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Enhancement of Industrial Hydroformylation Processes by the Adoption of Rhodium-Based Catalyst: Part I

DEVELOPMENT OF THE LP OXO^{SM} PROCESS TO THE COMMERCIAL STAGE

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The adoption of a low-pressure rhodium-based catalyst system in place of high-pressure cobalt for the hydroformylation of propylene by reaction with carbon monoxide and hydrogen to produce butyraldehydes (an 'oxo' reaction) has brought large cost benefits to oxo producers. The benefits derive from improved feedstock efficiency, lower energy usage and simpler and cheaper plant configurations. The technical and commercial merits of the 'LP Oxo^{SM} Process' for producing butyraldehydes have made it one of the best known applications of industrial-scale chemistry using a platinum group metal (pgm). Today, practically all butyraldehyde is made by rhodium catalysis, and this should provide convincing encouragement to researchers who are keen to exploit pgms as catalyst research materials, but are apprehensive as to the implications of their very high intrinsic value. It should also encourage developers and designers responsible for turning pgm chemistry into commercial processes, who may be daunted by problems such as containment and catalyst life. This article (Part I) reviews the background to the LP Oxo^{SM} Process, and its development to the point of first commercialisation. Part II, covering some of the key improvements made to the process and its use in non-propylene applications, will appear in a future issue of Platinum Metals Review.

2-Ethylhexanol (2EH) is the most widely used ('workhorse') plasticiser alcohol, and butanols – the normal and *iso* isomers – are used as solvents or chemical intermediates. Both 2EH and butanols are derivatives of butyraldehyde made from propylene by hydroformylation. From the early 1940s until the early 1980s, the world's major producers of 2EH and butanols operated propylene hydroformylation (often termed 'oxo') processes for producing the required butyraldehyde using a cobalt catalyst system. This delivered poor conversion and low selectivity of the principal feedstock, propylene, to the desired products, in complex and cumbersome plants operating at high pressure.

The 'Low Pressure Oxo' process (LP Oxo^{SM} Process) was developed and then licensed to the oxo industry through a tripartite collaboration beginning in 1971. The principals were Johnson Matthey & Co. Ltd. (now Johnson Matthey PLC), The Power-Gas Corporation Ltd. (a former name of Davy Process Technology Ltd., now a subsidiary of Johnson Matthey PLC) and Union Carbide Corporation (now a subsidiary of The Dow Chemical Company). Using rhodium-based catalysis, the LP Oxo^{SM} Process offered such great economic advantages over the established cobalt-catalysed processes, as well as technical elegance, that many cobalt systems were replaced by brand new plants. In the thirty years or so since the LP Oxo^{SM} Process was first introduced, it has maintained its position as the world's foremost oxo process, having undergone much improvement and refinement. About two thirds of the world's butyraldehyde is now produced in LP Oxo^{SM} plants. Most LP Oxo^{SM} systems are licensed plants, nearly all of which have been built under licences granted by Davy Process Technology (1) working in cooperation with The Dow Chemical Company (2); the remainder are plants owned and operated by Dow's Union Carbide subsidiary (3).

This article (Part I) reviews the background to the LP Oxo^{SM} Process, addressing some of the challenges that faced its developers and designers in planning the first commercial plant, and during the period immediately following commercialisation. Insights are given on the chemical function of the homogeneous liquid-phase catalyst system. In Part II, some examples of advancements of the technology in the years following the first round of licensing will be outlined.

The Beginnings of the Development

Commercialisation of the LP Oxo^{SM} Process was the culmination of an intensive joint effort in chemistry and engineering by the three companies, dating back to 1964. Early exploratory work by the chemicals producer Union Carbide in the U.S.A. demonstrated promise for rhodium coordination complexes in solution as hydroformylation catalysts at low pressure, yielding a high proportion of the straight-chain aldehyde product and with high enough catalyst productivity to justify examining the commercial potential of rhodium. The company obtained a basic patent for this work in 1970 (4). In operating a number of high-pressure oxo plants, Union Carbide had become very familiar with cobalt systems and their shortcomings, and viewed the potential for rhodium with guarded excitement. At that time, all industrial oxo production used the classic high-pressure cobalt process described below, or a modification of it.

