The development of the Low Pressure (LP) Oxo Process from initial laboratory experiments to the position today in which 13 commercial plants are operating or under construction throughout the world is a classic story of chemical innovation and its application on a large industrial scale.

The technical and commercial success of the process has been brought about by close collaboration between three companies operating in widely diverse business areas and on both sides of the Atlantic — Union Carbide Corporation, Johnson, Matthey & Co., Ltd. and Davey McKee (London) Ltd.

Many people from all three of the “Tripartite” companies — people representing all the chemical, engineering and commercial disciplines — have played a part in achieving the prominence which the LP Oxo Process has attained today.

The background

More than 40 years ago, the German chemist Otto Roelen, working in the laboratories of Ruhchermie 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 essentially an aldehyde with very little ketone formation, and the reaction was renamed “Hydroformylation”. In current practice, both names are used, but “oxo” is clearly the more convenient and more internationally recognisable name.

The process was commercialised in Germany during the early 1940s, and has been widely used throughout the world since the late 1940s. The major application of the process is in the production of alcohols, produced from the corresponding aldehydes by hydrogenation, and today a range of
<table>
<thead>
<tr>
<th>Starting Olefin</th>
<th>Product(s)</th>
<th>End use applications</th>
</tr>
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<tbody>
<tr>
<td>Ethylene ($C_2$)</td>
<td>n-Propyl alcohol, propionic acid</td>
<td>Solvent, Printing inks, Grain preservative, Agricultural chemicals</td>
</tr>
<tr>
<td>Propylene ($C_3$)</td>
<td>Butyl alcohols, Butyrodehydes, Octanol (2-ethyl Hexanol)</td>
<td>Solvents, Paints, Adhesives, Plasticisers, Agricultural chemicals</td>
</tr>
<tr>
<td>Butene ($C_4$)</td>
<td>$C_8$ alcohols, $C_{10}$ alcohols</td>
<td>Lubricants, Catane-improvers, Oil additives, Metal extractive agents, Plasticisers</td>
</tr>
<tr>
<td>Pentene ($C_5$)</td>
<td>$C_6$ alcohols</td>
<td>Oil additives, Plasticisers</td>
</tr>
<tr>
<td>Hexene ($C_6$)</td>
<td>$C_7$ aldehydes</td>
<td>Fragrances</td>
</tr>
<tr>
<td>$C_{7-11}$</td>
<td>$C_8-C_{12}$ alcohols</td>
<td>Plasticisers</td>
</tr>
<tr>
<td>$C_{11-10}$</td>
<td>$C_{12}-C_{20}$ alcohols</td>
<td>Detergents</td>
</tr>
</tbody>
</table>

J. L. Stewart, B. Sc., ARTC, C. Chem., MIIC, Ph.D.

We greatly regret to report that Dr. J. L. Stewart, the author of this article and a man closely identified for more than 10 years with the successful development of the technology it describes, died just a few weeks before its publication.

Jim Stewart was an Associate Director with Davy McKee (London) Ltd. He was Manager of the LP Oxo Business Area, and as such was responsible, primarily to Davy McKee but also to the Tripartite as a whole, for the terms of LP Oxo Licence Agreements. Jim joined the then Power Gas Corporation Ltd. in 1969, and was Business Development Manager prior to his involvement in LP Oxo.

A tribute to him from some of his principal colleagues appears at the end of the article.

Table 1: Uses for Oxo products

Prior to the existence of oxo technology, 2EH was produced from acetylene or ethylene by a series of steps yielding successively acetaldehyde, crotonaldehyde and normal butyraldehyde. The oxo reaction enabled normal butyraldehyde to be produced in one step from propylene. Normal butyraldehyde can readily be converted to a $C_4$ aldehyde which on hydrogenation yields 2EH.

Total installed capacity throughout the world to produce butyraldehydes using PVC, and produced by the esterification of phthalic anhydride with 2EH. Table 1 summarises the principal applications for oxo products.

