

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

KEY IMPROVEMENTS TO RHODIUM PROCESS, AND USE IN NON-PROPYLENE APPLICATIONS

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Part I of this article (1), which appeared in the July 2007 issue of Platinum Metals Review, described the substantial cost and technical benefits brought to the hydroformylation of propylene with carbon monoxide and hydrogen (an 'oxo' reaction) by replacing the previous high-pressure cobalt-catalysed technology with a low-pressure rhodium-based catalyst system (the LP OxoSM Process). The background to the rhodium process and its development to the point of first commercialisation were reviewed. This article (Part II) covers some of the improvements made to the LP OxoSM Process after the early plants started operation, and its uses in non-propylene applications.

The 'Low Pressure Oxo' process (LP OxoSM 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 OxoSM 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 OxoSM 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 OxoSM plants. Most LP OxoSM systems are licensed plants, nearly all of which have been built under licences granted by Davy Process Technology (2) working in cooperation with The Dow Chemical Company (3); the remainder are plants owned and operated by Dow's Union Carbide subsidiary (4).

The first commercial plant to use the LP OxoSM Process was a unit built by Union Carbide at Ponce in Puerto Rico for producing 136,000 tonnes per annum of butyraldehydes. The Ponce plant started operation in 1976. By the end of 1982, Davy Process Technology had licensed and designed ten LP OxoSM plants that were built around the world. All these plants employed a homogeneous triphenylphosphine (TPP)-modified rhodium catalyst, and *in situ* gas stripping was adopted to separate the butyraldehyde product from the rhodium-containing catalyst solution which remained in the oxo reactor. (The flowscheme for an LP OxoSM plant employing this gas recycle principle is described in Part I (1).) Adopting gas recycle not only led to a simple and affordable process flowsheet, it also provided 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.

From Gas to Liquid Recycle

Once the gas recycle technology had been proven, and market interest in the LP OxoSM Process was intensifying, Union Carbide and Davy Process Technology turned their attention to a new

flowsheet concept employing the 'liquid recycle' principle. This involved separating the reaction product from the catalyst solution in equipment outside the oxo reactor, using a sequence of vapour flashing (resulting from an abrupt pressure reduction) and vaporisation using a suitable external heat source. Reaction solution from the back-mixed reactor was continuously fed to this equipment, in which the greater part of the butyraldehyde and reaction byproducts present in the feed were separated from the rhodium-bearing catalyst solution, which was recycled to the reactor. The net rate of removal by external vaporisation of products and byproducts matched their rate of production in the reactor, so as to maintain a constant catalyst solution inventory. The liquid recycle flowsheet also included the means to recover and recycle dissolved reactants present in the separated product stream.

Apart from these basic principles of liquid recycle, much attention had to be given to the operating conditions under which vaporisation of products would occur, particularly the duration for which catalyst would be exposed to a raised temperature outside the equable environment of the reactor. Earlier deactivation studies in the laboratory and the successful operation of the Ponce plant had given valuable insights in this regard. It had become evident that decomposition of the triphenylphosphine (TPP)-rhodium complex – a potential concern – should be avoidable. A proprietary vaporisation system design emerged from the efforts of specialist engineers working alongside the process developers.

The overriding merit of the liquid recycle approach was that by decoupling the hydroformylation reaction step from the physical process of product/catalyst separation, it became possible to adopt operating conditions in the reactor to optimise the balance of production rate (or reaction 'speed'), selectivity and (catalyst) stability – the 'three Ss'. The technique adopted exemplified the challenge facing the developers and designers of commercial liquid phase homogeneous catalyst systems, that of balancing the 'three Ss' by imaginatively addressing the issue of product/catalyst separation. Here, decoupling reaction from separation would, for example, obviate the necessity to run the reactor at temperatures dictated by product stripping requirements.

The introduction of liquid recycle therefore provided the plant operator with more degrees of freedom to get the best performance from an oxo reaction system than hitherto had been possible. For Davy Process Technology and Union Carbide, it would open up new possibilities for the LP OxoSM Process in terms of catalyst selection and its application with olefins other than propylene.

