS uses similar technology with the addition of a butene recycle loop in a plant at Feluy, Belgium that began operations in mid-1992 and at Joffre, Alberta (Canada) that became operational in May 2002. The resulting product distribution is as follows:

Percent by Weight

C ₄	0
C ₆ -C ₁₀	70-77
C ₁₂ -C ₁₄	21-28
C ₂₀₊	2

Due to INEOS' product distribution, the company is the second-largest producer of C₆-C₁₀ LAOs. A linear alpha-olefin plant using this ethylene oligomerization process started up in 1990 at Nizhnekamsk in the Tatar Republic of Russia. Capacity for the plant is currently 90 thousand metric tons. Only one of two lines is operational since it restarted in 1998 after a period of inactivity.

SHELL'S ETHYLENE OLIGOMERIZATION (SHELL HIGHER OLEFINS PROCESS—SHOP)

Shell first commercially used the SHOP technology at its Geismar, Louisiana plant in 1977. Unlike the Ethyl and CPChem processes, which use a triethylaluminum catalyst, the ethylene oligomerization step in SHOP is based on a non-Ziegler catalyst system. SHOP's initial products are even-numbered carbon linear alpha-olefins from C₄ to C₂₀₊. Shell distills selected individual carbon-number products in the C₄-C₂₀ range and also supplies blends. The alpha-olefins not separated for sale are converted to C₈-C₁₈₊ internal olefins via a series of isomerization and disproportionation steps. The internal olefins are subsequently converted via a modified oxo process to detergent-range primary alcohols or sold.

This process selectively yields high-purity linear alpha-olefins and detergent-range internal olefins. The SHOP process is very flexible and alpha-olefins can be withdrawn for sale or converted into internal olefins as desired. Detergent-range internal olefins can be used for manufacture of alcohols, sold or recycled. This flexibility allows Shell to meet a wide range of product demands. Shell developed this process to fit its own special situation as a major supplier of detergent surfactants and intermediates, in particular detergent-range alcohols and/or their ethoxylates.

The initial step of the process is conducted at moderate temperatures (80-120°C) and pressures (1,000-2,000 psi). The ethylene is oligomerized to C₄-C₂₀₊ linear alpha-olefins using a proprietary liganded nickel catalyst system. The chain-length distribution of alpha-olefins from the oligomerization step can be varied over the following range:

Percent by Weight

C ₄	7-14
C ₆	8-15
C ₈	9-14
C ₁₀	8-12
C ₁₂	8-10
C ₁₄	7-8
C ₁₆	6-7
C ₁₈	5-8
C ₂₀₊	14-42

The C₄-C₂₀ alpha-olefins are distilled from the mixture and separated into high-purity individual components and blends to be marketed as Shell's Neodene[®] linear alpha-olefins. Typical linear alpha-olefin content ranges from 94% to 99% for C₄-C₂₀, with the hexene-1 fraction being the most pure. Impurities include internal olefins, paraffins and branched olefins. Shell has the highest linearity of alpha-olefin producers.

In the next step of the process, Shell converts C_4 and C_{20+} alpha-olefin fractions and a selected portion of the alpha-olefin products to C_{11} - C_{14} detergent-range internal olefins by isomerization and disproportionation reactions. The olefin fractions are first purified using absorbent beds and then isomerized at moderate temperatures (80-140°C) and pressures (50-250 psi) using a proprietary catalyst. The internal olefins are then disproportionated, using a catalyst and reaction conditions similar to the isomerization step, to new pairs of internal C_4 - C_{20+} odd- and even-numbered carbon chain lengths. This disproportionation of the internal olefins yields 10-15% by weight of detergent-range C_{11} - C_{14} product per pass. These olefins are then recovered by distillation. The remaining olefins are recycled through the disproportionation or isomerization and disproportionation steps.

After distillation, the C_{11} - C_{14} internal linear olefins are converted via a modified oxo process to Neodol[®] detergent-range alcohols; 80% is linear alcohol and the remainder is the 2-methyl isomers. In addition, some quantities of C_9 - C_{11} alcohols are made from processing C_8 - C_{10} internal olefins. (alpha-Olefins can also be processed directly through the oxo alcohol unit.) Internal olefins in the C_8 - C_{18} range are also offered on the merchant market.

In addition to the Geismar, Louisiana facilities, SHOP is also used in the Shell Chemicals UK Ltd. plant in Ellesmere Port (Stanlow), United Kingdom, which has been operating since the fall of 1982.

IDEMITSU'S ETHYLENE OLIGOMERIZATION PROCESS

Idemitsu commercialized its own process at a plant that started up in Japan in mid-1989. This process, also based on ethylene oligomerization, utilizes a proprietary zirconium-based catalyst system. The reported advantage of this process is that it produces fewer branched and internal olefins and fewer waxes are formed. Recommended reaction conditions are 100-150°C at pressures of more than 355 psi. Product distribution can be controlled within the constraints of the geometric pattern by appropriately selecting the reaction conditions and catalyst concentration and composition.

VISTA'S ALFENE[®] PROCESS

CONDEA Vista Company (now Sasol since the company acquired CONDEA Vista in 2001), developed its Alfene[®] process for the production of linear alpha-olefins, but has not commercialized it. This process parallels its Alfol[®] ethylene oligomerization process for the production of linear alcohols and uses a Ziegler-type low-temperature ethylene growth stage with triethyl-aluminum similar to the Amoco process. The triethylaluminum is separated from the displacement product by formation of a complex and a proportion of the lower olefins is recycled to the growth reaction step. This process also yields a Poisson distribution of LAOs.

EXXON'S ETHYLENE OLIGOMERIZATION PROCESS

Exxon Research and Engineering Company has a low-pressure, low-temperature variation of the ethylene oligomerization process that uses a soluble catalyst derived from alkyl aluminum halides and transition metal compounds. Products are high-purity (greater than 98%) linear alpha-olefins with an even number of carbon atoms. Product distribution, which follows a geometric pattern, can be controlled by altering the process conditions. This process has not been commercialized.

DUPONT'S VERSIPOL™ PROCESS

DuPont has developed a one-step ethylene oligomerization process using its Versipol™ family of catalysts (such as a mixture of an iron tridentate catalyst and an alkyl aluminum cocatalyst) in the production of LAOs with low capital and operating costs and high product purity (98%). This system offers greater flexibility in the selection of the LAO product distribution. DuPont is offering this technology for license.

SABIC/LINDE ALPHA-SABLIN™ PROCESS

Linde and SABIC (Saudi Arab Basic Industries Corporation) developed their linear alpha-olefins technology in partnership under the commercial name of alpha-SABLIN™. alpha-SABLIN™ utilizes a two-component catalyst system for homogenous, liquid-phase ethylene oligomerization. The catalyst system consists of a proprietary zirconium (Zr) compound used in conjunction with an aluminum alkyl cocatalyst, providing narrow carbon-number distributions. The product has more branching in the higher-range alpha-olefins.

The LAOs are fed into a series of conventional separation columns to obtain the desired product cuts. The high-selectivity, one-stage reactor is claimed to produce high-purity products that do not require secondary stages, such as superfractionation distillation towers for removal of side products. Technical features of the process include reduced reaction temperature and pressure in the oligomerization reactor, improved control of molecular weight distribution of reactor products, and high product selectivity and purity because of a nonnoble metals catalyst. The relative distribution of the different olefins produced by alpha-SABLIN™ technology is shown in the table below.

**Product Distribution of LAOs
Using alpha-SABLIN™ Technology
(percent)**

C ₄	27
C ₆	23
C ₈	18
C ₁₀	11
C ₁₂	8
C ₁₄₋₁₈	10
C ₂₀₊	3

SOURCE: CEH estimates.

According to Linde, alpha-SABLIN™ offers more moderate reaction conditions and the highest flexibility to produce alpha-olefins in different product ranges as compared to other LAO technologies. Thus, the technology has an advantage that it can be changed to match the products demand.

OTHER ALPHA-OLEFIN SYNTHESIS ROUTES

SASOL'S PURIFICATION PROCESS

Sasol Chemical Industries of South Africa has built a plant for recovering C₅-C₈ alpha-olefins. The Sasol process is unique in that the alpha-olefins are produced from a gasification plant and Fischer-Tropsch conversion. Coal is converted to crude gas under pressure, high temperature and in the presence of steam

and oxygen. After purification, the synthesis feed gas is sent to reactors for Fischer-Tropsch conversion, in which hydrogen and carbon monoxide react in the presence of an iron-based catalyst and pressure to yield a broad spectrum of hydrocarbons in the C₁-C₂₀ range. Prefractionation splits out the alpha-olefins and a second (etherification) stage converts branched-chain olefins into heavy ethers that are distilled out from the primary linear olefin stream. The final stage consists of superfractionation and distillation to separate out the impurities (mainly paraffins and cyclic olefins) and to produce pure hexene-1, pentene-1 and octene-1.

The purification facility came on stream in 1994. Higher olefins can also be recovered and the company is planning to do so.

PARAFFIN WAX CRACKING

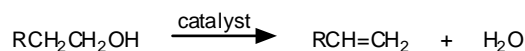
Until the introduction of the oligomerization route, linear alpha-olefins were produced by thermally cracking waxy paraffins found in crude oils. The LAOs produced by cracking contained both odd- and even-numbered carbon chains with lengths ranging from C₅ to C₂₀₊. Paraffin wax cracking was less efficient than ethylene oligomerization processes since it was energy-intensive, it did not yield as pure a product and it contained higher levels of internal olefins, dienes and paraffin impurities. Limited feedstock supplies also contributed to its demise.

The process was conducted in the vapor phase at relatively low cracking temperatures followed by rapid quenching to prevent side reactions such as isomerization or cyclization. Using a purified paraffin feedstock resulted in linear alpha-olefins of 90% purity by weight.

This technology is no longer in use commercially. Until 1985 Chevron Chemical Company produced linear alpha-olefins by thermal cracking of paraffin waxes at Richmond, California. The Royal Dutch/Shell Group also produced linear alpha-olefins by wax cracking at Pernis, Netherlands and at the Berre, France facility, but these plants have been permanently shut down since 1986.

DEHYDRATION OF ALCOHOLS

The dehydration of primary alcohols was the first commercial process for linear alpha-olefins. Linear primary alcohols, when vaporized and passed over a heated catalyst, lose a water molecule to yield an alpha-olefin of the same carbon number.



