

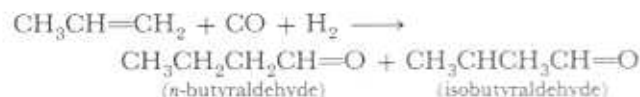


## Low-pressure oxo process yields a better product mix

New oxo chemistry developed by Union Carbide, Davy Powergas and Johnson Matthey also features low capital needs, effective use of feed, and negligible environmental impact.

□ A switch from the conventional cobalt-based to a new rhodium-based catalyst has greatly enhanced the oxo process. For developing and commercially implementing the technology that underlies this switch, Union Carbide Corp., Davy Powergas Ltd. and Johnson Matthey and Co. Ltd. (U.K.) win the 1977 Kirkpatrick Chemical Engineering Achievement Award.

Called the Low Pressure Oxo (LPO) process, the improved method is embodied in a 300-million-lb/yr propylene-to-butyraldehyde plant that Union Carbide started up at Ponce, Puerto Rico, early in 1976. Like any other oxo plant, it makes aldehyde by a hydroformylation reaction of olefin with a mixture of carbon monoxide and hydrogen (i.e., water gas, or synthesis gas):



But the use of a triphenylphosphine-modified rhodium catalyst, instead of the conventional cobalt hydrocarbonyl or the sometimes-employed tributylphosphine-modified-cobalt version, leads to a host of technical and economic attractions.

The most important of these is the product mix from

the plant. Manufacture of butyraldehyde from propylene, the main commercial application of oxo chemistry, has for many years been plagued by an unfortunately low ratio of valuable *n*-butyraldehyde to less-desirable isobutyraldehyde in the product mix. When homogeneous cobalt hydrocarbonyl catalyst is used, this ratio has been 3:1 to 4:1, according to Union Carbide. The LPO process, by contrast, allows ratios of 10:1 or greater. And it does so without requiring the relatively high temperature needed when cobalt is modified with tributylphosphine to improve its isomer ratio.

Hand in hand with the high yield of *n*-butyraldehyde in the new process is a very low incidence of the other side reactions prevalent with the cobalt-catalyzed process. These include: hydrogenation of propylene to propane; hydrogenation of butyraldehyde to butanol; reactions of the butanols to yield esters and acetals; and formation of heavy aldehyde-condensation products. A key reason is that the LPO process operates at 80 to 120°C, whereas conventional cobalt-catalyzed manufacture requires 140 to 180°C, and the tributylphosphine-modified-cobalt approach needs 180 to 200°C.

More significant than the temperature difference, however, is the low pressure at which the LPO process operates: only 200 to 400 psi, in contrast with 4,000 to 5,000 psi and 800 to 1,500 psi for the two cobalt-based