Another advantage of the liquid recycle approach was that the oxo reactor could be reduced in size. With gas recycle, it was necessary to allow a significant excess reaction volume, to accommodate expansion of the liquid phase by the entrainment of bubbles from a large gas flow. With no such gas flow required with liquid recycle, most of this volume allowance could be dispensed with. This was particularly significant for gas recycle plant operators who had decided to enlarge their production capacities. By converting their plants from gas to liquid recycle, they could almost double the production capacities of their existing oxo reactors.

With oxo plants becoming larger in size, the adoption of liquid recycle resulted in designs of lower cost, mainly as a result of the elimination of the cycle compressor and the use of smaller reactors. Practically all LP OxoSM plants designed since the mid 1980s employ liquid recycle, to which several of the early gas recycle designs have also been converted. Plant operators welcome the added operating flexibility, enabling them to optimise reaction conditions to their production capacity and product mix requirements.

The Introduction of a Bisphosphite-Modified Rhodium Catalyst

A continuing programme of investment by Davy Process Technology and Union Carbide in research and process development aimed at improving and refining the LP OxoSM Process, coupled with the substantial operating experience accumulated from Union Carbide's own oxo plants and more than twenty plants built by others under licence, have, over the years, resulted in considerable improvements to the original process. The technical and commercial appeal of the LP OxoSM Process over competing processes has, if anything, increased. The discovery and successful use of catalyst reactivation

(discussed in Part I (1)), and the process enhancements resulting from the move from gas to liquid recycle are just two examples of the improvements made.

The quest for improvement has not been confined to the TPP-modified rhodium system. Today, several LP OxoSM plants are producing butyraldehyde using a more advanced bisphosphite-modified rhodium catalyst developed by Union Carbide. The chemical characteristics, intrinsic activity, stability and regioselectivity of this catalyst show marked differences from those of the TPP-modified catalyst still used in most operating plants. The challenge of recent years has been how best to capitalise on the excellence of some attributes of bisphosphite catalysts where it most counts, i.e. in terms of feedstock utilisation efficiency, selectivity to normal butyraldehyde, rhodium inventory and catalyst life.

It had been known for many years before the introduction of bisphosphites that phosphite-modified rhodium catalysts are very reactive and show good regioselectivity (i.e. selectivity to the straight chain aldehyde) in comparison with phosphine-modified catalysts. Conventional phosphites, however, had been found to be unstable in the presence of aldehydes. This limitation was overcome through the development of bisphosphite ligands.

The preparation, structural features and performance in hydroformylation by bisphosphites were discussed by Union Carbide's David R. Bryant at the Royal Society of Chemistry Dalton Division's Fourth International Conference on the Chemistry of the Platinum Group Metals in 1990 (5, 6). Then,

in 1992, at a meeting of the American Chemical Society (7), Dr Bryant discussed the new-found place for bisphosphite-modified rhodium catalysts, describing them as the fourth generation of oxo catalysts, following the first-generation unmodified cobalt, then phosphine modified cobalt, then phosphine-modified rhodium catalysts. Several Union Carbide patents (e.g. 8–10) disclosed a large number of bisphosphite-modified rhodium catalyst systems that are much more active than those based on TPP, with much higher selectivity to the linear aldehyde possible. Certain Union Carbide patents also gave methods for stabilising bisphosphite-modified catalysts.

Preparing the bisphosphite ligands from substituted biphenols imparts the high degree of steric hindrance needed to achieve the good regioselectivity sought in some hydroformylation applications, for instance in the production of butyraldehydes.

The molecular structure of TPP and a general representation of a bisphosphite are shown in Figure 1. The chemical nature of the group bridging the two phosphite groups has a crucial bearing on hydroformylation performance. The bridge could be specifically configured to encourage high normal to *iso* selectivity at an acceptable reaction rate by the appropriate choice of substituents X₃, X₄, Y₃ and Y₄ in Figure 1.

It is thought that the bisphosphite ligand functions in a hydroformylation environment by doubly coordinating rhodium to form a bidentate complex. The favourable steric environment thus created around the rhodium is the likely cause of the high

