ALCOHOLS, HIGHER ALIPHATIC, SYNTHETIC PROCESSES

1. Introduction

Higher aliphatic alcohols (C_6–C_{18}) are produced in a number of important industrial processes using petroleum-based raw materials. These processes are summarized in Table 1, as are the principal synthetic products and most important feedstocks (qv). Worldwide capacity for all higher alcohols was approximately 5.3 million metric tons per annum in early 1990, 90% of which was petro-

Table 1. **Synthetic Industrial Processes for Higher Aliphatic Alcohols**

Process	Feedstock(s)	Principal products	Worldwide capacity, millions of tons
Ziegler (organo-aluminum)	ethylene, triethyl-aluminum	primary C_6–C_{18} linear alcohols	0.3
oxo (hydroformylation)	olefins based on ethylene, propylene, butylene, or paraffins	primary alcohols	4.2
aldol	*n*-butyraldehyde	2-ethylhexanol	[a]
paraffin oxidation	paraffin hydrocarbons	secondary alcohols	0.2
Guerbet	lower primary alcohols	branched primary alcohols	[b]
Total			*4.7*

[a] Included in oxo process total.
[b] Less than 0.05.

leum-derived. Table 2 lists the major higher aliphatic alcohol producers in the world in early 1990.

By far the largest volume synthetic alcohol is 2-ethylexanol [104-76-7], $C_8H_{18}O$, used mainly in production of the poly(vinyl chloride) plasticizer bis(2-ethylhexyl) phthalate [117-81-7], $C_{24}H_{38}O_4$, commonly called dioctyl phthalate [117-81-7] or DOP (see PLASTICIZERS). A number of other plasticizer primary alcohols in the C_6–C_{11} range are produced, as are large volumes of C_{10}–C_{18} synthetic, mainly primary, alcohols used as intermediates to surfactants (qv)

Table 2. **Major C_6 and Higher Aliphatic Alcohol Producers**[a]

Company and location	Capacity 10^3 t/yr	Alcohol products	Feedstock
		Ziegler process	
Condea Chemie, Brunsbuettel, Germany	70	*n*-C_6,C_8,C_{10},C_{12},C_{14},C_{16},C_{18},C_{20}	ethylene
Ethyl Corp, Houston, Tex., U.S.	111	*n*-C_6,C_8,C_{10},C_{12},C_{14},C_{16},C_{18},C_{20}	ethylene
State, Ufa, USSR	48	*n*-C_6,C_8,C_{10},C_{12},C_{14},C_{16},C_{18},C_{20}	ethylene
Vista Chemical, Lake Charles, La., U.S.	100	*n*-C_6,C_8,C_{10},C_{12},C_{14},C_{16},C_{18},C_{20}	ethylene
Ziegler subtotal	*329*		
		Guerbet process	
Henkel, Duesseldorf, Germany	2	*i*-C_{16},C_{18},C_{20},C_{22},C_{24},. . .,C_{36}	linear alcohols
Guerbet subtotal	*2*		
		Caustic fusion process	
Witco Chemical, Dover, Ohio, U.S.	7	2-octanol	castor oil
Caustic fusion subtotal	*7*		

Table 2 (*Continued*)

Company and location	Capacity 10^3 t/yr	Alcohol products	Feedstock
		Fatty acid hydrogenation processes	
ATOCHEM SA, Lavera, France	7	n-C_7	castor oil
Cocochem, Batangas, Philippines	25	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Colgate, Barangay, Philippines	4	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Oleofabrik, Aarhus, Denmark	5	n-C_{16},C_{18}	palm oil, tallow
State, Kedzierzyn, Poland	10	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Fatty acid hydrogenation process	*51*		
		Methyl ester hydrogenation process	
ATUL, India	3	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Aegis, Jalagon, India	5	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Condea Chemie, Brunsbuettel, Germany	30	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Henkel, Duesseldorf, Germany	130	n-C_8,C_{10},C_{12},C_{14},$C_{16}C_{18}$	coconut oil, tallow
Henkel, Boussens, France	50	n-C_8,C_{10},C_{12},C_{14},C_{16},C_{18},C_{20},C_{22}	coconut oil, other fats
Hüls AG, Marl, Germany	10	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Kao Corp, Wakayama, Japan	15	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Marchon (Albright & Wilson), Whitehaven, UK	25	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
New Japan Chemical, Tokushima, Japan	15	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Philippinas Kao, Jasaan, Philippines	30	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Procter & Gamble, Kansas City, Kan., U.S.	45	n-C_8,C_{10},C_{12},C_{14},C_{16},C_{18}	coconut oil, tallow
Procter & Gamble, Sacramento, Calif., U.S.	54	n-C_8,C_{10},C_{12},C_{14},C_{16},C_{18}	coconut oil, palm oil
Sherex, Mapleton, Ill., U.S.	7	oleyl alcohol, n-C_{18}	tallow, soybean oil
Sinopec, Shanghai, China	15	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
State, Radleben, Germany	10	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil
Synfina-Oleofina, Ertvelde, Belgium	30	n-C_8,C_{10},C_{12},C_{14},C_{16}	coconut oil

Table 2 (*Continued*)

Company and location	Capacity 10^3 t/yr	Alcohol products	Feedstock
Methyl ester hydrogenation process subtotal	*474*		
		Oxidation processes	
Japan Catalytic Chemical, Kawasaki, Japan	12	*sec*-$C_{11},C_{12},C_{13},C_{14},C_{15}$	*n*-paraffins
State, Angarsk, USSR	45	*i*-$C_{10},C_{11},C_{12},C_{13},C_{14},C_{15},C_{16},C_{17},C_{18}$	*n*-paraffins
State, Ufa, USSR	90	*sec*-$C_{11},C_{12},C_{13},C_{14},C_{15},C_{16}$	*n*-paraffins
State, Volgodonsk, USSR	45	*n*-$C_{10},C_{11},C_{12},C_{13},C_{14},C_{15},C_{16},C_{17},C_{18}$	*n*-paraffins
Oxidation subtotal	*192*		
		Oxo process	
Enichem, Augusta, Italy	50	*n*-C_7 to C_{15}	*n*-paraffins
Exxon Chemical France, Harnes, France	125	*i*-C_8,C_9,C_{10}; *n*-C_9,C_{11},C_{13},C_{15}	polygas olefins, alpha olefins
Exxon Chemical Holland, Rozenburg-Europort, Netherlands	200	*i*-$C_8,C_9,C_{10},C_{13},C_{16}$	polygas olefins
Exxon Chemical, Baton Rouge, La., U.S.	295	*i*-C_6 to $C_{10},C_{12},C_{13},C_{16}$; *n*-$C_7,C_9,C_{11}$	polygas olefins, alpha olefins, butene
Hoechst, Oberhausen-Holten, Germany	40	*i*-C_{10},C_{13}	propylene
ICI, Teeside, United Kingdom	250	*i*-C_8,C_9,C_{10}; *n*-C_9 to C_{15}	polygas olefins, alpha olefins
India Nissan Chemical Ind., Baroda, India	13	*i*-$C_7,C_8,C_9,C_{10},C_{11}$	polygas olefins
Mitsubishi Kasei, Mizushima, Japan	25	*i*-C_9	butenes
Mitsubishi Kasei, Mizushima, Japan	30	*n*-$C_7,C_9,C_{11},C_{13},C_{15}$	ethylene
Mitsubishi Petrochemical, Yokkaichi, Japan	30	*n*-$C_{12},C_{13},C_{14},C_{15}$	*n*-paraffins
Nippon Oxocol, Ichihara, Japan	85	*i*-C_7,C_9,C_{10},C_{13}	polygas olefins