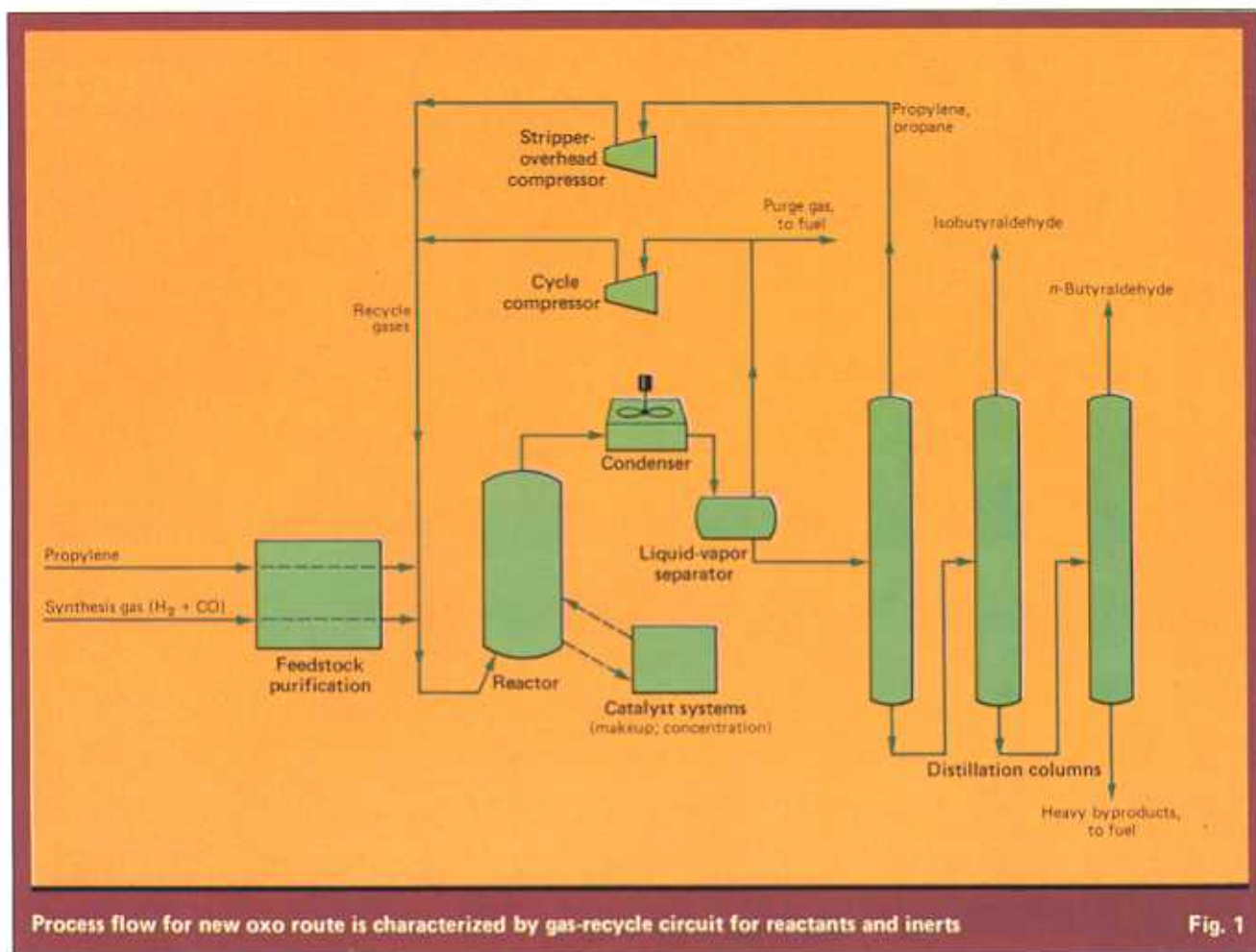


Fig. 1

versions. The resulting saving in capital, operating and maintenance costs is obvious. For instance, there is no need to compress the synthesis gas. This, together with the fact that only minimal distillation is needed in the process, helps keep energy requirements likewise low.

Environmental impact is negligible, points out Union Carbide. The process has only two effluent streams: a liquid containing the minor output of heavy byproducts, and a gas stream. Both can be used as fuel.

The triphenylphosphine-modified rhodium catalyst not only brings about all these advantages; there are also some other attractions that directly center upon the catalyst system itself. The LPO flowsheet was designed to minimize in-process rhodium inventory and losses, and there is no need for a catalyst-recycle system. If the catalyst is accidentally poisoned or deactivated, the rhodium can be recovered with little loss, using techniques developed by Johnson Matthey.

In the conventional oxo process, by contrast, the cobalt hydrocarbonyl is generated at high pressure, either outside or inside the hydroformylation reactor. Because the catalyst is volatile, and stable only in the presence of carbon monoxide, it must be decomposed before the reaction product is recovered. The cobalt-catalyst recovery cycle is traditionally cumbersome and costly.

## Process flow

The flow diagram shows the LPO process to be both elegant and simple (Fig. 1). The synthesis-gas and propylene streams are first purified via proprietary solid-adsorbent techniques developed by Union Carbide and Davy Powergas, to remove catalyst poisons such as hydrogen sulfide or carbonyl sulfide. Then they join with recycle gas, and the combined stream enters the base of the hydroformylation reactor through a distributor. Here, the rhodium-based catalyst is present in a homogeneous liquid phase, dissolved together with free triphenylphosphine in a mixture of butyraldehyde and heavy byproducts from aldehyde trimerization.

The discovery that these aldehyde-condensation products are good solvents for the catalyst was important to the development of the commercial process. It allows the unit to operate without need for other solvents, and forestalls the need for a catalyst-recycle step.

Because the catalyst is very active, only a low rhodium concentration of several hundred parts-per-million is needed. The triphenylphosphine level is kept much higher—typically, several percent by weight. This favors production of the *n*- isomer, as explained below.