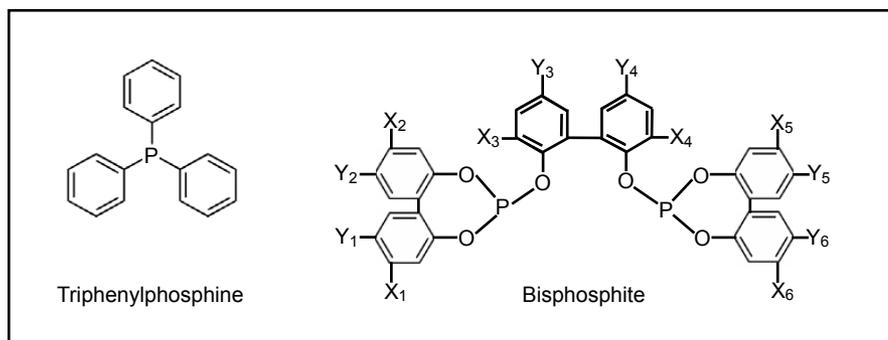


Fig. 1 Structures of triphenylphosphine and bisphosphite ligands. For butyraldehyde production, high normal to *iso* selectivity at an acceptable reaction rate is encouraged by the appropriate choice of substituents X₃, X₄, Y₃ and Y₄

regioselectivity mentioned above.

Union Carbide found that with propylene, it was possible to select in the laboratory a suitable bisphosphite-modified rhodium catalyst that would show about 30 times the activity of a TPP-modified catalyst, while achieving extraordinarily high selectivity to normal butyraldehyde and using lower ligand concentrations. Since bisphosphite-ligated catalyst complexes were viewed as having great potential, Union Carbide had devoted a substantial R&D effort to resolving issues over their stability in commercial hydroformylation environments. Union Carbide were confident that they had found a way forward to the first commercial use of these catalysts.

The successful adoption of the liquid recycle principle in many operating LP OxoSM plants by the early 1990s had opened the way to specifying a commercial propylene hydroformylation process incorporating a bisphosphite-modified catalyst that would offer much appeal over its TPP counterpart. On the basis of test work they had performed in the laboratory, Union Carbide believed that they had discovered how best to utilise and sustain the high activity of bisphosphite-modified catalyst in a commercial environment. The first commercial plant to use the catalyst system was built by Union Carbide at its petrochemical complex at St. Charles, Louisiana, U.S.A., for producing 136,000 tonnes per annum of butanol from propylene. Production started in 1995.

In designing the plant, the concentration of rhodium in the catalyst was set at about one third of that for a TPP-modified catalyst system, and the operating temperature of the catalyst and the reaction pressure were reduced. Catalyst productivity, relating the rate of production to catalyst volume, was not altered drastically from that for which the TPP-modified catalyst plants had been designed. It was thought better to exploit improved catalyst activity by reducing the rhodium inventory and in reducing byproduct formation to improve feedstock efficiency, rather than by making reactors smaller. In selecting the operating temperature, known factors influencing catalyst stability were also considered.

The Dow Chemical Company, which acquired Union Carbide in 2001, today operates two plants at the St. Charles site employing the LP OxoSM Process

using LP OxoSM SELECTORSM Technology, using a proprietary bisphosphite-modified rhodium catalyst. Further plants have been licensed to deploy the same catalyst system, one of which operates in Malaysia; the latest SELECTORSM 30 licence was granted earlier this year (2007) for a butanols plant to be built in the Kingdom of Saudi Arabia. The bisphosphite is introduced to the process as the NORMAXTM Catalyst compound, which is available from The Dow Chemical Company.

The experience gained from more than eleven years of operation of the first St. Charles plant and process refinements made in recent years have provided the technical platform for the 'SELECTORSM 30' Technology that Davy Process Technology offers for licence in collaboration with Dow. The brand name is derived from the ratio of normal to *iso*-butyraldehyde of 30:1 that the process is capable of achieving through the use of NORMAXTM Catalyst.

While the SELECTORSM 30 Technology has aroused much interest, Davy Process Technology and Dow are seeing a sustained interest in the TPP-modified catalyst technology for use in propylene applications. This is now marketed under the brand name 'SELECTORSM 10' Technology. As the name implies, this refers to the normal to *iso* ratio of 10:1 with which the TPP process is usually associated. Just this year (2007), Davy Process Technology granted a licence to a Chinese company for a plant for producing approximately 250,000 tonnes per annum in total of 2EH and normal plus *iso*-butanols employing SELECTORSM 10 Technology. This will be the largest LP OxoSM plant in Asia.

TPP or Bisphosphite?

Many factors influence the choice of route for producing oxo derivatives from propylene, and the following highlights some of the parameters on which the choice of ligand can have a significant bearing.

