ALCOHOLS, HIGHER ALIPHATIC, SURVEY

1. Survey and Natural Alcohols Manufacture

Monohydric, aliphatic alcohols with a hydrocarbon chainlength of C6 and above are referred to as higher alcohols. For commercial products, the alcohol group is usually found in the primary position, although secondary alcohols are occasionally seen. The hydrocarbon portion of the molecule is hydrophobic, while the hydroxyl group provides a reactive site for attaching a strong hydrophilic species. The combination of hydrophilic and hydrophobic properties in the same molecule yields an extremely good surfactant, readily biodegradable (see DETERGENCY; SURFACTANTS). Detergent alcohols generally have a hydrocarbon chainlength of C12 and above with at least 35% linear chains. Plasticizer alcohols generally have a chainlength of C6 to C13 (excluding C12 and C13 linear) with a structure that is either linear or highly branched.

Both natural (oleochemical) and synthetic (petrochemical) routes are used to make the higher alcohols. Plasticizer alcohols are made primarily by the synthetic route, with only minor quantities obtained from natural feedstocks. Detergent alcohols are made by both routes, with global capacity currently split 50/50 synthetic/natural. The natural route is based on vegetable and animal fats, principally coconut, palm kernel, and tallow. The products are essentially all even chain length (ie, C12, C14, ...) and 100% linear. The synthetic route is based on ethylene chain growth, and is classified as either Ziegler or oxo. The Ziegler process produces linear, even-chain products, while the oxo process produces a mixture of branched and linear, even- and odd-chain products (see Synthetic Processes section).

Global production of plasticizer alcohols was about 3,400,000 tons in 1995, with demand expected to increase 3.1% during the period 1995–2000. Primary end uses are for flexible PVC and for surface coatings applications in construction or automobile manufacturing. Global production of detergent alcohol was about 2,000,000 tons in 1998, with demand expected to increase by 2.5% during the period 1995–2000. Ethoxylates, sulfates, and ethoxysulfate derivatives account for about 84% of U.S. consumption of detergent alcohols in 1995. Various other derivatives account for 11%, with the balance being free alcohol consumption.

1.1. Detergent Range Alcohols.

Detergent range alcohols can be categorized into mid cut (C12–C15) and heavy-cut (C16 and greater) chain lengths, depending on the distillation range where they are separated. Mid cut alcohols are most preferred for detergent use, as these chain lengths provide an optimum tradeoff between surfactancy on the one hand and (lack of) crystallinity on the other. Heavy cut alcohols are used more for health and personal care applications. Mid cut alcohols are produced and distributed as either a pure component or a mixture of two or three components (ie, C12/C13 or C12/C14), while heavy cuts are primarily a single chain length (ie, C16 or C18). Oleyl alcohol (*cis*-9-octadecenol) is the most abundant of the unsaturated alcohols and occurs widely as a wax ester in fish and marine mammal oils. It consitutes 70% of the alcohols in wax esters of sperm body oil.

Long-chain alcohols $>$C18 are generally of much less commercial importance (1). C20 alcohol [629-96-9] is made commercially through one or more synthetic routes. Applications are as chemical intermediates for rubber, plastics, and textiles. C22 alcohol [661-19-8] is made commercially by reduction of behenic acid or behenic methyl esters. Applications include lubricants and synthetic fibers. Even-chain C24–C32 alcohols are derived from various natural waxes, including carnauba, beeswax, and Chinese insect wax. Applications are similar to that of C22 alcohol. Wool grease from sheep also contains higher alcohols as wax esters, and is a minor commercial source of alcohol.

1.2. Plasticizer Range Alcohols.

C6–C11 and C13 alcohols are available as pure materials or as complex mixtures. In general, the linear alcohols are available as pure materials, and are referred to as "-yl alcohols." There is no single dominant linear alcohol product, as the entire C6–C11 range is about equally important. The branched alcohols are generally available as mixtures, and are referred to as "isoalcohols" or "-anol." 2-Ethyl hexanol is by far the most important branched alcohol.

2. Physical Properties

Table 1 lists some of the basic physical properties of linear and branched higher alcohols (2). Table 2 lists the key thermal, flammability, and critical properties of the linear alcohols (3). In Table 1, it can be seen that specific gravity, boiling point, melt point, and viscosity are all a linear or a polynomial function of chain length. The branched alcohols have properties that are similar to the linears for equal carbon number, with the exception that melt point is

Table 1. **Physical Properties of Higher Aliphatic Alcohols**

IUPAC name	CAS Registry Number	Molecular formula	Other common names	Specific gravity 20 °C	Bp, °C 101.3 kPa	Mp, °C	Viscosity mPa s	Solubility, in water	% by wt of water	Solubility in other solvents
					Primary normal aliphatic					
1-hexanol	[111-27-3]	$C_6H_{14}O$	*n*-hexyl alcohol	0.8212	157	−44	5.9	0.59	7.2	petroleum ether, ethanol
1-heptanol	[111-70-6]	$C_7H_{16}O$	*n*-heptyl alcohol	0.8238	176	−35	7.4	0.1		
1-octanol	[111-87-5]	$C_8H_{18}O$	*n*-octyl alcohol	0.8273	195	−15.5	8.4	0.06	4.5	petroleum ether, ethanol
1-nonanol	[143-08-8]	$C_9H_{20}O$	*n*-nonyl alcohol	0.8295	213	−5	11.7			
1-decanol	[112-30-1]	$C_{10}H_{22}O$	*n*-decyl alcohol	0.8312	230	7	13.8		2.8	petroleum ether, ethanol benzene, glacial acetic
1-undecanol	[112-42-5]	$C_{11}H_{24}O$	*n*-undecyl alcohol	0.8339	243	16	17.2	< 0.02		
1-dodecanol	[112-53-8]	$C_{12}H_{26}O$	lauryl alcohol	0.831 [a]	138 [b]	24	18.8	[d]	1.3	
1-tetradecanol	[112-72-1]	$C_{14}H_{30}O$	myristyl alcohol		158 [b]	38		< 0.02	nil	petroleum ether, ethanol
1-hexadecanol	[36653-82-4]	$C_{16}H_{34}O$	cetyl alcohol		177 [b]	49	53 cAt 60 °C	0.06	nil	petroleum ether, ethanol
1-octadecanol	[112-92-5]	$C_{18}H_{38}O$	stearyl alcohol		203 [b]	58	7 [c]	[d]	nil	
1-eicosanol	[629-96-9]	$C_{20}H_{42}O$	arachidyl alcohol		251 [b]	66		[d]	nil	petroleum ether, ethanol
1-hexacosanol	[506-52-5]	$C_{26}H_{54}O$	ceryl alcohol			80		[d]		ethanol, ether
1-triacontanol		$C_{30}H_{62}O$	myricyl alcohol	0.777		88		[d]		benzene, ethanol, ether
9-octadecen-1-ol	[143-28-2]	$C_{18}H_{36}O$	oleyl alcohol	0.8484	205–210	6				ethanol, diethyl ether
					Primary branched aliphatic					
2-methyl-1-pentanol	[105-30-6]	$C_6H_{14}O$	2-methylpentyl alcohol	0.8254	148		6.6	0.31	5.4	
2-ethyl-1-butanol	[97-95-0]	$C_6H_{14}O$	2-ethylbutyl alcohol	0.8348	147	−114				
2-ethyl-1-hexanol	[104-76-7]	$C_8H_{18}O$	2-ethylhexyl alcohol	0.834	184	−70	9.8	0.07	2.6	ethanol, diethyl ether
3,5 dimethyl-1-hexanol	[13501-73-0]	$C_8H_{18}O$		0.8297	182.5					ethanol
2,2,4 trimethyl-1-pentanol	[123-44-4]	$C_8H_{18}O$		0.839	168	−70				ethanol
3,5,5 trimethyl-1-hexanol		$C_9H_{20}O$		0.83	197		15			
iso-octadecanol		$C_{18}H_{38}O$	isostearyl alcohol			0	48			

[a] At 24 °C.
[b] At 1.33 kPa pressure.
[c] At 60°C.
[d] insoluble.