Alcohols containing between 3 and 20 carbon atoms is produced on a large scale using oxo technology. The major uses for these alcohols are as solvents and as intermediates for the production of plasticisers, lubricants, detergents and other surfactants. The production of plasticiser alcohols is the major application of oxo technology, and of these, 2-ethylhexanol (2EH) is the most important. Plasticisers are added to polymers to give a product which is more flexible than the polymer alone, and most plasticisers are esters formed from an alcohol and a dibasic acid or acid anhydride. The "workhorse" of the plasticiser industry in most countries of the world is dioctylphthalate (DOP), widely used in the production of flexible...
selectivity could be achieved to the straight-chain (normal) aldehyde product. Professor Wilkinson's work was undertaken with the support of Johnson, Matthey & Co. Ltd., a UK company long established in precious metal refining and processing. Johnson Matthey approached Davy McKee (then The Power Gas Corporation Ltd.) and proposed that the two companies joined forces to develop and exploit the rhodium-catalysed process.

At about the same time, and quite independently of the research work in the U.K., Union Carbide Corporation research personnel at South Charleston, West Virginia, had also established that rhodium co-ordination complexes in solution showed promise as hydroformylation catalysts at low pressure to give a product containing a high proportion of the straight-chain aldehyde product. In 1970, Union Carbide, who were then operating a number of oxo plants using cobalt catalyst at high pressure, decided that they would not themselves install a rhodium catalysed process on a commercial scale because of the depressed state of the oxo alcohols market at that time.

Johnson Matthey and Davy McKee became aware of Union Carbide's work in the area when the first patents were published and the three companies agreed to meet to determine whether a joint development programme might be more effective than proceeding independently. These meetings resulted in the signature by the three companies of an agreement in 1971 (the Tripartite Agreement). The Agreement foresaw three successive phases of collaboration. In the first phase, each of the parties was to disclose in confidence to the others the results of its work to date. If all three parties were then willing to continue, the second phase was to be the development of definitive design data for a commercial scale plant to produce butyraldehydes from propylene, together with an assessment of the techno-economic merits of the new process relative to the cobalt catalysed technology then existing. The third phase would be to undertake a campaign to license the process on the commercial scale.

The tripartite

In the mid 1960s research work was being carried out in many industrial and academic laboratories with the objective of improving the efficiency of the oxo process as then in use commercially on a large scale. Several research projects were investigating the potential of catalyst systems other than those using cobalt – the only oxo catalyst in use industrially at that time – and particular attention was focussed on another metal in Group VIII of the Periodic Table, rhodium.

Professor Geoffrey Wilkinson (now Sir Geoffrey Wilkinson, Nobel Laureate) at Imperial College, London, showed that rhodium could be highly active as a hydroformylation catalyst at lower pressure than was possible with cobalt, and that, by using a suitable co-ordination complex of rhodium with an organo-phosphorus ligand, high oxo technology exceeds 3 million metric tonnes per year.
terms which reflected the economic advantage which the rhodium process offered.

By 1973, process design and optimisation studies had shown that a viable commercial process was possible which offered substantial savings in both capital and operating costs relative to existing technology. This information together with an improved market for oxo alcohols, led Union Carbide to decide to build a plant to produce 300 million lb/year of butyraldehydes at their Ponce, Puerto Rico site. Union Carbide installed a pilot plant at Ponce to obtain data specific to the qualities of propylene and synthesis gas available there and to provide information as an input to the commercial plant design being carried out by Davy McKee. In addition, Union Carbide decided to build a plant at Texas City, Texas to produce propionaldehyde from ethylene using the same rhodium catalysed process.

In January 1976, the Ponce plant started up and the LP Oxo Process to produce butyraldehydes became a commercial reality. Plant start-up was trouble-free and design output and feedstock efficiencies were rapidly attained. Relative to the high pressure cobalt catalysed plant which the new unit replaced, plant operation proved to be extremely simple and reliable. Excluding interruptions for reasons external to the LP Oxo plant (e.g. shortage of propylene or synthesis gas; power failure), the plant was available for operation for more than 99% of the first 12 months.

In 1977, Union Carbide, Johnson Matthey and Davy McKee jointly received the Kirkpatrick Award for “outstanding group effort in new chemical engineering technology” following the development and commercialisation of the LP Oxo Process.