The NORMAXTM Catalyst today offers the highest commercially proven isomer selectivity in favour of normal butyraldehyde production. The SELECTORSM 30 Technology will therefore appeal strongly where the production of 2-ethylhexanol (2EH) from the available propylene is to be maximised. Put simply, production of 2EH using SELECTORSM 30

will typically consume between 6 and 7% less propylene than with SELECTORSM 10, solely as a result of the improved selectivity of conversion to the normal aldehyde. Further improvements in efficiency can result from the reduced formation of byproducts arising from the lower operating temperatures used with the NORMAXTM Catalyst as compared with TPP, and also because of lower propylene purge losses. Plant owners having access to lower-grade, cheaper propylene streams, may also find the NORMAXTM Catalyst system attractive because its high activity will effectively handle dilute feed-streams, such as refinery-grade propylene.

Questions concerning the stability of bisphosphite-modified rhodium catalysts in commercial service (and there were many!) have been conclusively answered by excellent experience with those plants now using NORMAXTM Catalyst. This has indicated that exceptional rhodium catalyst life can be expected. In the more than eleven years since the first LP OxoSM plant utilising NORMAXTM Catalyst went into operation at St. Charles, no replacement of the original oxo catalyst charge has been necessary. Furthermore, the rhodium usage has been extremely small. The same picture has emerged for the second St. Charles plant and the licensed plant in Malaysia.

The manufacturing cost per kilogramme of NORMAXTM Catalyst is higher than that of TPP. The cost difference is largely compensated for by the large differences in the quantities of these ligands that are needed to operate commercial plants. This is because the benefits of the bisphosphite-modified catalysts are best realised with the ligand present at much lower concentrations in the catalyst solution than is the case with TPP-modified systems. Experience has shown that for commercial propylene systems, the contribution to the cash cost of production by rhodium and ligand for the SELECTORSM 30 Technology is very comparable to its equivalent for SELECTORSM 10. Typically, for the TPP system, the contribution is about U.S.\$2 to U.S.\$3 per tonne of butyraldehyde, whereas for systems employing NORMAXTM Catalyst, it is about U.S.\$5 per tonne.

Other factors are influencing licensees of the LP OxoSM Process in their choice of ligand. The highest

possible selectivity to normal butyraldehyde is not always the priority. Some oxo producers desire to produce *iso*-butyraldehyde to make derivatives such as neopentylglycol, for use in speciality polyesters, or other polyols going into, for instance, volatile free film-formers. The NORMAXTM Catalyst would be inappropriate in such cases. The butyraldehyde section of a 2EH plant licensed in 2003 by Davy Process Technology was designed to use TPP with the capability of being able to vary the normal to *iso* product ratio from 12:1 to only 6:1 – to provide good flexibility in the amount of *iso*-butyraldehyde coproduct.

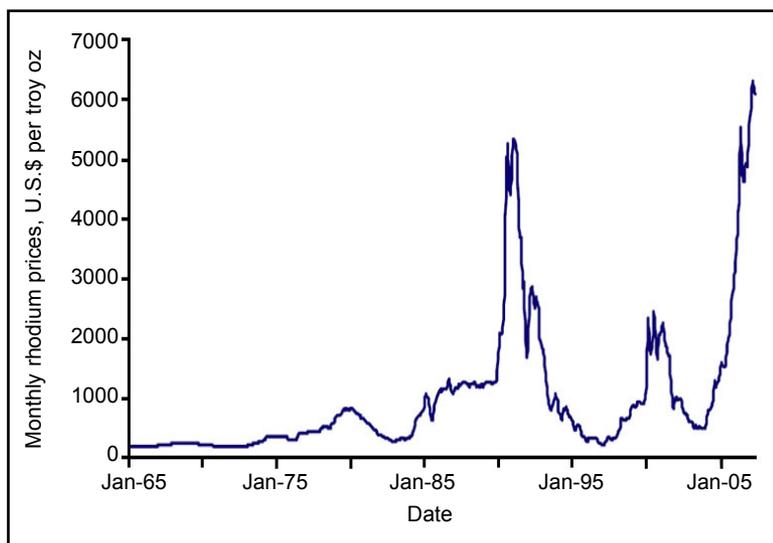
The Influence of Rhodium Metal Prices

The price of rhodium metal has varied enormously in the forty years since rhodium first attracted serious attention for hydroformylation catalysis. This variation is plotted in Figure 2 (11, 12).

