DAVID BRYANT WINS PERKIN MEDAL

Senior corporate fellow at Union Carbide is honored for improvements to hydroformylation of olefins

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Leaders of the world of chemistry will assemble at a banquet at the Plaza Hotel in New York City this week to honor research chemist David R. Bryant as he receives the 1998 Perkin Medal for outstanding contributions to applied chemistry. Bryant, who is a senior corporate fellow at the technical center of Union Carbide, South Charleston, W.Va., has perfected the company’s array of low-pressure processes for hydroformylation of olefins.

Hydroformylation products such as propionaldehyde (made from ethylene) and butyraldehyde (made from propylene) are intermediates in the manufacture of dozens of solvents, plasticizers, lubricants, stabilizers, and other performance chemicals. Licensing of the Union Carbide process by other firms has made it the most used hydroformylation technology worldwide.

The American Section of the London-based Society of Chemical Industry awards the Perkin Medal annually to an outstanding chemist chosen by officers of the American Section of SCI, the American Chemical Society, the American Institute of Chemists, the American Institute of Chemical Engineers, the Electrochemical Society, and the American Section of Société de Chemie Industrielle.

Bryant was born in Greensboro, N.C., in 1936. He received a bachelor’s degree in chemistry magna cum laude from Wake Forest University, Winston-Salem, N.C., in 1958, and a Ph.D. degree in organic chemistry from Duke University in 1961. He joined Union Carbide at South Charleston that year and has remained there since. Or as it seems to Bryant himself, “I started as a child with a Gilbert chemistry set, and I ended up spending my whole career at Union Carbide.”

Bryant started at the company in an exploratory group. “We could do whatever we wanted,” he recalls, “but often no one cared about the results. So I resolved to work on things that would end up in a plant, even if it was only a pump I could look at.” Bryant started work on the low-pressure hydroformylation process in 1967, and his results have ended up in dozens of plants worldwide.

Commenting on his overall approach to technological innovation, Bryant reflects: “Early on, you want to get hits. With business has to have an answer, you have to give them your recommendation and accept that you’ll sometimes be wrong.”

Bryant advocates having many approaches to problem solving. He is attracted to what is called “strong inference,” which sets an experiment to compare two hypotheses rather than to disprove one. That way one ends with a stronger hypothesis rather than none at all.

Hydroformylation is also called the oxo process and its products are called o xo chemicals. It was discovered by Otto Roelen of Ruhrchemie in Holten, Germany, in 1938. Roelen used a cobalt-thorium catalyst to make propionaldehyde from ethylene, carbon monoxide, and hydrogen.Temperatures ranged from 100 to 200 °C and pressures from 3,000 to 6,500 psi.

With propylene, the product was a 2:1 mixture of butyraldehyde and its branched isomer, isobutyraldehyde. For most applications, however, linear chains are preferred to branched structures. So work at Union Carbide for which Bryant is being honored has focused on bringing down the temperature and pressure while increasing the selectivity for straight chains.

As Bryant puts it, “Hydroformylation is a balancing act. There are four problems: speed, selectivity, catalyst stability, and separation of the catalyst. People have made different trade-offs.” Cobalt is not a very active catalyst, which leads process chemists to raise temperatures. High temperatures tend to decompose the cobalt carbonyl and hydrate catalytic species, so operators raise hydrogen and carbon monoxide pressures to keep the catalyst in solution. High temperatures also degrade selectivities as side reactions become fast enough to be a problem. Such side reactions include hydrogenation of aldehydes to alcohols and of olefins to alkanes, aldol additions of aldehydes to give dimer aldehydes and ester triols, hydroformylation of aldehydes to formate esters, and reaction of aldehydes with by-product alcohols to give acetals.
Oxo chemicals are key intermediates

The catalyst system that Union Carbide developed beginning in 1967 was a rhodium complex with triphenylphosphine. This catalyst enabled use of temperatures of 100 °C and pressures of 200 psi, while reaching ratios of linear to branched products of 10:1.

Bryant recalls a number of factors that influenced the particular development path that the low-pressure process took. One influence was that Union Carbide decided to license the process beginning in 1975 through a consortium with precious-metals purveyor Johnson Matthey and an engineering construction firm then called Davy Powergas. Success with licensing encouraged management to continue to improve the process.

A second influence was Union Carbide's focus on butanol as its desired end product. The company did not shy away from licensing every improvement in its top-of-the-line technology once it had been perfected in its own facilities.

A third influence was the emotional as well as economic concern not to lose costly rhodium circulating in solution. Another precious metal used in other processes at the time was palladium. Users of palladium kept buckets under every valve, pump, and vessel in their plants for fear of loss.

This concern spelled success for a gas-recycle variation of the oxo process. In this variation, hydrogen and carbon monoxide blow through the reaction, volatilizing and carrying aldehyde products away from the rhodium catalyst, which does not circulate.

As Union Carbide developed experience in handling precious metals in circulating systems without loss, the company developed a liquid-recycle variation. That variation offers independent control of high molecular weight condensation by-products (the "heavies") and product removal.

Speaking on the importance of research to a company, Bryant says: "R&D provides options. Find out what things are possible, so that when a business opportunity appears, you can check to see what options are available, how to change practices in the plant."

Of his own role over the years, he says: "I’ve been involved in recruiting people who come in and training them in the culture of research here. As they present their ideas, I’ve tried to guide them toward the ones that are most likely to have industrial application."