This process has not been used since 1966 when Archer Daniels Midland Company discontinued production of alpha-olefins.

ISOMERIZATION OF INTERNAL OLEFINS

Although internal olefins can be isomerized to yield linear alpha-olefins, they are themselves valuable intermediates in processes such as the synthesis of oxo alcohols and linear alkylbenzenes. They are not considered to be an economical feedstock for the manufacture of alpha-olefins.

SUPPLY AND DEMAND BY REGION

NORTH AMERICA

PRODUCING COMPANIES

The following table presents North American producers of LAOs (all three can produce their own ethylene feedstock):

North American Producers of Linear alpha-Olefins				
Company and Plant Location	Annual Capacity as of Mid-2010 (thousands of metric tons)			Remarks
	C ₄ ^a	C ₆₊	Total	
Chevron Phillips Chemical Company LP Olefins and Polyolefins Business Unit Cedar Bayou, TX	102	601	703	Listed capacity is for LAOs in the C ₄ -C ₃₀₊ range. The company markets individual linear alpha-olefins in the C ₄ -C ₁₈ range and C ₂₀ -C ₂₄ , C ₂₄ -C ₂₈ and C ₃₀₊ fractions. Captive uses include polyalphaolefins, polyethylene comonomers and lube additives. alpha-Olefins are sold under the trademark AlphaPlus [®] NAO.
INEOS Joffre, Alberta, Canada	--	265	265	Current capacity represents the normal alpha-olefins production in the C ₆ -C ₁₈ range, but is flexible. C ₄ is recycled to produce higher olefins. The company markets individual linear alpha-olefins in the C ₆ -C ₁₄ range and C ₁₂ -C ₁₄ , C ₁₄ -C ₁₆ and C ₁₆ -C ₁₈ fractions. Captive uses include polyalphaolefins. In 2005, Innovene (formerly BP's olefins and derivatives business) was fully acquired by INEOS. The company started production at its 250 thousand metric ton-per-year plant at Joffre, Alberta, Canada in late 2001. Capacity was increased by 15 thousand metric tons since 2007.
Shell Chemical Company Geismar, LA	34-41 ^b	880 ^c	921	Existing capacity is for C ₄ -C ₂₀ alpha-olefins. Capacity includes alpha-olefins that are converted to internal olefins that, in turn, are consumed to make detergent and other alcohols or sold. The company markets individual linear alpha-olefins in the C ₄ -C ₂₀ range and C ₁₂ -C ₁₄ , C ₁₄ -C ₁₆ , C ₁₆ -C ₁₈ and C ₁₄ -C ₁₈ fractions. Most butene-1 is captively consumed in the SHOP process and for polybutene-1 production. Internal olefins and alpha-olefins are sold under the trademark Neodene [®] .
Total	136-143	1,746	1,889	

- a. Includes only C₄ produced by ethylene oligomerization. There are other producers of C₄ (butene-1) from other sources not included in this report.
- b. Shell consumes some of its 1-butene internally in its I/D unit for conversion to longer-chain internal olefins. The assignment of the volume of C₄ and C₆₊ is arbitrary, but may approximate current practices.
- c. The volume assigned to C₆₊ olefins includes alpha- and internal olefins. This volume is estimated based on the difference between Shell's total capacity and its C₄ capacity of 41 thousand metric tons.

SOURCE: CEH estimates.

The preceding table includes capacity to produce butene-1 by means of ethylene oligomerization. Chevron Phillips Chemical and Shell isolate butene-1 from their ethylene oligomerization plants. Both producers use captive ethylene for making LAO. For more information on butene-1 from other sources, see the CEH *Butylenes* marketing research report.

All three LAO producers use their own process to manufacture alpha-olefins, each process yielding different chain-length distributions. See the **MANUFACTURING PROCESSES** section for a description of the distribution patterns for each process. An ongoing concern of producers is the need to adjust process conditions to maximize the value of their production by increasing production of chain lengths in high demand and minimizing production of chain lengths with low demand. However, limitations of each process, laws of stoichiometry and practical considerations (e.g., the high costs of repeated recycling) place limits on the flexibility of the chain-length distribution pattern. Producers inevitably manufacture some chain lengths in excess of existing demand, although they have often been successful in finding new consumers for these cuts. Producers try to minimize butene-1 production since they compete on the merchant market with lower-cost raffinate-derived butene-1 produced by ExxonMobil and Texas Petrochemicals. On some occasions, a very small proportion of fractions that cannot be sold at prices above fuel value can be used as a fuel in the plant or sold for this purpose.

Shell's higher olefin process (SHOP) includes the capability to convert excess alpha-olefins to C₈-C₁₈₊ internal olefins via a series of isomerization and disproportionation steps. Its annual capacity for internal olefins is approximately 250 thousand metric tons. Most of the internal olefins are subsequently converted via a modified oxo process to detergent-range primary alcohols or plasticizer-range alcohols, but some are sold. See the **MANUFACTURING PROCESSES** section for information on this process.

Sasol plans on constructing a hexene-1 and octene-1 plant in the United States with a combined annual capacity of 100 thousand metric tons. The process will use Sasol tetramerization technology and construction is slated to commence in 2011. The plant will be located at Sasol's Lake Charles, Louisiana chemical complex.

CPChem plans to build a hexene-1 plant with over 200 thousand metric tons of capacity at its Cedar Bayou, Texas, complex. The plant is expected to start up in first-quarter 2014, using CPChem's proprietary selective hexene-1 process.

PRODUCTION

The following table presents North American production of LAOs:

North American Production of Linear alpha-Olefins^a
(thousands of metric tons)

1995	1,202
1996	na
1997	1,313
1998	1,366
1999	1,409
2000	1,415
2001	1,508
2002	1,558
2003	1,732
2004	1,815
2005	1,760
2006	1,791
2009	1,575
2010 ^b	1,650

a. Includes butene-1 from ethylene oligomerization.

b. Projected estimate.

SOURCES: (A) *NPRA Quarterly Report*, National Petrochemical Refiners Association (data for 1997-2001).

(B) CEH estimates (data for 1995 and 2002-2010).

North American production of LAOs (including butene-1) from ethylene oligomerization reached 1,575 thousand metric tons, valued at \$1.8 billion in 2009. North American capacity utilization during 2009 was approximately 84%.

The following table presents North American production of butene-1 and C₆ and higher alpha-olefins:

North American Production of Linear alpha-Olefins
(thousands of metric tons)

	Butene-1 ^a	C ₆ and Higher		Total	Total
		C ₆ -C ₁₀	C ₁₁ and Higher		
2003	147	787	798	1,585	1,732
2006	118	745	928	1,673	1,791
2009	115	680	780	1,460	1,575

a. Data include only butene-1 produced by ethylene oligomerization.

SOURCE: CEH estimates.

For historical production and sales of linear alpha-olefins, please see **APPENDIX**.

CONSUMPTION

The following table presents North American consumption of linear alpha-olefins:

North American Consumption of Linear alpha-Olefins						
	Main Carbon Number Range	2009		2014		Average Annual Growth Rate, 2009-2014 (percent)
		Thousands of Metric Tons	Percent of Total	Thousands of Metric Tons	Percent of Total	
C₆ and Above (alpha and internal)						
Polyethylene Comonomers	6-8	673	45	762	46	2.5
Oxo Alcohols						
Detergent Alcohols	12-20 ^a	200	13	221	13	2.0
Plasticizer Alcohols	6-10 ^a	25	2	22	1	-2.5
Polyalphaolefins ^b	10, 8-12	201	13	256	16	5.0
Oil Field Drilling Fluids	16-18	90 ^c	6	100	6	2.1
Other Lubricant Additives	16-24	38	3	39	2	0.5
Alkyldimethylamines						
and Dialkylmethylamines	8-18	66	4	15	1	-25.6 ^d
Alkenylsuccinic Anhydrides	16-20	25	2	29	2	3.0
Fatty Acids (C ₇ -C ₉)	6-8	19	1	22	1	3.0
alpha-Olefin Sulfonates	14-16	14	1	15	1	1.4
Linear Alkylbenzene	10-14	9	1	9	1	-1.0
Linear Mercaptans	6-16	8	1	8	1	2.0
Aluminum Alkyls	6-8	7	0	8	1	2.7
Chlorinated alpha-Olefins	10-16	5	0	5	0	0
Alkyldiphenylether Disulfonates	12-14	4	0	4	0	2.0
Other ^e	6+	22	1	24	1	1.8
Total		1,406	93%	1,539	93%	1.8%
C₄ (Butene-1)						
Polyethylene Comonomers ^f	4	90	6	--g	--	--
Polybutene-1 ^f	4	--g	--	--g	--	--
Aluminum Alkyls	4	--g	--	--g	--	--
Butylene Oxide ^f	4	--g	--	--g	--	--
C ₅ Aldehydes ^f	4	--g	--	--g	--	--
Linear Mercaptans ^f	4	--g	--	--g	--	--
Other ^f	4	10	1	110	--	2.5 ^h
Totalⁱ		100	7%	110	7%	1.9%
Total		1,506	100%	1,649	100%	1.8%

a. The carbon number range is for olefins in the form consumed for these end uses. Data include internal olefins that are made from C₄ and higher alpha-olefins; estimates, therefore, include C₄ in addition to higher alpha-olefins.

b. Most PAOs are based on C₁₀; C₈ and C₁₂ are also used to make PAOs.

c. Although relatively small compared with C₁₆-C₁₈ usage, beginning in 2003, includes 9-11 thousand metric tons of C₁₄ for off-shore and onshore drilling as well as C₁₄ ester (from LAO).

d. The consumption of LAOs for the production of ADMA will decline at a high average annual rate as a result of P&G's feedstock switch from LAOs to natural fatty alcohols in 2010.

e. Other uses include those described later in the consumption section, as well as inventory changes and any products burned for fuel value.

- f. Most C₄ (butene-1) markets are also supplied from refinery sources. Estimates in the table include only butene-1 supplied by LAO producers. See the CEH *Butylenes* marketing research report for estimates of total butene-1 consumed. Because producers have a choice of butene-1 suppliers, the amount supplied by LAO producers can vary from year to year.
- g. Since butene-1 from both LAO production and refinery sources is sold into these applications, the total volume of butene-1 from LAO production consumed is not easily estimated for these applications. Thus, any such use of LAO-derived butene-1 is included in the value shown in the Other category.
- h. The volume and growth rate shown for the butene-1 derived from LAOs does not represent a composite of growth in the individual market segments as shown in the table. Instead, it reflects the assumption that all butene-1 produced from ethylene oligomerization will find a home in the overall butene-1 market and that growth will be driven by the higher fractions of LAOs.
- i. Total butene-1 excludes butene-1 consumed by Shell to make internal olefins for oxo alcohol production or for export. The volume of butene-1 consumed for Shell's oxo alcohol production is included in the consumption shown under plasticizer and detergent alcohols in the table.

