Industrial Low Pressure Hydroformylation: Forty-Five Years of Progress for the LP OxoSM Process

A long standing collaboration between Johnson Matthey and Dow continues to sustain the high standing of their oxo technology through innovative solutions to address the changing needs of the global oxo alcohol market.

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Since the mid-1970s when the ‘Low Pressure Oxo’ process (LP OxoSM Process) was first commercialised, it has maintained its global position as the foremost oxo process, offering particular appeal to independent producers of commodity plasticisers facing increasing regulatory pressure. The story of this important industrial process is told from its early beginnings when laboratory discoveries by independent groups of researchers in USA and UK revealed the remarkable ability of organophosphine containing rhodium compounds to catalyse the hydroformylation reaction, and describes how its development, exploitation and continuing industrial relevance came about by collaboration between three companies: The Power-Gas Corporation, which later became Davy Process Technology before becoming part of Johnson Matthey; Union Carbide Corporation, which became a wholly owned subsidiary of The Dow Chemical Company; and Johnson Matthey.

Introduction

The LP OxoSM Process is the rhodium-catalysed hydroformylation process in wide use today in a variety of industrial applications. These applications have been developed, co-marketed and licensed as a cooperation between affiliates of The Dow Chemical Company (‘Dow’) and Johnson Matthey or their predecessors, for over 45 years.

The LP OxoSM Process first made an impact in the 1970s when its technical elegance, environmental footprint and economics attracted huge attention by the world’s producers of normal butyraldehyde for conversion to the plasticiser alcohol 2-ethylhexanol (2EH).

The Early Dominance of Cobalt Catalysis

Hydroformylation is the reaction of an unsaturated olefinic compound with hydrogen and carbon monoxide to yield an aldehyde. In the case of the widely practised hydroformylation of propylene, the olefin (usually present in chemical or polymer grade propylene) is reacted with a mixture of hydrogen and carbon monoxide (in the form of synthesis gas), to produce two aldehyde isomers (normal butyraldehyde and iso-butyraldehyde) according to Equation (i):

$$2\text{CH}_3\text{CH}==\text{CH}_2 + 2\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + (\text{CH}_3)_2\text{C(H)CHO}$$ (i)
The hydroformylation reaction was first reported by Dr Otto Roelen of Ruhrchemie AG, Germany, in 1938 and was given by German researchers the description of ‘oxo’ synthesis. Alcohols synthesised by the hydrogenation of aldehydes produced from hydroformylation tend therefore to be called oxo alcohols. Roelen’s discovery was to lay the foundation for bulk organometallic chemistry and the application of homogeneous catalysis on an industrial scale. He originally employed as a catalyst a mixture containing cobalt, thorium and magnesium oxide that was commonly used for Fischer-Tropsch synthesis and later speculated that cobalt hydridocarbonyl \((\text{HCo(CO)}_3)\) was the catalytically active species. He realised that the catalytic mechanism was homogeneous in nature (for example \((1, 2)\)). The Second World War hindered Ruhrchemie’s attempts to complete the construction of a first industrial oxo plant for producing fatty alcohols from Fischer-Tropsch olefins, and in the following years Ruhrchemie commercialised a number of hydroformylation processes using homogeneous cobalt catalyst for use in the production of detergent and plasticiser alcohols. By the end of the 1960s most plants were using the ‘classic’ cobalt process employing \(\text{HCo(CO)}_3\), operating at very high pressures in the range of 200 to 450 bar and temperatures between 140°C and 180°C, although a modification of this catalyst, cobalt hydridocarbonyl trialkylphosphine \((\text{HCo(CO)}_3\text{PR}_3)\), had been commercialised enabling the hydroformylation of propylene to occur at about 50 bar. This phosphine modified cobalt catalyst also gave improved selectivity to the preferred normal butyraldehyde, the isomer ratio \((\text{n:i ratio})\) being about 7:1 rather than the 3:1 that was typical of the classic cobalt process. To this day, cobalt catalysts are still being used industrially in some hydroformylation applications, especially in the manufacture of detergent alcohols from long chain olefins produced by ethylene oligomerisation and the production from butene dimers and propylene trimer of the plasticiser alcohols iso-nonyl alcohol \((\text{INA})\) and iso-decyl alcohol \((\text{IDA})\) respectively.