Table 2. **Thermal, Flammable, and Critical Properties of Higher Aliphatic Alcohols**

	n-hexanol	*n*-octanol	*n*-decanol	*n*-dodecanol	*n*-octadecanol
specific heat, cal/g °C		0.65		0.63	0.6
heat of fusion, kcal/gmol		10.1	10.3	8.3	17.7
heat of vaporization, cal/g	106	98	85	77	67
reference temp, °C	190	224	246	247	242
heat of combustion, kcal/gmol		1262	1577		
surface tension, dyn/cm	24.5	26.1			
thermal conductivity, cal/cm h °C	1.34	1.37	1.41	1.46	1.58
dielectric constant	13.3	10.3			
critical temperature, °C	340	387	425	460	545
critical pressure, MPa	3.5	3.0	2.6	2.3	1.7
flash point, °C	55	85	103	113	127
fire point, °C	68	96	116	138	193
autoignition temperature, °C				244	260

significantly lower for the branched molecules. The plasticizer alcohols are slightly soluble with or in water, but the detergent alcohols are generally insoluble with or in water. Branching does not have a significant impact on water solubility.

In Table 2, it can be seen that heat of fusion, thermal conductivity, critical temperature, and flammability generally increase with chain length. Critical pressure and heat of vaporization are an inverse function of chain length. However, the reference temperature for the heat of vaporization increases over the range of C6–C18 chain lengths. Specific heat is relatively constant over the range of chain lengths listed.

3. Chemical Properties

There are three principal types of reactions involving alcohols (4). These are the reactions involving the O-H bond, reactions involving the C-O bond, and reactions with the alkyl portion of the molecule (ie, the C-H bond of the α carbon). Examples of each type are shown below. Alcohols, like water, can act as both weak acids or weak bases. Reactions are generally done in the liquid phase, using either homogeneous or heterogeneous catalysts. The products of each reaction are useful as valuable chemical intermediates and end products.

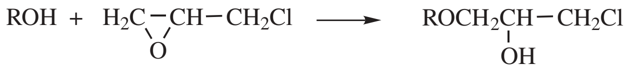
3.1. Reactions Involving the O-H bond

Sulfation

$$\mathrm{ROH} + \mathrm{SO_3} \longrightarrow \underset{\text{alkyl hydrogen sulfate}}{\mathrm{ROSO_3H}}$$

$$\mathrm{ROSO_3H} + \mathrm{NaOH} \longrightarrow \underset{\text{sodium alkyl sulfate}}{\mathrm{ROSO_3Na}} + \mathrm{H_2O}$$

Etherification



$$\mathrm{ROH + \underset{O}{H_2C{-}CH}{-}CH_2Cl \longrightarrow ROCH_2\underset{OH}{CH}{-}CH_2Cl}$$

epichlorohydrin alkyl chlorohydrin ether

Alkoxidation

$$\mathrm{ROH + M} \longrightarrow \underset{\text{alkoxide}}{\mathrm{ROM} + \tfrac{1}{2}\mathrm{H_2}}$$

$$\mathrm{M = Al, Mg, Na, K, etc.}$$

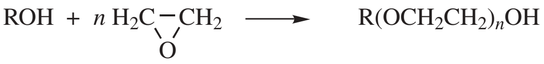
3.2. Reactions involving the C-O bond

Esterification

$$\mathrm{ROH + R'COOH} \longrightarrow \mathrm{R'COOR + H_2O}$$

$$\mathrm{ROH + R'COOR''} \longrightarrow \underset{\text{alkyl ester}}{\mathrm{R'COOR + R''OH}}$$

Ethoxylation



$$\mathrm{ROH} + n\,\mathrm{\underset{O}{H_2C{-}CH_2}} \longrightarrow \mathrm{R(OCH_2CH_2)_{\mathit{n}}OH}$$

polyethoxylated alcohol

Halogenation

$$\mathrm{ROH + HX} \longrightarrow \underset{\text{alkyl halide}}{\mathrm{RX + H_2O}}$$

Dehydration

$$\mathrm{RCH_2CH_2OH} \longrightarrow \underset{\text{olefin}}{\mathrm{RCH = CH_2 + H_2O}}$$

Amination

$$\mathrm{ROH + R'NH_2} \longrightarrow \underset{\text{amine}}{\mathrm{RNHR' + H_2O}}$$

3.3. Reactions with the α-Carbon

Oxidation

$$\mathrm{RCH_2OH} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \underset{\text{aldehyde}}{\mathrm{RCH{=}O + H_2O}}$$

$$\mathrm{RCH{=}O} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \underset{\text{carboxylic acid}}{\mathrm{RCOOH}}$$

Dehydrogenation

$$\mathrm{RCH_2OH} \longrightarrow \underset{\text{aldehyde}}{\mathrm{RCH{=}O}} + \mathrm{H_2}$$

4. Shipment and Storage

Higher alcohols are available in bulk quantities in 208-L (55-gal) drums, 23,000-L (6000-gal) tank trucks, 75,000-L (20,000-gal) tank cars, and marine barges. In addition, some of the plasticizer alcohols are available in bottles and cans, ie, for perfume applications. Higher-melting alcohols (C16 and greater) are also generally available in a flaked form in 22.7-kg (50-lb) polyethylene or paper lined bags. Linear and branched alcohols of 6–9 carbon atoms are classified as combustible for shipment by the U.S. DOT due to their low flash points. Alcohols of C10 and above are classified as nonhazardous. The higher alcohols in anhydrous form do not attack common metals. They may be stored in mild steel, but to avoid iron contamination a liner of zinc silicate, epoxy phenolic, or high baked phenolic may be used (5). For high melting alcohols, and for low melting alcohols under cold climate conditions, insulated tanks and heating coils of stainless steel are required. High temperatures should be avoided during storage to maintain product quality. This can be accomplished by using hot water or low pressure steam on heating coils during meltout to avoid hot spots, and by maintaining temperature at 10°C above the melting point. Carbonyl formation during storage may be minimized with a nitrogen blanket. Moisture in the atmosphere may be excluded by storing the product under a blanket of inert gas or by installing a dehumidifier. In order to minimize any danger of fire in the handling of plasticizer range alcohols, tanks should be grounded, have no interior sources of ignition, be filled from the bottom of the tank to prevent static sparks, and be equipped with flame arrestors.

5. Health and Safety Factors

The higher alcohols are among the less toxic of commonly used industrial or household chemicals. Toxic effects generally decline as chain length increases. Table 3 summarizes the toxicological properties of the higher alcohols (6).

The acute oral toxicity data on the higher alcohols indicate a low order of toxicity by the oral, dermal, or inhalation routes of exposure (6). Higher alcohols are poorly absorbed through the skin. The rate of dermal uptake for the neat material was found to decrease with increasing carbon number. Human repeated skin patch tests with a 1% alcoholic solution of C12–C15 alcohols indicate very slight to mild irritation which is nonfatiguing or sensitizing (6). Primary human skin irritation of C16 and C18 alcohols is nil, as these products have been historically used in cosmetic and personal care products. Inhalation hazard is slight, due to the low vapor pressure of these materials. However, sustained breathing of alcohol vapor or mist is to be avoided, in order to minimize any aspiration hazard.