The gaseous reactants pass from small bubbles (with high interfacial area) into the liquid phase, where reac-



Butyraldehyde plant employing low-pressure oxo process at Ponce, Puerto Rico, started up extremely smoothly during early 1976. Figs. 2 and 3

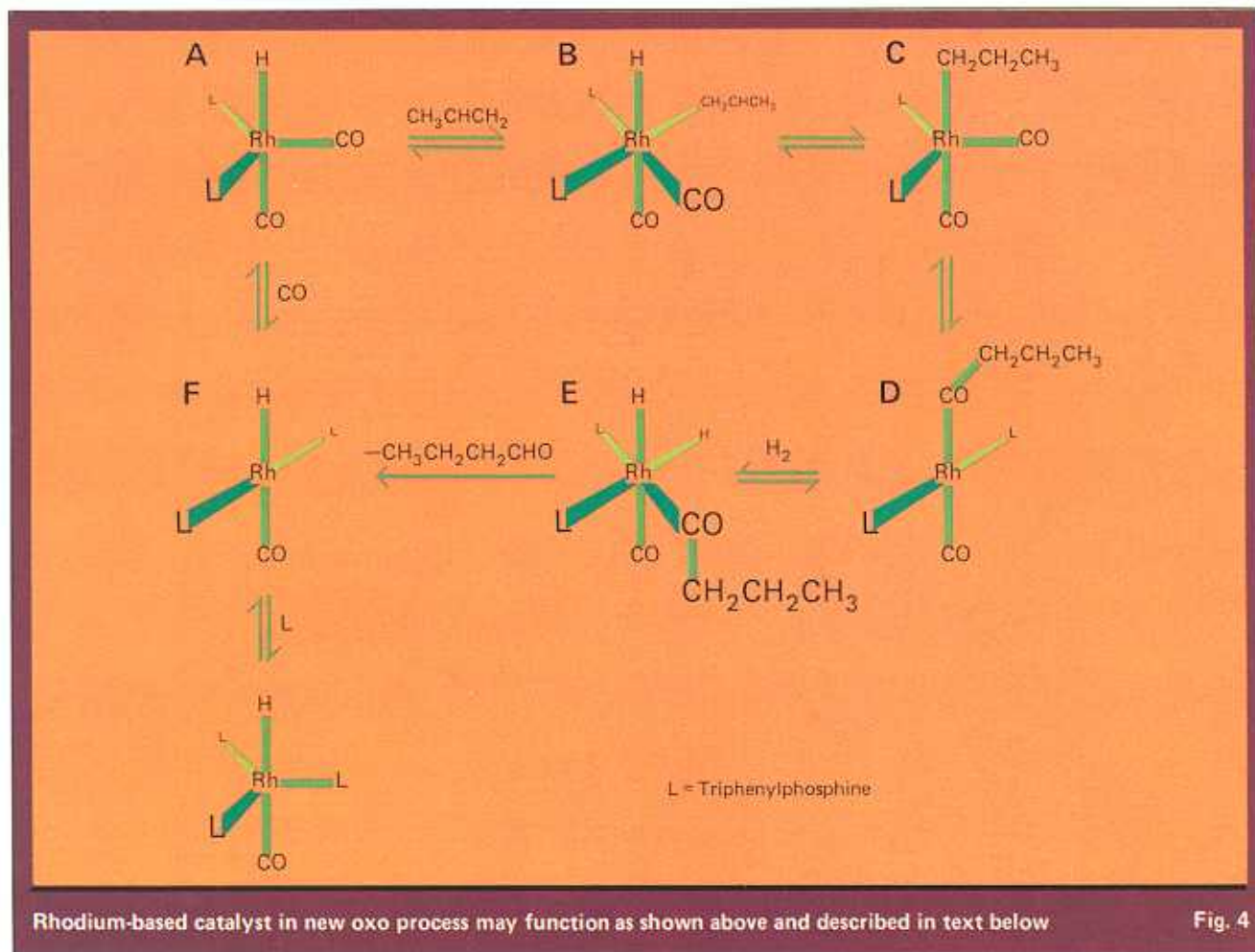


tion takes place. It can be carried out at 80 to 120°C. Heat of reaction is taken out partly via vaporization of aldehydes into the overhead gas stream, and partly by circulating a coolant through coils inside the reactor.