**The Beginnings of the LP Oxo\textsuperscript{SM} Process**

In the 1960s researchers at the chemicals producer Union Carbide Corporation (now a wholly owned subsidiary of The Dow Chemical Company, USA) in Charleston, West Virginia, USA, and a group led by the late Professor Sir Geoffrey Wilkinson (later to become a winner of the Nobel Prize for Chemistry) at Imperial College London, UK, found independently that rhodium compounds containing organophosphines could catalyse the hydroformylation reaction at mild temperatures and pressures and with high selectivity to linear aldehydes \((2, 3)\). Wilkinson’s research was supported by the precious metal refiner and processor Johnson Matthey who supplied rhodium through a loan scheme inaugurated in 1955 that did much to foster university research in platinum group metals chemistry in the UK and overseas. Wilkinson later proposed that the rhodium complex responsible for catalysing hydroformylation reactions was \((\text{RhH(CO})(\text{PPh}_3)_3)\) and that high selectivities to normal aldehyde could be achieved using a large excess of phosphine ligand \((\text{for example (4, 5)})\). In the late 1960s Johnson Matthey and The Power-Gas Corporation decided to seek worthwhile opportunities to collaborate in research projects. The Power-Gas Corporation was a full services engineering and construction contractor of considerable international repute with a strong process engineering base, and had recently restructured its research and development activities meaning it was looking for process development projects. By early 1970, The Power-Gas Corporation had broadly confirmed in its Stockton-on-Tees laboratory Wilkinson’s proposition that high \(\text{n:i ratios}\) can be obtained with a large excess of phosphine. Further encouraged by preliminary process engineering evaluation work, The Power-Gas Corporation concluded in a 1970 letter to Johnson Matthey that a proposition for a low pressure propylene hydroformylation process using a homogeneous rhodium based catalyst would be “economically attractive when compared with what we currently know of processes as they are operated today”. By the middle of the year, Johnson Matthey and The Power-Gas Corporation had entered into a new, but far more wide-reaching collaboration aimed at developing a commercial, licensable hydroformylation process initially directed at the conversion of propylene to 2EH. The agreement was followed by co-ordinated programmes of further research, testing and studies of reaction kinetics in the laboratories of both companies. The Power-Gas Corporation did process scale-up work and process designs based on predicted optimum reaction conditions. Johnson Matthey investigated how it would manufacture commercial quantities of a suitable rhodium catalyst precursor and also economically manage the recovery of rhodium...
from used catalyst. Based on information describing Union Carbide Corporation’s activity found in literature searches, Johnson Matthey and The Power-Gas Corporation decided to visit Union Carbide Corporation in the USA in October 1970. It became evident from early discussions that Union Carbide Corporation had made significant progress on the experimental front but also that Wilkinson’s results complemented the Union Carbide Corporation findings. After confidential disclosures had been made between them, three independent companies in different, but overlapping, fields found they had mutual and complementary interests and contributions to make in developing potentially revolutionary chemical technology:

- Union Carbide Corporation: A chemicals producer having experience in the operation of cobalt oxo systems with their huge shortcomings. Union Carbide Corporation regarded the potential for rhodium with guarded excitement and in the early 1970s was awaiting market conditions to improve before deciding whether or not to develop a commercial rhodium process for its own use in a new oxo plant
- Johnson Matthey: A precious metal refiner and processor seeking opportunities to increase its product range and market reach
- The Power-Gas Corporation: A process engineering contractor with wide experience in chemical projects, international sales and marketing, which saw the potential relationship between oxo synthesis chemistry and the design and supply of plants for producing gases, notably hydrogen and carbon monoxide, on which it had a long history.

In August 1971, the parties agreed to collaborate to develop and market low pressure rhodium catalysed oxo technology for use with certain olefinic feeds.