Table 2 (*Continued*)

Company and location	Capacity 10^3 t/yr	Alcohol products	Feedstock
Shell Chemical, Stanlow, UK	90	n-C_{10},C_{11},C_{12},C_{13},C_{14},C_{15}	ethylene
Shell Chemical, Geismar, La., U.S.	272	n-C_7,C_8,C_9,C_{10},C_{11},C_{12},C_{13},C_{14},C_{15}	ethylene
Sterling, Texas City, Tex., U.S.	102	n-C_7,C_9,C_{11},C_{13}	alpha olefins
Unipar, Sao Paulo, Brazil	20	i-C_{10},C_{13}	propylene
Oxo process subtotal	*1627*		
		Oxo / aldol processes	
Aristech, Pasadena, Tex., U.S.	86	2-ethylhexanol	propylene
BASF, Ludwigshafen, Germany[b]	100	i-C_9;n-C_9,C_{11},C_{13},C_{15}	butenes, polygas olefins, alpha olefins
BASF, Ludwigshafen, Germany	150	2-ethylhexanol	propylene
BASF, Freeport, Tex., U.S.	30	2-ethylhexanol	propylene
BASF Espanol SA, Tarragona, Spain	30	2-ethylhexanol	propylene
Celanese Mexicana, Celaya, Mexico[c]	70	2-ethylhexanol	acetaldehyde
Chemicke Zavodi, Litwinov, Czechoslovakia	30	2-ethylhexanol	propylene
Chisso, Goi, Japan	50	2-ethylhexanol	propylene
Ciquine, Camacari, Brazil	74	2-ethylhexanol	propylene
Elekieroz do Nordeste, Igarassue, Brazil[c]	15	2-ethylhexanol	acetaldehyde
Hoechst, Oberhausen-Holten, Germany	200	2-ethylhexanol	propylene
Hüs AG, Marl, Germany	200	2-ethylhexanol	propylene
Jilin, Jilin, China	50	2-ethylhexanol	propylene
KII, Koper, Yugoslavia	42	2-ethylhexanol	propylene
Kyowa Yuka, Yokkaichi, Japan	100	2-ethylhexanol	propylene
Lucky, Naju, Korea	120	2-ethylhexanol	propylene
Mitsubishi Kasei, Mizushima, Japan	146	2-ethylhexanol	propylene
National Organic, Bombay, India	8	2-ethylhexanol	propylene
Neste Oxo, Ornskoldsvik, Sweden	10	2-ethylhexanol	n-butyraldehyde

Table 2 (*Continued*)

Company and location	Capacity 10^3 t/yr	Alcohol products	Feedstock
Neste Oxo, Stennungsund, Sweden	126	2-ethylhexanol	propylene
Shell Chemical, Deer Park, Tex., U.S.	27	2-ethylhexanol	propylene
Sinopec, Daqing, China	50	2-ethylhexanol	propylene
Sinopec, Yan Shan, China	20	2-ethylhexanol	propylene
Sinopec, Yueyang-shibequ, China	10	2-ethylhexanol	propylene
Sinopec, Zibo, China	50	2-ethylhexanol	propylene
Societe Oxo-Chemie, Lavera, France	105	2-ethylhexanol	propylene
State, Burgas, Bulgaria	20	2-ethylhexanol	propylene
State, Beijing, China	10	2-ethylhexanol	propylene
State, Leuna, Germany	40	2-ethylhexanol	propylene
State, Schkopau, Germany	40	2-ethylhexanol	propylene
State, Rimnicu Vilcea, Romania	20	2-ethylhexanol	propylene
State, Timisoara, Romania	60	2-ethylhexanol	propylene
State, Angarsk, USSR	45	2-ethylhexanol	propylene
State, Omsk, USSR	45	2-ethylhexanol	propylene
State, Perm, USSR	90	2-ethylhexanol	propylene
State, Saluwat, USSR	45	2-ethylhexanol	propylene
Texas Eastman, Longview, Tex., U.S.	98	2-ethylhexanol	propylene
Tonen, Kawasaki, Japan	50	2-ethylhexanol	propylene
Union Carbide Corp., Texas City, Tex., U.S.	54	2-ethylhexanol	propylene
Zaklady Azotowe, Kedzierzyn, Poland	100	2-ethylhexanol	propylene
Oxo/aldol subtotal	*2616*		
Total world	*5298*		

[a] Data from Refs. 1–6.
[b] Oxo/dimersol process.
[c] Aldol process.

for detergents. Other lower volume synthetic alcohol application areas include solvents and specialty esters.

2. The Ziegler Process

The Ziegler process, based on reactions discovered in the 1950s, produces predominantly linear, primary alcohols having an even number of carbon atoms. The process was commercialized by Continental Oil Company in the United States in 1962, by Condea Petrochemie in West Germany (a joint venture of Continental Oil Company and Deutsche Erdöl, A.G.) in 1964, by Ethyl Corporation in the United States in 1965, and by the USSR in 1983.

Four chemical reactions are used to synthesize alcohols from aluminum alkyls and ethylene (qv).

Triethylaluminum Preparation

$$2\ \mathrm{Al} + 3\ \mathrm{H_2} + 6\ \mathrm{C_2H_4} \longrightarrow 2\ (\mathrm{C_2H_5})_3\mathrm{Al}$$

Chain Growth

$$(\mathrm{C_2H_5})_3\mathrm{Al} + 3x\ \mathrm{C_2H_4} \longrightarrow \left[\mathrm{C_2H_5(C_2H_4)}_x\right]_3\mathrm{Al}$$

Oxidation

$$2\ \left[\mathrm{C_2H_5(C_2H_4)}_x\right]_3\mathrm{Al} + 3\ \mathrm{O_2} \longrightarrow 2\ \mathrm{Al}\left[\mathrm{O(C_2H_4)}_x\mathrm{C_2H_5}\right]_3$$

Hydrolysis

$$2\ \mathrm{Al}\left[\mathrm{O(C_2H_4)}_x\mathrm{C_2H_5}\right]_3 + 3\ \mathrm{H_2O} \longrightarrow 6\ \mathrm{C_2H_5(C_2H_4)}_x\mathrm{OH} + \mathrm{Al_2O_3}$$

This process is currently used by Vista Chemical, successor to Continental Oil Company's chemical business, and by Condea. In the Ethyl Corporation process dilute sulfuric acid is used in place of water in the hydrolysis step; producing alum rather than alumina.

2.1. Triethylaluminum Preparation. Triethylaluminum [97-93-8], $C_6H_{15}Al$, can be prepared by a two-step or a one-step process. In the former, aluminum [7429-90-5], Al, powder is added to recycled triethylaluminum and the slurry reacts first with hydrogen [1333-74-0], H_2, to produce diethylaluminum hydride [871-27-2], which in the second step reacts with ethylene [74-85-1], C_2H_4, to produce triethylaluminum. In the one-step process, hydrogen and ethylene are simultaneously fed to the reactor containing the aluminum slurry.