Meanwhile, independent research by the late Professor Sir Geoffrey Wilkinson (5–7) (later to win a Nobel Prize for Chemistry) at Imperial College, London, supported by the precious metal refiner and processor Johnson Matthey, produced results using a suitable coordination complex of rhodium (e.g. (5)) which basically reproduced or complemented the Union Carbide findings. Johnson Matthey in turn approached The Power-Gas Corporation (now Davy Process Technology). The engineering contracting company drew on its strong background in process engineering to investigate the commercial potential for a low-pressure route to butyraldehyde. With the publication of patents by Union Carbide (e.g. (4)) and Johnson Matthey (e.g. (5)), the three parties realised that they had a common interest, so in 1971 they launched a joint development programme to convert the laboratory rhodium-oxo chemistry into a commercial process with a view to exploiting its technical merit.

The focus of the collaboration was a process for the hydroformylation of propylene using a mixture of carbon monoxide and hydrogen (in the form of synthesis gas) to produce normal butyraldehyde and *iso*-butyraldehyde according to Reaction (i):

$$2CH_3CH{=}CH_2 + 2CO + 2H_2 \rightarrow \underset{\text{normal butyraldehyde}}{CH_3CH_2CH_2CHO} + \underset{\textit{iso}\text{-butyraldehyde}}{(CH_3)_2C(H)CHO} \quad \text{(i)}$$

The normal butyraldehyde isomer is usually more highly valued than *iso*-butyraldehyde. A much improved normal-to-*iso* yield ratio observed in the laboratory with rhodium catalysis, as compared with the then-current commercial cobalt systems (i.e. about ten as opposed to typically between three and four) was unquestionably a key driver for collaborative development. The high selectivity of conversion of propylene to normal butyraldehyde has since become a hallmark of the LP Oxo^{SM} Process.

The collaborators' success in exploiting their development efforts (8) would eventually result in the LP Oxo^{SM} Process becoming the technology of choice for many of the world's oxo producers, with whom Davy Process Technology negotiated licences on behalf of the collaborators. The high reputation which the process would acquire because of its operating excellence and low production costs, and a sustained growth in the markets for the end products, drove investment in continuing research and process development programmes aimed at improving the technology to ensure the long-term sustainability of the process.

The Uses and Market for Butyraldehyde

The major use of butyraldehydes was, and still is, for the production of 2EH and butanols; see Figure 1. Normal butyraldehyde has always been the more valuable of the two aldehyde isomers, because unlike *iso*-butyraldehyde, it can be used to produce 2EH, by a sequence involving an aldol condensation reaction followed by hydrogenation of the aldol product. Furthermore, normal butanol, produced by the direct hydrogenation of normal butyraldehyde, usually offers solvent and derivative value superior to that of *iso*-butanol. The world production levels of 2EH and normal and *iso*-butanols combined are presently about 2.5 million and 4.5 million tonnes respectively (9).

In today's marketplace, butanol and its derivatives have gained prominence from the long-term growth potential of water-based coatings (such as indoor paints), driven by environmental considerations, with demand for butyl acrylate and methacrylate esters particularly strengthened by this trend. Meanwhile, most of the world's 2EH is esterified with phthalic anhydride to produce di(2-ethylhexyl) phthalate (DEHP), often referred to as dioctylphthalate or DOP, a plasticiser in wide use for the production of flexible PVC. DOP has been around for a long time, and its market is somewhat mature. Increasing amounts of 2EH are, however, being esterified with acrylic acid to produce 2-ethylhexyl acrylate, used for adhesives, resins for latex, paper coatings and textile finishing. 2EH is also used to produce 2-ethylhexyl nitrate, a diesel fuel additive, and also lubricant additives. Propylene hydroformylation is increasingly being used as the first step in the production of 2-ethylhexanoic acid, the wide applications of which include alkyd resins and adhesives for laminated glass. Therefore, the range of product applications linked to propylene hydroformylation is increasing, and the growth in global demand for butyraldehyde is between about 2% and 3% per year.

The Classic Cobalt 'Oxo' Route

In 1938, the German chemist Otto Roelen, working in the laboratories of Ruhrchemie AG, discovered that it was possible to react a mixture of carbon monoxide and hydrogen with an olefin to form products containing oxygen. Roelen's initial work identified aldehydes and ketones in the product, and the reaction was named the 'oxo' reaction. Later work established that using olefins other than ethylene, the product is principally an aldehyde, with very little ketone formation, and the reaction was renamed 'hydroformylation'. Both names are in common use, but 'oxo' has become the more convenient and more internationally recognisable name.