Commercialisation and Start of Licensing

A collaborative process engineering and plant design exercise by Power-Gas Ltd (the new name of The Power-Gas Corporation) and Union Carbide Corporation resulted in even better economics of the propylene LP OxoSM Process than previous studies. An upturn in the market was followed by a decision by Union Carbide Corporation to build a plant at Ponce, Puerto Rico having a nameplate capacity of 136,000 tonnes per year of normal and iso-butyaldehydes to replace a cobalt catalysed plant. The new plant would use the homogeneous triphenylphosphine (TPP) modified rhodium catalyst discovered by Union Carbide Corporation and proposed by Wilkinson. Union Carbide Corporation took the precaution of building a pilot plant at Ponce so that operating data could be available during the construction of the main plant. The choice of location meant the catalyst could be tested using the commercial feedstocks that were to be used in full-scale operations. Data from the pilot plant tests calibrated the process engineering design of the commercial plant that was being carried out by Davy Powergas (another name changel) in London. Following its decision to build a butyraldehyde plant, Union Carbide Corporation decided to fast-track an ethylene hydroformylation project at Texas City, USA. The plant started operations in April 1975 ahead of the Ponce plant, which started in January 1976. The commissioning of both plants went smoothly and plant performance was better than expected. At Ponce, the rhodium catalyst operated at less than 20 bar and at a temperature between 90ºC and 100ºC, much milder conditions compared to cobalt. The isomer ratio, comfortably above 10, showed a more than threefold improvement and the lower reaction temperature resulted in significantly less byproduct formation. The product aldehyde was much ‘cleaner’, resulting in cost savings in product work-up and eliminating the effluent treatment measures that were needed during cobalt operations (6). With the Ponce plant continuing to operate well and very reliably, uncertainties about the robustness of the rhodium catalyst and the reliability of kinetic models developed in the laboratory abated. Projections of catalyst life and rhodium related costs were looking much more favourable than had been assumed. The expected large improvements in yield to desired product normal butyraldehyde, utility costs and environmental impact were confirmed. A new propylene oxo process was heralded that was far superior to the cobalt process Union Carbide Corporation had built and operated at Ponce – which shared many of the characteristics of the cobalt technology then being used by most of the world’s 2EH producers. The investment capital needed for a LP OxoSM Process plant was less than for a cobalt plant equivalent because of a simpler flow-sheet, cleaner product and other factors. The lower operating pressure meant in most cases expensive compression of the incoming synthesis gas could be avoided.

In 1977, Union Carbide Corporation, Davy Powergas Ltd and Johnson Matthey won the prestigious Kirkpatrick Chemical Engineering Achievement
Award “for outstanding group effort in new chemical engineering technology commercialised in the last two years”. In its dissertation the award sponsor, *Chemical Engineering*, stated the new LP OxoSM Process “yields a better product mix and also features low capital needs, effective use of feed, and negligible environmental impact” (7). With such a testimonial the Ponce plant became the target of numerous client visits and by the end of 1978 several companies had committed to build LP OxoSM process plants under licences granted by Davy Powergas in conjunction with Union Carbide Corporation.

Behind the successful commercialisation of the LP OxoSM Process, both Union Carbide Corporation and Davy had intensified their development work in laboratories in the UK and the USA. This was initially aimed at improving the LP OxoSM Process for propylene applications, then the single focus of market interest. An early effort was made in the laboratory by Union Carbide Corporation to find a way to mitigate the negative cost impact of what was termed ‘intrinsic’ catalyst deactivation. This was predictable deactivation attributable to the formation of clusters of monomeric rhodium species, as distinct from deactivation caused by external causes such as the presence of poisons in the feedstocks (6). Union Carbide Corporation’s efforts were to pay dividends (see later). Away from the laboratory, Davy process engineers had visited Union Carbide Corporation plants to gather design and operating data on the industrial scale conversion of butyraldehydes to alcohol end products. This led to the two companies agreeing the process basis of alcohol technology offerings sought by licensees wishing to use ‘Union Carbide Corporation and Davy’ technology for both the propylene hydroformylation step and the conversion of butyraldehydes to 2EH and possibly normal and iso-butanols. See Figure 1.

**The Early Licensed Plants**

In May 1980, the first two licensed plants to be completed went into operation – in Sweden and in the Federal Republic of Germany (*Figures 2 and 3*). These had a combined nameplate capacity of over 300,000 tonnes per year of butyraldehydes. Ten years on, nine further plants had started: three in Japan, two in China and plants in the Republic of Korea, the USA, Poland and France. By 1990, the LP OxoSM process was producing about 1.5 million tonnes per year of butyraldehydes, about half of this from seven cobalt ‘conversion’ projects. By 2000, no butyraldehyde was being produced by cobalt technology anywhere except in Russia, which remains so today. All the licensed plants used the TPP-modified rhodium catalyst giving typical n:i ratios of *circa* 10:1 to 12:1. The catalyst existed in the same medium as the feedstocks and liquid reaction products in stirred, back-mixed reactors. The plants used the ‘gas recycle flow-sheet’ employing *in situ* gas stripping to separate reaction products from catalyst to provide a simple and affordable process design. In Part I of a two-part article (6), Tudor and Ashley explained the thinking behind this choice of flowsheet. Central to this was uncertainty and concerns regarding catalyst deactivation and the containment or loss of expensive rhodium. Union Carbide Corporation operators found it easy to operate gas recycle reactors to achieve smooth, stable and dependable plant performance without undue concerns about the life or security of the rhodium catalyst, and gas stripping was accordingly adopted as the norm for all of the first generation of plants using the LP OxoSM Process. Laboratory work by Union Carbide Corporation on intrinsic deactivation had led to the discovery of a catalyst reactivation technique that could in effect reverse in days the effect of months of progressive activity decline because of rhodium clustering (6). Most of the early licensees