2.2. Chain Growth. Triethylaluminum reacts with ethylene in controlled, highly exothermic, successive addition reactions to produce a spectrum of higher molecular weight alkyls of even carbon number. The distribution of chain lengths in the chain growth mixture corresponds closely to the Poisson equation (7). Side reactions lead to small deviations from the Poisson distribution, greater deviations being observed at higher reaction temperatures. Some

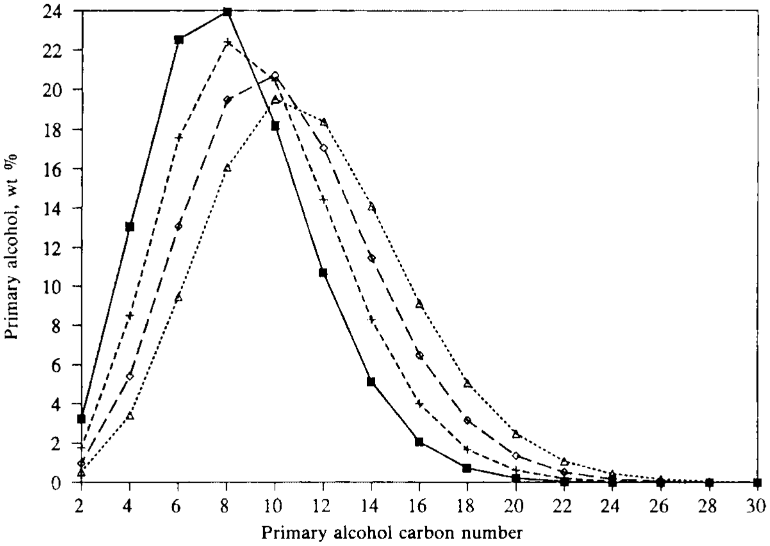


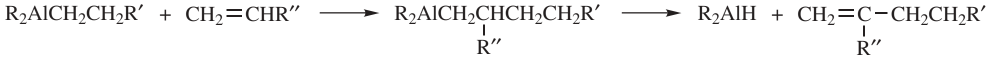
Fig. 1. Ziegler ethylene chain growth. Theoretical (Poisson) distribution of primary alcohols at (–■–) 2.5, (– + –) 3.0, (–◇–) 3.5, and (··△··) 4.0 moles of ethylene per $\frac{1}{3}$ mole aluminum. Courtesy of Ethyl Corporation.

control of the distribution is obtained by adjustment of triethylaluminum–ethylene ratio as shown in Figure 1. In the Ethyl process, steps are taken to produce a longer chain fraction (predominantly C_{12}–C_{18}) that is sent to the oxidation step, and a shorter chain fraction (predominantly C_2–C_{10}) that is recycled for additional chain growth. The final product distribution is about 15–25% C_6–C_{10} and 75–85% C_{12}–C_{18} (8). This approach permits changes in the carbon number distribution of the alcohol product as best fit market demands. A comparison of typical commercial product distributions in the Ethyl and Vista processes is shown in Figure 2.

There are two important side reactions, particularly above 120°C: (*1*) aluminum alkyls decompose to form dialkylaluminum hydrides and alpha olefins (the dialkylaluminum hydrides rapidly react with ethylene to regenerate a trialkylaluminum);

$$R_2AlCH_2CH_2R' \longrightarrow R_2AlH + CH_2{=\!=}CHR'$$

and (*2*) alpha olefins can react with trialkylaluminum to produce branched aluminum alkyls and branched olefins.



$$R_2AlCH_2CH_2R' + CH_2{=}CHR'' \longrightarrow R_2AlCH_2\underset{\displaystyle R''}{\underset{|}{C}}HCH_2CH_2R' \longrightarrow R_2AlH + CH_2{=}\underset{\displaystyle R''}{\underset{|}{C}}{-}CH_2CH_2R'$$

This second reaction leads to the small amount of branching (usually less than 5%) observed in the alcohol product. The alpha olefins produced by the first reaction represent a loss unless recovered (8). Additionally, ethylene polymerization

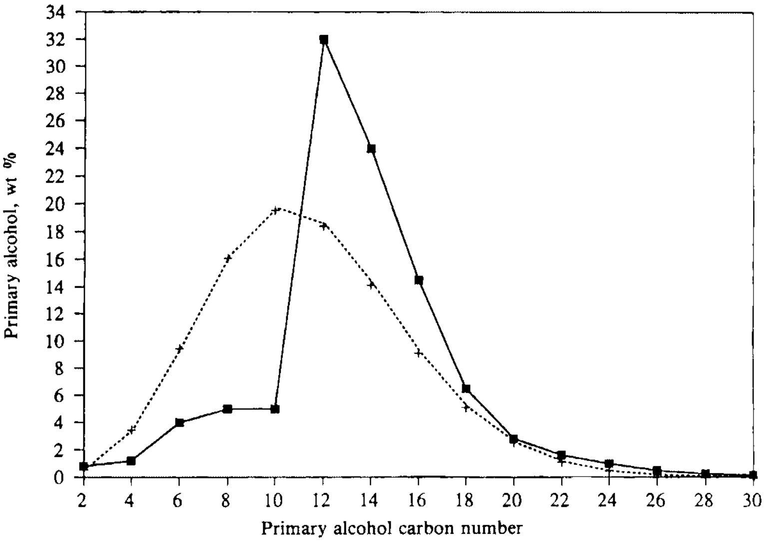


Fig. 2. Estimated primary alcohol distributions for (■) Ethyl Corporation-modified Ziegler and (+) Vista Corporation Ziegler, at 4.0 moles ethylene per $\frac{1}{3}$ mole aluminum. Courtesy of Ethyl Corporation.

during chain growth creates significant fouling problems which must be addressed in the design and operation of commercial production facilities (9).

2.3. Oxidation. Aluminum alkyls are oxidized to the corresponding alkoxides using dry air above atmospheric pressure in a fast, highly exothermic reaction. In general, a solvent is used to help avoid localized overheating and to decrease the viscosity of the solution. By-products include paraffins, aldehydes, ketones, olefins, esters, and alcohols; accidental introduction of moisture increases paraffin formation. To prevent contamination, solvent and by-products must be removed before hydrolysis. Removal can be effected by high temperature vacuum flashing or by stripping.

2.4. Hydrolysis. Aluminum alkoxides are hydrolyzed using either water or sulfuric acid, usually at around 100°C. In addition to the alcohol product, neutral hydrolysis gives high quality alumina (see ALUMINUM COMPOUNDS); the sulfuric acid hydrolysis yields alum. The crude alcohols are washed and then fractionated.

Mild steel is a satisfactory construction material for all equipment in Ziegler chemistry processes except for hydrolysis. If sulfuric acid hydrolysis is employed, materials capable of withstanding sulfuric acid at 100°C are required: lead-lined steel, some alloys, and some plastics. Flow diagrams for the Vista and Ethyl processes are shown in Figures 3 and 4, respectively.