The process was commercialised in Germany during the early 1940s, and was then widely used throughout the world from the late 1940s onwards. The classic oxo process uses a cobalt catalyst in solution, operating at very high pressure in the range 200 to 450 bar and at temperatures in the range 140 to 180ºC. The active compound is cobalt hydridocarbonyl $HCo(CO)_4$. A very high CO pressure is needed to ensure catalyst stability during hydroformylation. The catalyst has to be decomposed before the reaction product can be recovered; therefore the process involves a cumbersome and costly catalyst recovery cycle. Using propylene as feedstock, the ratio of normal to *iso* products is typically between about three and four,

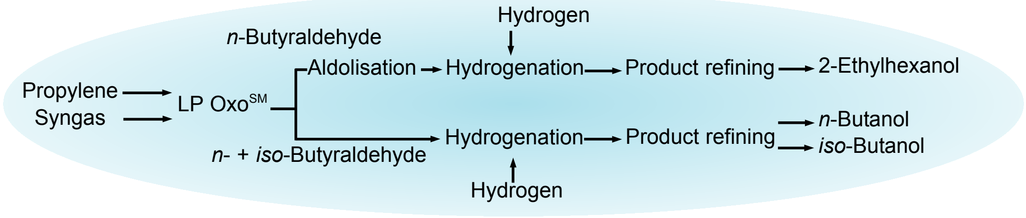

Fig. 1 Schematic showing the production of oxo alcohols from propylene by the LP Oxo^{SM} Process

and the severe operating conditions mean that there is a high level of byproduct formation. Derivatives of butanol present in the reaction product could adversely affect the environmental impact of the process. The two or three high-pressure cobalt plants remaining in operation for producing 2EH and butanols are very inefficient. They require considerable operator attention, are costly to maintain, and leave a poor impression on the environment.

A modification of the classic cobalt process was commercialised in the 1960s, using as the catalyst cobalt hydridocarbonyl trialkylphosphine, $HCo(CO)_3PR_3$. The process operates at a lower pressure than the 'classic' process (around 50 bar), although a higher temperature is needed. With propylene, the product shows much-improved linearity, the normal-to-*iso* ratio being around seven. The better selectivity to normal butyraldehyde is, however, partly offset by an increase in reaction byproducts and an unavoidable production of alcohols during oxo synthesis.

The Appeal of Rhodium-Catalysed Hydroformylation

The first commercial plant to employ the LP Oxo^{SM} Process to produce butyraldehydes successfully started up in 1976. It was built by Union Carbide at its petrochemical complex at Ponce, Puerto Rico, with a capacity of 136,000 tonnes per annum. As a result, the collaborators saw much interest in the technology from both existing and new oxo producers. By the end of 1982, Davy Process Technology had licensed and designed ten LP Oxo^{SM} plants that were built around the world.

Several advantages of the LP Oxo^{SM} Process appealed at that time. The high activity and good stability of the rhodium catalyst meant that it was not necessary to use the very high pressures needed with cobalt to retain catalyst integrity. The LP Oxo^{SM} Process operated at less than 20 bar, and a lower reaction temperature of between 90 and 100°C resulted in less byproduct formation. The lower temperature also brought other advantages over cobalt catalysis. Overall, the product mix from the reaction was much 'cleaner' and free of many of the components formed using cobalt chemistry. For example, the absence of butanol in the product meant that esters and acetals were not formed – unlike with the cobalt process, for which special measures were often needed to reduce their environmental impact. With LP Oxo^{SM}, the product could be worked up using a much simpler system and, very significantly, the selectivity of conversion of propylene to the preferred normal butyraldehyde was much better than with cobalt, the normal to *iso* ratio being improved about three-fold. These characteristics meant that propylene could be converted to normal butyraldehyde more effectively and efficiently than had hitherto been possible. The lower operating pressure compared with cobalt eliminated or reduced the need for compression of the incoming synthesis gas, and with a simpler distillation system needed to work up the product butyraldehyde, overall energy demand was reduced.

In the thirty years since rhodium was first used commercially in hydroformylation, rhodium chemistry of one form or another has been adopted to meet at least 95% of world butyraldehyde demand. First- and subsequent-generation LP Oxo^{SM} plants account for more than 60% of this; see for example Figure 2. (It is believed that the only remaining cobalt-based butyraldehyde production plants are in Russia, all other cobalt plants having been shut down, with many of them being replaced by LP Oxo^{SM} plants.) Rhodium catalysis has also made inroads into non-propylene hydroformylation applications, and the possibilities here may well increase with time. Some of these applications will be discussed in Part II.