Reactor effluent is removed in the gaseous phase, passing through entrainment separators that minimize rhodium loss. This effluent then goes to a condenser where aldehydes and byproducts drop out; this mixture is removed in a separator. The liquid stream from the separator contains appreciable amounts of dissolved gases, mainly propylene and propane. A product stripping column distills these out. The liquid stream from this stripper goes through two distillation columns in series that remove *iso*- and *n*-butyraldehyde as overhead products, respectively. The only liquid effluent from the overall operation is the small byproduct stream that leaves the bottom of the second column; this stream can be used as fuel.

The propylene-rich overhead product from the stripping column is compressed and recycled into the gas stream to the reactor. Meanwhile, the overhead gas from the liquid-vapor separator likewise is compressed and recycled, after a portion of it is bled off in a purge stream that controls the level of propane and other inert gases (e.g., methane introduced with the feedstock) in the gas circuit. By regulating the flow of this purge gas, the operators can control the reaction pressure very accurately. The purge stream is the only gaseous effluent from the operation; and, like the liquid effluent, it can be used as fuel.

A key feature of the process is its use of the gas-recycle system, as described above. It makes possible the notably simple process flowscheme, because: (1) reactor byproducts can be easily removed (in the gas purge-



Rhodium-based catalyst in new oxo process may function as shown above and described in text below

Fig. 4

stream and in the bottoms from the final distillation column) at their rate of formation; (2) the rhodium catalyst remains in the reactor, with only minimal loss; (3) distillation of reaction solution for product recovery is avoided, so the catalyst need not be exposed to high temperatures (nor to oxygen that could leak in if the solution were vacuum-distilled).

The plant also includes equipment for periodic (and infrequent) makeup and removal of catalyst. Whenever catalyst must be added, an undisclosed convenient rhodium compound is dissolved along with triphenylphosphine into butyraldehyde, and this concentrated catalyst-precursor solution is pumped into the reactor. The system is designed in such a way that air cannot contact the catalyst solution and that operators are not exposed to malodorous aldehyde vapors.

Occasionally, a simple system concentrates a batch of the reaction solution, to recover catalyst at the end of its useful life. This is accumulated, then shipped to Johnson Matthey for rhodium recovery.

### No squandering

A major advantage of the process is its efficient use of feedstock, which is especially valuable in light of current high valuations put upon propylene and synthesis gas.

Typical feedstock consumption is 750 kg of propylene

(94 mole percent), and 740 normal m<sup>3</sup> of synthesis gas (99 mole percent), per 1,000 kg of *n*-butyraldehyde. The conventional oxo process, by contrast, is said to consume 930 kg of propylene and 1,200 m<sup>3</sup> of synthesis gas.

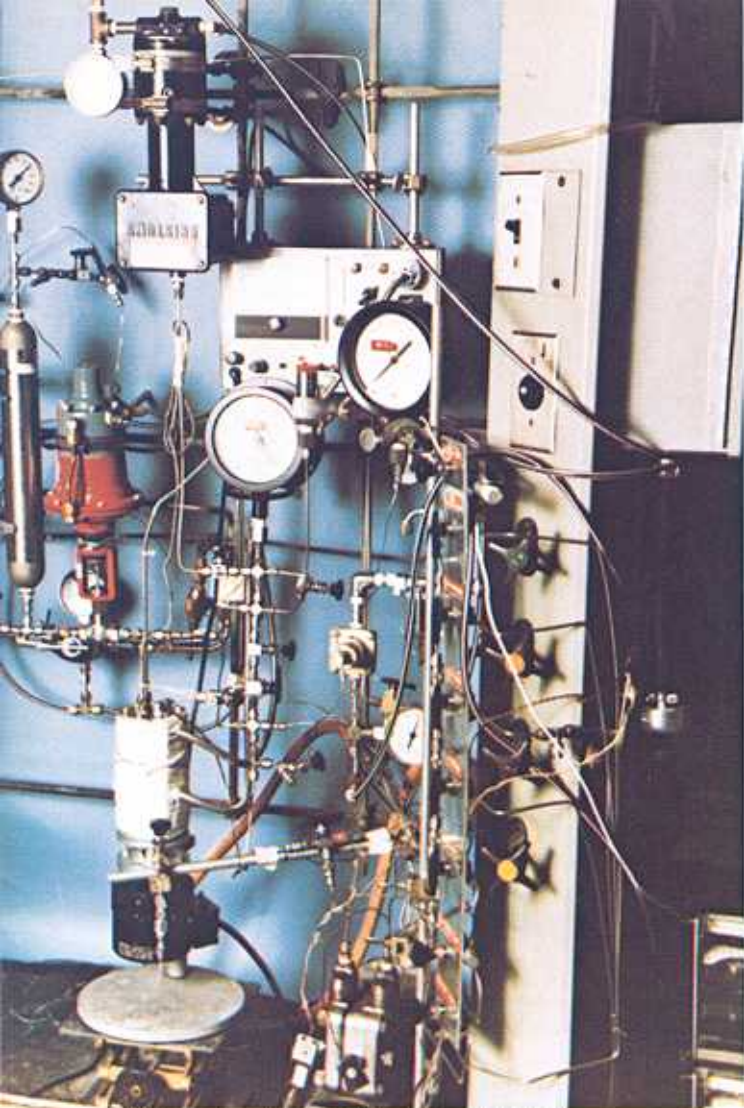
Catalyst usage is very efficient, too, because of the long catalyst life and the minimal loss during operation. Thus, catalyst cost is only a fraction of the total-product cost; and it is believed to be the same or slightly lower than that for the best of the conventional oxo processes.