The technology

The aldehyde product from the Oxo reaction contains one more carbon atom
than the starting olefin and, with propylene as the feedstock, the product is a mixture of normal and iso-butyraldehydes as shown in Figure 1. Such a mixture can readily be hydrogenated and fractionated to give normal and iso-butanol, or fractionated to give normal butyraldehyde which can be converted into 2-ethylhexanol via aldolisation and hydrogenation as shown in Figure 2.

Conventional Processes
The process based on Roeland's original work uses a cobalt catalyst in solution and operates at pressures in the range 250–350 atmospheres and at temperatures in the range 140–180 deg. C. The active catalyst is a cobalt hydridocarboxyl HCo(CO)₅ and the operating conditions chosen are necessary because of catalyst instability at lower pressures. Under these conditions, several side reactions take place with loss of propylene to propane and to aldehyde condensation products. Some hydrogenation of aldehyde to alcohol occurs in the oxo reactor and this leads to the formation of further by-products in the form of acetals and esters. In addition to the loss of valuable feedstock to these unwanted by-products, the separation and purification of the products is a difficult and expensive operation. Using propylene as feedstock, the ratio of normal to iso-products is about 3:5:1.

In a modification of the process, the catalyst used is a cobalt hydridocarbonyl trialkylphosphine HCo(CO)₅PR₃. This enables the operating pressure to be reduced to 40–50 atmospheres but at the higher temperature of 180–200 deg. C. These conditions significantly increase the ratio of normal to iso-products, but this is offset by higher production of alcohols in the reactor and greater loss of propylene to propane.

In both these versions of the cobalt-catalysed process, the separation of the products from the catalyst and the recovery of cobalt in a form suitable for re-use is a complicated and relatively expensive operation.

LP Oxo Process
A flowsheet of the process is shown in Figure 3. The process is simple, uses few items of equipment and operates at modest temperature and pressure. Incoming synthesis gas, without the need for compression downstream of the reformer or partial oxidation plant, is used to strip unreacted propylene and gaseous inerts dissolved in the liquid product. The resultant gas stream, together with propylene feedstock in the vapour phase, enters the base of the oxo reactor through a distributor. The reactor contains a solution of rhodium catalyst and triphenylphosphine (TPP) in butyraldehyde and higher boiling aldehyde condensation products. The fact that the catalyst and TPP are soluble in butyraldehyde means that no extraneous solvent is necessary.

Reaction takes place in the homogeneous liquid phase and butyraldehyde product leaves the reactor as vapour. Additionally, the small amount of higher molecular weight byproducts are also removed as vapour at their rate of formation. The reaction is exothermic, part of the heat of formation being removed by vapourisation of the liquid and part by exchange with cooling water in a closed system.

The product vapour is condensed and separated from unreacted propylene and gaseous inerts which are compressed and recycled to join the synthesis gas stream. The liquid product, following stripping of most of the dissolved gases by incoming synthesis gas, is fractionated to remove the final traces of dissolved gaseous inerts and propylene.

This gas stream is compressed and recycled to the oxo reactor after removal of a purge stream to prevent the build-up of inerts in the system. Separation and purification of normal and iso-butyraldehydes is carried out by fractionation (not shown).

The LP Oxo Process is radically different from conventional oxo technology:
- in catalytic system
- in operating conditions
in product pattern
in raw material efficiencies
in simplicity of design and operation.

The key features of the process stem from the use of rhodium as the catalytic metal in the form of a co-ordination complex with carbon monoxide and triphenylphosphine. The activity and stability of the active catalyst species are such that the oxo reaction can be carried out at much lower pressure (ca. 20 atmospheres) and temperature (ca. 100 deg. C) than is possible with cobalt catalysed processes. This offers substantial savings in investment and operating costs.

The rhodium catalysed reaction is more selective in forming butyraldehydes from propylene than is the case using cobalt — there is very little coproduction of butanols in the LP oxo reaction and consequently insignificant formation of acetol and ester impurities. The loss of propylene by hydrogenation to propane is minimal. The product is essentially a mixture of normal and isobutyraldehydes together with a small amount of higher molecular weight by-products. This leads to simplified and thus less expensive separation and purification of the products. The absence of significant co-production of butanols is advantageous when the only desired end product is 2EH — in cobalt processes, coproduction of butanols is inevitable.