Table 3. **Toxicological Properties of Higher Alcohols**

	Acute oral rat LD_{50}	Acute dermal rabbit LD_{50}	Skin irritation rabbit	Eye irritation rabbit
n-hexanol	4.7	>5	severe	severe
2-ethylhexanol	3	2.3	slight-moderate	moderate-severe
iso-octanol	2	>2.6	moderate	severe
isodecanol	8	3	moderate	severe
n-undecanol	3	>5	moderate	
n-dodecanol	>11		slight-moderate	
n-tetradecanol	>5	>5		
n-hexadecanol	>8.4	>2.6	slight	slight
n-octadecanol	>8	>3	slight	slight

6. Economic Aspects

Global production of detergent range alcohols in 1998 was about 2,000,000 tons. Production is growing by 3–4% per year in the period 1995 to 2000.

During the 1990s, virtually all new plant capacity added has been based on natural feedstocks, largely in the countries of Malaysia, Indonesia, and Japan. The Philippine producers have been largely overtaken by new Indonesian and Malaysian capacity. This is a reversal of the global trend during the 1960s–1980s, when synthetic alcohol capacity was increasing while natural capacity was flat. The current trend for adding natural alcohol capacity is driven largely by geographical considerations of supply and demand. Demand is increasing 6% in Asia vs. 3–4% in North America and Europe. Asian countries also have an abundant supply of coconut and palm kernel oil, and a desire to harvest and export these commodities. Much of the growth in production between 1995 and 2005 will be for export to developing and Western countries. China will also be an emerging market, for both production and consumption.

Growth in the industry in recent years has been limited by supply (7). By year 2000, new debottlenecked capacity should be on-line in Germany, Italy, and the U.S. New plant construction for synthetics is also planned for Condea and Shell in the U.S. and Sasol in South Africa. Currently, worldwide production capacity is about evenly split between synthetics and naturals. The preponderance of natural producers in Asia is contrasted by a much stronger position by synthetics in North America. Europe is about evenly split. For either approach, cost of production is affected by both feedstock costs and co-product value, and these costs are largely determined in other markets. Figure 1 shows the historical cost for ethylene (8) vs. coconut oil (9), which are the key starting materials for synthetic and natural alcohols, respectively. Due to the cyclic nature of these raw material costs, there are periods of time when natural alcohols have a cost advantage and other periods when synthetic alcohols have the upper hand. Consumer preferences are segmented, with synthetic alcohols preferred for household and industrial applications and natural alcohols preferred for health and personal care. In countries such as Germany and Japan, the naturals are also preferred by consumers for their renewable source of supply. For most applications, linear synthetic alcohols can be used interchangeably with natural

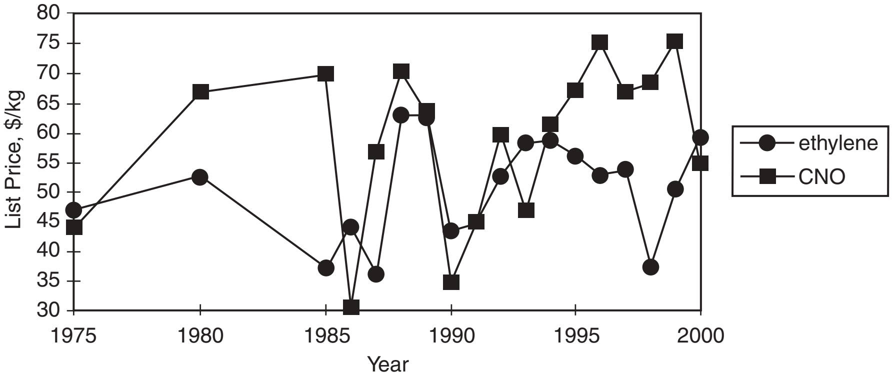


Fig. 1. List price of ethylene vs. conconut oil: 1975–2000.

alcohols except where minor amounts of chain branching or secondary alcohols are absolutely prohibited.

Global producers of detergent range alcohols are numerous. In 1999 there were five in the U.S., ten in Europe, and numerous others in Asia. Table 4 shows relevant information on the five U.S. producers; representative list prices for natural alcohols are given in Table 5 (10). Most major customers have contracts at prices lower than at list. Also, several producers are planning to expand plant capacity in the next few years.

Global production of plasticizer alcohols was 3,400,000 tons in 1995, of which 1,058,000 tons was U.S. About 40% of U.S. consumption is as 2-ethylhexanol. Consumption is equally split among North America, Europe, and Asia. Global demand is projected to increase by 3.1% per year over the period 1997–2002.

Global producers of plasticizer alcohols are numerous. In 1996 there were 11 U.S. producers and at least 15 global producers. Exxon and Eastman

Table 4. **Detergent Alcohol Producers in U.S.**

Producer	Process	Capacity, tons (1999)	Products	Trade names
P&G	natural methyl ester	80,000	C12–C18	CO, TA
Cognis	natural methyl ester	40,000	C12–C18	Lorol
Shell	synthetic modified oxo	250,000	C12–C15	Neodol
BPAmoco	synthetic modified Ziegler	60,000–95,000	C12–C32	Epal
Condea	synthetic Ziegler	60,000	C12–C28+	Alfol

Table 5. **Natural Detergent Alcohol List Pricing (1999)**

Alcohol	Price, U.S. $/kg, fob
C12–C14	1.54
C16	1.65
C18	1.65

Table 6. **Plasticizer Alcohol List Pricing (1996)**

Material	Price, US. \$/kg, fob	Manufacturer
n-hexanol	2.09	Exxon, Condea, BPAmoco
isohexyl alcohol	1.45	Exxon
n-octanol	2.27	BPAmoco, Condea, P&G, Cognis
2-ethylhexanol	1.23	BASF, Eastman, Union Carbide, Shell
n-decanol	2.02	Exxon, Shell, BPAmoco, P&G, Cognis, Condea
isodecyl alcohol	1.12	Exxon
tridecyl alcohol	1.58	Exxon

Chemicals are the largest U.S. producers. Rather than listing all producers, Table 6 shows typical manufacturers and list prices of some of the common types of plasticizer alcohols (11).

The U.S. market possesses the best economic conditions for continued growth in consumption in the near future. Usage for plasticizers (flexible PVC) and for acrylate/methacrylate esters (surface coating and textiles) are both driving demand. Long term, Asia is the focus of global producers due to emerging strong demand and insufficient local production. Plant capacity has been added in the U.S. during the 1990s by BASF, Condea Vista, and Shell, and globally by Eastman and Exxon.

Particular alcohols are chosen for plasticizer production based on physical properties. In addition to performance, cost is extremely important. The branched chain alcohols are consistently less expensive than the comparable linear alcohols, primarily because propylene feedstock for branched alcohols is consistently less expensive than the ethylene feedstock used for linears. Manufacturers of plasticizer alcohols general sell some of their material to the merchant market and save the rest for internal or “captive” use, largely for production of phthalate plasticizers.

7. Analytical Methods

Higher alcohols analysis is done to determine the chain-length distribution as well as to determine the level of minor components present, which may impact product performance.

Gas chromatography (GC) is used to measure chain-length distribution for mixed products and purity for single-chain products. The composition of both linear and branched alcohols can be characterized by this method. In case of overlapping peaks on the chromatograms, more sophisticated techniques such as GC-mass spec or nuclear magnetic resonance (nmr) can be applied.

Minor components are generally measured by wet titration techniques. This includes % moisture, color, carbonyl value, hydroxyl value, saponification value, acid value, and iodine value (12). Carbonyl value is expressed as ppm of $C{=}O$ equivalent in the product and is a measure of product oxidation, which is associated with dark color and off-odor. Hydroxyl value is expressed as mg of KOH equivalent to the hydroxyl content of one gram of product and is an indication of the overall alcohol purity. Saponification value is expressed as mg of KOH

Table 7. **Reference Test Methods for Analysis**

Analysis	Reference Test Method No.
acid value	AOCS Te 1a-64
saponification value	AOCS TL 1a-64
moisture	AOCS Tb 2-64
hydroxyl value	AOCS Cd 13-60
iodine value	AOCS Tg 1a-64
peroxide value	AOCS Cd 8-53
color (APHA)	ASTM D 1209
density	ASTM 1298
flash point	ASTM D92

required to saponify esters and acids in one gram of product and is an indication of the sum of the levels of these components in the product. Acidity is commonly expressed as acetic acid equivalents/100 g of product for plasticizer alcohols and as mg KOH/g of product for detergent-grade alcohols. Iodine value is expressed as g I_2/100 g of product and is an indication of the degree of unsaturation (double bonds) present. An iodine value of 0 is completely saturated.