2.5. Environmental Considerations. Environmental problems in Ziegler chemistry alcohol processes are not severe. A small quantity of aluminum alkyl wastes is usually produced and represents the most significant disposal problem. It can be handled by controlled hydrolysis and separate disposal of the aqueous and organic streams. Organic by-products produced in chain growth

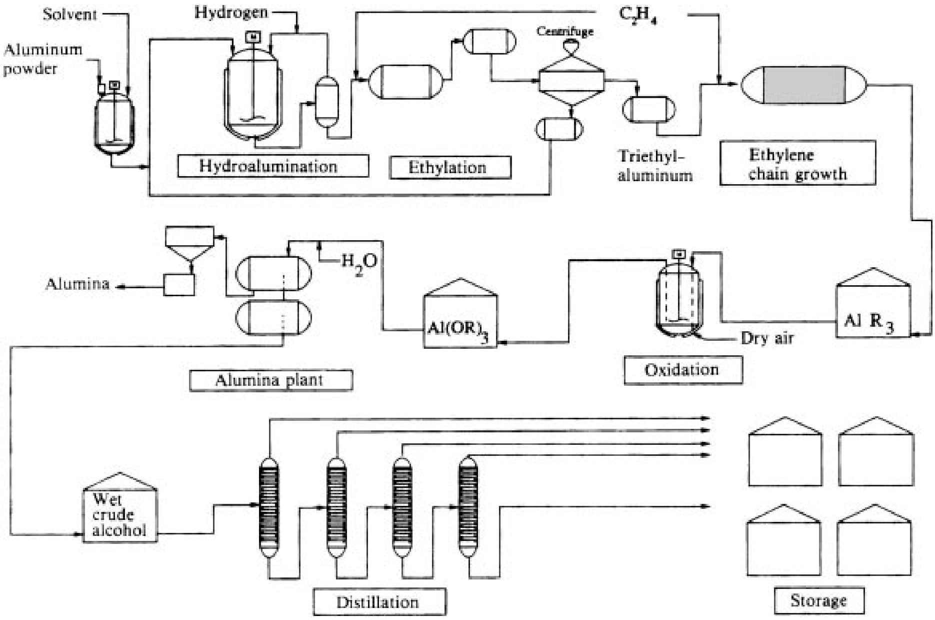


Fig. 3. Flow diagram for the Vista Corporation primary alcohols plant, Lake Charles, Louisiana. Courtesy of Vista Corporation.

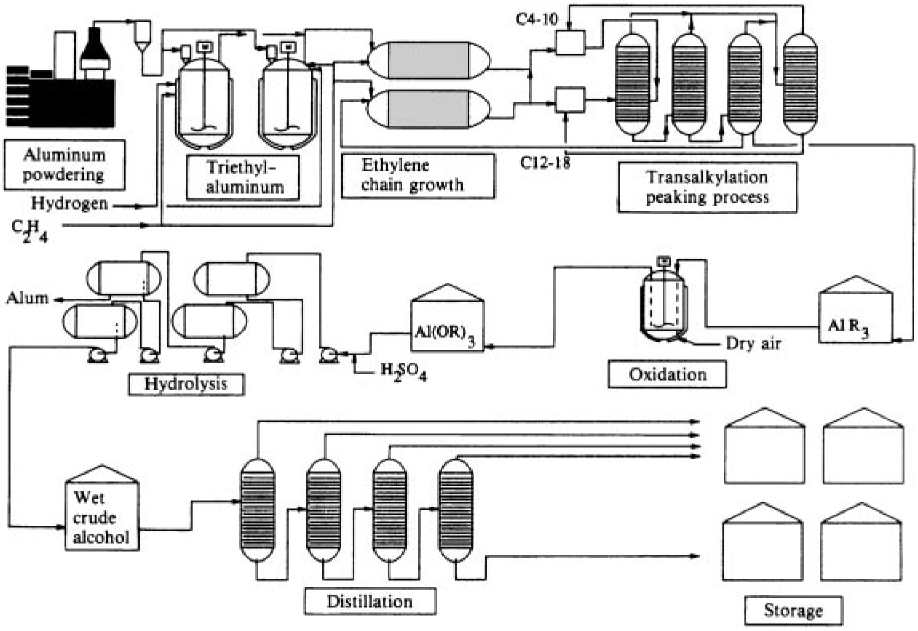


Fig. 4. Flow diagram for the Ethyl Corporation primary alcohols plant, Houston, Texas. Courtesy of Ethyl Corporation.

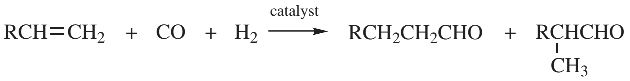
and hydrolysis can be cleanly burned. Wastewater streams must be monitored for dissolved carbon, such as short-chain alcohols, and treated conventionally when necessary.

3. The Oxo Process

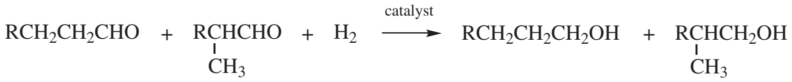
The oxo or hydroformylation reaction was discovered in Germany in 1938 (10) and was first used on a commercial scale by the Enjay Chemical Company (now Exxon) in 1948. By 1990 the total world alcohol capacity based on this general technology was over four million metric tons per year (see Oxo process).

The structures and, hence, the properties of the higher oxo alcohols (C_6–C_{18}) are a function of the oxo process and the olefin employed. All the oxo products are primary alcohols and contain one more carbon atom than the feedstock olefin. They differ in two respects from natural alcohols and from Ziegler products, both of which are linear and of even carbon number. First, depending on the feedstock, they contain either even and odd carbon numbers or all odd carbon numbers. Second, the oxo products all have more branching. Branched olefin gives completely branched products; linear olefin gives some 2-methyl branching, the extent of which is dependent on the process. From a conventional cobalt-catalyzed process, the typical product of a linear olefin is 40–50% branched. Modified catalysts reduce branching to 15–25%.

3.1. Process Technology. In a typical oxo process, primary alcohols are produced from monoolefins in two steps. In the first stage, the olefin, hydrogen, and carbon monoxide [630-08-0], react in the presence of a cobalt or rhodium catalyst to form aldehydes, which are hydrogenated in the second step to the alcohols.

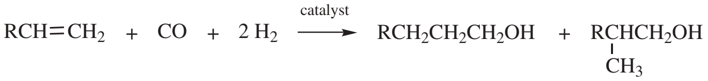


$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO + R\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO$$



$$RCH_2CH_2CHO + R\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CH_2OH + R\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$$

The oxo catalyst may be modified to function as a hydrogenation catalyst as well and, using a 2:1 ratio of hydrogen to carbon monoxide, alcohols are produced directly.



$$RCH{=}CH_2 + CO + 2\,H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CH_2OH + R\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$$

These reactions are applicable to most monoolefins and are used to obtain a large number of commercial products.

3.2. Cobalt Catalyst, Two-Step, High Pressure Process. The olefin, with recycle and makeup cobalt catalyst at 0.1–1.0% concentration, is preheated and fed continuously to the oxo reactor together with the synthesis gas at a

1–1.2:1 H_2 to CO ratio. The reaction is conducted with agitation at 20,300–30,400 kPa (200–300 atm) and 130–190°C. Liquid hourly space velocity (LHSV) in the reactor is 0.5–1.0. The reaction is highly exothermic, 125 kJ/mol (54,000 Btu/lb-mol), and requires cooling. The intermediate aldehyde is hydrogenated to the alcohol at 5,070–20,300 kPa (50–200 atm) and 150–200°C using a catalyst containing copper, zinc, or nickel. The crude product is then fractionated (Fig. 5). The plant may be operated continuously or on a campaign basis with subsequent blending of the alcohols to give the desired product. The reactor and parts exposed to aldehydes or acids are constructed of alloy steel; the remainder is of carbon steel.

The cobalt catalyst can be introduced into the reactor in any convenient form, such as the hydrocarbon-soluble cobalt naphthenate [61789-51-3], as it is converted in the reaction to dicobalt octacarbonyl [15226-74-1], $Co_2(CO)_8$, the precursor to cobalt hydrocarbonyl [16842-03-8], $HCo(CO)_4$, the active catalyst species. Some of the methods used to recover cobalt values for reuse are (11): conversion to an inorganic salt soluble in water; conversion to an organic salt soluble in water or an organic solvent; treatment with aqueous acid or alkali to recover part or all of the $HCo(CO)_4$ in the aqueous phase; and conversion to metallic cobalt by thermal or chemical means.

