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PERP PROGRAM

Report Abstract

Oxo Alcohols
PERP06/07-8

February 2009

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For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: <http://www.chemsystems.com>.

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INTRODUCTION

The Oxo process, more formally known as hydroformylation, is the common name for a reaction of an olefin with carbon monoxide and hydrogen to give an aldehyde. Subsequent hydrogenation of the aldehyde leads to an oxo alcohol.

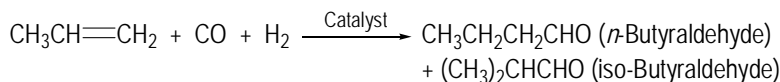
The chronological development of oxo alcohol process technology is illustrated below:

- 1938** Oxo process discovered by Otto Roelen of Ruhrchemie using a cobalt catalyst.
- 1940s/1950s** Various companies develop their own versions of the oxo process (e.g., ICI, BASF, PCUK, Eastman).
- 1960s** Shell develops a modified cobalt process, using ligands such as phosphines or phosphites. ICI improved its High Pressure Oxo Process with an unliganded rhodium catalyst.
- 1970s** Union Carbide Corporation, Davy Process Technology, and Johnson Matthey developed the LP Oxo (modified rhodium) process, using triphenylphosphine ligand (PPh₃). Key features are much lower operating pressure and good normal to iso ratio. Aldehyde is separated as vapor in the original gas recycle version of the flowsheet.
- 1980s** Rhône-Poulenc/Ruhrchemie develops a two-phase process using a water-soluble modified rhodium catalyst with TPP sulfonate ligand.
- UCC and Davy developed a liquid recycle variation of the LP Oxo process offering advantages over gas recycle for some situations.
- BASF starts up an LP Oxo process.
- Early 1990s** UCC and Davy, (see note below) improves the LP Oxo process capable of taking both propylene and raffinate-2 feeds, including commercially available mixed butene streams, for the production of butanols, 2-EH and 2-PH. The process uses a highly active modified rhodium catalyst system and has a "single-pass" flow scheme, which is simpler than the earlier gas or liquid recycle LP Oxo variants.
- Late 1990s** BASF patents butadiene route to *n*-butanol/*n*-butyraldehyde.
- Early 2000s** Davy and Johnson Matthey license their Johnson Matthey Oxo Alcohols Process™ (formerly the ICI High Pressure Oxo Process) for the production of higher oxo alcohols (INA and IDA) from iso-octene and iso-nonene. Key features are minimum byproduct formation.

Note: Union Carbide Corporation is now a wholly owned subsidiary of the Dow Chemical Company, while Davy Process Technology Limited is a wholly owned subsidiary of Johnson Matthey.

CHEMISTRY & CATALYSTS

The reaction involves the addition of CO and hydrogen to a terminal double bond, and was adapted widely for use with propylene to prepare butyraldehydes according to the following equation.

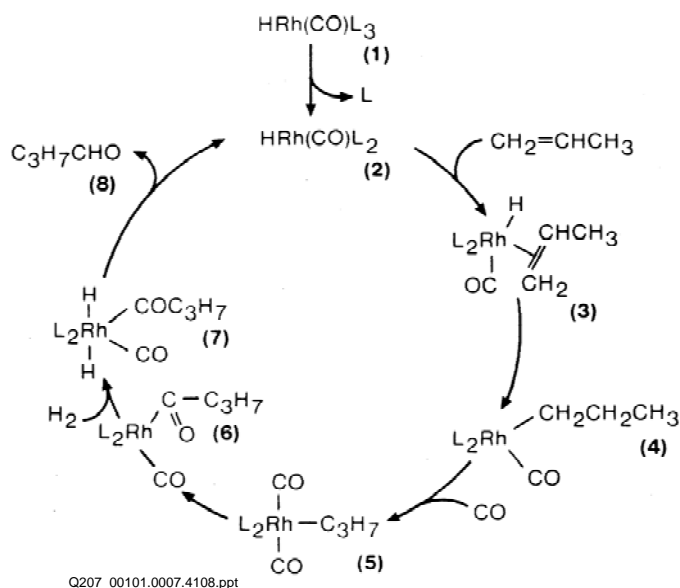


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Roelen's catalyst comprised dicobalt octacarbonyl, $(\text{Co})_2(\text{CO})_8$. There are two major problems encountered with using cobalt catalysts for hydroformylation. The first is that in order to achieve reasonable olefin conversion, relatively high temperatures and pressures are needed. The second problem is a relatively high selectivity to the branched aldehyde species.

Considerable research and development effort has been expended to improve the efficiency of the oxo process and particularly to improve the yield of linear aldehydes. Although modification to the operating conditions, e.g., H_2/CO ratio in syngas, pressure, temperature and catalyst concentration, were modestly successful, much better results were obtained by modification of the original $(\text{Co})_2(\text{CO})_8$ catalyst. The effort has resulted in different catalyst systems being developed over the years. The reaction cycle for linear hydroformylation is given in the mechanism shown in the figure below.