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**Fig. 1.** Schematic showing the production of oxo alcohols from propylene by the LP OxoSM Process
butyraldehyde plant built by Chemische Werke Huels at Marl, Federal Republic of Germany, taken in 1980

Fig. 3. The Davy, Union Carbide Corporation and Johnson Matthey start-up advisory team at the Marl plant, taken in 1980

included in their plants the equipment needed to achieve such catalyst reactivation and used it to good effect to carry out repeated reactivations on what was essentially a single rhodium catalyst charge. This drastically reduced the need for off-site rhodium recovery and the reprocessing of recovered rhodium to the catalyst precursor.

Liquid Recycle Opens Up New Horizons

In the first half of the 1980s, with original concerns about catalyst life and security largely behind them, Union Carbide Corporation and Davy turned their attention to a new flowsheet concept employing the ‘liquid recycle’ principle. This involved separating the reaction products from the catalyst solution in equipment outside the oxo reactor, using a proprietary design of vaporiser (8). By decoupling the hydroformylation reaction step from the physical process of product and catalyst separation, it became possible to choose a reaction regime to optimise the reaction conditions without, for example, having to use temperatures high enough to ensure effective product removal by gas stripping. Liquid recycle would also enable designers to significantly reduce the size of reactors, which for gas recycle had to be large enough to accommodate expansion of the liquid phase by the entrainment of bubbles from a large recycle gas flow. Such were its benefits that nearly all plants designed after the late 1980s used liquid recycle. Several of the earlier licensees, eager to exploit freed-up reactor volume, switched from gas to liquid recycle operation, in some cases nearly doubling the outputs of their oxo units from the same reactors.

Liquid recycle technology is today extensively used with enormous success across all applications of the LP OxoSM Process. It has provided designers greater scope for chemical engineering creativity when evaluating flow-sheet options for catalyst innovations and new non-propylene developments.

Polyorganophosphite-Modified Rhodium

The early 1990s saw the emergence of a more advanced polyorganophosphite-modified catalyst that would offer considerable appeal over its TPP counterpart, giving a much improved \( n:i \) ratio and other benefits (8). Polyorganophosphite-modified rhodium catalysts are very reactive and show good regioselectivity (selectivity to the straight chain aldehyde) in comparison with phosphine-modified catalysts such as TPP. Union Carbide Corporation overcame a major limitation of these new ligands, namely their instability in the presence of aldehydes, through the discovery and development of ligand stabilisation systems. Union Carbide Corporation first used the new ligand in 1995 in a new butanol plant at St Charles, Louisiana, USA, in the anticipation it would deliver an \( n:i \) ratio of about 30:1. The design of this plant, with certain improvements and
accumulated operating know-how became the basis of an advanced propylene LP OxoSM Process using polyorganophosphite-modified catalyst. Compared to TPP, it offered significant improvements to feedstock utilisation efficiency, selectivity to normal butyraldehyde, rhodium inventory and catalyst life. The success of technology, design and operating measures that Union Carbide Corporation had developed in the laboratory to overcome concerns about the stability of the polyorganophosphite-modified catalysts had pleased Union Carbide Corporation enormously, the catalyst at St Charles showing remarkable robustness and no signs of activity loss over a prolonged period, with hardly any rhodium usage. A significant gain (by about 7%) in yield to normal butyraldehyde and the reduced operator attention and plant down-time needed to operate the polyorganophosphite catalyst and manage its life cycle stood out as particular cost benefits compared to TPP.

Today, two Union Carbide Corporation owned butanol plants use the polyorganophosphite-modified catalyst using 'LP OxoSM SELECTORSM 30' technology, so named to reflect its proven capability of achieving an n:i ratio of at least 30:1. Seven of nine propylene plants so far licensed to use SELECTORSM 30 are in operation, including two examples of where existing licensees elected to retrofit the technology into TPP plants originally built many years earlier to use (retrospectively called) 'SELECTORSM 10' technology. Some of these plants now achieve n:i ratios greater than 30:1.