SOURCE: CEH estimates.

North American alpha-olefin consumption, which reached 1,506 thousand metric tons in 2009, decreased at an average annual rate of approximately 2% during 2006-2009 compared to an average annual increase of 3.6% during 2003-2006. Most of this decrease took place in 2008 and throughout most of 2009. The economic crisis negatively affected consumption of LAOs in most applications, particularly comonomers used for the production of polyethylene (LLDPE and HDPE), the largest consuming market. By the end of 2009, production of HDPE and LLDPE was up significantly over 2008, but not quite to 2006 levels. As of August 2010, consumption of LAOs in most major-consuming markets was up as the economy improved and markets tried to regain volume lost during the economic recession.

The fastest-growing markets are those that use LAOs as raw materials (largely C₁₀) for polyalphaolefins (for synthetic lubricants), as comonomers (C₄-C₈) in polyethylene, in drilling fluids (C₁₆-C₁₈), and for alkenylsuccinic anhydrides (ASA). Although growing more slowly, detergent-range alcohols absorb large volumes of LAOs as raw materials, mainly in the mid-range (C₈-C₁₄). These variations in current and projected growth of end-use markets that require different chain lengths present special problems to producers. As already described, alterations in the process conditions permit producers to make adjustments to meet market demand, but since some imbalance persists, wide variations in prices for the various chain lengths often are employed to further balance demand.

Total North American alpha-olefin consumption is expected to increase at an average annual rate of approximately 2% during 2009-2014, reaching 1.65 million metric tons in 2014.

The following table presents historical consumption of North American linear alpha-olefins:

Historical North American Consumption of Linear alpha-Olefins
(thousands of metric tons)

	Main Carbon Number Range	1995	1999	2003	2006
C₆ and Above (alpha and internal)					
Polyethylene Comonomers	6-8	277	413	483	656
Alcohols					
Detergent Alcohols	12-20 ^a	231	277	256	242
Plasticizer Alcohols	6-10 ^a	125	125	116	70
Polyalphaolefins ^b	10, 8-12	131	147	178	219
Oil Field Drilling Fluids	16-18	23	73	79 ^c	84 ^c
Other Lubricant Additives	16-24	27	39	40	42
Alkyldimethylamines and Dialkylmethylamines	8-18	29	31	58	64
Fatty Acids (C ₇ -C ₉)	6-8	20	29	29	25
Alkenylsuccinic Anhydrides	16-20	16	21	23	25
alpha-Olefin Sulfonates	14-16	11	13	14	13
Linear Alkylbenzene	10-14	11	23	11	10
Linear Mercaptans	6-16	6	8	9	8
Aluminum Alkyls	6-8	5	6	7	8
Chlorinated alpha-Olefins	10-16	7	7	6	6
Alkyldiphenylether Disulfonates	12-14	3	4	4	4
Other ^d	6+	20	21	22	23
Total		941	1,235	1,336	1,499
C₄ (Butene-1)					
Polyethylene Comonomers ^e	4	55	95	91	95
Polybutene-1 ^e	4	23	-- ^f	-- ^f	-- ^f
Aluminum Alkyls	4	4	5	-- ^f	-- ^f
Butylene Oxide ^e	4	14	-- ^f	-- ^f	-- ^f
C ₅ Aldehydes ^e	4	5	-- ^f	-- ^f	-- ^f
Linear Mercaptans ^e	4	3	-- ^f	-- ^f	-- ^f
Other ^e	4	3	19	16	12
Total^g		107	119	107	107
Total		1,048	1,354	1,443	1,606

a. The carbon number range is for olefins in the form consumed for these end uses. Data include internal olefins that are made from C₄ and higher alpha-olefins; estimates, therefore, include C₄ in addition to higher alpha-olefins.

b. Most PAOs are based on C₁₀; C₈ and C₁₂ are also used to make PAOs. Beginning in 2006, includes C₈-C₁₂.

c. Although relatively small compared with C₁₆-C₁₈ usage, beginning in 2003, includes 9-11 thousand metric tons of C₁₄ for offshore and onshore drilling as well as C₁₄ ester (from LAO).

d. Other uses include those described later in the consumption section, as well as inventory changes and any products burned for fuel value.

- e. Most C₄ (butene-1) markets are also supplied from refinery sources. Estimates in the table include only butene-1 supplied by LAO producers. See the CEH *Butylenes* marketing research report for estimates of total butene-1 consumed. Because producers have a choice of butene-1 suppliers, the amount supplied by LAO producers can vary from year to year.
- f. Since butene-1 from both LAO production and refinery sources is sold into these applications, the total volume of butene-1 from LAO production consumed is not easily estimated for these applications. Thus, any such use of LAO-derived butene-1 is included in the value shown in the Other category.
- g. Total butene-1 excludes butene-1 consumed by Shell to make internal olefins for oxo alcohol production or for export. The volume of butene-1 consumed for Shell's oxo alcohol production is included in the consumption shown under plasticizer and detergent alcohols in the table.

SOURCE: CEH estimates.

The estimates for C₄ (butene-1) demand include only the material supplied from alpha-olefin plants. See the discussion sections for estimates of total butene-1 consumed from all sources. Butene-1 from LAO production is disposed of as a relatively low-value coproduct (often below the price of ethylene) in a larger butene-1 market served by other sources. Consequently, its distribution within market segments is difficult to quantify and can vary significantly from year to year. Furthermore, growth for butene-1 from LAOs is driven by its supply, which depends upon demand for the other LAO fractions, rather than demand within the actual markets for butene-1. Thus, LAO producers will dispose of butene-1 within its markets at whatever price they can obtain, so long as it is above fuel value. For this reason, the markets for butene-1 are shown separately in the table, following those that consume the higher fractions. In addition, some butene-1 is converted to higher carbon-numbered internal olefins for conversion to alcohols by Shell in its isomerization/disproportionation unit. Most of the resulting olefins are internally consumed to produce plasticizer and detergent alcohols and this volume is accounted for within these two categories in the consumption table. Some internal olefins are exported to other countries.

For historical U.S. consumption (excluding Canada) of linear alpha-olefins, please see **APPENDIX**.

The end-use market discussion that follows presents each segment in order of market size (largest first), regardless of chain length (i.e., whether from butene-1 or higher LAOs).

Polyethylene Comonomers

Linear alpha-olefins, specifically butene-1 (C₄), hexene-1 (C₆) and octene-1 (C₈), are used as comonomers in the production of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) resins. This category also includes the even lower-density products (i.e., polyolefin plastomers and elastomers) that are made by the same processes. HDPE and LLDPE are both linear polyethylenes produced in low-pressure processes; LAOs are not consumed for production of conventional branched low-density polyethylene (LDPE) resins made in high-pressure processes. The LAO comonomers create short-chain branching in the polymer that prevents polymer chains from packing together tightly, thus lowering product density. The higher the comonomer concentration, the lower the density of the resin. In addition to controlling density, alpha-olefin comonomers modify the processing and mechanical properties of the polymer. The chain length of the comonomer also influences these properties. Hexene-1 and butene-1 are comonomers used in HDPE (slurry phase), and in gas phase and solution phase LLDPE. Octene-1, demand for which has remained strong in recent years, is used in solution-phase LLDPE plants.

The following table presents North American consumption of comonomers in PE production in 2009:

**North American Consumption of Comonomers in
Polyethylene Production—2009
(thousands of metric tons)**

	From Ethylene Oligomerization	From Non- oligomerization Sources	Total	
			Thousands of Metric Tons	Percent of Total
Total	763	101	864	100%
Butene-1	90	101	191	22.1
Hexene-1	351	--	351	40.6
Octene-1	322	--	322	37.3
Total	763	101	864	100%

SOURCE: CEH estimates.

The following table presents North American comonomer use in PE by type:

**North American Comonomer Use in
Polyethylene by Type—2009
(thousands of metric tons)**

	C ₄	C ₆	C ₈	Total
LLDPE	191	235	193	619
HDPE	--	116	--	116
Plastomers/Elastomers	--	--	129	129
Total	191	351	322	864

SOURCE: CEH estimates.

Overall use of LAO comonomer from LAO producers is expected to grow at a more modest average annual rate of 2.1% during 2009-2014. This growth primarily reflects increasing production of plastomers and elastomers in North America during this time period and increased production of LLDPE in 2010. In terms of LAO comonomer consumption for the combined production of LLDPE and HDPE, growth will be relatively flat. As of mid-2010, North American production of HDPE and LLDPE was higher than in 2009, driven by exports to regions with high demand and improved domestic demand. Although there is a shift in production and consumption of PE to regions such as China where demand is considerably higher or to regions where feedstocks are cheaper (Middle East) and demand is strong, North American shale gas developments should positively affect U.S.-based producers of ethane and ethylene in terms of low/competitively priced feedstocks. This will in turn have a positive effect on North American production of PE.

New PE process and catalyst technologies have been commercialized during the last decade that have provided a better balance of processability and physical properties. Conventional Ziegler-Natta catalysts contain many reactive sites with varying levels of reactivity, resulting in variations in the polymers produced. The newer metallocene catalysts are single-site catalysts that provide identical reactive sites that allow the resin producer to maximize desired physical properties. The distinguishing characteristic of resins produced using metallocenes is a narrow molecular weight distribution. Metallocenes also provide

far better control of comonomer incorporation, molecular weight and crystalline structure. This overall capability to control polymer properties results in improvements in tailoring polyethylenes to meet processor and user needs. In some cases, these improvements will also permit the use of lower levels of comonomer to achieve the same properties as existing products containing higher comonomer levels.

Further developments of this technology have led to the development of low-modulus copolymers designed to compete with elastomers and flexible polymers in the 0.860-0.910 density range. These resins have very high comonomer levels, ranging from 10% to 30%; resins with 10-20% comonomer content are being called polyolefin “plastomers,” while resins with 20-30% comonomer content are considered polyolefin elastomers. The new resins are opening new markets for PE, competing with materials such as plasticized PVC, EPDM elastomers and EVA copolymers.

