High Pressure Hydroformylation in the Chemical Industry

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Abstract

Higher oxo alcohols are intermediates for large-scale applications, such as plasticizers, detergents and fuel additives, as well as being useful in the synthesis of fine chemicals such as vitamins or flavors and fragrances. Many of these alcohols are still made using high pressure technologies. Advantages and disadvantages of different technologies presently in use or being developed are discussed. In particular, efforts to decrease raw material costs, e.g. by increasing yield, or investment, e.g. by decreasing pressure, will be highlighted.

Text

The hydroformylation of olefins, with ca. 9 mio tons of production annually, is one of the largest homogeneously catalyzed processes in the chemical industry. And it is, with ca. 1.5 mio ton/year, a core technology of BASF. The BASF portfolio of aldehydes and alcohols produced in this manner spans the range from C3 to C15 as well as encompassing polymers and a number of specialties. Such aldehydes and alcohols are the key to a wide spectrum of value added products, such as plasticizers, detergents and fuel additives. They also serve as intermediates in the synthesis of fine chemicals such as vitamins and flavors and fragrances.

The olefins available determine the technology used in production. Lower olefins, *e.g.* ethylene, propylene and butenes, are typically hydroformylated under low pressure conditions using ligand modified rhodium catalysts. Worldwide, the hydroformylation of propylene alone accounts for approximately two thirds of the production volumes. Accordingly, such systems have been intensively investigated in the last decade and have reached a high degree of development. They will not be the topic of this particular discussion.

Higher olefins, such as C12/C14-α-olefins based on ethylene; trimers of propylene; dimers and trimers of butenes, are typically hydroformylated under high pressure conditions. At BASF, such products make up about 20 % of the total capacity. Although a tremendous amount of research has been done on alternatives for such processes, they remain in use for two major reasons: catalyst reactivity, as they allow the conversion of “difficult”, *i.e.* branched, internal olefins, and process advantages when handling high boiling products. These considerations can be illustrated quite nicely by looking at the usage of the C4-fraction coming out of a typical steam cracker.

Approximately 10 % of the output of the naphtha crackers commonly found in Europe consists of C4-products. This mixture of butadiene, butenes and butanes can be extracted or selectively hydrogenated to remove butadiene. Isobutene is extracted from the resulting raffinate I to yield raffinate II, a mixture of linear butenes and butanes.

Dimerization of the linear butenes in raffinate II yields a mixture containing n-octenes (ca. 6 %), 3-methylheptenes (ca. 60 %) and 3,4-dimethylhexenes (ca. 34 %). These olefins are obtained as a mixture of structural and positional isomers. Amongst other things, this means that the olefins become more difficult to hydroformylate with increasing conversion, as the percentage of branched, internal isomers in the remaining olefins increases. The mixture

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of isomeric nonanols obtained after hydroformylation and subsequent hydrogenation is mainly used to produce plasticizers. The butanes, so called Raffinate III, are sent back to the cracker as feed.

The hydroformylation of such highly substituted olefins has been traditionally carried out with high pressure cobalt catalysts. The BASF process consists of hydroformylation with $HCo(CO)_4$, catalyst removal using oxygen in the presence of aqueous acid (*i.e.* formation of aqueous Co^{2+}), separation of the organic product phase and the aqueous catalyst phase, and recycle of Co^{2+}_{aq} under regeneration of $HCo(CO)_4$. This process takes advantage of the clean redox chemistry of cobalt and has the additional advantage of a non-distillative catalyst separation step. This advantage in process technology can be used for other substrates.

Isobutene can be polymerized to yield polyisobutene, which can be hydroformylated to yield a mixture of polymeric alcohols and aldehydes, which can be further functionalized to yield polyisobuteneamine. Polyisobuteneamine, Keropur®, is a fuel additive which inhibits valve incrustation. This is an example of an innovative, high value product, whose production demands catalyst removal from completely water insoluble, non-volatile polymeric intermediates.

The two major advantages of the BASF process are that high boiling (or completely involatile products such as polyisobutene oxo product) can easily be recovered, and that the catalyst accepts all olefins (such as the internal, branched isomers found in octene isomer mixtures). The drawbacks are that high pressures and temperatures are necessary, and that the coproduction of high boilers and paraffins is quite high.

These drawbacks and advantages are also present in the Kuhlmann process carried out by Exxon. This process takes advantage of the acidity of the cobalt catalyst and thus also has the advantage of an aqueous extractive catalyst separation step. An additional disadvantage of this process is salt formation, as the aqueous cobaltate solution formed by deprotonation in the catalyst separation step has to be acidified to generate active $HCo(CO)_4$ once more. A particular advantage, however, is that a non-aqueous catalyst feed can be generated, which allows access to interesting options in the process technology.

The desire to improve olefin usage (*i.e.* by reducing the formation of high boilers and paraffins) has led to numerous attempts to develop rhodium-based technologies. $HRh(CO)_4$ as can be used under much milder conditions as the cobalt system and delivers almost pure aldehyde products. It is also not acidic and can be used under neutral conditions, minimizing certain types of highboiler formation. These advantages are counterbalanced by the extremely high cost of rhodium, leading to enormous process effort to minimize losses, as well as to the lack of the process technological options made available by cobalt's redox and acid/base chemistry.