Table 7 shows reference test methods commonly used to analyze the higher alcohols. Methods are from the American Oil Chemists Society (13) and the American Society for Testing and Materials.

8. Specifications and Standards

Commercially available materials are found as both pure components and mixtures. Sales brochures from commercial manufacturers provide further details (14). Even-chain alcohols are produced from natural fats and oils and from the Ziegler process, and are highly linear. Odd-chain alcohols are produced by oxochemistry, and have some branched chains. Linear, detergent-range alcohols are marketed in the U.S. by P&G, Cognis, and Condea. These materials are available as 95–99% pure C12, 14, 16, and 18 alcohols, and also as blends, eg, a 70/30 blend of C12 and C14 alcohols. C16 and C18 alcohols are also available as National Formulary (NF) grade, for cosmetic or pharmaceutical applications. Condea is the only company to produce C20 and C22 alcohols for health and personal care applications. P&G and Cognis exclusively use natural fats and oils, while Condea uses both oleochemical and petrochemical routes. Branched, detergent-range alcohols are marketed in the U.S. by Shell. They are 80% linear, with the balance being random alkyl branched chains. These are typically 50/50 mixtures of even and odd chains, eg, C12 and C13, or C14 and C15. Table 8 displays information

Table 8. **Detergent Alcohol Chain Length, Linerity**

Manufacturer	Product name	Chain length	% Linear
P&G	CO-1270	70/30 blend of C12/C14	100
Cognis	LOROL C1695	95% C16	100
Condea	Alfol 18, Nacol 18	99% C18	> 98
Shell	Neodol 45	50/50 blend of C14/C15	80

Table 9. **Properties of Commercial Linear Detergent Range Alcohols**

Descriptive name	Hydroxyl value mg KOH/gr	Saponification value	Carbonyl value, ppm	Acid value	Iodine value	Melting point, °C	Color, APHA	Moisture %	Hydrocarbon %
lauryl (99% C12)	301	0.2		0.02	0.2	22	5	0.03	0.2
lauryl (68% C12)	285	0.2		0.02	0.2	22	3	0.04	0.2
C12–C13	289		40	0.01		20	5	0.02	0.2
cetyl	229	0.4		0.1	0.6	48	5	0.04	0.1
stearyl	206	0.5		0.1	0.6	58	5–10	0.03	0.2
oleyl	206	0.5		0.1	94	4		0.03	

Table 10. **Plasticizer Alcohol Chain Length, Linearity**

Manufacturer	Product name	Chain length	% Linear
Condea	Alfol 6	99.5% C6	> 98
PG	CO-898	98% C8	100
Cognis	Lorol C1098	98% C10	100
BPAmoco	Epal 810	50/50 C8/C10	> 98
Shell	Linevol 79	97% C7-C9	80
Exxon	Exxal 6	5% ethylbutanol, 60% methyl pentanol, 35% *n*-hexanol	35
Exxon	Nonanol	80% 3,5,5 trimethyl hexanol	< 20
BASF	2-ethylhexanol	99.5% 2-ethyl hexanol	0

on detergent alcohol chain length and linearity, while Table 9 focuses on other physical properties of interest.

Linear, plasticizer alcohols are marketed in the U.S. by P&G, Cognis, Condea, and BPAmoco. These materials are available as 95–99% pure C6, C8, and C10 alcohols, and also as blends, eg, a 45/55 blend of C8 and C10 alcohols. P&G and Cognis utilize natural fats and oils exclusively, while Condea and BPAmoco use petroleum based feedstocks.

A range of branched, plasticizer range alcohols are marketed in the U.S. by Shell and Exxon. Both pure materials and mixtures are available. Shell produces odd-chain C9–C11 alcohols with 80% linearity. Exxon produces highly branched even- and odd-chain C6–C13 alcohols, the major isomers of which are mono-, di-, tri-, or tetramethyl branched molecules. 2-Ethyl hexanol is produced and marketed in the U.S. by BASF, Union Carbide, and Eastman.

Table 10 displays information on chain length and linearity for various plasticizer alcohols, while Table 11 focuses on other physical properties.

9. Manufacture from Fats and Oils

9.1. Feedstocks and Intermediates. Both methyl esters and fatty acids are suitable intermediates for manufacture of higher natural alcohols.

Table 11. **Properties of Commercial Plasticizer Alcohols**

Descriptive name	Hydroxyl value mg KOH/g	Carbonyl value, ppm	Acidity % as acetic	Color, APHA	Moisture %	Boiling range °C	Flash point °C
hexanol	548		0.001	5	0.05	152–160	63
2-ethyl hexanol	431		0.005	5	0.05	182–186	
isooctyl alcohol	429	100	0.001	5	0.05	186–193	84
isononyl alcohol	380	100	0.001	5	0.05	204–216	91
octanol	431		0.005	5	0.03	184–195	88
decanol	355	50	0.005	5	0.03	226–230	113
tridecanol	283		0.001	5	0.03	254–263	127

Triglycerides from either vegetable or animal sources are the feedstocks used to produce either of these intermediates. Triglycerides consist of three fatty acid chains attached to a glycerine backbone. The fatty acid chain lengths range from C6 to C22. The most useful chain lengths for detergent applications are C12 and C14. Health and personal care applications are more oriented towards C16 and C18. Common triglyceride feedstocks are coconut oil and palm kernel oil for detergent applications, and tallow, palm, or soybean oil for cosmetic applications. Less common is rapeseed oil as a feedstock for behenyl or eurucyl alcohol and castor oil as a feedstock of hydroxy-stearyl alcohol.

As the more widely used intermediate, methyl esters can be made by transesterification of fatty triglycerides or by direct esterification of fatty acids.

Transesterification of triglycerides with methanol is the predominant process for manufacture of methyl esters. The reaction occurs readily at atmospheric pressure at a temperature of 50–70°C using carbon steel equipment and an akaline catalyst. Both triglyceride and methanol are dried to minimize the conversion of alkaline catalyst into soap.

$$C_3H_5(OOCR)_3 + 3\ CH_3OH \longrightarrow 3\ RCOOCH_3 + C_3H_5(OH)_3$$

These mild reaction conditions require that any trace fatty acids present in the fat be neutralized chemically (alkali refining) or removed physically (steam refining) prior to the base catalyzed transesterification. Removal of fatty acids is not required if the reaction is carried out with an acid catalyst, or if it is carried out under pressure (10 MPa) at a temperature of about 240°C with an alkaline catalyst. The latter is advantageous in that lower grades of triglyceride can be used, but this is balanced by the need for a higher excess of methanol and higher equipment pressure ratings than for the conventional process.

The reaction can be done either batchwise or continuous. It is advantageous to have mixing present in the early stages of the reaction to enhance miscibility among the reactants. After reaction, the mixture is settled and the glycerol is recovered in methanol solution in the lower layer. The catalyst and excess methanol are removed from the ester, which can then either be fed directly to the alcohol making process, or distilled to remove impurities or to purify the chain length distribution (15).