How the LP Oxo^{SM} Process was Developed

The active catalyst used in the LP Oxo^{SM} Process is a hydridocarbonyl coordination complex of rhodium, modified with triphenylphosphine (TPP) ligand. The catalyst is formed, under process conditions, from rhodium acetylacetonato carbonyl triphenylphosphine ($Rh(acac)(CO)PPh_3$ or 'ROPAC'), or a suitable alternative catalyst precursor. From the outset, the process concept involved a homogeneous liquid-phase catalyst, in which the active catalyst species

Fig. 2 2-Ethylhexanol plant built by Sinopec Qilu Petrochemical Co. Ltd., China, employing the LP Oxo^{SM} *Process*

are dissolved in the reaction mixture along with reactants and reaction products, that is, normal and *iso*-butyraldehyde and high-boiling aldol condensation byproducts. The beauty of this route is that no extraneous solvent is necessary. A characteristic of fully mixed homogeneous catalyst systems is that short molecular diffusion ranges encourage high reaction rates. These were achieved at laboratory scale, suggesting that rhodium concentrations in the low hundreds of parts per million (ppm) would be suitable. This in turn implied affordable rhodium inventories for commercial-scale plants, provided that the rhodium could be sufficiently protected from poisoning and that excessive deactivation could be avoided.

In the early stages of development, Union Carbide needed to relate the rates of propylene hydroformylation and of the main byproduct-forming reaction, i.e. the hydrogenation of propylene to propane, to the main process variables. A statistical approach was used to design a set of laboratory experiments to develop kinetic models to determine these relationships. Models were also developed for the rate of formation of heavy byproducts resulting from aldehyde condensation reactions. Drawing upon these mathematical models, Davy Process Technology was able to optimise relationships among equipment size and cost, reactant concentrations, feedstock consumption, and rhodium inventory, seeking the lowest possible overall production cost.

The Design of the First Commercial Process

A key challenge to the developers and designers of a first commercial LP Oxo^{SM} Process, resulting from the intrinsic characteristics of the homogeneous catalyst system, was how best to separate the butyraldehyde product from the reaction mixture. The solution adopted needed to address key factors such as losses of unrecoverable reactants and product, energy usage and capital cost. There were however two very important additional considerations that were directly linked to the use of a pgm of high intrinsic value: firstly, rhodium containment, and secondly, the impact of process design on catalyst stability and catalyst life. For the former, the physical loss of even relatively small amounts of rhodium had to be avoided. As to the latter, much care had to be applied to the design of the complete catalyst system, including the facilities needed for preparing, handling, treating and processing the raw materials and the various rhodium-containing streams. The object was to avoid design measures that might unduly harm the catalyst, thus shortening its useful life.

At the outset of commercialisation, there was considerable uncertainty as to the likely lifetime of a rhodium catalyst charge in a commercial plant. Moving up from the laboratory to industrial scale was not seen in itself as significantly influencing catalyst life; the more salient issue was that during laboratory testing, it had not been possible to replicate completely the operating regime to which the catalyst system would be subjected in a commercial plant, due to various limitations, and this introduced its own uncertainties. Only a certain amount could be learned in the laboratory about the tendency for the catalyst to lose activity.

It was recognised, for example, that the catalyst stability observed in small-scale rigs using high-purity feedstocks could not reflect the effects on catalyst life of impurities present in commercial feedstocks. Nor, with the limitations of rig design and scope, would it be possible to simulate the long-term effects on the catalyst of operating conditions that could well occur in the plant but cannot be reproduced in the laboratory. Such conditions might negatively impact catalyst life. The predictive models for deactivation rates based on laboratory studies therefore had their limitations, and considerable further effort would be needed here as the technology developed. Despite the uncertainties, the conceptual process design for the first commercial application of the LP Oxo^{SM} Process built in as much protection for the rhodium as was thought desirable. The degree of protection was based on the known science, or, where there were large gaps in knowledge, on what was considered intuitively correct, in either case bearing in mind capital cost constraints.

The fact that the rhodium catalyst used in small-scale rigs was not seeing representative commercial feedstocks, and the concerns this raised with respect to catalyst life, had to be addressed before the flowsheet for a commercial plant could be outlined. Early poisoning studies in the laboratory by Union Carbide had concluded that the propylene and synthesis gas mixtures produced in industrial-scale plants were likely to contain impurities that could either poison the rhodium or inhibit its performance. To put that problem into perspective, it is useful to look at some data for the scale of butyraldehyde production that was then being contemplated: based on predictive models generated from laboratory results, a commercial plant designed to produce 100,000 tonnes per annum of normal butyraldehyde would need a charge equivalent to about 50 kg of fresh rhodium. Given the rhodium metal price at the time, the replacement value of this rhodium was about U.S.$1 million (allowing for the processing charge). During one year of operation, each kilogram of rhodium, if it could last that long in service, would be exposed to more than 2,500,000 times its own mass of commercial feedstocks. The question was whether there could be present in that huge quantity of raw materials enough harmful contaminants, albeit at low concentrations, to threaten serious damage to the catalyst, even destroying its activity, within an unacceptably short period of plant operation. The answer was a resounding 'yes'.