Linear Hydroformylation Reaction Cycle



The original catalyst for linear hydroformylation was the so called Wilkinson catalyst comprising rhodium chloride and triphenylphosphine (PPh_3) ligands. The catalyst was originally developed for hydrogenation processes and then extended to hydroformylation. Triphenylphosphine (TPP) modified rhodium catalyst systems were widely used from the 70s through the early 90s in industrial oxo synthesis. This system has not been applied to the

hydroformylation of higher olefins because less volatile aldehydes cannot be distilled from the phosphine-rhodium complex without decomposition of the complex. Other drawbacks of this system are limitations on the ratio of linear to branched aldehyde products and unsuitability for hydroformylation of butene-2 due to short catalyst life. Newer catalysts have been developed and these are discussed in the report.

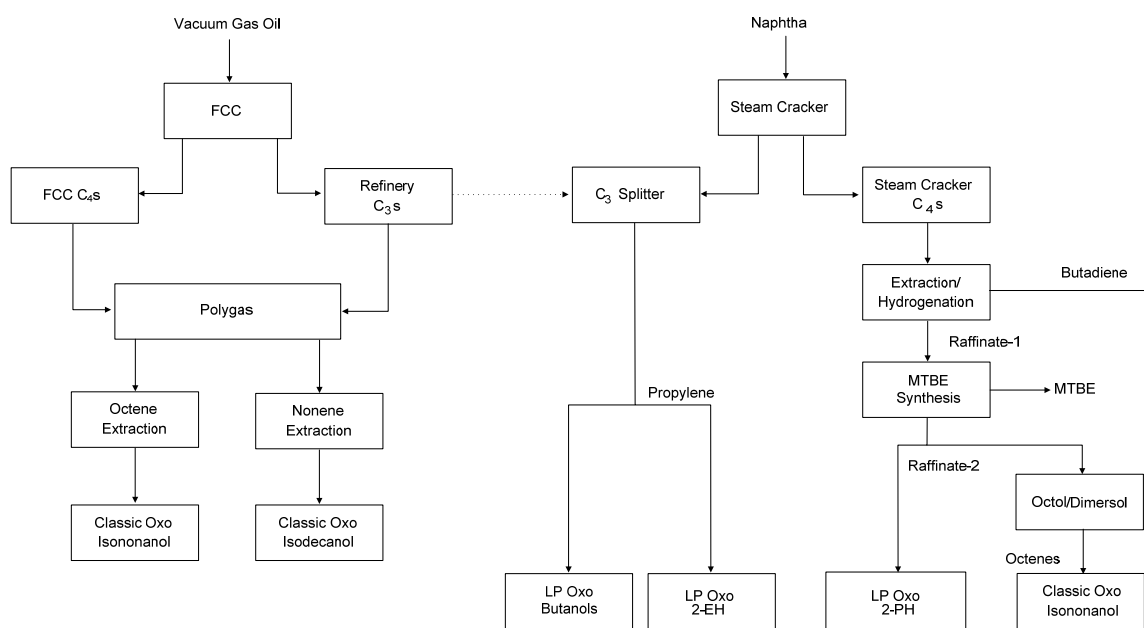
Although there are several versions of oxo aldehyde processes using different catalyst systems, the hydrogenation steps to produce oxo alcohols are believed to be very similar for many producers.

FEEDSTOCKS AND PRODUCTS FROM OXO ALCOHOLS

The chemical feedstocks used to produce oxo alcohols include propylene and butylenes, as exemplified by the figure below. (In the Figure, 2-EH is 2-Ethylhexanol & 2-PH is 2-Propylheptanol.) Depending on the process and product, propylene is used in contained and pure forms. Alpha olefins from ethylene oligomerization can also be hydroformylated to produce detergent range alcohols, but these are not considered in detail as part of this study.

Feedstocks and products from the oxo alcohols produced are discussed in the report.

Process Routes to C₄/C₈-C₁₀ Plasticizer Oxo Alcohols



CURRENT COMMERCIAL OXO ALCOHOLS TECHNOLOGIES

Various oxo processes by Davy-Dow, Ruhrchemie-Rhône-Poulenc, Johnson Matthey-Davy, Shell, and the old industrial oxo process based on an unmodified cobalt carbonyl hydride catalyst are compared in this section of the report.

The following technologies are discussed:

- Production of Isodecanol by the hydroformylation of nonenes using the classic unmodified cobalt catalyst system, followed by hydrogenation of the resulting aldehydes.
- Dow & Davy Butyraldehyde production using LP Oxo SELECTORSM Technology with NORMAXTM Catalyst.
- Celanese RCH Butyraldehyde production using rhodium-based oxo process.
- Dow and Davy Valeraldehyde (i.e. Pentanaldehyde) Production using LP Oxo SELECTORSM Technology.
- *n*-Butanol production by hydrogenation from *n*-butyraldehyde synthesized by oxo reaction.
- 2-Ethylhexanol production from oxo synthesized *n*-butyraldehyde by aldol condensation & hydrogenation.
- 2-Propylheptanol production from oxo synthesized C₅ aldehyde isomers via aldol condensation & hydrogenation.
- Davy/Johnson Matthey technology for processing of C₆-C₁₄ (linear or branched) olefins into C₇-C₁₅ alcohols, e.g. production of isononanol for subsequent use in plasticizer production.
- Production of oxo alcohols using Axens Dimersol X process for selective dimerization or co-dimerization of propylene-rich and/or butene-rich streams from steam crackers or FCC units.