The Propylene LP OxoSM Process Today

The introduction of the polyorganophosphite-modified catalyst system in place of TPP has boosted propylene efficiencies and cut costs needed for seeing out the complete rhodium life cycle. In addition, various patented process enhancements have been introduced and the economics of practically all areas of the flow-sheet improved. Today the process is the source of about 70% of the world’s butyraldehyde and about 90% of licensed-in propylene oxo technology. Nearly all licensees convert butyraldehyde products to 2EH or butanols, and the aldehyde to alcohols part of the flow-sheet has been progressively improved through studies, development projects and catalyst programmes. These have improved the aldol condensation step, and for hydrogenation introduced improved catalysts and reactor designs. On the latter, major capital savings have been made by making more use of liquid phase hydrogenation in place of vapour phase which was used in earlier designs, eliminating the need for a cycle compressor and simplifying the reactors.

Non-Propylene Applications of the LP OxoSM Technology

By the early 1990s, shifts in markets and client enquiries called for a broader reach of possible applications for the LP OxoSM technology. In response, Union Carbide Corporation and Davy set new development trajectories that eventually resulted in new licence offerings for several non-propylene applications.

C7 and Longer Chain Alpha Olefins

The first non-propylene applications were two plants licensed and built by Sasol at Secunda in South Africa. Both of them produced alcohols from alpha olefins sourced from fuel product streams from Sasol’s coal based ‘Synthol’ Fischer Tropsch operations. The first started production in 2002 of C12–C13 ‘Safol®’ detergent alcohols using a C11–C12 olefin fraction as feed (Figure 4). The second was commissioned in 2008 for producing octanol from a 1-heptene fraction for subsequent conversion to co-monomer grade 1-octene. The designs of both plants resulted from development programmes by Davy at their Technology Centre in Teesside, UK, tightly tailored to Sasol’s requirements.

[Image of surfactant alcohol plant built by Sasol at Secunda, Republic of South Africa]
The detergent alcohol development, being the first, was the most demanding and at the outset two areas stood out as being crucial to a successful outcome. Both stemmed from the characteristics of the designated Sasol C11–C12 alpha olefins feed. Firstly, Davy’s lack of familiarity with such feeds and the uncertainty of how the Sasol feed would perform over time under hydrosyngmentation conditions suggested innovative techniques would be needed to identify and remove impurities that could harm the rhodium catalyst. Secondly, there would be a need for continuous purging of high boiling ultra-heavy reaction byproducts and this could be a source of significant rhodium ‘loss’ placing an undue burden on the economics of the process. This could be so despite Sasol engaging a third party precious metal refiner to recover and reprocess that rhodium off-site.

In the commercial plant, the feed was to be separated as a C11–C12 cut in a fractionation system before being treated primarily to remove impurities known to be detrimental to the oxo catalyst. Early screening tests done by Davy on the reactivity of representative samples of the pre-treated C11–C12 cut were promising, but it became evident that amongst the huge number of chemical constituents of the feed was at least one ‘bad actor’, possibly several, affecting the rhodium catalyst. It took considerable experimentation – some of it very conjectural – and then further testing in the mini-plant proving run (see below) to develop and prove a further pretreatment step for removing suspected offenders from the feed to acceptable levels. A need to address the extent of rhodium loss in the ultra-heavies’ purge stemmed from the high molecular weights of aldehyde products and the very high boiling, undesirable byproducts formed from aldehyde condensation and other reactions. This meant that whatever operating regime was adopted to effect the physical separation of desired aldehyde product from catalyst and reaction byproducts, rhodium catalyst would be present in the necessary ultra-heavies’ purge. This too got much attention during the mini-plant run and data collected on the extent of purging needed provided the basis of projections of the economic implications for the commercial plant.

Davy custom built a ‘mini-plant’ that was configured to simulate the entire olefin to alcohol processing scheme proposed by Davy when fed with Sasol supplied C11–C12 feed. This was used for a four-month demonstration run of the process, at the end of which Davy had done all the testing and evaluation considered necessary and had assembled sufficient data to provide a platform for the design of the commercial plant as well as projections of its performance, including the expected rhodium usage. Davy subsequently used data on reaction kinetics and other information obtained from the proving run to do the process design of a commercial plant with a throughput about 20,000 times greater.

Before the start-up of the Safol plant, Davy and Sasol discussed the potential benefits of a patented proprietary rhodium recovery process that was being developed by Davy. The proposition was a process that would remove and recover most of the largely deactivated rhodium present in the ultra-heavies purge stream before recycling that rhodium for reuse in the reaction system as active catalyst. Tests done by Davy later confirmed the effectiveness of the patented technology and a compelling economic case emerged for it being adopted by Sasol. Its use would eliminate much of the cost burden of having to engage a precious metal refiner to extract the rhodium in the purge. Sasol built the rhodium recovery process to work in conjunction with both the Safol plant and the new octanol plant, which have shared its large benefits since.