The catalyst solution contains a substantial excess of triphenylphosphine. As described later, the effect of excess TPP is to favour the formation of normal rather than isobutyraldehyde. Typically normal to iso ratios of 10:1 are achieved commercially. This has a major impact on the economic attractiveness of the process for two reasons:
(i) normal butanol as a solvent is preferred to iso-butanol and commands a higher price, and
(ii) iso-butyraldehyde cannot undergo aldolisation/hydrogenation to 2EH.

The quantity of iso-butyraldehyde produced by conventional cobalt technology has invariably exceeded the
available market outlets and large quantities of iso-butyraldehyde have as a consequence been used as fuel or have been recycled as feedstock to the synthesis gas producing plant. Overall, the selectivity of the rhodium catalyst to butyraldehydes at high normal to iso-ratio has a profound effect on consumption of propylene and synthesis gas per unit of useful product.

The active catalyst is a co-ordination complex of rhodium hydridocarbonyl modified with triphenylphosphine. The reaction sequence with propylene is even now not fully known, but is certainly that shown in Figure 4. Rhodium is introduced to the oxo reactor in the form of a solution of a stable crystalline compound dissolved in normal butyraldehyde and complex A is formed in the presence of carbon monoxide and triphenylphosphine. Under reaction conditions, complex A first adds a molecule of propylene and then, following a series of structural rearrangements and the addition of a molecule of hydrogen, butyraldehyde is released with the formation of complex F. Addition of a molecule of carbon monoxide regenerates complex A.

A key feature of the process is that the reaction is carried out in the presence of a large excess of triphenylphosphine. This results in the formation of complex A containing 2 TPP molecules, in preference to an alternative structure containing only a single TPP molecule.

It is likely that the predominance of complex A is the main factor which enables a high ratio of normal to iso-butyraldehyde to be produced, due to the steric effect of the relatively bulky TPP molecules inhibiting the bonding of a propylene molecule other than via the terminal carbon atom.

The industrial use of a catalyst system containing a metal as expensive as rhodium — currently priced at US $19,000 per kg (more expensive than gold at current prices) — obviously makes economic sense only if certain key criteria are met:

(i) the quantity of rhodium “in process” must be as small as possible to minimise initial investment and working capital cost;

(ii) the amount of rhodium lost during plant operation must be minimal;

(iii) the active life of the catalyst must be as long as possible; and

(iv) the method of treating deactivated catalyst and its conversion back to an active catalytic form must be carried out at minimum cost with minimum losses as rapidly as possible.

All these requirements are satisfied by the LP Oxo Process as a result of the initial and more recent process.
development work. The activity of the catalyst is such that the rhodium concentration in the reactor is measured in parts per million. The design of entrainment separators removing liquid from product vapour leaving the reactor is such that operating experience has shown the carry-over of rhodium in the product to amount to a few parts per billion. The operating life of a catalyst charge is typically 15–20 months before replacement is necessary.

In summary, the LP Oxo Process represents a significant technical and economic advance over prior technology, with substantial savings in investment and operating costs. The process makes efficient use of increasingly expensive primary hydrocarbon resources, requires fewer operating and maintenance personnel and is environmentally “clean”. The only discontinuous waste streams are small quantities of gas and liquid which are usable as high-grade fuel. Figure 5 presents a comparison of the LP Oxo Process with the older cobalt-catalysed oxo technology.

<table>
<thead>
<tr>
<th></th>
<th>HP Cobalt</th>
<th>LP Oxo</th>
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<tbody>
<tr>
<td>Reaction pressure (ATM)</td>
<td>250–350</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>140–180</td>
<td>ca.100</td>
</tr>
<tr>
<td>Product n : i ratio</td>
<td>3.5 : 1</td>
<td>10 : 1</td>
</tr>
<tr>
<td>Propylene consumption</td>
<td>965</td>
<td>720</td>
</tr>
<tr>
<td>(kg per 1000 kg n-Butyraldehyde)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syn gas consumption</td>
<td>1100</td>
<td>722</td>
</tr>
<tr>
<td>(Nm3 per 1000 kg n-Butyraldehyde)</td>
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</tbody>
</table>

The licensees

By the terms of the Tripartite Agreement, one of the tasks allocated to Davy McKee is the negotiation and signature of LP oxo licence agreements on behalf of itself, Union Carbide and Johnson Matthey. To date, 10 licences have been granted to 9 companies throughout the world.