3.3. Modified Cobalt Catalyst, One-Step, Low Pressure Process.

The distinguishing feature of this process, as commercialized by Shell, is catalysis by a cobalt–carbonyl–organophosphine complex such as $[Co(CO)_3P(C_4H_9)_3]_2$ (12). The olefin, using recycle and makeup catalyst at about 0.5% concentration, and synthesis gas at a 2–2.5:1 H_2 to CO ratio, react at 6,080–9,120 kPa (60–90 atm) and 170–210°C for detergent range alcohols. Lower pressures (3,040–7,080 kPa) are employed for *n*-butanol [71-36-3] and 2-ethylhexanol production. LHSV in the reactor is 0.1–0.2. The catalyst is highly selective for hydroformylation of 1-olefins at the terminal carbon atom; this results in a product from a linear feedstock which is up to 75–85% linear, having mainly 2-methyl isomers as branched components. The product is alcohol rather than aldehyde, because the modified catalyst promotes hydrogenation; and, because it is such an effective hydrogenation catalyst, approximately 10% of the olefin feed is also converted to paraffins. Because rapid isomerization of intermediates occurs under the reaction conditions, high primary alcohol selectivity can be obtained from internal olefins as well as from alpha olefins. After degassing and vacuum flashing, the crude alcohols are washed with caustic to convert esters to alcohols, water-washed, and distilled. Purified alcohols are then finished by hydrogenation and filtration (13).

Significant differences in this modified process include use of a lower pressure, slightly higher temperature, lower LHSV, formation of alcohol in one processing step, and a higher hydrogenation of the olefins to paraffins. The process is operated commercially by Shell Chemical U.S.A., Shell Chemical UK, and Mitsubishi Petrochemical exclusively for detergent range alcohols. Detergent range alcohols produced by the Shell process are particularly well-suited for downstream production of ethylene oxide adducts, which are major Shell Chemical products. The process schematic is shown in Figure 6.

Rhodium Catalysts. Rhodium carbonyl catalysts for olefin hydroformylation are more active than cobalt carbonyls and can be applied at lower

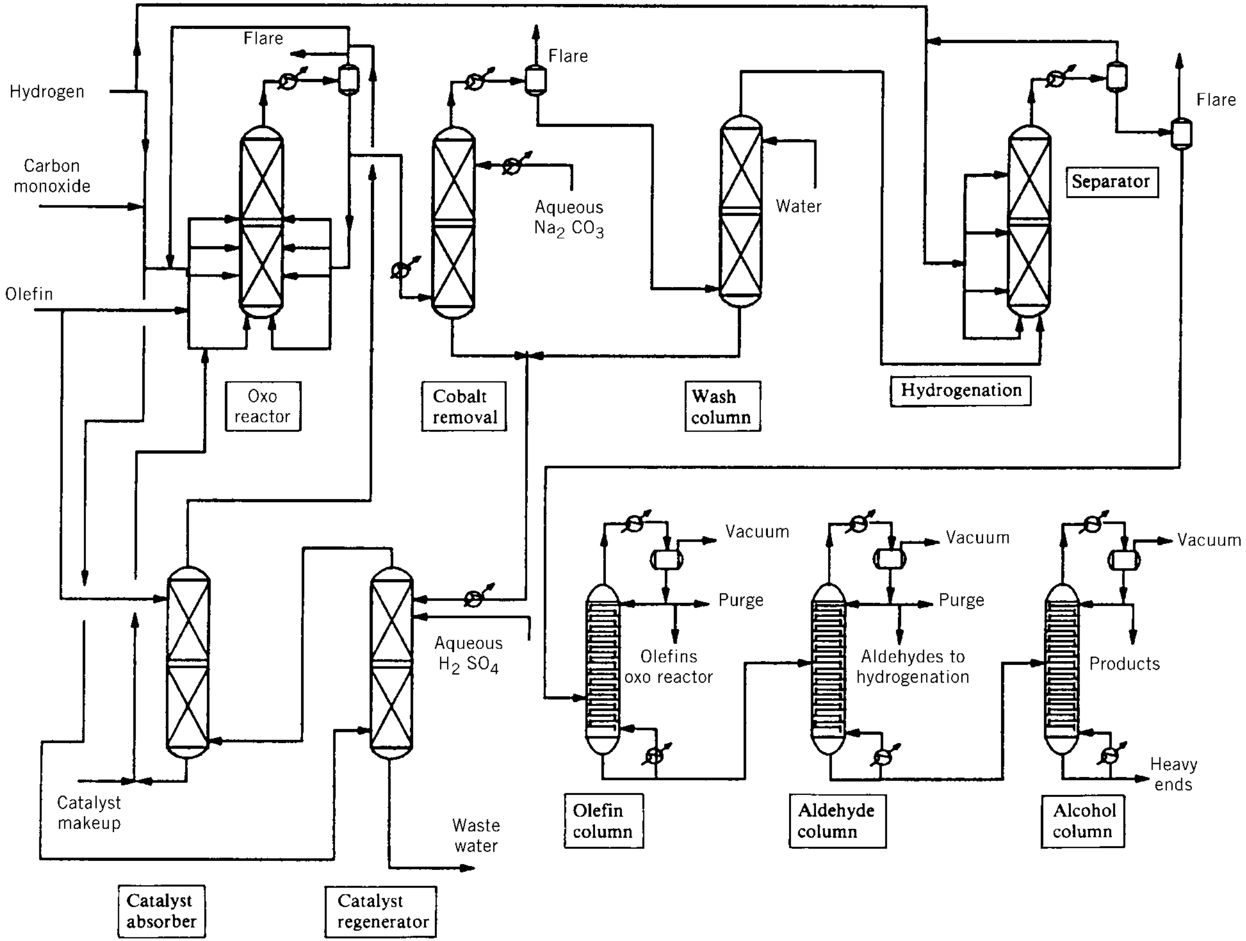


Fig. 5. Flow diagram for oxo alcohol manufactured by the two-stage process. Courtesy of the Ethyl Corporation.