Despite this, the rhodium catalyst is so reactive at 600 bar, that it can be used in such low concentrations that catalyst recovery and recycle is not necessary. This type of technology is not suitable for the production of commodity chemicals such as plasticizers and detergents. It is, however, a useful option when synthesizing intermediates for fine chemicals such as vitamins or flavors and fragrances.

Synetix (now a part of Johnson-Matthey and formerly the catalyst research of ICI) has described an interesting alternative for rhodium recovery in patents.[i] The catalysis is carried out in a range from 200-300 bar and the ligand exchange chemistry of such metal carbonyls is used to "harvest" rhodium out of the raw product streams. Lightly basic ion exchange resins contain tertiary amine groups, which complex rhodium under low pressure conditions and hold it in the resin bed. After being loaded, the beds are incinerated and the rhodium recovered. The technology is straightforward, efficient and has the advantage that the products do not have to be vaporized. A cost effective form of bed regeneration has unfortunately not yet been described in the literature.

All of the drawbacks referred to above in the discussion of the various process variants can immediately be reformulated as research goals. Improving usage of branched, internal olefins (*i.e.* by reducing the formation of high boilers and paraffins) is of major importance. Of equal importance is a reduction of investment costs through the development of low or medium pressure processes (< 100 bar).

A number of interesting ideas have been discussed in the literature (usually in patents). Only a few examples, which have been chosen in order to illustrate particular points of interest, will be discussed here.

Oxeno, for example, has described a process for recycling unconverted olefins back to the cobalt high pressure reaction.[ii] This process takes advantage of hydrogenation catalysts, which hydrogenate aldehydes to alcohols but do not hydrogenate olefinic double bonds. The stationary concentration of "difficult" olefins in the oxo reactor can be raised this way without having to distill the olefins from the aldehyde/alcohol mixture. A distillation at this stage would lead to higher highboiler formation due to increased thermal stress for the more sensitive aldehydes.

Celanese described an interesting ligand system, which was tailored to stabilize the rhodium carbonyl catalyst during distillation.[iii] Of interest here was the effort made to find a system, in this case a bis-etherchelate, which does not slow down the active catalyst during use. The use of a rhodium high pressure system, which was not described in detail, to hydroformylate propylene in a 100,000 t/year plant was described in press releases soon thereafter.[iv] Such catalysts are extremely unselective with respect to product linearity and yield much larger quantities of isobutyraldehyde as the well-known highly selective, 2-phase, low pressure systems described in great detail in the mid-90s.

Shell made enormous efforts in the 90s to develop medium pressure palladium systems (ca. 70 bar). Amongst other things, pilot plant tests for a production process for detergent alcohols based on linear, internal SHOP-olefins were described.[v] Cationic palladium complexes with chelating phosphine ligands were used as catalysts. The pressure reduction as well as the extractive workup describe were quite attractive from an investment point of view. Although the patent examples describe an advanced state of development, it does not appear that Shell actually commercialized this process.

Meeting the goals necessary to replace the well established high pressure synthesis has been extremely demanding. At this point, there is no really convincing technical solution in this area. This has led to the need for alternative routes to similar products. This type of strategy can be illustrated using the synthesis of 2-propylheptanol, a new plasticizer alcohol.

The established C_{10}-plasticizer alcohol, a mixture of isomeric isodecanols, is obtained *via* the cobalt catalyzed high pressure hydroformylation of trimerpropylene. Trimerpropylene is the mixture of isomeric C_9-olefins (structural and positional isomers), obtained as the name implies *via* oligomerization of propylene. This feedstock exhibits the same problems in reactivity as the octene isomer mixtures mentioned above, and has the additional drawback that its price is coupled to that of propylene, which has become relatively expensive due to high demand.

As discussed previously, one approach to improving this process would be to find a better catalyst for such internal, branched isomers. A low pressure process would, of course, be most desirable. As pointed out above, this has proved to be difficult. Another approach, however, is to build a "better" alcohol and simultaneously address the feedstock situation.

The rhodium catalysed, low pressure hydroformylation of the linear butenes in Raffinate II yields n-valeraldehyde. The base catalyzed aldol condensation of n-valeraldehyde yields 2-propylheptenal and water. Hydrogenation of this unsaturated intermediate leads to 2-propylheptanol. This synthesis is analogous to the well known synthesis of 2-ethylhexanol. It has the twin advantages of being a higher alcohol (C_{10}) synthesis based on low pressure technology and of being based on an economically attractive feedstock, Raffinate II. BASF announced plans for the construction of a world scale plant for propylheptanol in the United States early in 2005.[vi]

References

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[i] WO 02/20451

[ii] EP 1 172349

[iii] WO 97/49490

[iv] Press release Hoechst AG, Chemical Week Nov. 4, 1998

[v] EP 0 922691

[vi] Press release BASF, March 21, 2005