**Normal Butenes to 2PH**

In the 1980s the phthalate ester of the ‘workhorse’ C8 plasticiser alcohol 2EH – the ‘C8’ plasticiser di-octyl phthalate (DOP) (or di-2-ethylhexyl phthalate (DEHP)) – was coming under increasing regulatory pressure and polyvinyl chloride (PVC) plasticiser producers were paying increasing attention to higher molecular weight ‘C9’ and ‘C10’ phthalate plasticisers produced from C9 and C10 alcohols. These phthalates, containing 9 and 10 carbon atoms in each ester chain respectively, had better migration and volatility (fogging) properties and were seen as being more suitable for PVC uses where these and other properties, such as their good weathering behaviour, were especially required. A few oxo operators were manufacturing INA or IDA from butene dimers and propylene trimers – produced by oligomerisation of refinery light olefins – respectively. Market outlets for their corresponding phthalate plasticisers, diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP), had been established, and some of them were niche applications that could bear a price premium compared to DOP. Overall however, their usages were small compared to DOP partly because of the wide availability of the latter. DOP was also...
cheaper, largely because of the low production cost of 2EH compared to INA and IDA. With market interest in these higher molecular weight plasticisers increasing because of their perceived environmental, health and safety performance advantages, several companies, most of them 2EH producers, contacted Union Carbide Corporation and Davy with an interest in the production from normal butenes of 2-propylheptanol (2PH), a C10 alcohol. No 2PH was then being made industrially but Union Carbide Corporation and Davy saw the results of tests from a number of sources showing the promise of the phthalate ester of 2PH, DPHP, as a PVC plasticiser. DPHP displayed some of the performance characteristics of DINP and DIDP and was also seen as a potential substitute for DOP in some PVC applications.

Before these early signs of market interest, Union Carbide Corporation and Davy had anticipated the potential attractions of a 2PH process and had conducted hydroformylation trials in the laboratory with 1-butene using TPP-modified rhodium catalyst. The proposed 2PH process was similar to the 2EH process Davy had already licensed with a notable exception. Experimental work had shown the ratio of normal to branched valeraldehyde product achievable with TPP was about 20:1 compared to the 10:1 to 12:1 typical of propylene. The expensive aldehyde isomer separation step needed for 2EH production was therefore omitted before aldol condensation and hydrogenation steps and product 2PH refining. This meant the commercial 2PH product would actually contain 2-propylheptanol as the principal component (meaning >85%) in an isomeric mixture of C10 alcohols. And with butene feeds other than higher value co-monomer grade 1-butene then having transfer prices typically between 55 and 70% of the price of purchased propylene, early studies had indicated that 2PH produced from a refinery sourced raffinate-2 stream could be produced with a significant cost advantage over 2EH. This meant the commercial 2PH product would actually contain 2-propylheptanol as the principal component (meaning >85%) in an isomeric mixture of C10 alcohols. And with butene feeds other than higher value co-monomer grade 1-butene then having transfer prices typically between 55 and 70% of the price of purchased propylene, early studies had indicated that 2PH produced from a refinery sourced raffinate-2 stream could be produced with a significant cost advantage over 2EH. This TPP based technical platform formed the basis of the responses to early market interest in 2PH, but later on it was further enhanced following the introduction of more advanced proprietary ligands. Potential 2PH producers tabled C4 feed-stream specifications with significant concentrations of 1-butene and 2-butene (both cis- and trans-) as well as non-reactive butanes. The use of the much more reactive proprietary ligand in place of TPP meant the less reactive 2-butene component was now able to contribute significantly to product yield. It could therefore convert a much larger slice of the C4 feed-stream to 2PH, meaning higher normal butene conversion efficiencies while preserving relative isomer selectivities. Eventually, as the pull from PVC producers seeking greater versatility and improved long-term property retention in plasticisers intensified, several oxo producers instigated projects to build the first 2PH plants. In 2007, and after Davy Process Technology had become part of Johnson Matthey, Dow and Johnson Matthey licensed a normal butenes hydroformylation facility in Europe using a proprietary ligand modified rhodium catalyst system to produce mixed valeraldehyde from a C4 raffinate feed for conversion to 2PH. Following the successful start of this plant in 2009, a second licensed plant started in Asia in 2012. Soon afterwards two Chinese companies launched 2PH projects, both incorporating Dow and Johnson Matthey hydroformylation, aldol and hydrogenation technology. The first of these, with a capacity of 60,000 tonnes per year, successfully started operations in 2014. The second is being built by a licensee in the Shaanxi Yanchang Petroleum group for producing 80,000 tonnes per year of 2PH in tandem with butanols.