Linear low-density polyethylene (LLDPE) resins

All linear low-density polyethylene (LLDPE) resins are copolymers of ethylene with higher alpha-olefin comonomers such as butene-1, hexene-1 and octene-1. Polyethylene resins are generally characterized by density and melt index. In general, LLDPE resins have densities ranging from 0.916 to 0.940.

Generally, LLDPE resins are produced by both liquid-phase and gas-phase processes. Almost all plants that can make LLDPE as a primary product are actually linear polyethylene plants that are also capable of producing HDPE; however, these “swing plants” are usually operated on a dedicated basis to make predominantly one or the other product for extended periods. Frequent switches between LLDPE and HDPE are costly and not practiced routinely. The most commonly used commercial process for making LLDPE is Dow’s (formerly Union Carbide’s) gas-phase Unipol® process. In this process, butene-1 or hexene-1 is copolymerized with ethylene in a fluidized-bed reactor. Another widely used process is INEOS’ gas-phase fluidized-bed process, which can use C₄ or C₆ (hexene-1 or 4-methylpentene-1) feed; no 4-methylpentene-1 is currently used in the United States. In 2009, INEOS Licensing announced that their Innovene process can use C₈ comonomer instead of the traditional C₄ or C₆. Significant quantities of LLDPE are also produced by Dow’s solution-phase process, which copolymerizes octene-1 with ethylene. Several other producers can also use octene-1 to make LLDPE.

Desired properties, economic considerations and process determine the choice of comonomer. Butene-1 is less expensive than hexene-1 and octene-1. However, LLDPE resins based on hexene-1 and octene-1 are increasingly attractive, despite higher costs, because of the excellent properties imparted to the copolymer product, including greater tear strength and stress crack resistance.

Comonomers are used either alone (copolymer) or in combinations (terpolymer). Although levels of comonomers incorporated in LLDPE can be as low as 3%, an average level is now between 10% and 14%. Until 1984, most LLDPE resins were based on butene-1 comonomer, which provided sufficiently high performance properties to compete with LDPE. During the mid-1980s, Union Carbide began to increase its production of resins based on hexene-1. Currently, butene-1 is still the largest-volume comonomer consumed for LLDPE resins. However, hexene-1 and octene-1 are expected to continue to take market share from butene-1 during the next few years.

North American production of LLDPE resins amounted to approximately 6.0 million metric tons in 2009. Approximately 65% of this amount was in the United States and the balance in Canada. Consumption in film is by far the largest market. Other significant end uses for LLDPE in North America include injection molding, rotomolding, sheet, and wire and cable. The rapid growth of LLDPE following its introduction in the early 1980s was due primarily to its success in capturing a major portion of existing polyethylene

film markets. LLDPE quickly penetrated established LDPE film markets where its lower prices and higher strength properties could offer improved performance and cost savings through product downgauging. LLDPE has been most successful in consumer, institutional and industrial garbage bags and liners.

Octene-based LLDPE and further improvements in hexene-1-based resins have further expanded the market for LLDPE resins and fueled a rapid growth rate that has exceeded GDP. Improvements in manufacturing and fabrication technologies continue to open up new markets and applications. North American consumption of LAOs for the production of LLDPE is expected to increase at an average annual rate of 1.0% during 2009-2014. The largest-volume growth will be in film applications, followed by injection molding and sheet.

For detailed information on LLDPE resins, see the CEH *Linear Low-Density Polyethylene (LLDPE) Resins* marketing research report.

High-density polyethylene (HDPE) resins

Approximately 13% of comonomer demand is for the production of high-density polyethylene (HDPE) resins. Linear polyethylene resins with densities of over 0.940 are classified as HDPE resins. They are produced in a variety of low-pressure processes based on different catalyst systems. The processes can be classified into three basic groups according to their reaction conditions—gas phase, slurry phase and solution phase. The most widely used process for producing HDPE in the United States is the Phillips process (slurry phase), followed by Dow's Unipol® process (gas phase). The Phillips process uses hexene-1 comonomer, while the Unipol® process can use either hexene-1 or butene-1 comonomer. Octene-1 is used only in facilities that use the solution process, the largest of which is Dow's. See the CEH *High-Density Polyethylene Resins* marketing research report for information on other processes to make HDPE.

High-density polyethylene homopolymers (i.e., those made solely from ethylene) have high stiffness properties; however, they are susceptible to environmental stress cracking in the presence of many liquids, such as household detergents. The incorporation of C₄-C₈ alpha-olefins at a rate of 0.5-3% by weight greatly increases environmental stress crack resistance (ESCR). Comonomers also increase the impact strength and provide some increase in chemical resistance. The addition of comonomer also decreases the density of the polymer, resulting in a softer, more flexible plastic. The resulting reduction in stiffness can be compensated for in the product design by molding a container with slightly thicker walls. HDPE copolymers have densities of 0.94-0.96.

In 2009, the average comonomer content for all HDPE was 1.5%. Hexene-1 accounted for the majority of comonomer demand, followed by butene-1; octene-1 accounted for a negligible amount of comonomer demand. The relative comonomer share is not expected to change significantly during the next few years.

In 2009, 7.7 million metric tons of HDPE resins were produced in North America. HDPE resins are converted to end products by blow molding or injection molding and by variations of the extrusion process. Blow-molded applications represent the largest end use for HDPE resins in North America, accounting for 38% of domestic consumption in 2009. The largest application in the blow-molding area is for milk bottles; this application and the smaller-volume market for water bottles do not require copolymer resin. This application has surpassed that of the bottles for household industrial chemicals (e.g., bleaches, dishwashing and laundry detergents, pesticides, and swimming pool chemicals), now the second-largest use in the blow-molding category. The resins used in this market are generally copolymers

with good ESCR. The use of virgin HDPE resin in household industrial chemicals containers has declined because of the increasing use of recycled resin and source reduction, including lightweighting of bottles and the development of reusable rigid containers that can be refilled using flexible pouches. These trends will continue for the next few years, resulting in a further decline in the use of virgin HDPE in this market. Also included in the blow-molded category are other consumer-oriented bottles, pails and drums, motor oil bottles, and automotive fuel tanks.

Injection-molding applications account for approximately 19% of HDPE demand. A wide variety of items are made by injection molding, including shipping pails; crates, trays and cases; food containers; and housewares.

Extrusion processes convert HDPE into film and sheet, pipe and conduit, wire and cable insulation, and profiles. Film and sheet applications are expected to grow strongly during the next few years. Film applications have been growing well because of the continued displacement of paper products by plastics, as well as substitution of high-molecular-weight HDPE for LLDPE in high-strength film applications. Uses include production of retail bags, including T-shirt bags, trash can liners, and food and nonfood packaging. The fastest-growing use for HDPE is for sheet applications, especially for geomembranes used as liners for landfills, ponds, reservoirs and canals.

North American consumption of LAOs for production of HDPE resins is expected to remain relatively flat during 2009-2014.

For additional information on HDPE and its markets, see the CEH *High-Density Polyethylene Resins* marketing research report.

Elastomers and plastomers

Plastomers and elastomers have densities in the 0.860-0.915 range and are produced by the same processes as LLDPE, but the level of comonomer use is in the 20-30% range. Growth in the consumption of plastomers and elastomers has been dramatic in recent years, and growth is expected to continue at a rate of approximately 10% per year during 2009-2014. Approximately 129 thousand metric tons of comonomer were consumed in this segment in 2009 and growth in its usage should continue at the same rate as for the elastomers and plastomers. Octene-1 is the largest-volume comonomer used in this market segment. Dow Chemical and ExxonMobil are the major North American producers of these products. In August 2010, Dow announced plans to increase its specialty elastomers capacity in Texas and Spain.

Oxo Alcohols

Oxo technology utilizing a linear alpha-olefin feed is currently used by Shell in both plasticizer-range and detergent-range alcohol production. As of late 2006, Sterling Chemicals (which also manufactured plasticizer-range alcohols via oxo technology utilizing a LAO feed) ceased production of C₇, C₉ and C₁₁ linear alcohols. For the purposes of this report, plasticizer-range alcohols are defined as monohydric aliphatic primary alcohols containing four to eleven carbon atoms, and detergent-range alcohols are similar products that contain twelve or more carbon atoms. Oxo processes, formally termed *hydroformylation*, involve the addition of synthesis gas (carbon monoxide and hydrogen) to either end of an olefinic bond. Most processes follow this step with hydrogenation of the resultant aldehyde to the respective alcohol in a second reactor. Hydroformylation of even-carbon LAOs yields odd-numbered linear alcohols.

Shell has developed a major modification to the oxo process. The alpha-olefins not separated for sale are converted to C₈-C₁₈₊ internal olefins via a series of isomerization and disproportionation steps in its SHOP plant. (See the **MANUFACTURING PROCESSES** section for more information on this process.) Some internal olefins are subsequently converted via a modified oxo process to detergent-range primary alcohols. Shell's process performs both hydroformylation and dehydrogenation of the intermediate aldehyde in the same reactor.

Detergent alcohols

Approximately 200 thousand metric tons of alpha-olefins were consumed by Shell to produce similar amounts of detergent alcohols in 2009. The remaining detergent alcohol production is based on either ethylene, using Ziegler chemistry, or conversion of natural fats and oils, especially coconut oil, tallow and palm kernel oil.

Shell Chemical is the only company that produces detergent alcohols (C₁₂ and higher) from LAOs in the United States, with a nameplate capacity of 286 thousand metric tons at Geismar, Louisiana. In 2002, Shell completed an expansion of 102 thousand metric tons of capacity, for a specific range of mono-methyl branched alcohol. In 2003, an equivalent capacity was placed on standby and as of mid-2010 this had not changed.

Most of Shell's plant is devoted to the production of detergent-range alcohols; however, it also produces some C₉-C₁₁ linear alcohols for plasticizer and detergent applications, as well as other oxo alcohols derived from branched olefins. Shell captively consumes most of its alcohol production to make alcohol ethoxylates. The balance is accounted for by merchant sales (including exports) of detergent alcohols, sold under the trademark Neodol®.

Demand for detergent alcohols from all sources is expected to grow at an average annual rate of approximately 2.5% during 2009-2014. Since 2003, the detergent alcohols industry had experienced some tightness. The idling of Shell's 102 thousand metric tons of capacity greatly reduced the industry's operating capacity. This combined with increasing demand for alcohols resulted in tight supplies of mid-cut (C₁₂-C₁₄) alcohols during intervals of 2006-2007. However this tightness eased with the increase of net imports of detergent alcohols in 2008, as new natural alcohol plants come on line in Southeast Asia and Brazil. It is likely that imports of alcohols from Asia will continue to increase. Consumption of LAOs for detergent alcohols will grow at an average annual rate of 2.0% per year over 2009-2014.