The poisoning studies carried out by Union Carbide had shown that certain likely contaminants such as hydrogen sulfide and carbonyl sulfide (often found in commercial propylene and synthesis gas streams), and organic chlorides often seen in propylene, were definite catalyst poisons. Other impurities, in particular dienes present in propylene, had shown strong inhibiting effects on the rhodium catalyst. Impurities that might catalyse the aldol condensation reaction had also been considered. If this reaction were allowed to occur to excess, it would produce too many high-boiling byproducts in the reactor. Having identified target impurities, and quantified the problem in terms of the permissible concentrations of those impurities in raw material streams to be fed to commercial plants, new analytical techniques were required. Their sensitivity and repeatability had to be sufficient to measure the target impurities present in real feed streams down to sub-ppm levels. Armed with such analytical methods, Davy Process Technology built laboratory rigs to develop and characterise processing schemes, employing heterogeneous catalysts and adsorbents for removing (to desired residual levels) the potentially troublesome impurities likely to be found in commercial propylene and synthesis gas streams.

The impurity guard beds and other purification plant that Davy Process Technology developed for commercial feedstocks ultimately featured in the design of commercial LP Oxo^{SM} plants, and were to contribute to ensuring that catalyst deactivation rates in the operating plants were within permissible limits.

Using the Gas Recycle Principle

To address the key challenge of how best to separate the products and byproducts of the oxo reaction from the catalyst, several distillation columns were proposed in an early LP Oxo^{SM} flowsheet. However, it was felt that this scheme would only exacerbate concerns regarding catalyst deactivation. Thermodynamic modelling, in conjunction with the kinetic models, revealed that it should be possible to remove from the catalyst solution the reaction products, including high-boiling aldol condensation byproducts, by means of gas stripping. This emerged as the makings of the 'gas recycle flowsheet' adopted for the first commercial LP Oxo^{SM} plant, and several subsequent plants.

The flowscheme of an early LP Oxo^{SM} plant employing the gas recycle principle is shown in Figure 3. A stirred, back-mixed reactor is configured in a loop, also containing a gas recycle compressor, product condenser and liquid-vapour separator. The catalyst solution, containing liganded rhodium and excess triphenylphosphine (TPP) dissolved in the products and byproducts of hydroformylation, is retained in the stirred reactor. The incoming fresh raw materials, after pretreatment to remove impurities, merge with recycled gas containing the chemical components of the synthesis gas and vaporised organics from the reactor, to enter the base of the reactor through distributor spargers. The gaseous reactants pass as bubbles of small size (and hence large interfacial area) into the liquid phase, where reaction takes place at a closely controlled temperature, typically selected between 90 and 100°C. While oxo synthesis takes place in the reactor, the reaction products are stripped from the catalyst solution by an upward gas flow. Heat of reaction is taken out partly *via* the latent heat of vaporisation of aldehydes into the gas, and partly by circulating a coolant through coils inside the reactor. The products are condensed from the gas/vapour effluent leaving the top of the reactor, and the resulting liquid products are separated from the recycle gas. The gas/uncondensed vapour is then recompressed for recycling to the reactor. Operating conditions, in particular the gas recycle rate, are set so that all liquid products leave the system at the same rate at which they have been formed, so that