Since 2008, the global use of 2PH has increased more strongly than either of the other higher plasticiser alcohols INA and IDA. Its C10 phthalate ester has been widely accepted as a PVC plasticiser in Europe, the USA and China. By 2019, the global annual production of 2PH is expected to exceed 500,000 tonnes, of which over two thirds will be made using a butene fed LP OxoSM facility. Commercial C4 streams suitable for feeding to plants utilising the Dow and Johnson Matthey 2PH technology include raffinate streams from steam naphtha crackers: either raffinate 2 largely depleted of iso-butene, such as streams available from methyl tert-butyl ether (MTBE) plants or raffinate 3 rich in 2-butene, the latter being raffinate 2 after its more highly valued 1-butene component has been removed. Another possible C4 source is the waste 2-butene stream from a methanol to olefins plant. The very fact that a 2-butene stream can be an economically viable feed is proof of the high activity and versatility of the Dow and Johnson Matthey catalyst, especially when one considers the reactivity in hydroformylation of 2-butene (cis- and trans-) is as low as one fiftieth that of 1-butene. Other potential feed sources could conceivably be C4 olefinic fractions from Fischer-Tropsch plants. All of the above sources are likely to be cheaper than the olefins feeding 2EH, INA or IDA plants.
Where there is interest from a 2EH or butanols producer in making 2PH if market conditions suit, Johnson Matthey can design cost effective flexible LP OxoSM plants capable of using propylene and butene as separate feedstocks either continuously or intermittently.

The Alcohol Products from C3 and C4 Hydroformylation and their Uses

Butyraldehyde is mainly used in the production of 2EH and butanols. Of the two isomers, normal butyraldehyde is the more valuable, because unlike iso-butyraldehyde, it can be used to produce 2EH. Also, normal butanol usually offers solvent and derivative value superior to that of iso-butanol. A small outlet for normal butyraldehyde is trimethylolpropane used as a building block in the polymer industry.

Large quantities of 2EH are esterified with phthalic anhydride to produce the PVC plasticiser DEHP, often referred to as DOP. While strong demand for DEHP in Asia has sustained a global growth rate of about 2.5%, regulatory pressures have meant Western Europe and the USA now together account for less than 5% of world usage, with demand in the former practically zero. In recent years increasing amounts of 2EH have been used to produce di(2-ethylhexyl) terephthalate (DEHTP) or diocytol terephthalate (DOTP), using dimethyl terephthalate or purified terephthalic acid as the other primary input. Not being an ortho-phthalate plasticiser like DEHP, DOTP has a growing use as a replacement for DEHP, in particular, without any negative regulatory pressure. Increasing amounts of 2EH are being esterified with acrylic acid to produce 2-ethylhexylacrylate, used in the production of homopolymers, copolymers for caulks, coatings and pressure-sensitive adhesives, paints, leather finishing and textile and paper coatings. 2EH is also used to produce 2-ethylhexyl nitrate, a diesel fuel additive and also lubricant additives.

Normal butanol is used industrially for its solvent properties, but by far its largest use is as an industrial intermediate. Butyl acrylate is widely used in the production of homopolymers and copolymers for use in water-based industrial and architectural paints, enamels, adhesives, caulks and sealants, and textile finishes. Butyl methacrylate’s uses include the manufacture of acrylic sheet, clear plastics, automotive coatings and other lacquers. n-Butyl acetate is an industrial solvent and artificial flavourant and is used in various coatings, floor polishes, textiles and as a gasoline additive.

Iso-butyraldehyde has a multitude of uses as an intermediate – to name a few, pharmaceuticals, crop protection products and pesticides. A key outlet is neopentylglycol (NPG) or 2,2-dimethyl-1,3-propanediol, produced by the aldol condensation of iso-butyraldehyde and formaldehyde. NPG is mainly used as a building block in polyester resins for coatings, unsaturated polyesters, lubricants and plasticisers. Iso-butanol has similar properties to normal butanol and may be used as a supplement or replacement for it in some applications. More specific uses include industrial coatings and cleaners, de-icing fluids, flotation agents, textiles and as a gasoline additive. It is also an intermediate for agricultural chemicals and for glycol ethers and esters. An outlet for iso-butyric acid, the oxidation product from iso-butyraldehyde, is a monoester of trimethyl pentanediol which has a use as a coalescing agent for latex paints.