Direct esterification of fatty acids to produce methyl esters is done in either a batch or a continuous process.

$$RCOOH + CH_3OH \longrightarrow RCOOCH_3 + H_2O$$

The batch reaction is done at pressures of about 1 MPa and temperatures of 200–250°C. Molar ratios of methanol:fatty acid are about 3–4:1. Water is removed to drive the reaction to a high conversion. The continuous process is done under similar conditions of pressure and temperature in a countercurrent reaction column where methanol is absorbed from the bottom and reacted while water (and excess methanol) are desorbed from the top. The methyl ester is taken off the bottom of the reactor, sent to a flash tank to remove methanol, and then distilled. Advantages of the continuous process are that a lower excess of methanol is required (molar ratio of 1.5:1), and the reaction time is much shorter.

The direct esterification process is advantageous for making esters with a higher chain length purity than the parent triglycerides, eg, separation of the fatty acid into a stearine and an olein fraction.

Fatty acids are less widely used as an intermediate than methyl esters. Most of the equipment has to be made of corrosion-resistant material, the fatty alcohol process has to be designed for a higher pressure and temperature, the catalyst has to be acid resistant, and the finished product tends to be slightly higher in hydrocarbons. On the other hand, fatty acids are more widely available than methyl esters for those who are purchasing, rather than producing the intermediate material. In addition, the fatty acid process avoids the use of methanol, a flammable solvent subject to local environmental regulations. In commercial processes, the fatty acid material is typically reacted with fatty alcohol to form a wax ester; this intermediate then undergoes hydrogenolysis to the alcohol. Lurgi has licensed the wax ester technology to several companies in Europe and Asia, including Albright and Wilson, PT Aribhawana Utama, Condea Vista, and United Coconut Chemicals (16).

To prepare fatty acid feedstock for fatty alcohol making, triglyceride feedstock must be hydrolyzed with water to fatty acid and glycerine.

$$C_3H_5(OOCR_3 + H_2O \longrightarrow 3\,RCOOH + C_3H_5(OH)_3$$

The hydrolysis can be done at atmospheric pressure with sulfuric or sulfonic acids or at high pressure with or without a catalyst (zinc oxide, magnesium oxide, or lime). High pressure continuous processes are most commonly practiced. The fatty acids are purified by distillation or separated into individual chain lengths by fractional distillation (17).

9.2. High Pressure Hydrogenolysis. Fatty acids or methyl esters are converted into fatty alcohols in the presence of a heterogeneous catalyst. The reaction for the methyl esters is:

$$RCOOCH_3 + 2\,H_2 \longrightarrow RCH_2OH + CH_3OH$$

There are two major processes in use: slurry based and fixed bed. Procter & Gamble and Kao practice the slurry based process while Cognis and Oleofina practice fixed bed.

Figure 2 shows a process flow diagram for the methyl ester, slurry catalyst process. Dry methyl ester, hydrogen, and catalyst slurry are fed to a series of vertical reactors operated at 250–300°C and 20–30 MPa. The reactors are tubular and contain no packing. Approximately 20 moles of hydrogen per mole of ester are fed to the reactors providing heat, agitation, and chemical reduction. Catalyst is typically copper chromite, which results in the hydrogenation of carbon double bonds as well as reduction of the methyl ester group. Catalyst usage is typically 2 kg/ton of alcohol. The product stream from the last reactor is cooled and separated into liquid and gaseous phases. The gaseous phase, rich in H_2, is recycled back to the reactors. Catalyst is removed from the liquid phase, and most of the catalyst is recycled to the reactors while a small amount is purged and replaced with fresh catalyst. Purged catalyst is landfilled, regenerated, or sold to a reclaimer to recover copper metal. The liquid phase is stripped of

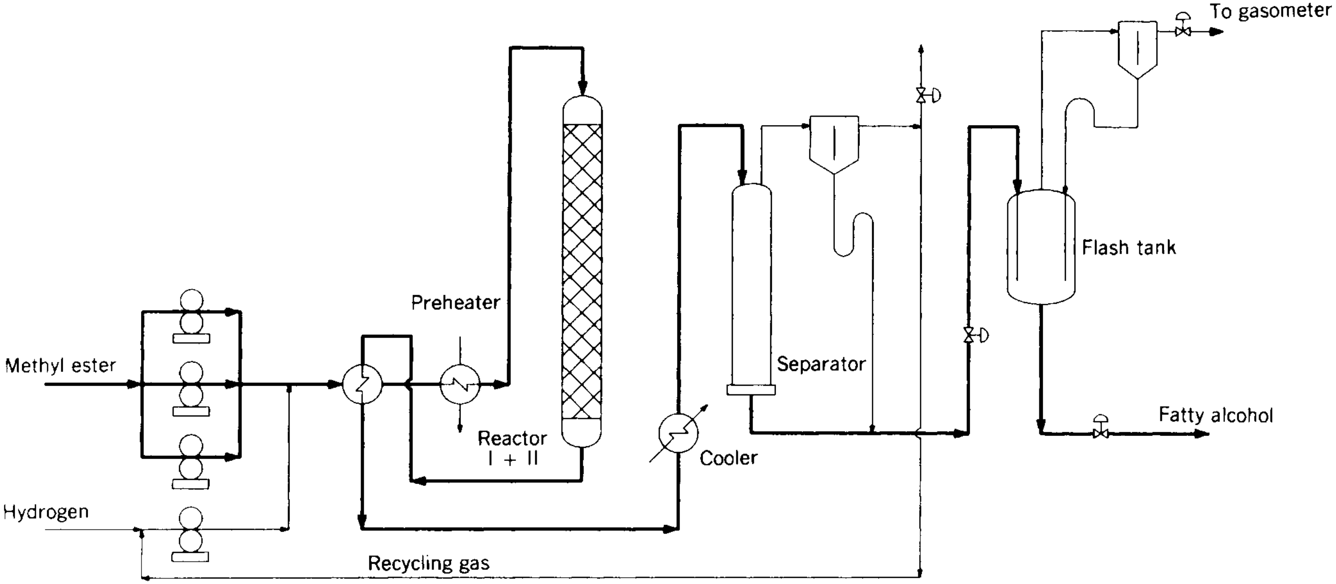


Fig. 2. Methyl ester, slurry catalyst process.

methanol, the latter being recycled back to the methyl ester reactors. Stripped crude alcohol is distilled to remove heavy impurities and optionally to fractionate into individual chain lengths. Still bottoms, primarily fatty-fatty ester, are recycled while a small amount are purged. A similar flowsheet is used for the fatty acid based, wax ester process (18).

There are a number of advantages for the fixed bed process compared to the slurry process, including lower catalyst usage (typically 0.8–1.0 kg/tonne of alcohol), improved process reliability, and better alcohol quality, with lower hydrocarbon content and lower saponification values. The low saponification value allows one in many cases to avoid alcohol distillation and rework of the unreacted methyl ester. The key disadvantages of the fixed bed include the need for higher ester feed quality to avoid poisoning the catalyst with sulfur, glycerine, glycerides, or soap. (19). Also, an increase in operating temperature, typically used near the end of the bed lifetime, can compromise product quality and cause elevated levels of hydrocarbon and dialkyl ether. A bed lifetime of 12 mo is typical. Either liquid-phase (trickle-bed) or vapor-phase hydrogenation can be used in the fixed bed. The process conditions for the liquid phase process are 200–225°C and 20.7 MPa, with a molar ratio of hydrogen to methyl ester of 20–100. Supported catalysts such as 20–40% copper chromite on a silica gel carrier are typically used. The catalyst must have high mechanical stability in order to withstand the stresses exerted by the gas–liquid film in the reactor. The vapor-phase process differs in the temperature and pressure requirements (225–250°C and 3.4 MPa); also the molar ratio of hydrogen to methyl ester is 200 or greater. The catalyst is compact pelletized. The high amount of recirculated gas provides fast removal of the heat of reaction, keeping side reactions such as hydrocarbon formation very low.