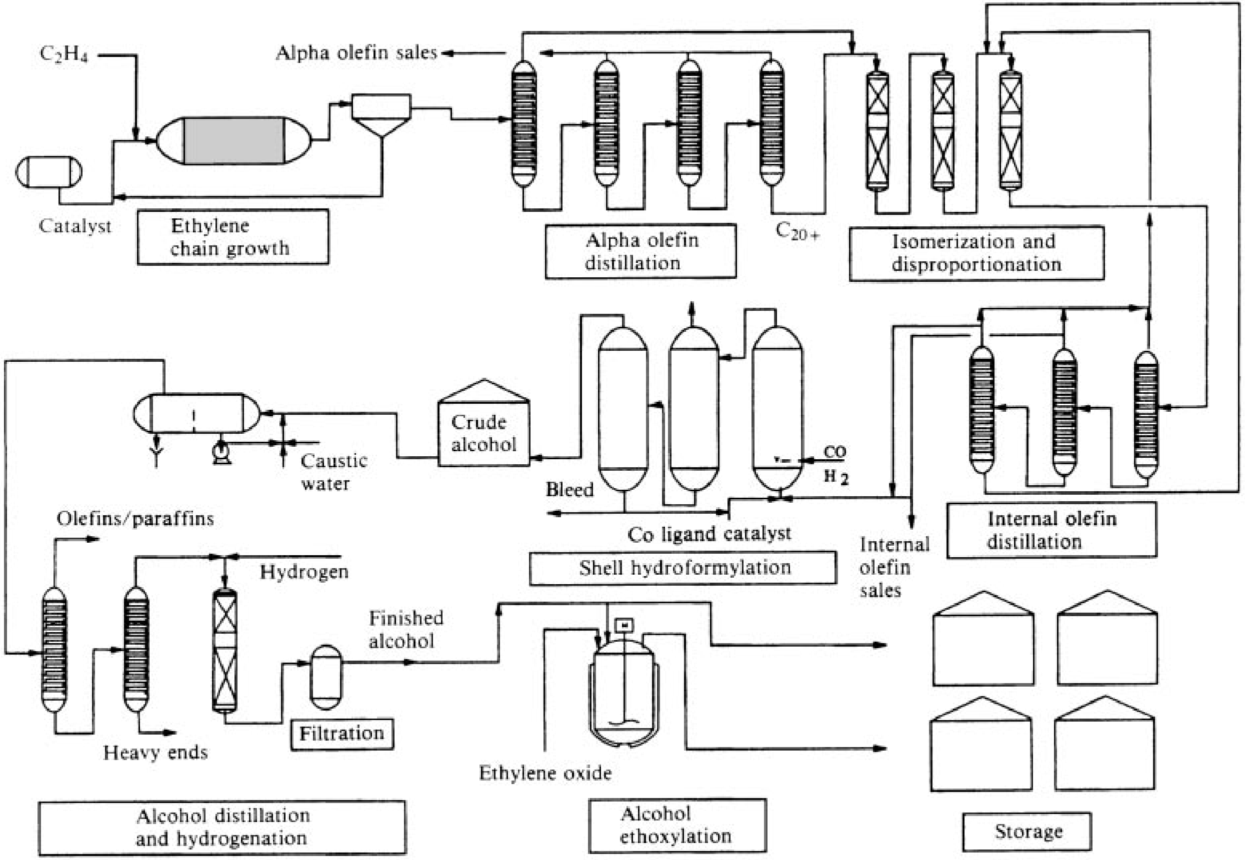


Fig. 6. Flow diagram for the Shell Chemical alcohol-olefin complex, Geismar, Louisiana, and Stanlow, United Kingdom. Courtesy of the Shell Chemical Corporation and the Ethyl Corporation.

temperatures and pressures (14). Rhodium hydrocarbonyl [75506-18-2], $HRh(CO)_4$, results in lower *n*-butyraldehyde [123-72-8] to isobutyraldehyde [78-84-2] ratios from propylene [115-07-1], C_3H_6, than does cobalt hydrocarbonyl, ie, 50/50 vs 80/20. Ligand-modified rhodium catalysts, $HRh(CO)_2L_2$ or $HRh(CO)L_3$, afford *n*-/iso-ratios as high as 92/8; the ligand is generally a tertiary phosphine. The rhodium catalyst process was developed jointly by Union Carbide Chemicals, Johnson-Matthey, and Davy Powergas and has been licensed to several companies. It is particularly suited to propylene conversion to *n*-butyraldehyde for 2-ethylhexanol production in that by-product isobutyraldehyde is minimized.

3.4. Olefin Sources. The choice of feedstock depends on the alcohol product properties desired, availability of the olefin, and economics. A given producer may either process different olefins for different products or change feedstock for the same application. Feedstocks believed to be currently available are as follows.

Propylene. 2-Ethylhexanol is now produced almost entirely from propylene, with the exception of a minor portion that comes from ethylene-derived acetaldehyde.

Polygas Olefins. Refinery propylene and butenes are polymerized with a phosphoric acid catalyst at 200°C and 3040–6080 kPa (30–60 atm) to give a mixture of branched olefins up to C_{15}, used primarily in producing plasticizer alcohols (isooctyl, isononyl, and isodecyl alcohol). Since the olefins are branched (75% have two or more CH_3 groups) the alcohols are also branched. Exxon, BASF, Ruhrchemie (now Hoechst), ICI, Nissan, Getty Oil, U.S. Steel Chemicals (now Aristech), and others have all used this olefin source.

Other Dimer Olefins. Olefins for plasticizer alcohols are also produced by the dimerization of isobutene [115-11-7], C_4H_8, or the codimerization of isobutene and *n*-butene [25167-67-3]. These highly branched octenes lead to a highly branched isononyl alcohol [68526-84-1] product. BASF, Ruhrchemie, ICI, Nippon Oxocol, and others have used this source.

The Dimersol process (French Petroleum Institute) produces hexenes, heptenes, and octenes from propylene and linear butylene feedstocks. This process is reported to produce olefin with less branching than the corresponding polygas olefins. BASF practices this process in Europe.

Normal Paraffin-Based Olefins. Detergent range *n*-paraffins are currently isolated from refinery streams by molecular sieve processes (see ADSORPTION, LIQUID SEPARATION) and converted to olefins by two methods. In the process developed by Universal Oil Products and practiced by Enichem and Mitsubishi Petrochemical, a *n*-paraffin of the desired chain length is dehydrogenated using the Pacol process in a catalytic fixed-bed reactor in the presence of excess hydrogen at low pressure and moderately high temperature. The product after adsorptive separation is a linear, random, primarily internal olefin. Shell formerly produced *n*-olefins by chlorination–dehydrochlorination. Typically, C_{11}–C_{14} *n*-paraffins are chlorinated in a fluidized bed at 300°C with low conversion (10–15%) to limit dichloroalkane and trichloroalkane formation. Unreacted paraffin is recycled after distillation and the predominant monochloroalkane is dehydrochlorinated at 300°C over a catalyst such as nickel acetate [373-02-4]. The product is a linear, random, primarily internal olefin.

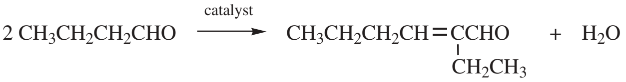
Ethylene-Based Olefins

Aluminum Alkyl Chain Growth. Ethyl, Chevron, and Mitsubishi Chemical manufacture higher, linear alpha olefins from ethylene via chain growth on triethylaluminum (15). The linear products are then used as oxo feedstock for both plasticizer and detergent range alcohols; and because the feedstocks are linear, the linearity of the alcohol product, which has an entirely odd number of carbons, is a function of the oxo process employed. Alcohols are manufactured from this type of olefin by Sterling, Exxon, ICI, BASF, Oxochemie, and Mitsubishi Chemical.

Catalytic Oligomerization. Shell Chemical provides C_{11}–C_{14} linear internal olefin feedstock for C_{12}–C_{15} detergent oxo alcohol production from its SHOP (Shell Higher Olefin Process) plant (16,17). C_9–C_{11} alcohols are also produced by this process. Ethylene is first oligomerized to linear, even carbon–number alpha olefins using a nickel complex catalyst. After separation of portions of the α-olefins for sale, others, particularly C_{18} and higher, are catalytically isomerized to internal olefins, which are then disproportionated over a catalyst to a broad mixture of linear internal olefins. The desired C_{11}–C_{14} fraction is separated; the lighter and heavier fractions are recycled to the isomerization/disproportionation section. The SHOP process has been described in detail in the literature (18) and is shown schematically in Figure 6.