Rhodium supply is not likely to be a problem, even though rhodium is a rare metal. Its use for oxo processes should have no significant impact on the overall rhodium market; and Johnson Matthey believes that reserves are adequate for 200 years. As noted above, the rhodium in the spent catalyst is recoverable.

### How the catalyst works

Because the rhodium complex that provides the catalysis is formed under hydroformylation-reaction conditions, there is no need for complicated catalyst-synthesis and handling steps.

The exact reaction mechanism is not certain, but is believed to follow the sequence set out in Fig. 4. The starting point is the rhodium coordination complex shown at A, in which the rhodium atom carries five labile-bonded ligands: two that are triphenylphosphine, two that are carbon monoxide, and one hydrogen. In



Mini-reactor at South Charleston, W. Va., generated data for reaction-rate model Fig. 5

the first step, this takes on propylene as an additional ligand, resulting in the structure shown at B.

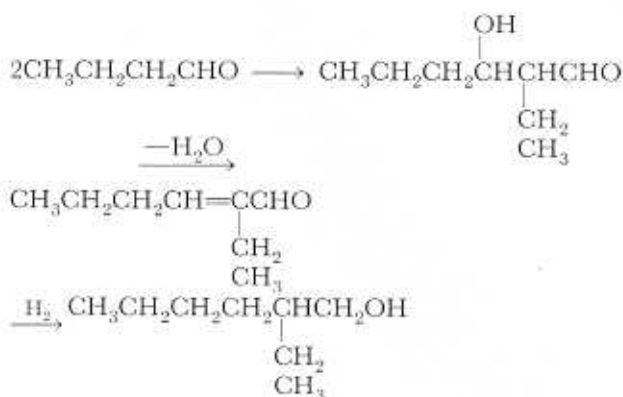
This propylene complex rearranges to the alkyl complex shown at C, which undergoes carbon monoxide insertion to form the acyl complex illustrated at D. Oxidative addition of hydrogen gives the dihydroacyl complex shown at E. Finally, hydrogen transfers to the acyl group, and butyraldehyde is formed along with the species shown at F. Coordination with carbon monoxide returns the complex to the state shown at A (while coordination with triphenylphosphine also produces a "byproduct" complex having three triphenylphosphine ligands and only one carbon monoxide ligand).

The presence of excess triphenylphosphine, under the low-pressure conditions of the reaction, favors the high selectivity for normal aldehyde. This excess suppresses the dissociation of species A into one containing only a single phosphine ligand. By favoring the presence of species A in contact with the propylene, the steric effect of the two bulky triphenylphosphine ligands favors a high ratio of primary alkyl—if fewer such ligands were present, more propylene would form secondary alkyl groups, leading to more isobutyraldehyde.

### Commercial significance

The high ratio of *n*-butyraldehyde to isobutyraldehyde is an asset because the former commands a better

market. Each compound can be hydrogenated to the corresponding alcohol; and, of these two alcohols, *n*-butanol generally outperforms isobutanol in most end-uses, such as solvent applications. Further, *n*-butyraldehyde differs from its iso sister because it can be a precursor to 2-ethylhexanol, via this reaction sequence of aldol condensation, dehydration, and hydrogenation:



Large quantities of 2-ethylhexanol esterified with phthalic anhydride move to market in the form of dioctyl phthalate, a highly important plasticizer for making flexible polyvinyl chloride. Total world markets for 2-ethylhexanol and butanols derived from butyraldehyde exceed 6 billion lb/yr.