Figure 3 shows the process flow diagram for the methyl ester, fixed-bed catalyst process. Methyl ester is mixed with fresh and recycled hydrogen and preheated prior to entering the top of the reactor. The effluent is cooled and separated into liquid and gaseous fractions. The gaseous phase, which is rich in hydrogen, is recycled to the reactor, while the liquid phase is expanded into a flash tank to remove methanol. The stripped, crude alcohol generally does not require further distillation, unless fractionation into narrower cuts is desired.

Zinc containing catalysts (ie, zinc chromite) can be used at higher temperatures (275–325°C) and pressures of 25–30 MPa to convert unsaturated esters into unsaturated fatty alcohols using a fixed-bed process. Selectivity is sufficiently high that unsaturated fatty alcohols with iodine values up to 170 are reported (17). Producers of oleyl alcohol are Cognis, Salim Oleochemicals, Witco, and Rhone-Poulenc NA. Unsaturated fatty alcohols can also be made from lauric oils by selective hydrogenation of the unsaturated C18 methyl ester fraction, which has been separated by fractional crystallization (20).

9.3. New Manufacturing Trends. During the 1990s, several new trends emerged in the field of high-pressure hydrogenolysis. This included both new process technology and new catalysts. While many of these developments are by themselves not significant enough to retrofit existing plants, several of them are being incorporated into the construction of new natural alcohol plants.

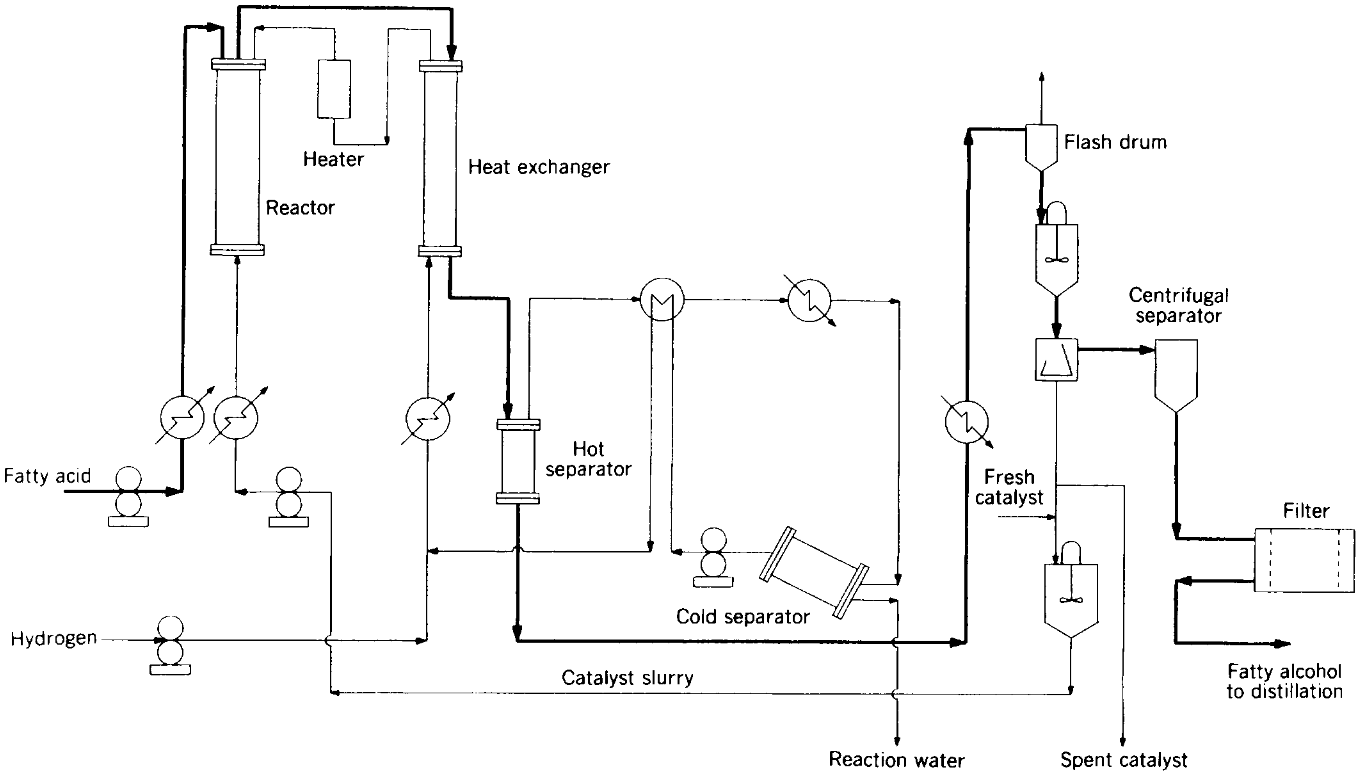


Fig. 3. Methyl ester, fixed-bed catalyst process.

9.4. Fatty Acid to Methyl Ester Conversion. In order to provide flexibility in feedstock usage, Kvaerner (formerly Davy Process Technology) has developed a new continuous countercurrent reactor to convert fatty acids to methyl esters (21). In some parts of the world, fatty acids are more widely available than methyl esters for those producers who do not have equipment for methanolysis of triglycerides. A solid resin acid catalyst developed by Rohm and Haas is used in the Kvaerner process. The resin is reported to be low cost, have long life, be easily separated from the product and have very high ($> 99.5\%$) conversion to the ester. This catalyst avoids some of the issues of previous esterification routes, which used sulfonic acid liquid catalysts that were corrosive to the reactor, were difficult to separate from the product, and thereby led to residual catalyst poisoning of the hydrogenation catalyst.

9.5. Low-Pressure Fixed-Bed Process. Kvaerner has also developed a totally vapor phase, fixed bed process for methyl ester feedstocks that is lower in pressure (3.4 vs 20.7 MPa) than the conventional fixed bed or slurry process (22). A promoted copper catalyst is used and selectivity is claimed to be 99%, but conversion is not specified. Methyl ester purity requirements are 99.8% as a feedstock for hydrogenation. This purity can be generated in the Kvaerner fatty acid to methyl ester conversion process described above. A very high ratio of hydrogen:methyl ester is used to keep the reaction completely in the vapor phase, and the capital associated with this somewhat offsets the benefits of lower-pressure operation.

Process benefits in the reactor reportedly include better contact between the hydrogen and the methyl ester, better heat contact and removal, and shorter residence time. Product benefits reportedly include lower by-products, such as hydrocarbons, as a result of the lower operating temperature. An integrated fatty acid–methyl ester–fatty alcohol plant located in the Philippines and operated by Primofina Oleochemicals, was successfully started up in 1997, but later shut down due to financial difficulties.

9.6. Direct Hydrogenolysis of Triglycerides. Several patents (23) were issued in the 1990s by Henkel (now Cognis) concerning direct hydrogenation of triglycerides. On paper, the process should be less costly than either the fatty acid or the methyl ester route, since there are fewer processing steps involved and hence lower capital investment as well as lower labor and utilities. However, propylene glycol, rather than glycerine, is the main co-product generated from the process, and during the period 1981–2000, the average list price for these materials was \$1.23/kg and \$1.65/kg, respectively (24). Under these conditions, the cost of fatty alcohol is approximately equal for both processes.

9.7. Hydrogenolysis in the Presence of Hydrocarbons under Supercritical Conditions. Another process technology being developed in the 1990s was hydrogenation under supercritical conditions (25). By adding a mutual solvent, ie, propane or butane, to methyl esters and hydrogen, the whole mixture is brought to a supercritical state. In this way, the gas to liquid mass transfer resistance of hydrogen is minimized. The result is an increase in the rate of hydrogenation by several orders of magnitude. Fatty alcohols have been produced on a pilot scale at about 250°C, 15.2 MPa, and a reaction time of 3 s using a fixed-bed process. Conversion and selectivity were both above 95%. For comparison, conventional reaction times for the fixed bed are on the order of 30 min to 2 h. From a capital standpoint, the advantage of a significant reduction in reactor volume is clearly offset by the requirement to separate and recycle the solvent back to the reactor. The inventors are reportedly looking for a commercial opportunity to scale up the process.