The main component of commercially produced 2PH is 2-propyleheptane-1-ol derived from the normal valeraldehyde present in the product from the hydroformylation of normal butenes. Other lesser components are 4-methyl 2-propyl 1-hexanol and 5-methyl 2-propyl 1-hexanol, derived from branched aldehyde isomers in the aldol condensation feed. The phthalate ester of 2PH is di-(2-propylheptyl) phthalate as its principal component, giving the plasticiser the generic name DPHP. It is a versatile PVC plasticiser with impressive weathering and low fogging properties making it particularly suitable for tough outdoor uses such as roofing membranes and tarpaulins, automotive, wires and cables and cable ducts.

LP OxoSM Technology Today

In 2001 Union Carbide Corporation became a wholly owned subsidiary of The Dow Chemical Company. In 2006 Davy Process Technology became part of Johnson Matthey. The process development and marketing collaboration today between Johnson Matthey and Dow Global Technologies, Inc, has its roots in the historic 1971 agreement between Union Carbide Corporation, Johnson Matthey and The Power-Gas Corporation, but now spans more olefins giving it a broader market reach. To date, 53 LP OxoSM technology projects have now been licensed, six of them for non-propylene applications. The collaboration is as close and focused as it ever was, and the resolve...
of Dow and Johnson Matthey is to sustain the place for LP OxoSM Technology as the premier oxo technology in the world through safe, innovative, low environmental impact and cost advantaged technical solutions, forever pushing the boundaries of the technology even further. Germane to many further developments will be the role for advanced ligand systems that have already boosted propylene and butene efficiencies and cut costs needed for seeing out the complete rhodium life cycle. Some new developments are already at the stage where they can be licensed for commercial use.

Examples of New Developments

Propylene \( n:i \) Ratio Flexibility

In those instances where operators are seeking a wide flexibility in the butyraldehyde isomer ratio, ‘Variable SELECTORSM Technology has been developed that enables the \( n:i \) ratio to be adjusted on-line within the range of 2:1 and 30:1 to suit market conditions by adjusting operating parameters.

INA from Butene Dimer and, the “All Singing, All Dancing” Oxo Plant?

The global plasticiser market is currently about 8 million tonnes per year and is growing at around 3 to 4% per year. The market share of the C9 phthalate DINP has increased in recent years and the consequential growing global demand for INA, currently about 1.4 million tonnes per year, is being met by new projects announced for Asia. A first INA plant in China started production in 2015. The superior migration and fogging properties and more favourable toxicological profiles of C9 and C10 phthalate plasticisers compared to DEHP should ensure sustained growth in the use of both DINP and DPHP.

To meet the growing demand for INA, Dow and Johnson Matthey have developed a new low pressure rhodium catalysed INA process in pilot plants at Dow and Johnson Matthey (see Figure 5) using commercially produced butene dimer feedstock. One of its key attributes is it can be retrofitted to existing 2EH or butanol plants built by licensees of the LP OxoSM Process, creating for them and for new licensees the opportunity to run flexible product oxo plants to best exploit market conditions. And with the 2PH process being similarly retrofittable, one can now envisage an oxo producer having flexible access to say, refinery sourced C3 and C4 olefins, building a single, highly flexible, LP OxoSM facility using advanced, dependable technologies to selectively deliver any and all of 2EH, INA and 2PH – as well as butanols. Collectively, the three higher alcohols supply more than two thirds of a very diverse plasticiser market.

Fig. 5. Johnson Matthey oxo pilot plant for INA process development at Stockton-on-Tees, UK

References

The Authors

Richard Tudor retired from Davy Process Technology in 2011 as Vice President, Oxo Business following an involvement of over 35 years in the company’s oxo licensing activities, initially in a technical capacity becoming Process Manager. His first commercial role was a broad remit as the company’s Licensing Manager, following which he ran the oxo business for over 20 years. He graduated in Chemical Engineering from the University of Manchester, UK, and is a Fellow of the Institution of Chemical Engineers and a former member of the Licensing Executives Society. Between 2011 and 2016 he continued working for Johnson Matthey as licensing consultant.

Atul Shah is Licensing Development Director at Johnson Matthey, London, UK. He has worked on many oxo alcohol projects globally and has played a leading role in Johnson Matthey’s oxo alcohols licensing business for over 30 years, both in technology and business development. Atul graduated from the University of London with a BSc (Eng) in Chemical Engineering and joined Davy in 1984, which became part of Johnson Matthey in 2006. He holds an MBA and is a Fellow of the Institution of Chemical Engineers.