Approximately 84% of 2009 detergent alcohol consumption was accounted for by three surfactants: alcohol ethoxylates (AE), alcohol sulfates (AS) and alcohol ether sulfates (AES). All three are used in household laundry detergents, which is the largest end-use category for these products. Since liquid laundry detergents contain on average higher surfactant levels than laundry powders, the consumer shift to liquids has led to an increasing use of the alcohol-based surfactants in this application. Large amounts of AES, which is derived from sulfating AE, are also used in hand dishwashing liquids. All three surfactants are also used in smaller-volume household (e.g., hard surface, rug and upholstery) cleaners. AS and AES are also used in significant volumes in personal care products (especially shampoos and soaps). In addition, all three are used in many industrial applications (e.g., emulsion polymerization, agricultural emulsifiers, industrial and institutional cleaners, and textile processing).

AS and AES compete with another large-volume anionic surfactant—linear alkylbenzene sulfonate (LAS)—and with nonionic surfactants. The relative costs of the competing surfactants depend largely on the prevailing prices for their raw materials (e.g., coconut oil, ethylene, benzene and n-paraffins). Since

these prices vary considerably over time, so do the prices for the surfactants derived from them, affecting their relative cost/performance advantages. As a result, reformulations are frequent and this market is internally dynamic.

The slight decrease in consumption of LAOs for the production of detergent alcohols during 2003-2006 can be attributed to several things. The use of AES grew more slowly during recent years, as detergent manufacturers partly offset the growth in the use of AES-containing laundry liquids by reducing its concentration in these detergents—a development that was mainly a consequence of higher alcohol and other raw material costs. The consumption of AS (and alcohol consumed to make it) has fallen since 2003 because of the declining use of laundry powders containing AS, as consumers switch to liquid laundry detergents that do not use AS. A significant reduction in LAO-derived detergent alcohol exports during 2007-2009 contributed to a decrease in consumption of LAOs for the production of detergent alcohols.

Other markets for detergent alcohols include polymethacrylate esters, fatty nitrogen derivatives, thio-dipropionate ester and alkyl glyceryl ether sulfonates (AGES). Detergent alcohols are also consumed directly in cosmetics and toiletries as emollients, in formulated lubricants used in the rolling of metallic foil or sheet stock, and in pharmaceutical preparations. For more details on markets for detergent alcohols, see the CEH *Detergent Alcohols* marketing research report.

Plasticizer alcohols

Approximately 25 thousand metric tons of alpha-olefins were consumed to produce similar amounts of C₇-C₁₁ oxo alcohols in 2009. This includes small amounts that were consumed for the production of surfactants.

As of August 2010, Shell is the only company that produces linear plasticizer alcohols (C₇-C₁₁) from LAOs in the United States. Shell produces C₇-C₁₁ linear alcohols for plasticizer and detergent applications as an adjunct to its Neodol® detergent-range alcohols. As previously mentioned, Shell converts C₆-C₁₀ internal olefins, which are obtained in its SHOP plant via isomerization and disproportionation of linear alpha-olefins, to a mixture of C₇-C₁₁ alcohols via a modified oxo reaction. These alcohols, sold as Linevol® 11, Linevol® 911 and Linevol® 79, are approximately 80% linear and 20% branched alcohols. Shell's flexible SHOP process can produce in any desired range; however, most of Shell's production is detergent alcohols and only a relatively small part of Shell's U.S. output is in the plasticizer range.

ExxonMobil purchases linear alcohols for the production of linear plasticizers. Sterling Chemicals ceased production of linear alcohols when it permanently shut down its 102 thousand metric ton-per-year oxo alcohols production unit in late July 2006—citing high raw material costs, raw material supply shortages and competing branched plasticizers as the reasons. BASF had marketing rights to Sterling's alcohol output, which was converted primarily to phthalate esters for BASF's Palatinol® line. Sterling will continue to produce phthalate esters for BASF with oxo alcohols supplied by BASF through 2013.

Linear alcohols were introduced into plasticizer markets because of the lower volatility, low-temperature stability and low water extraction that they impart to esters. C₇-C₁₁ alcohols are reacted most commonly with phthalic anhydride or, to a much lesser extent, with other acids, such as adipic acid, to produce the corresponding esters, which are used as plasticizers for flexible polyvinyl chloride (PVC) resins, especially those used in calendaring (e.g., coated fabrics and sheet goods) and when outdoor weathering resistance is required. They compete to a limited extent with the largest-volume plasticizers—di(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate (DINP)—which are branched plasticizers. The

linear C₇-C₁₁ plasticizers (e.g., ExxonMobil's Jayflex[®] 711) have distinct advantages in vinyl plasticizers for automotive upholstery and compartment interiors. While maintaining low-temperature flexibility, the linear phthalates reduce window fogging. Other uses for 711 phthalates include calendered sheet and film for swimming pool liners, roofing membranes, automotive body side molding, tarpaulins, and wire and cable jacketing.

Although their electrical resistivity is poorer than that of branched esters, high-molecular-weight linear phthalates are used in power transmission cable where temperature properties are important. The principal phthalate consumed for this use is diundecyl phthalate (DUP) made from C₁₁ alcohol.

Consumption of linear phthalates is also impacted by raw material price relationships (i.e., the ethylene/propylene price ratio). Fluctuations in consumption will continue whenever abrupt changes in typical feedstock price ratios occur.

The future production and consumption of linear plasticizers in the U.S. market will decrease over the next five years. Higher feedstock costs and the termination of feedstock sourcing of LAOs have dampened demand for linear plasticizers. Despite some advantages over branched plasticizers, some industry sources feel that linear plasticizers will be replaced by branched product over the long term. The consumption of LAOs for the production of C₇-C₁₁ linear alcohols is expected to decline at an average annual rate of 2.5% per year during 2009-2014.

For more information on plasticizers, including other smaller-volume plasticizers derived from C₇-C₁₁ alcohols and plasticizer alcohols, see the CEH *Plasticizers* and *Plasticizer Alcohols (C₄-C₁₃)* marketing research reports.

Polyalphaolefins

Polyalphaolefins (PAOs), also known as linear alpha-olefin oligomers, are base stock materials for synthetic lubricants for automotive, industrial and aviation applications. These synthetic base fluids have a uniform isoparaffinic structure similar to paraffinic mineral base stocks. Smaller but significant volumes of PAOs are used in other applications, including dielectric fluids and drilling muds, especially those used in offshore drilling applications. PAOs are produced by oligomerizing short-chain LAOs (largely C₁₀, but also C₈, C₁₂, and C₁₄; some companies may mix C₈, C₁₀ or C₁₂, C₁₄) using a promoted boron trifluoride catalyst in a one-step synthesis. Depending on reaction conditions, the typical oligomer mixture is 50-65% trimer and 10-15% dimer, with tetramer and higher oligomers making up the balance. The oligomers are converted to stable, high-purity isoparaffins through hydrogenation.

The following table presents North American producers of polyalphaolefins:

North American Producers of Polyalphaolefins

Company and Plant Location	Annual Capacity as of Mid-2010 (thousands of metric tons)	Trademark/Remarks
Albemarle Corporation Pasadena, TX	15.0	ExxonMobil's SpectraSyn® high viscosity PAOs are being manufactured under contract.
Chemtura Corporation Elmira, Ontario	15.8	Synton®. Specialty high viscosity PAOs. Capacity was increased by nearly 2 thousand metric tons in 2006.
Chevron Phillips Chemical Company LP Baytown, TX	48.0	Synfluid®. Captive LAOs (pure C ₁₀ or C ₁₂ for low viscosity PAOs).
ExxonMobil Chemical Company Beaumont, TX	84.5	SpectraSyn®. Includes capacity for both low and high viscosity PAOs.
INEOS Americas, LLC Deer Park, TX	78.0	Durasyn®. Captive LAOs.
Total	241.3	

SOURCE: CEH estimates.

ExxonMobil also produces higher-viscosity PAOs, which are used as base fluids in compounding higher-viscosity gear oils, greases, industrial oils, turbine oils and motor oils in blends with other synthetics and mineral oils.

In 2005 ExxonMobil increased capacity for high viscosity PAOs and upgraded low viscosity PAO production. In 2007, ExxonMobil underwent a debottlenecking to boost PAO capacity to help meet increasing market demand for the advanced high viscosity PAO. In December 2009, ExxonMobil announced a custom manufacturing agreement with Albemarle for the production of 15 thousand metric tons of high viscosity SpectraSyn® PAOs in Pasadena, Texas.

A high percentage of ExxonMobil's PAO production is consumed captively by its parent company for the manufacture of automotive and industrial oils and greases. The PAO made by Chevron Phillips, INEOS and Chemtura is sold to the merchant market.

North American production of PAOs in 2009 amounted to 195 thousand metric tons and required 201 thousand metric tons of LAOs, 65-70% of which was decene-1. Except for limited production by Chemtura in Canada, nearly all of the North American production of PAOs was accounted for by the three large U.S. producers. The following table presents U.S. consumption of LAOs for the production of PAOs:

**U.S. Consumption of Linear alpha-Olefins for Polyalphaolefins
(thousands of metric tons)**

	Polyalphaolefin Production	Linear alpha-Olefin Consumption^a
1976	10	11
1979	25	28
1980	25	29
1985	34	38
1990	48	49
1995	125	129
1999	142	147
2003	172	178
2006	213	219
2009	195	201
2010 ^b	210	216

a. The amount of decene-1 consumed for PAO varies depending on the process and the viscosity of the oligomer products. On average, 1.09 pounds of decene-1 were consumed per pound of PAO produced during 1976-1988; 1.03 pounds of decene-1 were consumed per pound of PAO beginning in 1989.

b. Projected estimate assuming strong second half of 2010.

SOURCE: CEH estimates.

