

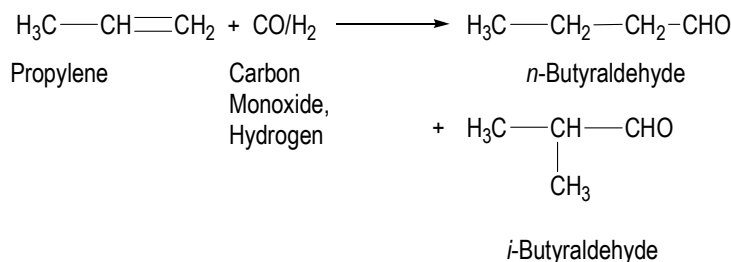
PERP Program – New Report Alert

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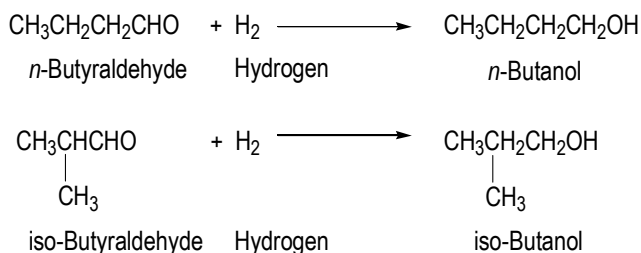
Nexant's ChemSystems Process Evaluation/Research Planning program has published a report, *Oxo Alcohols (01/02-8)*.

The oxo process, also known as hydroformylation, involves the reaction of an olefin with carbon monoxide and hydrogen to produce an aldehyde. The aldehyde can optionally be subjected to further hydrogenation to give the corresponding alcohol.

With propylene as the olefin feedstock, the hydroformylation reaction can be expressed as:

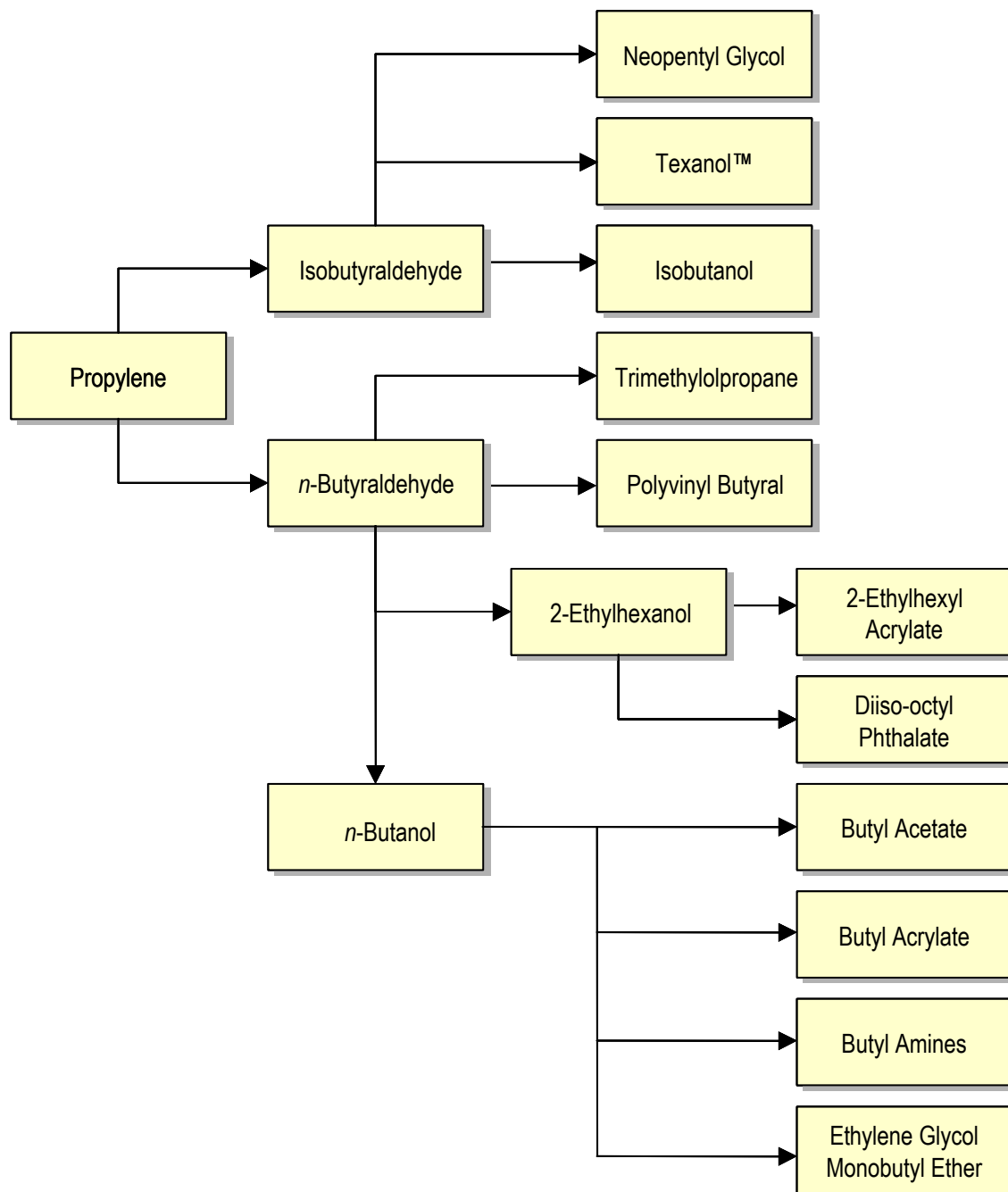


Production of the corresponding alcohols involves the following reactions:



The figure below illustrates some of the products made from the propylene-fed "Oxo" processes. C₄ aldehydes can be used as feedstocks for such products as polyvinylbutyral (from *n*-butyraldehyde) - a transparent high strength polymer, and neopentyl glycol (from *iso*-butyraldehyde) - a key component of powder coating resins. The alcohols themselves are used as solvents and intermediates in the production of plasticizers, e.g. diiso-octyl phthalate (DOP), and various components of paints, adhesives, textiles, etc. The manufacture of 2-ethyl hexanol involves the additional step of aldol condensation/dehydration of *n*-butyraldehyde.

Products from Propylene Hydroformylation



While propylene is the most common feed to the oxo process, butanes, octenes, and nonenes can be employed to give aldehydes and alcohols with one carbon more than the starting olefin. Thus, isononanol, isodecanol, and 2-propyheptanol can be produced, respectively, from mixed octenes, mixed nonenes, and mixed butanes (with aldol condensation/dehydration following hydroformylation).

Early versions of the oxo process used cobalt catalysts at high pressure (200 to 450 bar), and cobalt carbonyls or hydrocarbonyls formed the active catalyst species. The normal to iso (n/i) ratio of aldehyde product was typically about 4 for propylene feed and somewhat less for higher olefins. In the 1940s and 1950s various companies (e.g. BASF, ICI, PCUK, and Eastman) developed their own versions of this classic cobalt process. It is still widely used for olefin feeds higher than propylene, but is not actively offered for license.

Shell developed a modified process (commercialized in the 1960s) using cobalt catalyst modified by phosphite or phosphine ligands. This enabled the process to operate at a lower pressure, and gave improved linearity (n/i of 6 to 7) even when fed with internal olefins from its SHOP process. High linearity is regarded as desirable especially for detergent applications. Only Shell and its joint venture with Mitsubishi Petrochemical (MYKK) are currently using this technology.

In the 1970s Union Carbide, Davy McKee (now Davy Process Technology, DPT), and Johnson Matthey (UCC/Davy/JM) developed the "Low Pressure Oxo Process" using a rhodium catalyst modified with a triphenylphosphine ligand (TPP). This process operates at lower pressure and results in a higher n/i ratio of about ten. There are several variants of the LP Oxo process which use different modes of product/catalyst separation. For example, in the gas recycle version, the aldehyde product is removed directly from the reactor system as a vapor by gas stripping, a feature that so far has limited the commercial application of this technology to propylene feed. Gas recycle versions are commonly known in the industry as LP Oxo Mk I (for the very early versions) or Mk II (for the later version). In the liquid recycle mode, known as LP (Low Pressure) Oxo Mk III, a portion of the reactor medium is withdrawn in order to recover the aldehyde products as vapors by flashing them in a separate vessel and to recycle a rhodium containing solution back to the reactor. This operating mode has been made practical, at least in part, by the recognition of the favorable solvency properties of the aldehyde condensation products. Again, the direct product flash-off has limited the application of the Mk III version to olefins with low carbon number (C₃ to C₄). Many existing plants have been converted to LP Oxo, and most independent producers have selected this technology for new butanol and 2-EH capacity.

In the 1980s Rhône-Poulenc and Ruhrchemie (RP/RCH) developed a two-phase process using a water-soluble rhodium catalyst modified with TPP sulfonate ligand. Very high linearity (n/i of 19) can be achieved. The process is currently used by Hoechst for propylene feed. Other companies

such as BASF and Eastman operate oxo processes for propylene feed that may be similar to Dow/Davy technology.

Recent developments in the oxo technology area have focused on improving the existing modified rhodium process and adapting it for use with higher olefins. To this end, Dow/Davy developed a highly active bis-phosphite-modified rhodium catalyst that is capable of using both propylene and raffinate-2 feeds for butanol, 2-EH and 2-PH production. High catalyst activity allows this process to be run in “single pass” mode with no recycle requirement. The process is known as the LP Oxo Mk IV version. The potential advantage of this process is its flexibility to convert propylene or contained butylenes in the same reactor system.

Operating conditions, aldehyde selectivity, and isomer ratio are tabulated in the report for five distinct process/catalyst variations of hydroformylation.

Cost of production estimates are provided for *n*-butanol via two processes, 2-ethylhexanol via two processes, isononanol, isodecanol, and 2-propylheptanol.

The report discusses health, safety, and environmental concerns regarding phthalate plasticizers derived from various oxo alcohols by reaction with phthalic anhydride. The focus of this discussion is on evaluations and actions in Western Europe.

Consumption by application and production capacity are provided for *n*-butanol and 2-ethylhexanol in the United States and Western Europe. Capacity buildup for 2-EH in Asia in the 1997-2001 time frame has left the region balanced in the medium term and has exacerbated export problems for the North American and West European producers.

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