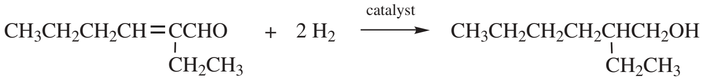
4. The Aldol Process

The important solvent and plasticizer intermediate, 2-ethylhexanol, is manufactured from *n*-butyraldehyde by aldol addition in an alkaline medium at 80–130°C and 300–1010 kPa (3–10 atm).



$$2\,CH_3CH_2CH_2CHO \xrightarrow{\text{catalyst}} CH_3CH_2CH_2CH{=}\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}CHO + H_2O$$

This step is followed by catalytic hydrogenation at 230°C and 5,070–20,300 kPa (50–200 atm).



$$CH_3CH_2CH_2CH{=}\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}CHO + 2\,H_2 \xrightarrow{\text{catalyst}} CH_3CH_2CH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2OH$$

The *n*-butyraldehyde may be obtained from acetaldehyde [75-07-0] by aldol addition followed by hydrogenation, or from propylene by the oxo process. This latter process is predominantly favored (Fig. 7).

The oxo and aldol reactions may be combined if the cobalt catalyst is modified by the addition of organic–soluble compounds of zinc or other metals. Thus, propylene, hydrogen, and carbon monoxide give a mixture of C_4 aldehydes and 2-ethylhexenaldehyde [123-05-7] which, on hydrogenation, yield the corresponding alcohols.

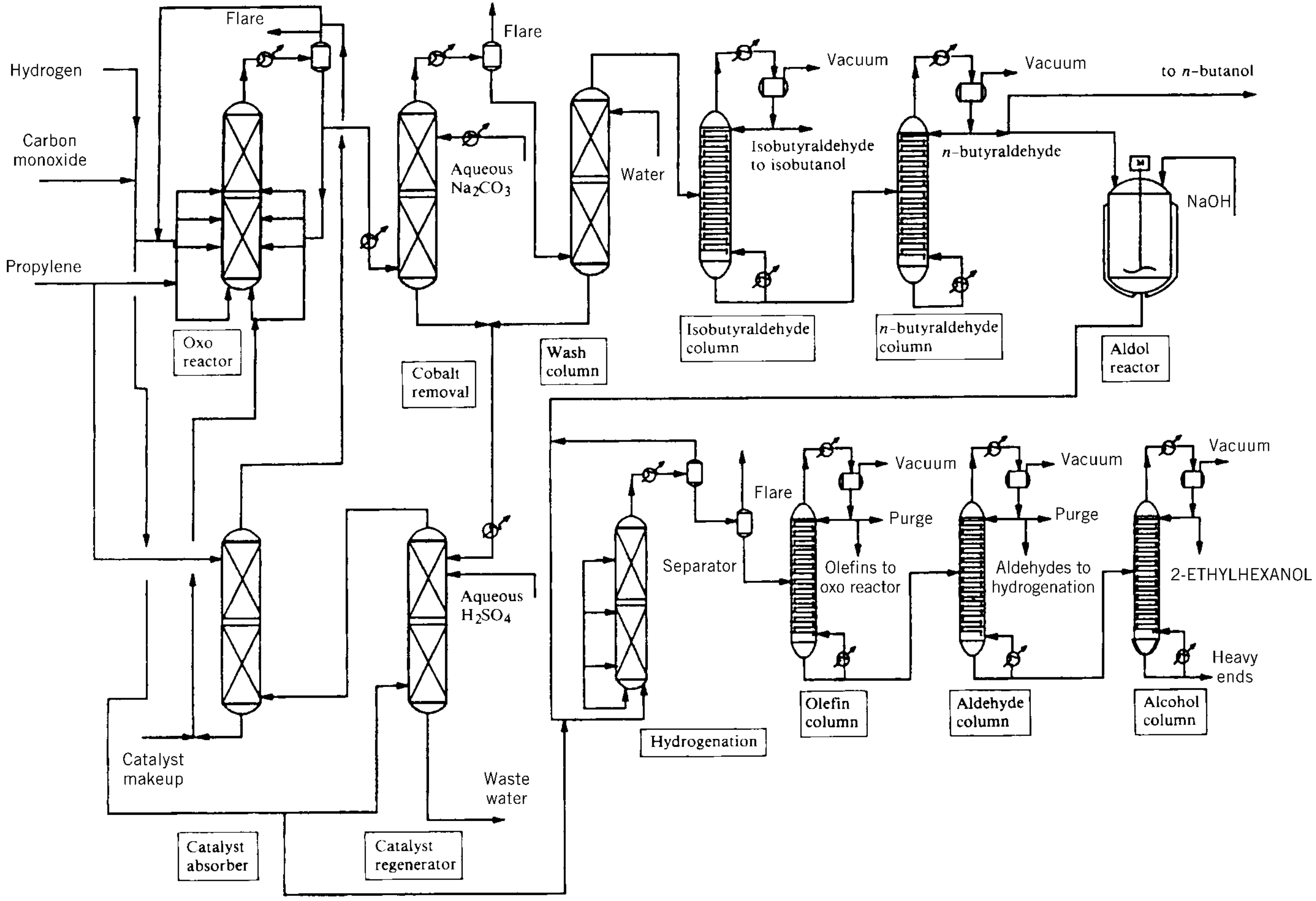


Fig. 7. Flow diagram for the oxo–aldol manufacture of 2-ethylhexanol.

5. The Paraffin Oxidation Process

Secondary alcohols (C_{10}–C_{14}) for surfactant intermediates are produced by hydrolysis of secondary alkyl borate or boroxine esters formed when paraffin hydrocarbons are air-oxidized in the presence of boric acid [10043-35-3] (19,20). Union Carbide Corporation operated a plant in the United States from 1964 until 1977. A plant built by Nippon Shokubai (Japan Catalytic Chemical) in 1972 in Kawasaki, Japan was expanded to 30,000 t/yr capacity in 1980 (20). The process has been operated industrially in the USSR since 1959 (21). Also, predominantly primary alcohols are produced in large volumes in the USSR by reduction of fatty acids, or their methyl esters, from permanganate-catalyzed air oxidation of paraffin hydrocarbons (22). The paraffin oxidation is carried out in the temperature range 150–180°C at a paraffin conversion generally below 20% to a mixture of trialkyl borate, $(RO)_3B$, and trialkyl boroxine, $(ROBO)_3$. Unconverted paraffin is separated from the product mixture by flash distillation. After hydrolysis of residual borate esters, the boric acid is recovered for recycle and the alcohols are purified by washing and distillation (19,20).

The product secondary alcohols from paraffin oxidation are converted to ethylene oxide adducts (alcohol ethoxylates) which are marketed by Japan Catalytic Chemical and BP Chemicals as SOFTANOL secondary alcohol ethoxylates. Union Carbide Chemical markets ethoxylated derivatives of the materials in the United States under the TERGITOL trademark (23).

6. The Guerbet Process

Higher molecular weight branched alcohols are produced by condensation of lower alcohols in the Guerbet reaction.

$$2\,RCH_2CH_2OH \longrightarrow RCH_2CH_2\underset{\underset{\displaystyle R}{|}}{C}HCH_2OH + H_2O$$

In earlier studies (24), the reaction was carried out at temperatures above 200°C under autogenous pressure conditions using alkali metal hydroxide or alkoxide catalysts; significant amounts of carboxylic acid, RCH_2COOH, were formed as were other by-products. More recent reports describe catalysts which minimize by-products: MgO–K_2CO_3–CuC_2O_2 (25), less basic but still requiring high temperatures; Rh, Ir, Pt, or Ru complexes (26); and an alkali metal alkoxide plus Ni or Pd (27), effective at much lower temperatures.

Some 2,000–3,000 t/yr of these specialty alcohols are produced in the United States (Exxon) and in Germany (Henkel) (28). Their high liquidity because of branching permits use of less volatile, higher molecular weight materials, reported to be less irritating than the lower molecular weight linear alcohol materials, in a variety of cosmetic products (29).