North American polyalphaolefin production increased steadily from the mid-1980s through 2007 before it decreased in 2008-2009. North American production of PAOs grew at an average annual rate of 5.5% during 2002-2006. During the period of 2004 through most of 2005, many PAO producers reported double-digit growth and operating rates over 90%. Strong demand for PAOs continued into 2006 and 2007 and operating rates remained high. However, by 2008 production (and hence LAO consumption) decreased with Hurricane Ike striking the U.S. Gulf Coast in the third quarter of 2008, followed by weak demand due to the economic recession. Weak economic conditions and a tight decene-1 supply kept production of PAOs from increasing throughout most of 2009. By the fourth quarter of 2009 things had started to improve and production and demand in 2010 (through August) have rebounded strongly compared to 2009 figures. Also, supply of decene-1 should improve with additional oversea LAO capacity.

Consumption of LAOs for the production of PAOs should average at least 5% per year during 2009-2014, assuming the impact of Group III lubricants or gas-to-liquid base (GTL) stocks on the PAO market will be minimal during this period. This also assumes an ample decene-1 supply during 2010-2014. The high performance of PAOs versus Group III base oils has allowed them to retain market share in those sectors that require this performance.

PAOs are usually considered the most versatile of all synthetic lubricants for automotive crankcase applications, which is their largest market. Compared with conventional mineral oil base stocks, they

have good lubricating properties over a wide temperature range; a high inherent viscosity index; low volatility; high thermal and oxidative stability; excellent response to antioxidants; and higher flash, fire and auto ignition points. The result is reduced engine friction, longer service life and improved efficiency under extreme cold weather conditions and high engine temperatures. PAOs are often used with lower levels of ester-type synthetic lubricants to correct seal-swelling problems that occur when they are used alone in some applications.

The market for PAOs in automotive crankcase lubricants appeared to have great growth potential, since only a very small percentage of U.S. passenger cars currently use synthetic lubricants. However, several refineries have made available increasing volumes of severely hydrocracked mineral oil-based stocks of high-viscosity index that are referred to as Group III lubricants. These new lubricants provide many, if not all, of the superior properties of the PAO-based lubricants and at a far lower cost than PAOs. Furthermore, Castrol won a court ruling in the United States that permitted the company to refer to its Group III-based lubricants as synthetic lubricants. However, PAO consumption in automotive crankcase lubricants may be boosted by the industry's trend toward longer service (drain) intervals—a trend that demands high performance base stocks such as PAOs. The volume of high-performance grade synthetic lubricants such as ExxonMobil's Mobil 1 and other PAO-based products continues to grow.

In addition to their use in automotive crankcase oils, synthetic lubricants are also consumed in automotive gear oils. These products were developed for heavy-duty trucks and other off-road vehicles to provide fuel economy and high-temperature/high-torque performance. The heavy-duty truck market suffered during the economic recession, and this sector primarily uses PAO-based synthetic lubricants for axle, transmission and driveline. Polyalphaolefin consumption in this sector is expected to exhibit above-average growth during 2009-2014, as markets rebound from the weak global economy.

Industrial applications have grown over the years. Because they provide longer drain intervals and may extend the life of equipment, synthetic lubricants can offer cost savings in some industrial applications. Use of synthetic lubricants based on PAO improves the efficiency of industrial gear systems compared with petroleum-based lubricants. A major use of PAO-based gear oils that has been showing rapid growth in recent years is lubrication of the gears of stationary diesel engines used in industry. Consumption of PAOs in industrial gear oils (primarily high-viscosity PAOs) is estimated to grow at an average annual rate of over 3% during 2009-2014.

Other large-volume lubricant applications for PAOs include compressor oils and hydraulic fluids (including automotive, aviation and industrial). Smaller-volume applications for PAO include aviation piston engine oils, greases, bearing oils, gas turbine lubricants, heat-transfer fluids, and transformer dielectric and insulation fluids.

PAOs compete for market share with dibasic esters and polyol esters in some industrial applications, but have the advantage of being less expensive than these other synthetics. For more information on polyalphaolefins and other synthetic lubricants, see the Specialty Chemicals Update Program *Synthetic Lubricants* report.

The consumption of PAOs in nonlubricant applications includes use in heat transfer fluids, transformer dielectric and insulation fluids, and drilling muds. Consumption in nonlubricant applications was 14 thousand metric tons in 2009. PAOs were used in drilling muds to help remove the cuttings, although they also lubricated the drill bit. Consumption of PAO for this purpose amounted to at least 18 thousand metric tons in 1995. However, it is believed they are no longer used in this application in the Gulf of Mexico because they do not meet regulations. PAOs were largely replaced in this application by the less costly C₁₆-C₁₈ olefins, either LAOs or isomerized LAOs.

Some industry sources feel that overall U.S. demand for PAOs (both low and high-viscosity) may grow more than 5% per year on average during 2009-2014. Polyalphaolefin demand will be driven by tightening emissions standards in the transportation industry (passenger vehicles and heavy-duty diesel).

Oil Field Drilling Fluids

LAO-based products in the C₁₆-C₁₈ range are used in oil field drilling muds as lubricants and to help remove cuttings. This application is identical to that previously described under **Polyalphaolefins**. The C₁₆-C₁₈-range LAOs have been found to provide equivalent performance at a lower price than the C₁₀-based PAOs. Consequently, they have been replacing the PAOs as well as the slow-to-biodegrade diesel oils in offshore drilling applications. The LAOs are either used as such or isomerized to internal olefins to lower their melting point. Approximately 90 thousand metric tons of C₁₄-C₁₈-range products and some lower or higher carbon-range products are used in this application. Although C₁₆-C₁₈ range is the most widely used for this application, C₁₄ usage has increased over the years in offshore drilling applications and it is also being used in onshore drilling, replacing some mineral products. The consumption of oil field drilling chemicals has increased over the years as a result of the shift from oil well drilling to natural gas well drilling. New gas wells are deeper and require more drilling fluids. However, consumption decreased in 2009 from 2008 levels as oil and natural gas exploration and production decreased—a consequence of lower demand for energy during the weak economic times and lower oil and natural gas prices.

It is difficult to predict a growth rate for LAO consumption in oil field drilling muds, especially given the current (August 2010) uncertain regulatory environment in the Gulf of Mexico. Consumption is likely to increase at a reduced rate of approximately 2.0-2.5% per year during 2009-2014. As the economy recovers from the global economic crisis, demand for oil and natural gas will increase, driving drilling activity and hence consumption of oil field drilling fluids. Higher oil and natural gas prices will also contribute to growth in drilling activity. Onshore drilling will help drive this growth. However, this growth rate could be lower if the U.S. EPA places additional environmental constraints on drilling companies in the Gulf of Mexico (where most of the consumption occurs). It does take into account the moratorium placed on drilling activity in the Gulf of Mexico in the second quarter of 2010 (set to expire on November 30, 2010) after the 2010 oil spill in the Gulf of Mexico. Should drilling companies ever be required to recover the cuttings from drilling operations, they might revert to the use of cheaper diesel fuel. Current practice permits dumping the cuttings, provided the material used has acceptable biodegradability and toxicity. Drilling companies have been forced to recover the cuttings off the coast of Norway in the North Sea; however, these regulations are considered unlikely to be imposed in the Gulf of Mexico. Shell supplies C₁₅-C₁₈, while INEOS and CPChem supply C₁₆-C₁₈ based fluids for this application. All these fluids are designed for and fully compliant with EPA regulations for use in the Gulf of Mexico.

Other Lubricant Additives

LAOs are incorporated in several types of compounds that have a variety of functions in lube oils. The production of these additives consumed 38 thousand metric tons of alpha-olefins in 2009. This amount can vary from year to year depending on the relative pricing of competing raw materials. Growth in North American consumption of lube oil additives in general is expected to average only 0.5% per year during 2009-2014. Consumption of LAOs for use in this application is estimated to grow at approximately the same rate.

Some of these lube oil additives are described briefly in the following paragraphs.

- **Synthetic Heavy Alkylates.** alpha-Olefins can be used to alkylate benzene, which is then sulfonated and neutralized to a calcium, magnesium or barium salt. These lube oil sulfonates are used as detergents in lube oils or in metalworking fluids. The main alpha-olefins consumed to produce lube oil additives are C₂₀-C₂₄ olefins, although some products use two alkyl groups containing shorter-chain olefins. The largest North American producers of lube oil additives based on alpha-olefins are The Lubrizol Corporation and Afton Chemical, although these companies may have some of their production toll produced by others (e.g., Pilot Chemical Co.). The two other large lube oil additive manufacturers, Chevron Oronite and Infineum (a Shell and ExxonMobil joint venture), make these products in Europe. Some lube oil sulfonates (probably less than 20%) used in automotive applications are based on natural petroleum sulfonates that do not consume LAO, but their use has been declining for years.
- **Phenates.** Linear alpha-olefins can also be used to alkylate phenols, which are then neutralized to calcium, magnesium or barium salts. Like the synthetic heavy alcohols, the alkyl phenol compounds function as detergent additives in lube oil applications. However, they are generally more expensive than SHA-type compounds and most are based on propylene tetramers and not LAOs. Chevron is believed to make some of these products based on LAO, but none is produced in North America.
- **Sulfurized Linear alpha-Olefins.** LAOs in the C₁₆-C₂₄ range are blended with an oleate ester or a triglyceride and this mixture is then sulfurized to a 5-20% sulfur content. Theoretically, any type of olefin, including internal, can be used for this sulfurized product, but in practice LAOs are the main olefins used. Sulfurized LAOs are used as an extreme-pressure agent in end uses such as metalworking, auto and industrial gear oils and greases, and to some extent hydraulic fluids.
- **Alkyl naphthalenes.** LAOs in the C₁₆-C₂₄ range are used to alkylate naphthalene, and the resulting product is used as a pour-point depressant. In this application, it competes with polymethacrylate-type pour-point depressants. These products are also used in some crankcase synthetic motor oils (e.g., Mobil 1[®]) as both lubricants and VI improvers. This latter use alone consumed approximately 4 thousand metric tons of LAOs in 2009.
- **Salicylates.** These products compete with sulfonates and phenates in lubricant additives and detergents. They are produced by Infineum (with headquarters based in Britain).

Alkenylsuccinic anhydrides (ASA) based on C₁₂-C₁₈ alpha-olefins can also be consumed for lube oil additives as corrosion inhibitors and frictional modifiers for crankcase oils and dispersants. Most, however, are based on propylene tetramers, rather than LAOs. Refer to the section on **Alkenylsuccinic Anhydrides** for information on alpha-olefin demand for ASAs for all other uses for these products. In addition, some dialkylbenzenes, which can be made from alpha-olefins, are also used in lube oil additives.