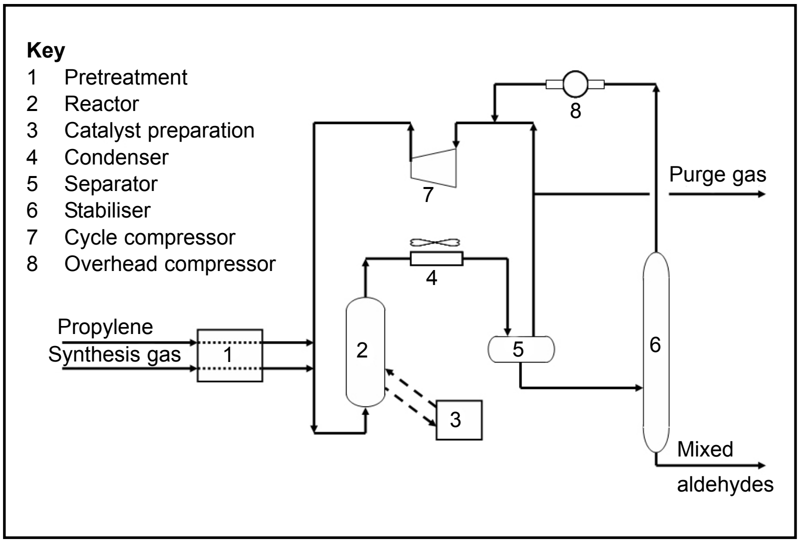

Fig. 3 Gas recycle flowsheet of an early LP Oxo^{SM} plant

the reactor inventory remains constant. Passive components in the synthesis gas, such as nitrogen, methane and carbon dioxide, along with propane present in the propylene or formed by hydrogenation, are purged in a blow-off to a fuel header, to prevent them from accumulating in the system. Unreacted propylene, propane, CO and hydrogen dissolved in the condensed product leaving the separator are removed from the product in a stabiliser column, and recompressed before being recycled to the reactor.

The basic flowscheme of the LP Oxo^{SM} Process emerged as both simple and elegant. The principle of using *in situ* gas stripping to separate product from the catalyst appeared sound, because the high molecular weight of the rhodium catalyst complex should mean that the loss by vaporisation of rhodium in the product would be practically zero. The rhodium catalyst was safely contained in the reactor, and provided sufficient energy could be imparted through the mixer impeller, the catalyst would be exposed to operating conditions more or less replicating those used in the laboratory. There was no reason for any significant amount of rhodium to leave the reactor during day-to-day operation, provided leakage was avoided and the physical entrainment of catalyst solution in the reactor overhead gas stream was minimised. Neither of these containment requirements were expected to pose undue difficulties. Catalyst leakage could be virtually eliminated by good engineering practice, including the careful selection of construction materials and mechanical seals for moving parts; entrainment could be dealt with by using proprietary, but inexpensive, entrainment filters on the overhead line from the reactor. The use of *in situ* stripping obviated the need to remove catalyst solution from the reactor to separate product using external distillation equipment, thereby eliminating any potential for increased catalyst deactivation due to concentrating the catalyst, and exposing it to higher temperatures than those used in the reactor.

The adoption of the gas recycle principle not only led to a simple and affordable process flowsheet, it also appeared to provide the best overall working regime for the catalyst, in terms of both loss prevention and deactivation, based on the 'state of the art' at the time.

Success from the First LP Oxo^{SM} Plant

Having decided to build a commercial plant at Ponce, Union Carbide erected a 200 tonnes per annum gas recycle pilot plant at the same site to test the process on the feedstocks available there, and to provide scale-up data. While the pilot plant was being built and commissioned, Davy Process Technology started the process and basic engineering design of the 136,000 tonnes per annum full-scale unit. This was to be built almost alongside the pilot plant. The process design was refined and further developed once operating data were available from the pilot plant, which continued to operate for a short time after the commercial unit first started up in January 1976.

The initial start-up of the full-scale Ponce plant was easier than anticipated. Excluding outside interruptions, the plant was online for all but one hour in its first month of operation. During its first year, its on-stream operational availability was greater than 99%. This contrasted with a typical availability of about 90% for a conventional cobalt-based oxo plant, based on Union Carbide's own experience. The operation continued to be marked by what was until then unusual ease, stability and smoothness. Design targets for productivity, selectivity, feedstock usage efficiency and product quality were all met. The ratio of normal to *iso*-butyraldehyde was usually controlled at around 10:1, but higher ratios up to 16:1 were achieved. Significantly, the costs attributable to catalyst were lower than expected, and the life of the first catalyst charge exceeded one year.

The reaction temperature was kept as low as possible, and in the range of about 90 to 100ºC, consistent with being able to achieve sufficient catalyst productivity from the volume of catalyst solution available to meet the production demands, and being able to control the liquid levels in the reactors. (Product stripping was easier at higher temperatures because of the higher vapour pressures of the products.) It was known that higher reaction temperatures would lead to an increased production of reaction byproducts and an increased rate of catalyst deactivation; effective temperature control was therefore important. The reaction temperature could be regulated very closely – to within ± 0.5°C. The operating pressure of the reactors was also well controlled at about 18 bar.

The process characteristics and control systems used meant that the unit needed little day-to-day operator attention. Again, this contrasted with experience on high-pressure cobalt plants. The rhodium unit could quickly be restarted from a full shutdown, and it was possible to restore production following outages much more rapidly than had been the case with cobalt.