### How the achievement evolved

Commercialization of the LPO process climaxed an intensive collaborative effort by the three companies in chemistry and engineering, stretching back to 1964.

Early exploratory work by Union Carbide showed that the rhodium-catalyzed hydroformylation of propylene could be carried out at low pressure, with high selectivity for the normal aldehyde and with high enough catalyst productivity to justify a look at possible commercial use of the rhodium. The company obtained a basic patent (U.S. 3,527,809, issued Sept. 8, 1970) covering this achievement.

Based on a series of statistically designed experiments, the company developed kinetic models relating propylene hydroformylation and hydrogenation rates to the main process variables, namely, temperature, catalyst used, and CO, hydrogen and propylene concentrations. Models were also developed for the rate of formation of heavy byproducts resulting from the aldehyde-condensation reactions.

In England, meanwhile, Davy Powergas and Johnson Matthey were linking forces for similar study—the former recognizing a chance to develop unique processes, and the latter particularly interested in rhodium-catalyzed hydroformylation reactions. Publication of patents made all three parties realize that they had a common interest, so in 1971 they entered into a joint development program to convert the laboratory rhodium-oxo chemistry into a commercial process.

Drawing upon Union Carbide's mathematical models for reaction and byproduct-formation rates, Davy Powergas was able to optimize relationships among equipment size and cost, reactant concentrations, feedstock consumption, and rhodium inventory, seeking the



Processing unit of Union Carbide uses new oxo technology to make propionaldehyde from ethylene at Texas City Fig. 6

lowest possible production cost. The models showed that light byproducts as well as the heavy aldehyde-condensation products could be taken out of the reactor solution by the gas-recycle stream. This was a far more attractive approach than using several distillation columns, as proposed in an earlier flowscheme.

The high productivity promised by the rhodium catalyst made it important that the reactor be designed to avoid mass-transfer limitations. This was a key consideration in selecting the reactor type and preparing its conceptual design.

Late in 1972, Union Carbide decided to commercialize the process, by building the abovementioned 300-million-lb/yr plant at the company's Ponce, Puerto Rico, petrochemical complex. To lay more groundwork for this project, the company also decided to first erect a 200-ton/yr pilot unit at the same site, to test the process on the feedstocks available there and to provide scaleup data. Davy Powergas engineers helped to design and engineer this pilot unit.

Meanwhile, process engineering for the commercial unit was also done by Davy Powergas. This effort began at the time that the pilot plant started operating, and it drew upon the results that became available from that operation. Those results were helpful for, among other things, the final design of the reactors. Detailed engineering of the full-scale plant was by Union Carbide.

Initial startup in 1976 was so easy that, excluding outside interruptions, the plant was online for all but one hour in its first month of operation. During its first year, it was available for onstream operation (again

excluding external interruptions) more than 99% of the time. This contrasts with about 90% availability for a conventional oxo plant, reports Union Carbide. The operation continues to be marked by unusual ease, stability and smoothness.

Design productivities, selectivities and feedstock-usage efficiencies have all been achieved, and product quality has met expectations. The ratio of *n*- to *iso* versions of butyraldehyde is normally controlled at around 10:1, but up to 16:1 has been achieved. Costs attributable to catalyst have been less than expected, and catalyst life exceeds one year.

A feature of the plant is its high degree of reaction control. Reaction temperature can be regulated to within  $\pm 0.5^\circ\text{C}$ , and pressure to within  $\pm 0.8$  psi, both computed over 8-h periods. The unit needs little operator attention.

From total shutdown, the unit can be brought back fully onstream in only 8 h. From outages due to dips in available power or similar causes, production can be restored in less than 45 min. Within 30 min of putting feedstock into the reactor, 80% of design output can be attained.

The LPO process has been licensed to Berol Kemi A.B., of Sweden, which is building a butyraldehyde plant scheduled to start up at Stenungsund in 1979. Meanwhile, Union Carbide itself is employing a variant of LPO to make propionaldehyde from ethylene and synthesis gas at Texas City, Tex., in a plant onstream since early 1975. It can operate at 150 million lb/yr, a rate which is about 50% above design capacity.