Alkyldimethylamines and Dialkylmethylamines

Alkyldimethylamines are produced from several different feedstocks in the United States—linear alpha-olefins, fatty alcohols or fatty acids. In the United States, two companies produced LAO-based alkyldimethylamines through 2009—Albemarle Corporation and The Procter & Gamble Company (P&G). In 2010, P&G switched feedstock for its tertiary amines from LAOs to natural fatty alcohols to supply its Kansas City plant. Albemarle also manufactures smaller volumes of dialkylmethylamines from LAOs. Lonza makes both types, but from detergent alcohols, while Akzo Nobel makes these amines from fatty nitriles (smaller volumes). It is believed that in 2009 all producers of alkyldimethylamines derived from LAOs or alcohols operated at or near capacity. In 2009, total alkyldimethylamine and

dialkylmethylamine production from all raw materials was 93-95 thousand metric tons, of which 83-85 thousand metric tons were derived from alpha-olefins. Approximately 65-67 thousand metric tons of C₈-C₁₈ alpha-olefins were consumed for their production in 2009. Because of P&G's feedstock switch in 2010, consumption of LAOs for the production of alkyldimethylamines will decrease at an average annual rate of approximately 25% during 2009-2014.

LAO-derived alkyldimethylamines are produced by reacting C₁₂-C₁₈ linear alpha-olefins with hydrogen bromide in the presence of peroxide catalysts to form an n-alkyl bromide. Reaction of these bromides with dimethylamine yields the corresponding alkyldimethylamines. Reaction of methylamine with two moles of the alkyl bromide yields a dialkyldimethylamine, but the latter types are based on C₈-C₁₀ LAOs.

P&G manufactures C₁₂-C₁₆ alkyldimethylamines at its Kansas City, Kansas plant, with an annual capacity estimated at over 60 thousand metric tons. It consumes most of them captively for the production of fatty amine oxides, but some are sold for use in making alkylbenzyltrimethylammonium salts (quaternaries or quats), used as biocides. P&G would prefer to use worldwide formulations for many of its products and must obtain the necessary raw materials either from local suppliers or by exporting product from its North American plants. For alkyldimethylamines, P&G appears to have found exporting product from its Kansas City plant to be more economical.

Albemarle manufactures ADMA[®] alkyldimethylamines and DAMA[®] dialkylmethylamines in Magnolia, Arkansas. Annual capacity for both the ADMA[®] and DAMA[®] types is 18-20 thousand metric tons. Albemarle's products are marketed as individual cuts of even-numbered carbon chains from C₈ to C₁₈ or as blends. Both ADMA[®] and DAMA[®] amines are sold largely for conversion to quats for biocides. Other applications include use in making fatty amine oxides, as well as quats and amine salts used in fabric softeners, hair conditioners, dye levelers, polyurethane foam catalysts and epoxide resin curing agents.

The largest application for alkyldimethylamines is for the production of fatty amine oxides (FAOs) produced from the reaction of alkyldimethylamines with hydrogen peroxide. The most common amine is C₁₂-C₁₄ alkyldimethylamine. Most of the production of fatty amine oxides is accounted for by P&G. Other major producers of fatty amine oxides are Lonza and Stepan Company.

Although mildly cationic in acidic solutions, amine oxides exhibit nonionic properties in neutral and alkaline pH ranges. They are good foam stabilizers, thickeners and emollients, as well as emulsifying and conditioning agents. They are very mild to the skin, an important attribute for dishwashing liquids. When used in combination with alcohol ether sulfates in dishwashing liquids, they provide superior foam stabilization properties in the presence of grease compared with the more commonly used alkanolamides. However, fatty amine oxides are considerably more expensive than alkanolamides and their use in dishwashing liquids is almost exclusively confined to the products of P&G, which has the advantage of a captive source of this surfactant.

Fatty amine oxides are used in some household cleaners and are also used as foam stabilizers and conditioning (i.e., antistatic) agents in shampoos and hair conditioners, as well as in some small-volume industrial applications.

Only slow growth is expected in the U.S. and Canadian markets for fatty amine oxides because of a strong consumer preference for automatic dishwashers, which use detergents that do not consume this surfactant. As already discussed, however, increasing volume may be used in other world areas by P&G, based on exported amines. See the CEH *Surfactants, Household Detergents and Their Raw Materials* marketing research report for additional information on fatty amine oxides.

The other major application for alkyldimethylamines is for the production of quaternary ammonium compounds. These products are produced by reacting the alkyldimethylamine with benzyl chloride (by far, the most common) or p-ethylbenzyl chloride, to produce alkybenzyltrimethylammonium (ABDM) salts. The alkyl group typically contains twelve to eighteen carbon atoms, depending on the desired properties, but the middle of this range (fourteen and sixteen carbon atoms) normally has the broadest spectrum of biocidal activity.

The other major class of quaternaries that can be derived from LAOs are dialkyldimethylammonium compounds made by quaternizing dialkylmethylamines with methyl chloride. Lonza is the largest producer of these particular compounds. Albemarle also produces DAMA[®] dialkylmethylamines from C₈-C₁₀ alpha-olefins and sells them to the merchant market. Both types of quaternaries are effective bactericides that are used in a variety of disinfectants and preservatives.

C₁₈ alkyldimethylamines are converted to alkyldimethylbenzylammonium chlorides for use as hair conditioning agents in shampoos, conditioners and cream rinses, where they provide softness as well as antistatic properties. For additional information on benzyl quats, see the CEH *Benzyl Chloride* marketing research report.

Lonza is the major producer of biocidal quaternaries derived from alkyldimethylamines, followed by Stepan Company. Lonza's plant for making the amines from alcohols has an estimated capacity of only 7-10 thousand metric tons per year and is believed to have operated at or near capacity in recent years. Stepan purchases its amine requirements. Stepan and Lonza are the major producers of hair-conditioning quats. For further information, see the Specialty Chemicals Update Program *Biocides* and *Cosmetic Chemicals* reports.

Alkyl betaines, which are amphoteric surfactants, are produced by reacting tertiary amines, such as alkyldimethylamine, with sodium chloroacetate. They can be used as surfactants in light-duty dishwashing liquids. P&G used an LAO-derived alkyl betaine in its Ivory[®] dishwashing liquid for several years, until the product was withdrawn in early 1992.

Alkenylsuccinic Anhydrides

Alkenylsuccinic anhydrides (ASAs) are produced by isomerizing an alpha-olefin to an internal olefin, which is then reacted with maleic anhydride to form the corresponding branched alkenylsuccinic anhydride. The most commonly used alpha-olefins are C₁₆-C₂₀, although other chain lengths are also used. Albemarle is the largest U.S. producer of ASAs. Other producers are Dixie Chemical Company, Milliken Chemical and Vertellus Specialties.

ASAs are consumed in a variety of applications, including paper sizes, lube oil additives, detergents, leather treatment and foods. Use in the paper industry for paper sizing is the largest application for ASAs. Sizes are used in and on paper and paperboard, primarily to make the products more resistant to water and other liquids and to control the spread of inks. ASAs are used as internal sizing agents that are added to the paper slurry prior to sheet formation. They are used in alkaline papermaking processes primarily for high-quality fine papers and gypsum wallboard liners. The other principal commercial alkaline internal sizing agents are alkyl ketene dimers (AKDs). AKDs, made from C₁₂-C₂₀ natural fatty acids, are used in the production of most paperboard made by alkaline processing; ASA sizes do not harden as well as AKDs, which is important in paperboard grades. Both ASA and AKD have a reactive end that binds to the cellulosic fibers and a hydrophobic tail that contributes to water repellency.

The use of ASAs and AKDs has grown because of the conversion of paper mills to alkaline processes during the late 1980s and early 1990s. Advantages of the alkaline process include reduced wood pulp requirements, increased strength, improved paper formation, improved printing performance, longer-lasting paper and a more cost-effective process overall for many mills.

ASAs and AKDs each have advantages and disadvantages associated with their use in the alkaline process. The main advantage of ASAs is that they cure rapidly on the paper machine, while AKDs require a longer off-machine cure time. A disadvantage associated with ASAs is their high reactivity, which requires that they be made into an emulsion at the mill and used immediately; AKDs are less reactive and can be shipped as an emulsion.

ASAs of various carbon numbers consume small quantities of alpha-olefins for other markets. Octenyl succinic anhydride, made from octene-1, is used in making derivatized starches used as thickening agents in foods, juices and puddings. The potassium or sodium salts of octenyl succinic anhydride are used as surfactants in industrial metal cleaners and institutional floor cleaners. ASA compounds derived from both C₁₆ and C₁₈ LAOs are used in finishes that soften leather and protect it from water penetration. Epoxy resins cured with C₁₆-C₂₀ ASAs have good electrical properties, flexural strength and hardness. Some ASAs based on C₁₂-C₁₈ LAOs are sold to the lube oil additives industry. These ASA compounds are processed to make derivatives that are used as corrosion inhibitors and frictional modifiers for crankcase oils and dispersants. Many of the ASA compounds used in lube oil additives, however, are based on propylene tetramers, rather than LAOs.

Approximately 25 thousand metric tons of alpha-olefins or internal olefins derived from LAO were consumed in the production of ASAs in 2009. Paper sizing accounted for 80% of the consumption and this use is expected to grow at an average annual rate of approximately 3% during 2009-2014. Many paper mills have converted from the acidic to the alkaline process. Other applications are not expected to exhibit much growth during this period.

Synthetic Fatty Acids (C₇-C₉)

OXEA produces heptanoic (C₇) and pelargonic (C₉) acids from hexene-1 and octene-1 olefins, respectively, at a 45 thousand metric ton-per-year plant at Bay City, Texas. OXEA's production of C₇ and C₉ acids was approximately 26 thousand metric tons in 2009, consuming 19 thousand metric tons of LAO. The acids are produced via a rhodium-catalyzed oxo process. Until this plant was commissioned in early 1980, semi-synthetic routes from natural feedstocks were the only sources of C₇ and C₉ fatty acids. Synthetic fatty acids produced by OXEA are more than 95% linear. This degree of purity allows them to be interchangeable in lubricant formulations with fatty acids derived from fats and oils that are available as 100% linear products.

The natural acids are produced as coproducts in the manufacture of other compounds, while the OXEA acids are primary products. Arkema imports natural heptanoic acid from its French operation, which steam-cracks methyl ricinoleate from castor oil to undecylenic acid and C₇ chain-length products, including heptanol and heptaldehyde. Undecylenic acid was previously the driving force for the operation, but increased demand for heptanoic acid has raised the emphasis on the C₇ fraction.