Rhodium is presently more than 25 times more expensive in U.S. dollar terms (11, 12) than it was when the strong economic drivers for rhodium first emerged in the early 1970s. While for plants operating the LP OxoSM Process, the variable cost contribution from rhodium is often barely U.S.\$1 per tonne of product, which is extremely modest, the rhodium price can have a large impact on the working capital needed for a new plant investment. In the early 1990s, the monthly rhodium metal price, having never previously been more than U.S.\$2000 per troy ounce, quite quickly rose to about U.S.\$5000 per troy ounce (12), where it remained for almost a year before easing right back to well below U.S.\$1000 per troy ounce. This increase in the rhodium price would have caused concerns among those companies contemplating investing in TPP/rhodium-based technology. Furthermore, it stimulated Union Carbide and Davy Process Technology into planning more proactively for a 'low rhodium' version of the LP OxoSM Process. Fortunately, at the time, the low-rhodium solution was already under development in the form of a modified version of the LP OxoSM Process using a more advanced bisphosphite-modified catalyst.

To put the effect of the rhodium price into a present-day perspective, even priced at U.S.\$5000 per troy ounce (the rhodium price at the time of writing

Fig. 2 Monthly rhodium prices from January 1965 to June 2007 (Source: Johnson Matthey Precious Metals Marketing, U.K.)



(early July 2007) is about U.S.\$6150 (12)), the cost to the plant operator of the least amount of rhodium possible to start a 150,000 tonnes per annum 2EH plant using SELECTORSM 10 Technology is in the order of U.S.\$9 million, which is more than 10% of the inside battery limit (ISBL) investment cost. In practice, the operator would probably wish to keep additional rhodium in reserve. Over a period of years, the rhodium inventory might well build to typically about one and a half times the initial requirement. The SELECTORSM 30 technology has the advantage that, with lower concentrations of rhodium used, the rhodium inventory of a plant can be reduced to less than one third of that needed for SELECTORSM 10.

With the rhodium price now having remained relatively high at over U.S.\$4500 per troy ounce for over a year (12), some operators of the TPP-based SELECTORSM 10 Technology will be considering a switch from TPP to the NORMAXTM Catalyst. If a much improved selectivity to normal butyraldehyde is a sufficient incentive, they could find that the asset value of surplus rhodium presently locked into a TPP-modified catalyst system (but recoverable from it) could easily pay for a project to convert their plants to SELECTORSM 30.

With product values (on a U.S. dollar per tonne basis) at best only quadrupling since the early 1970s, a 25-fold, even 10-fold increase in rhodium prices over the same period might have been expected to

undermine the sustainability of a commercial petrochemical process based on rhodium chemistry. In the case of the LP OxoSM Process, this situation has been avoided through advances in the technology such as those described in this article. The advances have tended to reduce the investment capital required per tonne of product, and have at least partly mitigated the requirement for extra working capital to establish rhodium inventories. The advances have also resulted in significant improvements in operating costs. The net effect of this is that today, oxo alcohols can be manufactured from propylene at a lower cost in real terms than ever before, despite the relatively high cost of raw materials resulting from expensive oil and the current level of the rhodium metal price. This cost-effectiveness has resulted not only from ingenious rhodium chemistry, but also from essential contributions from chemists, process developers and designers, not forgetting the plant operators.

LP OxoSM Today

The Dow Chemical Company and Davy Process Technology collaborate through their respective licensing organisations to market and license LP OxoSM Technology for use with propylene in plants employing either SELECTORSM 10 (TPP) or SELECTORSM 30 (NORMAXTM Catalyst) Technology. SELECTORSM 10 is suitable for a normal to *iso* ratio requirement of between about 6:1

and 14:1, and SELECTORSM 30 for between 22:1 and 30:1. Based on laboratory trials, a ratio of at least 35:1 is believed to be attainable commercially using the bisphosphite-modified rhodium catalyst employed in SELECTORSM 30 designs. As part of the LP OxoSM licence offering, technology is available for the production from butyraldehyde of 2EH, normal butanol or *iso*-butanol in any combination. Most of the thirty or so propylene-based LP OxoSM projects so far licensed involve 2EH and/or butanol plants designed by Davy Process Technology.