BIBLIOGRAPHY

"Alcohols, Higher" in *ECT* 1st ed., Vol. 1, pp. 315–321, by H. B. McClure, Carbide and Carbon Chemicals Corporation; "Alcohols, Higher, Synthetic" in *ECT* 2nd ed., Vol. 1,

pp. 560–569, by R. W. Miller, Eastman Chemicals Products, Inc; "Alcohols, Higher Aliphatic, Synthetic in *ECT* 3rd ed., Vol. 1 pp. 740–754 by M. F. Gautreaux, W. T. Davis, and E. D. Travis, Ethyl Corporation.

CITED PUBLICATIONS

1. Asociacion Petroquimica Latinomamericana, Anuario Petroquimico Latino Americano 1985, Buenos Aires, 1985.
2. J-P. Davreux, Synfina–Oleofina, 1988.
3. R. F. Modler, "Detergent Alcohols" in *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1987.
4. T. Gibson, "Plasticizer Alcohols" in *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1985.
5. T. Gibson, "Oxo Chemicals" in ref. 4.
6. G. R. Lappin, J. D. Wagner, Ethyl Corporation, 1989.
7. H. Weslau, *Justus Liebigs Ann. Chem.* **629**, 198 (1960).
8. U.S. Pat. 3,415,861 (Dec. 10, 1968), W. T. Davis and C. L. Kingrea (to Ethyl Corporation).
9. G. R. Lappin in G. R. Lappin and J. D. Sauer, eds., *Alpha Olefins Applications Handbook*, Marcel Dekker, New York, 1989, p. 36.
10. Ger. Pat. 849,548 (Sept. 15, 1952), O. Roelen (to Chemische Verwertungsgesellschaft Oberhausen GmbH).
11. H. Lemke, *Hydrocarbon Process.* **45**(2), 148 (Feb. 1966).
12. U.S. Pats. 3,239,569; 3,239,570; 3,239,571 (Mar. 8, 1966), L. H. Slaugh and R. D. Mullineaux (to Shell Oil Company); Brit. Pats. 988,941; 988,942; 988,943; 988,944 (Apr. 14, 1965) (to Shell Internationale Research Maatschappij NV).
13. E. D. Heerdt, Shell Development Co., personal communication, 1989.
14. Ger. Pat. 953,605 (Dec. 6, 1956), G. Schiller (to Chemische Verwertungsgesellschaft Oberhausen GmbH).
15. Ref. 3, 51–53.
16. Ref. 3, 54–57.
17. U.S. Pat. 3,647,906 (Mar. 7, 1972), F. F. Farley (to Shell Oil Company); U.S. Pat. 3,726,938 (Apr. 10, 1973), A. J. Berger.
18. E. R. Freitas and C. R. Gum, *Chem. Eng. Prog.*, 73 (Jan. 1979).
19. J. Kurata and K. Koshida, *Hydrocarbon Process.* **57**(1), 145 (Jan. 1978); N. J. Steens and J. R. Livingston, Jr., *Chem. Eng. Prog.* **64**(7), 61 (July 1968).
20. N. Kurata, K. Koshida, H. Yokoyama, and T. Goto, in E. J. Wickson, ed., *Monohydric Alcohols, ACS Symp. Ser. 159*, American Chemical Society Washington, D.C., 1981, 113–157.
21. I. M. Towbin and D. M. Boljanskii, *Maslo. Zhir. Prom.* **32**, 29 (1966).
22. H. Stage, *Seifen, Öle, Fette, Wachse* **99** (6/7), 143; (8), 185; (9), 217; (11), 299 (1973).
23. M. Tsuchino, and co-workers, *Paper no. 54 (I&*EC Div.), 196th National Meeting of the American Chemical Society, Los Angeles, September 25–30, 1988.
24. M. Guerbet, *J. Pharm. Chim.* **6**, 49 (1913); *Chem. Abstr.* **7**, 1494 (1913).
25. M. N. Dvornikoff and M. W. Farrar, *J. Org. Chem.* **22**, 540 (1957).
26. G. Gregorio and G. F. Pregaglia, *J. Organometall. Chem.* **37**, 385 (1972); P. L. Burk, R. L. Pruett, and K. S. Campo, *J. Mol. Catal.* **33**, 1, 15 (1985).
27. J. Sabadie and G. Descotes, *Bull. Soc. Chim. Fr.* **253** (1983).

28. K. Noweck and H. Ridder, *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., VCH Verlagsgesellschaft mbh, Weinheim, Germany, 1987, p. 288.
29. K. Klein, P. E. Bator, and S. Hans, *Cosmetics and Toiletries*, **95**, 70 (1980); A. J. O'Lenick, Jr., and R. E. Bilbo, *Soap, Cosmet. Chem. Spec.* **52** (April, 1987).

GENERAL REFERENCES

J. A. Monick, *Alcohols, Their Chemistry, Properties, and Manufacture*, Reinhold, New York (1968).

Ziegler Chemistry Processes; Triethylaluminum Synthesis

F. Albright, *Chem. Eng.* **74**, 179 (Dec. 4, 1967).
K. Ziegler and co-workers, *Angew. Chem.* **67**, 424 (1955).
K. Ziegler, *Erdöl Kohle* **11**, 766 (1958).
K. Ziegler and co-workers, *Justus Liebigs Ann. Chem.* **629**, 1 (1960).

Ziegler Chemistry Processes: Chain Growth

K. Ziegler, *Angew. Chem.* **64**, 323 (1952).
K. Ziegler, *Brennst. Chem.* **35**, 321 (1954).
K. Ziegler, *Angew. Chem.* **68**, 721 (1956).
K. Ziegler and co-workers, *Justus Liebigs Ann. Chem.* **629**, 121, 172 (1960).
K. Ziegler, *Angew. Chem.* **72**, 829 (1960).
K. Ziegler and H. Hoberg, *Chem. Ber.* **93**, 2938 (1960).

Ziegler Chemistry Processes: Displacement Reactions

K. Ziegler, H. Martin, and F. Krupp, *Justus Liebigs Ann. Chem.* **629**, 14 (1960).
K. Ziegler, W. R. Kroll, W. Larbig, and O. W. Steudel, *Justus Liebigs Ann. Chem.* **629**, 53 (1960).
K. Ziegler, in H. H. Zeiss, ed., *Organometallic Chemistry*, Reinhold, New York, 1960, p. 218 ff.

Ziegler Chemistry Processes: Oxidation

K. Ziegler, F. Krupp, and K. Zosel, *Justus Liebigs Ann. Chem.* **629**, 241 (1960).
K. Ziegler, F. Krupp, and K. Zosel, *Angew. Chem.* **67**, 425 (1955).

Oxo Processes

G. U. Ferguson, *Chem. Ind.* **11**, 451 (1965).
H. Weber and J. Falbe, *Ind. Eng. Chem.* **62**(4), 33 (Apr. 1970).
H. Weber, W. Dimmling, and A. M. Desal, *Hydrocarbon Process.* **55**(4), 127 (1976).

E. J. Wickson and H. P. Dengler, *Hydrocarbon Process.* **51**(11), 69 (1972).
J. Falbe, *Carbon Monoxide in Organic Synthesis*, Springer-Verlag, New York, 1970.
B. Cormels, in J. Falbe, ed., *New Synthesis with Carbon Monoxide*, Springer-Verlag, New York, 1980, p. 1–225.

Plant Locations, Capacities, Feedstocks

Refs. 1 through 6.

John D. Wagner
George R. Lappin
J. Richard Zietz
Ethyl Corporation