As early as April 1975, before the Union Carbide plant at Ponce was in operation, a licence to use the process was granted to Berol Kemfi AB in Sweden. The plant, now owned by Beroxo AB, a company jointly set up by Berol Kemfi and Statsforetag and located at Stemungsund on the west coast of Sweden, started up in May 1980 and has since successfully completed a 72-hour performance test. All guarantees pertaining to capacity, product quality and raw materials and utilities consumptions were passed.

The second licence was granted to Chemische Werke Hüls for a plant to be located at Marl in Germany. The LP oxo plant replaced a high pressure cobalt-catalysed process operated by Hüls and the conversion from cobalt- to rhodium-catalysed process operation by one of the world's largest producers of butyraldehydes underlines the significant advantages offered by the LP Oxo Process. The Hüls plant started up in June 1980 and 15 days after propylene was first introduced to the reaction section, a 72-hour performance test was successfully completed.

Advisory teams of chemists and chemical engineers representing each of the Tripartite companies were present at the start-up and performance test of both the Beroxo and Hüls plants.

Since that time four further licensees' plants have been successfully started up. These are owned by the following companies:
- Korea General Chemical Corporation, Republic of Korea
- Tonen Sekiyukagaku Kabushika, Japan
- Kyowa Yuka Co. Ltd., Japan
- Chisso Petrochemical Corporation, Japan

Licences have also been granted to the following companies, whose plants are at various stages of design and construction:
- China National Technical Import Corporation, People's Republic of China (2 plants)
LP Oxo plant of Chemische Werke Hüls AG at Marl, Germany.

Dr. J. L. Stewart
Many readers will already know that Dr. J. L. Stewart died peacefully at home recently after six months illness. Those who came into regular contact with him in the course of business came to have a high regard for him as a dedicated and meticulous worker whose common sense and dry humour made him a pleasure to work with. Many a problem was solved when he correctly pointed out the basic principle involved and insisted upon observing it. This regard was heightened after he became terminally ill. He approached this “inconvenience” in his usual manner, more concerned for the effect on others than any injustice to himself. From issuing firm guidance on the conduct of his own funeral to continuing interest in the latest Oxo plants and leaving his affairs in order, with no complaint of pain but rather insensitivity with his own weakness, he set an example which will not easily be forgotten.

The esteem for him by his associates was proved in full by the tens of messages of condolence from all parts of the world. These were a comfort to the wife and two daughters he left who have all our sympathy.

- Polimex-Cekop, People’s Republic of Poland
- Tenneco Chemicals Inc., U.S.A.

The total nameplate capacity for butyraldehyde licensed to date is in excess of 1.1 million metric tonnes per year. Negotiations are in progress with several other potential licensees. In addition to these licensee plants, Union Carbide have increased their own LP Oxo capacity with two additional plants located at Texas City, Texas.

The future
Technology advances inexorably, albeit as the result of conscious efforts by many people of all the scientific and engineering disciplines. No process technology, however much an advance over older methods, can maintain its competitive edge indefinitely unless it continues to develop and improve.

Today a substantial number of people in all three of the Tripartite companies are engaged in the study, optimisation and development of LP Oxo technology. This work is in two main areas:

(i) Developments relating to the design and operation of the process as at present used commercially. Already, several significant improvements have been devised and tested which lead to further economies in investment and operating costs compared with the process as originally flowsheeted.

(ii) Developments designed to extrapolate the existing low pressure rhodium-catalysed process to treat olefin feedstocks other than ethylene and propylene. Design data exist for a plant to convert butenes to valeraldehyde and by aldolisation/hydrogenation to a C10 alcohol, directly analogous to the propylene - 2EH route.

Laboratory work and process development are under way which will lead to the use of LP Oxo technology to produce other industrially important alcohols.