CURRENT TECHNOLOGY DEVELOPMENTS

Various developments with respect to catalyst improvements are discussed. For example:

- Ease of catalyst separation and recovery
- Development of heterogeneous hydroformylation catalysts
- New olefin oligomerization catalysts

ECONOMIC ANALYSIS

Several cases have been considered for the production of oxo alcohols at the same capacity. Furthermore, production cost estimates have been generated for the production of syngas (1:1) and mixed octenes since they are the raw materials used in the production of oxo alcohols. The selected cases are:

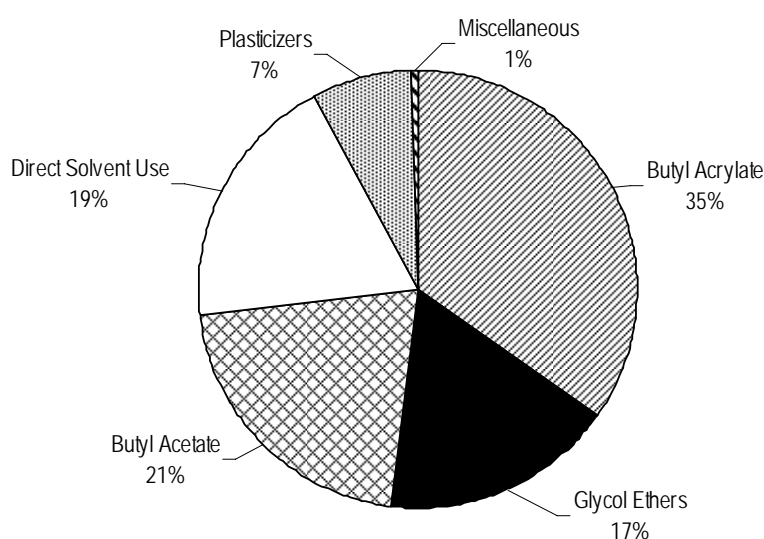
- 2-Ethylhexanol from propylene (Davy and Dow LP Oxo SELECTOR 30 Technology)
- *n*-Butanol from propylene (Davy and Dow LP Oxo SELECTOR 30 Technology)
- Isononanol from mixed octenes (Johnson Matthey Technology)
- Isodecanol from nonenes (Unmodified cobalt).
- 2-Propylheptanol from mixed butylene (Davy and Dow LP Oxo Technology)

It is not unusual in the chemical industry for raw materials prices to vary substantially over the course of the petrochemical cycle. Such variations can have a significant effect on production economics; 2-ethylhexanol, 2-propylheptanol, and isodecanol are no exception. To test the effect of raw materials on oxo alcohols production costs, a range of different, propylene and raffinate-2 prices were considered in individual sensitivity analyses.

COMMERCIAL ANALYSIS

The butanols business is driven by solvent applications particularly in emulsion and lacquers business. These water-based systems which have benefited from environmental considerations are closely allied to the construction business. Other uses are exemplified by the figure below displaying end-use for *n*-Butanol in Western Europe. The report gives more detail on the regional market review for *n*-butanol in Western Europe, as well as North America and Japan. Supply, demand, and trade data are given.

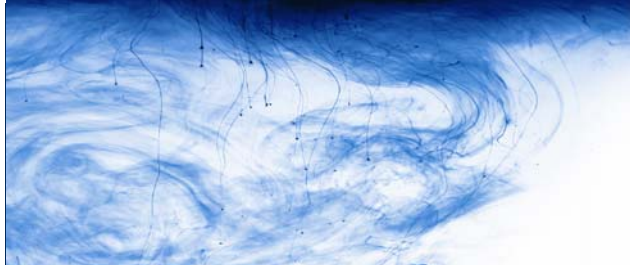
Western Europe *n*-Butanol Consumption by End Use, 2007



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The major use for 2-Ethylhexanol (2-EH) is in plasticizers, mainly diisooctyl phthalate (DOP). Phthalates were first produced in the 1920s, though they found limited commercial use. A smaller but significant and growing use is in the production of 2-ethylhexyl acrylate, a monomer used in acrylic copolymers for pressure sensitive adhesives and impact modifiers. Other uses include 2-ethylhexyl nitrates used as a cetane improver in diesel fuels. There are a number of specialty end-uses for 2-EH. More detail on 2-EH uses, as well as regional market reviews for North America, Western Europe and Japan are given. Supply, demand, and trade data is discussed.

Since the 1950s, large quantities of phthalates have been consumed to plasticize PVC. From the early 1980s, there have been concerns regarding the use phthalates and their effects on human health and the environment. A discussion of the Health, safety, environmental concerns on plasticizers is given in the report.



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