9.8. Biotechnology. Calgene cloned the reductase gene that is responsible for the synthesis of fatty alcohols in plants in 1992. They also reportedly were seeking to clone the ligase gene, which is responsible for the synthesis of long-chain liquid waxes from fatty alcohols in plants. Calgene reportedly plans to genetically engineer the reductase and ligase genes into rapeseed to allow for cost-effective natural production of fatty alcohols and long-chain liquid waxes in plants (26).

9.9. New Catalysts. Most catalysts for fatty alcohol production over the past 50 y have been based on Adkin's copper chromite catalyst (15). During the 1990s, alternatives to copper chromite were being investigated with the objective of replacing chromium as a promoter in the catalyst. This is because chromium is typically not recovered from spent catalyst, while copper is recovered and recycled. Positive results have been found by using zinc as the promoter in silica-supported copper catalysts (27). Another alternative catalyst (Ru-Sn-boride on alumina) was developed for low-pressure (1.5–5 MPa) hydrogenolysis of either saturated or unsaturated methyl esters into corresponding fatty alcohols. Yields of 90% have been demonstrated for saturated fatty alcohols, but only 60–80% yield has been demonstrated for oleyl alcohol (28).

10. Uses of Detergent-Range Alcohols

About 95% of the C12–C18 alcohols are converted to derivatives that are consumed in various end uses, while the remainder are consumed as the free alcohol. Major classes of applications include surfactants, lubricants, cosmetics and personal care, and pharmaceutical and medical products. Surfactants and lubricants tend to use alcohol derivatives, while the other applications tend to use the alcohol as is. Table 12 summarizes the list of applications.

10.1. Surfactants. In 1995, about 63% of the overall consumption of C12–C18 alcohols was as alcohol ethoxylates, half of which is subsequently converted to alcohol ethoxysulfate. Alcohol ethoxylates, ether sulfates, alcohol sulfates, alkyl glyceryl ether sulfonates (AGES), and alkylpolyglucosides (APG) are used as surfactants in household heavy-duty powders and liquids, light duty dishwashing liquids, other household cleaners, personal care products, and a variety of industrial, commercial, and institutional uses. These five surfactants account for about 84% of the 1995 U.S. consumption of detergent alcohols, excluding the C20+ products. Small volumes of fatty nitrogen derivatives are also used in household and industrial surfactants (9).

Consumption of ethoxylates and ether sulfates experienced strong growth during the 1990s due to displacement of LAS from laundry liquids and dishwashing liquids. Alcohol ethoxylates have better compatibility with complex enzymes increasingly used in liquid laundry products. They are also superior for cleaning body oil stains. The ether sulfates are more mild for dish applications. Both surfactants have better tolerance for hard-water ions than any anionic surfactant

Table 12. **Uses of Detergent Range Alcohols**

Industry	Use as alcohol	Use as derivative
detergent	emollient, foam control	surfactant, softener, bleaching agent, degreaser
petroleum and lubrication	drilling mud	emulsifier, lubricant, pour-point depressant
agriculture	evaporation suppressant, sprout inhibitor, debudding agent	pesticide, fungicide, emulsifier, soil conditioner, seed coating
plastics	mold release agent, antifoam, emulsion polymerization agent	stabilizer, uv absorber
textile	lubricant, foam control	emulsifier, softener, lubricant
cosmetics	softener, emollient, skin cleansing, gellant	emulsifier, biocide, hair conditioner, shower gel
pulp and paper	foam control	deinking agent
food	beverage additive	emulsifier, disinfectant
mineral processing	flotation agent	surfactant
pharmaceutical	performance enhancement	antiviral, antiulcer treatment
fuel additive	oxygenating agent	

available. Very low levels of specialty alcohol ethoxylates are used as emulsifiers in cleansing cremes and a few other personal care products. Alcohol ethoxylates are also used in textile processing and metal degreasing. Alcohol sulfates and ether sulfates are used in hard surface, rug and upholstery cleaners, shampoos, bubble baths, toilet soaps, and other personal care products in the U.S. Industrial uses include emulsion polymerization and agricultural emulsifiers. Alkyl glyceryl ether sulfonates and alkylpolyglucosides are small-volume, specialty surfactants. The former is used as a foam-boosting surfactant in light-duty liquid, shampoos, and combination soap-synthetic toilet bars. The latter is a nonionic surfactant with good solubility, foaming, and mildness and can be used in laundry, light-duty liquids, and personal care products. Fatty nitrogen derivatives include fatty amine oxides, ether amines, dialkyldimethylammonium quaternaries, and alkylbenzyldimethylammonium chlorides. Fatty amine oxides are surfactants used in light-duty dishwashing liquids, household cleaners, personal care products, and a few specialized industrial applications.

10.2. Lubricants. Polymethacrylate esters are employed in automotive and aircraft lubricating oils, as well as transmission and hydraulic fluids. They function as viscosity index improvers, pour-point depressants, and polymeric dispersants. Oligoesters of fatty alcohol and a pyrometallic anhydride are useful for waterproofing leather (29). An aqueous belt lubricant composition is based on fatty alcohol polyglycerol ethers (30). A lubricant for cold working of metals is based on monoalkyl ethers of polyethylene glycol and fatty alcohols (31). Lubricating and antifriction characteristics of water-based drilling fluids are improved by additives such as fatty alcohol or esterified or ethoxylated fatty alcohols (32). A corrosion inhibitor for gas pipelines and other steel surfaces is made by adding higher aliphatic alcohols to a mixture containing butanol, urea, various surfactants, and amines (33).

10.3. Cosmetics, Personal Care. C12, C14, and C16 alcohols are used in perfumes and fragrances. C18 alcohol is used in USP ointments (14).

In general, short-chain alcohols, particularly under about C16, tend to be irritants, while longer-chain aliphatic alcohols tend to be non irritating. C1216 alcohol is used as an emollient and bodying agent in hair care formulations. C16, C18, and C22 alcohols are used as a lubricant and bodying agent in skin care and hair care formulations. C20 alcohols are used as a lubricant and bodying agent in skin care formulations and also used in lipsticks, toothpastes, and perfume bases (34). A facial skin cleanser containing C16 and C18 alcohols and their ethoxylates is useful for removing sebum plaque (35). Other personal care applications include a cleansing bar with a moisturizing effect (36), cosmetic cleaning products with superior mildness via use of fatty alcohol polyglycosides (37), and a mild shower gel composition comprising fatty alcohol which imparts improved lathering and thickening properties (38).

Guerbet alcohols (2 alkyl-alcohols) and wax esters (alkyl alkanoates) are also commonly used for personal care applications. C12–C24 Guerbet alcohols are used in skin, hair, and stick applications, while C28–C36 Guerbet alcohols are used in stick and color cosmetic formulations. C24–C44 wax esters are used for cosmetics, pharmaceutical and candy coatings, and candles. The higher chain lengths (C36–C44) may be used as a replacement or extender for montan or carnauba wax.

10.4. Pharmaceutical, Medical. C18 alcohol has been approved as a direct and indirect food ingredient and as an ingredient in over-the-counter drugs. It is generally known that selected alcohols have some physiological activity. More specifically, the longer-chain alcohols, generally greater than C24, have benefits as anti-inflammatories and antiviral agents. C30 alcohol (triacontanol), in a suitable carrier, can be used as a treatment for inflammatory disorders such as herpes simplex, eczema, shingles, psoriasis, etc (39). C27 to C32 aliphatic alcohols are an effective topical anti-inflammatory and may also be used, in suitable carrier compositions, for treatment of virus induced disease and in prevention of infection by disease-causing virus (40). Natural mixtures of higher aliphatic primary alcohols, isolated from beeswax, are useful for antiulcer treatment (41). Perhaps the broadest medical claim associated with the higher alcohols refers to improved physical performance of athletes from ingestion of C24–C30 alcohols, which are active ingredients in wheat germ oil (42).