How the Catalyst Works

The active rhodium species for the LP Oxo^{SM} Process is formed under hydroformylation reaction conditions, and there is no need for complex catalyst synthesis and handling steps. The probable sequence of the reaction with propylene to form normal butyraldehyde is shown in Figure 4.

Rhodium is introduced to the oxo reactor in the form of a solution of ROPAC (a stable crystalline compound) in butyraldehyde. Complex **A** in Figure 4 is formed from the fresh rhodium in the presence of carbon monoxide and TPP. In this coordination complex the rhodium atom carries five labile-bonded ligands: two TPP, two carbon monoxide and one hydrogen. In the first reaction step, a propylene ligand is added to form complex **B**, which rearranges to the alkyl complex **C**. This undergoes carbon monoxide insertion to form the acyl complex **D**. Oxidative addition of hydrogen gives the dihydroacyl complex **E**. Finally, hydrogen transfers to the acyl group, and normal butyraldehyde is formed together with complex **F**. Coordination of **F** with carbon monoxide regenerates complex **A**.

Some *iso*-butyraldehyde is produced along with the normal butyraldehyde, but a high selectivity to the latter is ensured by exploiting a steric hindrance effect as follows. The reaction is carried out in the presence of a large excess of TPP. Under the low-pressure conditions of the reaction, the high TPP concentration suppresses the dissociation of complex **A** into one containing only a single phosphine ligand. If largely undissociated complex **A** is present, with its two bulky TPP ligands incontact with the propylene, then a high proportion of primary alkyl is favoured – if fewer such ligands were present, then more propylene would form secondary alkyl groups, leading to more *iso*-butyraldehyde.

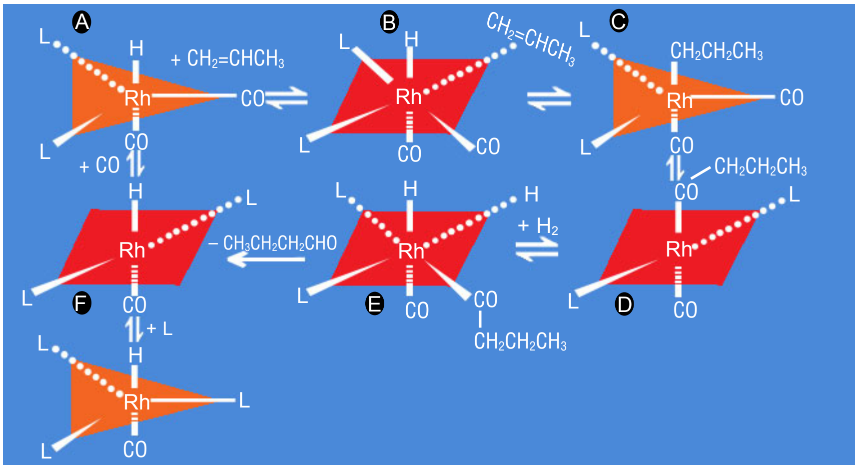

*Fig. 4 Probable reaction cycle for formation of normal butyraldehyde from propylene (L = triphenylphosphine (TPP); **A**: product of reaction of ROPAC with carbon monoxide and TPP; **B**: addition product of **A** and propylene; **C**: alkyl complex resulting from rearrangement of **B**; **D**: acyl complex resulting from carbon monoxide insertion to **C**; **E**: dihydroacyl complex resulting from oxidative addition of hydrogen to **D**; **F**: product of elimination of butyraldehyde from **E**)*

Measures to Deal with Catalyst Deactivation

The TPP-modified catalyst has a tendency to deactivate over time due to the formation from the monomeric rhodium species of rhodium clusters. This type of deactivation is termed 'intrinsic', to distinguish it from deactivation caused by an external source such as catalyst poisons present in the feedstocks. Catalyst management models were developed to help operators of the LP Oxo^{SM} Process to optimise the economic return from their catalyst charges, in recognition that intrinsic deactivation had to be tolerated to some extent. For example, operating temperatures could not be lowered to reduce catalyst deactivation if this also reduced catalyst productivity to uneconomic or unmanageable levels. Rhodium catalyst management guidelines from Union Carbide and Davy Process Technology recommended operating adjustments to compensate for deactivation, in response to accumulated operating data which indicated the time evolution of catalyst activity. The guidelines were couched so as to optimise the balance between reaction rate, selectivity to normal butyraldehyde and catalyst stability. While operators felt some obligation to comply with the licensor's recommendations, at least until performance warranties had been met, it was interesting to observe how the long-term catalyst operating strategies adopted by plant owners varied so widely between plants, depending on specific circumstances and preferences.