Other Applications of the LP OxoSM Process

The investment by Davy Process Technology and Union Carbide in research and process development has converted the early laboratory promise of rhodium chemistry into commercial realities of wide appeal. The oxo landscape has eventually changed as a result. The ongoing quest for technical excellence driven by the market for butyraldehyde and its derivatives has opened up applications for the LP OxoSM Process for non-propylene uses.

LP OxoSM Technology has been used to produce from normal butenes commercial quantities of 2-propylheptanol (2PH), an alternative plasticiser alcohol to 2EH in which there is a growing interest. The commercial 2PH product actually contains 2-propylheptanol as the principal component in an isomeric mixture of C10 alcohols. The phthalate ester plasticiser made from 2PH is often referred to as DPHP, or di(2-propylheptyl) phthalate. DPHP is gradually establishing a place in certain plasticiser markets in Europe and the U.S.A. because of environmental and other factors. It offers advantages as a plasticiser for flexible PVC applications where its low volatility, good long-term stability and excellent outdoor performance can be exploited.

The 2PH technology developed by Davy Process Technology and Union Carbide can operate with commercial C4 streams containing 1-butene and 2-butene such as raffinate 2 streams available from methyl *tert*-butyl ether (MTBE) plants. The high reactivity of a NORMAXTM bisphosphite-modified rhodium catalyst can be exploited so that both the 1-butene and the less reactive 2-butene present in the feedstream contribute as valuable reactive feed

components to ensure the best available overall product yield. Where there is interest from a 2EH producer in producing 2PH in order to exploit a suitable C4 feed source that is likely to be considerably cheaper than propylene, Davy Process Technology is able to design an LP OxoSM plant that is capable of producing either 2EH or 2PH separately by switching between propylene and butene feedstocks.

Should the 2EH/2PH producer have a particular requirement to gradually ramp up production of 2PH according to how the market is seen to develop, another possible approach is to produce the two plasticiser alcohols simultaneously by co-feeding propylene and butenes to the oxo system in appropriate proportions, finally separating the 2EH product from the 2PH product. If a co-feed route is adopted, it would be necessary to conduct separate aldol condensation steps on separated C4 and C5 aldehyde streams prior to a combined C8/C10 hydrogenation step, in order to maximise yields of desired products.

LP OxoSM Technology has also been developed for, and successfully operates under licence in, a plant for producing C12 to C15 surfactant range alcohols from C11 to C14 olefins derived from Fischer Tropsch synthesis. The plant capacity is 120,000 tonnes per annum. The technology is also being applied in a 125,000 tonnes per annum process plant now in construction for converting 1-heptene (extracted from Fischer-Tropsch products) to 1-octanol. The octanol product is to be used in the production of co-monomer grade 1-octene. Both these applications of the LP OxoSM Process were developed by Davy Process Technology at its Technology Centre at Stockton-on-Tees in the U.K. Figure 3 shows the 'Mini-Plant' employed for this purpose.

Conclusion

In recent customer surveys made on behalf of Dow and Davy Process Technology, operators of the LP OxoSM Process have commended the ease of operation and the low environmental impact of the plants, their high reliability and their low maintenance requirements.

A successful resolution of various issues in



Fig. 3 Oxo 'Mini-Plant' at Davy Process Technology's Technology Centre, Stockton-on-Tees, U.K.

rhodium catalyst management has been essential to the commercialisation of the process. This success should provide convincing encouragement to researchers, who are keen to exploit pgms as catalyst materials, but who are apprehensive as to the implications of their very high intrinsic value. It should also encourage developers and designers who

are entrusted with turning pgm chemistry into commercial processes, but who may be daunted by problems such as pgm containment and catalyst life.

The LP OxoSM Process is recognised as one of the best known applications of industrial-scale chemistry using a pgm. The promise of rhodium chemistry first observed forty years ago has transformed the manufacturing base of a petrochemical sector. Davy Process Technology and The Dow Chemical Company are continuing in their efforts to build on and extend the significant contribution made towards this transformation by the LP OxoSM Process. Their market focus and continuing efforts in research and process development programmes driven by a sustained market interest will likely mean that the LP OxoSM Process will continue to play an important role in industrial hydroformylation applications for many years to come.

LP OxoSM and SELECTORSM are service marks of The Dow Chemical Company.

NORMAXTM is a trademark of The Dow Chemical Company.

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