10.5. Other. Higher alcohol esters of thiodipropionic acid function as antioxidants and are effective in stabilizing polyolefins. Ether amines are often used in mining (ore flotation) applications. Dialkyldimethylammonium quaternaries are used for fabric softeners. Alkylbenzyldimethylammonium chlorides are used as active ingredients in fungicides, biocides, sanitizers, and disinfectants. An aqueous dispersion of C20–C36 alcohols for use in food and drinks offers good acid, salt, and heat resistance (43). C30 alcohol (triacontanol) accelerates growth in plants (44), and accelerates decomposition of sewage and reduces H2S (45). C14–C22 fatty alcohol is useful in dry cement compositions to reduce lime bloom, lime weeping, or crystallization of salts (46). Aqueous fatty alcohol dispersions (C10–C28) are useful as antifoam agents (47). An aqueous-based, solvent-free degreaser composition includes alcohol alkoxylates with a fatty alcohol moiety, alkoxylated fatty alcohol, and a fatty alcohol having an oxyethylate moiety (48).

Table 13. **Uses of Plasticizer Alcohols**

Industry	Use as alcohol	Use as derivative
plastics	emulsion polymerization	plasticizer, coatings
petroleum and lubrication	defoamer	lubricant,diesel additive
agriculture	stabilizer, tobacco sucker control	
mineral processing	extractant, antifoam	extractant, surfactant
paper	plasticizer	deinking agent
metal working	lubricant	lubricant, surfactant
cosmetics	fragrances, perfumes	sun protection products, gel sticks
health and personal care	antiseptics	fragrances

11. Uses of Plasticizer Alcohols

Plasticizer alcohols are either linear or branched C6 to C13 molecules (excluding C12 and C13 linears, which are detergent range). In 1997, about 54% of worldwide production was as 2-ethyl hexanol, 17% as C9 oxo alcohol, 12% as isodecyl alcohol, and 8% as C6–C11 linear alcohols. The remaining 9% is as branched C6 to C8 molecules. The plasticizer alcohols are used primarily in plasticizers, but they also have applications in a wide range of industrial and consumer products, as shown in Table 13 (11). As with the detergent range alcohols, the plasticizer alcohols are mainly consumed as derivatives.

11.1. Plasticizers. Phthalates, adipates, acetates, and trimellitates of C6–C13 alcohols are the lead types of plasticizers in use. Both linear and branched phthalates and adipates are used. Acetates and trimellitates tend to be exclusively branched. When ethylene prices rise in comparison to propylene, consumers tend to substitute branched phthalates for linear phthalates. The C7–C11 linear phthalates thrive better in markets where performance is more critical than price. At similar prices, linear phthalates provide better value than branched phthalates. Linear phthalates are characterized by superior low temperature properties and lower volatility; they are used in coated fabrics and sheet goods and when outdoor weathering resistance is required (swimming pool liners, roofing membranes, tarpaulins, and wire and cable jacketing). Linear phthalates based on alcohols greater than C9 have distinct advantages over branched phthalates in auto upholstery and compartment interiors; while maintaining low temperature flexibility, these linear phthalates reduce window fogging. Branched phthalates are used in applications such as vinyl flooring, carpet backing, and wire and cable jacketing. Adipates are used where low temperature flexibility is important, such as auto accessories, gaskets, hoses, and tubing. Acetates are based on branched alcohols such as isohexyl and isoheptyl and are used in application such as surface coatings. Trimellitates are used for wire and cable compounds, with trioctyl trimellitate and triisononyl trimellitate being the primary molecules (11).

11.2. Other Plastics Applications. 2-Ethyl hexyl esters of trialkyl phosphite serve as thermal stabilizers and antioxidants in plastics. Ba, Cd, and Zn salts of 2-ethyl hexanoic acid are used as PVC stabilizers. 2-Ethyl hexyl acrylate is used in emulsion polymers for pressure-sensitive adhesives. 2-Ethyl hexanol can be used directly or as an acrylate or methacrylate ester for surface coatings. Direct use is as a solvent in the electrodisposition of primer surface coatings in the automotive industry (11).

11.3. Surfactants. A number of surfactants are made from the plasticizer-range alcohols, using processes similar to that of detergent range alcohols, including ethoxylation, sulfation, and amination. Ethoxylated mixtures of C9–C11 linear alchols are used in hard surface cleaners and commercial detergents. Increased solubility and liquidity provide advantages over longer chain alcohols. Ethoxylates are also used for processing textiles, leather, pulp, and paper. C6–C10 and C8–C10 blends are used for ethoxylated/propoxylated/phosphated surfactants and C6–C10 sulfates and betaines. Automatic dishwasher formulations use propoxylated and ethoxylated linear alcohols. Ethoxylated tridecyl alcohol is used in nonionic surfactants, and the ether sulfate is used in a leading children's shampoo. 2-Ethyl hexanol is used as an additive in dispersing and wetting agents for pigment pastes, and as a sulfosuccinate molecule for wetting and scouring of textiles (11).

11.4. Lube Additives. 2-Ethyl hexyl based esters of C6–C10 dicarboxylic acids, glycols, or polyglycols are useful as greases and lubricants (49). Other branched alcohols are converted to molecules such as zinc diisodithiophosphate (ZDDP) and isodecyl methacrylate for high-temperature stability and cold weather flow in lubricants. 2-Ethyl hexanol is used as an ingredient in a fuel oil composition for diesel engines with decreased levels of particulates (50). 2-Ethyl hexyl nitrate is another type of diesel fuel additive that can be used at low levels to promote ignition (51). A lubricant composition containing 2-ethyl hexanol, dimer fatty acid, and a surfactant is effective in hot steel rolling mill operations (52). C6 and C8 alcohols can also be used for lamp oil and lighting fluids for charcoal grills as a nontoxic, clean-burning fuel with no color or odor (53).

11.5. Agricultural Chemicals. Plasticizer alcohols are used as solvents or as intermediates in the manufacture of insecticides and herbicides, including 2-ethyl hexyl esters of 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid. 2-Ethyl hexanol is also used as a carrier in microbiocidal compositions. Blends of C8 and C10 linear alcohols are used a plant growth regulators for tobacco sucker control.

11.6. Mining, Extraction. 2-Ethyl hexanol and various amine derivitives are used as a feedstock in the manufacture of extractants for heavy metals. Di-2-ethylhexyl phosphoric acid (DEHPA) and C8–C10 linear trialkyl amines are used for extraction of uranium ore. C8–C10 linear ether amines and isodecyl alcohol amines are used for flotation of taconite ores (54).

11.7. Solvents. 2-Ethyl hexanol is used as a direct solvent for defoaming in the paper, textile, and oil field industries (55). It is also used as a low-volatility ingredient in solvent blends for dyestuffs and coatings (ie, printing and stamp pad inks, dipping lacquers, etc), as well as an ingredient in solvent compositions to clean soil from dirty articles including metal, ceramic, and glass substrates (56). Quaternary amines used for deinking of paper, surfactants, flotation agents, and biocides also use 2-ethyl hexanol as a diluent (57).

11.8. Other Miscellaneous Applications. 2-Ethyl hexanol is used as a flow and gloss improver in baking finishes (58). Sun protection products are made with esters of 2-ethyl hexanol and *p*-methoxycinnamic acid (59). Benzylammonium chlorides of C8–C10 linear alcohols are used in hard surface cleaners and fungicides in institutional applications. Esters of 2-ethyl hexanol with salicylic acid have a variety of applications in the cosmetic, pharmaceutical, and food industries, as flavor and fragrance chemicals (60).

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COREY J. KENNEALLY
The Procter & Gamble Co.