Plant operators observed rates of catalyst deactivation that meant that a rhodium catalyst charge would typically last for about 18 to 24 months before its activity had declined to the point when it would have to be discharged from the reactor and replaced by a fresh catalyst charge.

The earliest LP Oxo^{SM} plants contained very simple equipment to concentrate the discharged spent catalyst solution. The idea was that concentrated catalyst, containing say 2000 ppm of rhodium, would be shipped to Johnson Matthey in the U.K., who would then recover the rhodium in a form suitable for reprocessing to ROPAC. But the logistics of actually reprocessing around 20 tonnes of concentrate for a typical plant were somewhat daunting. There were concerns about handling and transporting such material in such large quantities. With rhodium metal prices rising, the logistics might put the security of, say, U.S.$2 million worth of rhodium at undue risk. There were also uncertainties about what other substances might be present in the rhodium concentrate that could cause Johnson Matthey processing problems. Although metals like iron and nickel that are usually found in commercial feedstocks could be anticipated, would metal contamination compromise rhodium recovery? The requirement for off-site rhodium recovery from bulk catalyst solution detracted from the elegance of the LP Oxo^{SM} Process. Fortunately, by the time the first licensed plants actually started operation, Union Carbide had proven a catalyst reactivation technique that would virtually obviate off-site recovery.

Catalyst Reactivation

By the early 1980s, before any need had arisen to resort to off-site rhodium recovery, Union Carbide had developed a means to deal with the intrinsic deactivation – effectively by reversing it. This involved concentrating the spent catalyst and then treating the rhodium present in the resulting residue to convert it into a form capable of reactivation. The concentration process was carried out using specialised equipment (a proprietary evaporator) under very precise conditions, including high vacuum, designed to prevent catalyst damage. The overall process could conveniently be performed at the plant site, and required no chemical reagents. It resulted in a 'declustering' of rhodium to enable the restoration of activity once the treated residue had been returned to a hydroformylation environment. Eventually, all operators either added reactivation equipment to their plants, or arranged to share facilities. Catalyst reactivation was incorporated into the standard design of all new plants, and a measure of lost elegance was restored to the LP Oxo^{SM} Process!

The catalyst reactivation technique was used to carry out repeated reactivations of what was essentially a single catalyst charge. This drastically reduced the need for off-site recovery, which was normally deployed only on rhodium that could no longer be reactivated economically. In that case, the recovery could be performed on residues typically containing about 8000 ppm of rhodium, four times the concentration initially envisaged, thus improving the logistics and reducing the cost of off-site processing.

Conclusion

This article (Part I) has sought to demonstrate the initial promise of the LP Oxo^{SM} Process, employing rhodium-based catalysis, in terms of high availability, selectivity and productivity, low environmental impact and low maintenance. Part II, to be published in a future issue of *Platinum Metals Review*, will address subsequent key improvements to the process, and its use in non-propylene applications.

LP Oxo^{SM} is a service mark of The Dow Chemical Company.

References

1 Davy Process Technology Ltd.: http://www.davyprotech.com/

2 The Dow Chemical Company: http://www.dow.com/

3 Union Carbide Corporation: http://www.unioncarbide.com/

4 R. L. Pruett and J. A. Smith, Union Carbide Corporation, 'Hydroformylation Process', *U.S. Patent* 3,527,809; 1970

5 G. Wilkinson, Johnson Matthey, 'Improvements in Catalytic Hydrogenation or Hydroformylation', *British Patent* 1,219,763; 1971

6 M. L. H. Green and W. P. Griffith, *Platinum Metals Rev.*, 1998, **42**, (4), 168

7 W. P. Griffith, *Platinum Metals Rev.*, 2007, **51**, (3), 150

8 F. J. Smith, *Platinum Metals Rev.*, 1975, **19**, (3), 93

9 Production estimates provided by RXN Petrochemical Consulting Inc.: http://rxnpetrochem.com/page4.html

Further Reading

'Low-pressure oxo process yields a better product mix', *Chem. Eng. (New York)*, 5th December, 1977, **84**, (26), 110; marking the award of the 1977 Kirkpatrick Chemical Engineering Achievement Award to the winners: Union Carbide Corporation, Davy Powergas Ltd., and Johnson Matthey & Co. Ltd.

J. L. Stewart, 'LP Oxo^{SM} process – a success story', *Indications*, Winter 1982/83; the international journal of Davy McKee

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