Emery Oleochemicals (formerly Cognis Oleochemicals) coproduces pelargonic acid during the ozonolysis of oleic acid to azelaic acid. The largest use of pelargonic acid is for the production of sodium nonanoyl oxybenzene sulfate (NOBS), which is used by P&G as a bleach activator in some of its laundry detergents. Most of P&G's consumption is accounted for by Tide® with bleach, which was introduced in

the late 1980s. The bleach activator allows sodium perborate to function as a bleaching agent at the washing temperatures commonly used in North America. FutureFuel Chemical Company is the sole U.S. producer of NOBS. This use of pelargonic acid has grown from only 2-3 thousand metric tons in 1988 to approximately 14 thousand metric tons in 2009. However, growth in this application within North America has matured, especially since consumers are increasingly using liquid detergents, such as Liquid Tide®, which does not contain the bleach activator.

Other outlets for pelargonic acid include its use in the manufacture of synthetic lubricants (discussed later in this section), plasticizers and agrochemicals. For additional information on markets for heptanoic and pelargonic acids, see the CEH *Oxo Chemicals* marketing research report.

The major use of heptanoic acid and the second largest of pelargonic acid is neopolyol esters (NPEs) used for synlube base stock. Approximately 18 thousand metric tons of heptanoic acid and 4 thousand metric tons of pelargonic acid were consumed in NPEs in 2009. NPEs are made by the reaction of one or more organic acids with a polyfunctional alcohol (e.g., neopentyl glycol, trimethylolpropane or pentaerythritol) via a condensation reaction. In addition to heptanoic and pelargonic acids, valeric (C₅), 2-ethylhexanoic (C₈) and C₈ and C₁₀ natural fatty acids are commonly used to produce NPEs; valeric acid can also be derived from alpha-olefins via C₅ aldehydes. The largest market for NPEs is as synthetic lubricant base stocks for both military and commercial aircraft. Other lubricant market segments include automotive crankcases and refrigerators. As with valeric acid, NPEs produced with heptanoic and pelargonic acids are being increasingly used in non-CFC fluorocarbon cooling systems. The C₇ and C₉ acids face competition from C₈ and C₁₀ natural fatty acids derived from coconut oil. For additional information on neopolyol esters, see the Specialty Chemicals Update Program *Synthetic Lubricants* report.

Heptanoic acid was used for the production of tetraethylene glycol diheptanoate (4G7), a plasticizer for PVB resin. U.S. consumption of heptanoic acid in 4G7 declined dramatically during 2002-2005, as a result of DuPont's conversion to triethylene glycol di-2-ethylhexanoate (3GO) as its PVB plasticizer. Both Solutia and DuPont, the U.S. producers of PVB, now consume 3GO for their PVB operations.

Consumption of LAOs in the production of heptanoic and pelargonic acids is forecast to increase at an average annual rate of 2.5-3.0% during 2009-2014.

alpha-Olefin Sulfonates

alpha-Olefin sulfonates (AOS) are produced by the direct sulfonation of C₁₄-C₁₆ linear alpha-olefins with dilute sulfur trioxide (SO₃). This is followed by neutralization and hot hydrolysis of the intermediate reaction products with sodium hydroxide. The resulting AOS product, which is produced and sold mainly as a 40% active material, is actually a mixture consisting primarily of alkene-1 sulfonates, hydroxyalkane-1 sulfonates and some disulfonates. The U.S. industry is reportedly using a two-to-one C₁₄:C₁₆ blend for most applications. Three U.S. companies currently produce AOS in North America—Stepan Company, Rhodia and Pilot Chemical Company.

The presence of a double bond and a hydroxy group gives good solubility to alpha-olefin sulfonates and they are relatively stable at low pHs compared with the alcohol sulfates (AS) and alcohol ether sulfates (AES), with which they compete in many personal care applications. However, processing costs on a poundage basis are higher for AOS than for most commodity anionics, and various impurities have also made it less attractive for many large household uses, such as for laundry powders. Thus, the use of AOS in North America has been limited largely to some personal care (e.g., liquid hand soaps and shampoos) and industrial applications. The latter include its use in emulsion polymerization processes. AOS has also

been consumed in several oil field applications, including use as a foamer for well clean-out and, in the early 1980s, as a surfactant for steam-driven enhanced oil recovery techniques, but this use nearly disappeared as crude oil prices fell in the late 1980s.

Production of AOS was approximately 19 thousand metric tons in 2009, consuming 14-15 thousand metric tons of LAO. Overall growth for AOS is expected to average 1-1.5% annually during 2009-2014.

Linear Alkylbenzene

Linear alkylbenzene sulfonate (LAS) is a very-large-volume surfactant used in household and industrial detergents. It is produced by sulfonation of linear alkylbenzene (LAB) with oleum or a sulfur trioxide-air mixture. Most LAB is produced by alkylating benzene with normal paraffin-derived C₁₀-C₁₄ linear internal olefins or C₁₀-C₁₄ monochloroparaffins. However, Huntsman Chemical Corporation supplements its n-paraffin feedstock with purchased LAO. Internal olefins, derived from LAO in Shell's isomerization/disproportionation unit, can also be used for this purpose, but most of these products are exported for use in LAB production in other world areas. The paraffin-derived internal olefins are a far less costly source of raw materials than LAO, but the latter are used when paraffin-derived olefins are not available (as in many plants in Latin America and Southeast Asia) or to increase capacity utilization of plants or to adjust the chain-length distribution of the final product.

Annual U.S. consumption of LAO or internal olefins from LAO for LAB production is usually in the range of 11-14 thousand metric tons. Because of high capacity utilization of LAB plants and tight supplies and high prices for paraffins, consumption of LAOs in North America amounted to 23 thousand metric tons in 1999. However, by 2009, LAO consumption for this application declined to 9-10 thousand metric tons. North American LAB production and consumption decreased during 2002-2009. High raw material costs have caused some detergent manufacturers to reduce their cost by lowering surfactant levels, thus reducing LAB demand. Consumption in the United States is likely to decrease over the 2009-2014 period. (See the CEH *Linear Alkylate Sulfonates, Linear and Branched Alkylbenzenes and Surfactants, Household Detergents and Their Raw Materials* marketing research reports for additional information on LAB and LAS.)

Linear Mercaptans

Chevron Phillips and Arkema produce specialty linear, or normal, mercaptans from alpha-olefins. These companies also have facilities in Western Europe and supply virtually all international demand for linear mercaptans. Both U.S. producers have multipurpose equipment that can make a variety of linear, branched and cyclic mercaptans from different feeds. Arkema commercially produces C₄-C₁₂ linear mercaptans from alpha-olefins; it also produces very small amounts of C₁₄ and C₁₆ linear mercaptans. Chevron Phillips commercially produces normal C₄, C₆, C₈ and C₁₂ mercaptans from alpha-olefins.

The major markets for linear mercaptans are for agricultural chemicals and polymer modification. They are used primarily as an agricultural intermediate for the production of sodium n-butylmercaptide, which is consumed in the production of the organophosphate herbicides DEF® and Folex® (tribufos). These products are used as defoliant or desiccants to facilitate machine harvesting of cotton. Approximately 2-3 thousand metric tons of butene-1 were consumed in 2009 for the production of 3-4 thousand metric tons of n-butyl mercaptan; some of the butene-1 may have been supplied by alpha-olefin producers.

Less than 500 metric tons of hexene-1 are consumed annually for the production of n-hexyl mercaptan, also used as an agricultural intermediate.

n-Octyl mercaptan is consumed in fabric coating treatments by the textile industry, as a polymerization modifier in the manufacture of plastics and coatings and in the manufacture of pesticides, special papers and pharmaceuticals.

n-Decyl mercaptan production is very small and is used in only a few specialty proprietary applications. Its production by Arkema is currently alcohol-based and does not consume alpha-olefins.

n-Dodecyl mercaptan is used mainly as a polymerization regulator for polymers, primarily in plastics (e.g., polymethyl methacrylate) but also in rubbers. It is also used for ore flotation in the mining industry, particularly for copper ore; however, this use is more significant internationally than domestically. It is believed to be the largest-volume linear mercaptan.

Consumption of C₆-C₁₂ alpha-olefins for normal mercaptans amounted to approximately 8 thousand metric tons in 2009. In addition, some butene-1 was likely consumed that may have been supplied from alpha-olefin plants. Hexene-1 and dodecene-1 are believed to be consumed in the largest quantities, followed by butene-1, octene-1 and decene-1. Overall growth for linear mercaptans will be modest during the next few years because of the maturity of their markets.

Aluminum Alkyls

Approximately 7 thousand metric tons of LAOs (C₆-C₈ range) were consumed for the production of aluminum alkyls in 2009. Albemarle produces aluminum alkyls from alpha-olefins. Their largest use is for the production of Ziegler-Natta catalysts, used as polymerization catalysts (e.g., for polyolefins). Other uses include the production of organotins used as stabilizers for PVC or biocides. Growth in these applications was strong in the late 1990s with the increasing use of metallocene catalysts. Future growth is expected to average approximately 3% per year during 2009-2014.

Chlorinated Olefins

Chlorinated paraffin producers consumed approximately 5 thousand metric tons of C₁₀-C₁₆ alpha-olefins in 2009 to manufacture chlorinated olefins, which can be used as replacements for chlorinated paraffins. The largest use for chlorinated olefins and paraffins is in the metalworking industry where they are contained in coolants and lubricants. Growth in consumption of LAOs in this category will likely be minimal over 2009-2014. They are also used as secondary plasticizers, especially for polyvinyl chloride and as flame retardants. See the CEH *Normal Paraffins (C₉-C₁₇)* marketing research report for further information on chlorinated hydrocarbons.

Alkyldiphenylether Disulfonates

Alkyldiphenylether disulfonates were first produced by Dow Chemical U.S.A. and marketed under the trademark DOWFAX®. Dow currently supplies these products. Pilot Chemical Company manufactures and supplies alkyldiphenylether disulfonates. Alkyldiphenylether disulfonates can be manufactured by reacting an LAO with diphenyl ether; however, branched-chain olefins are also used as raw materials in their production. Each mole of the resulting alkyldiphenylether is then sulfonated with two moles of sulfur trioxide to produce a double ionic charge upon neutralization. The resulting product has greater dispersing power and higher solubility than most other surfactants.

