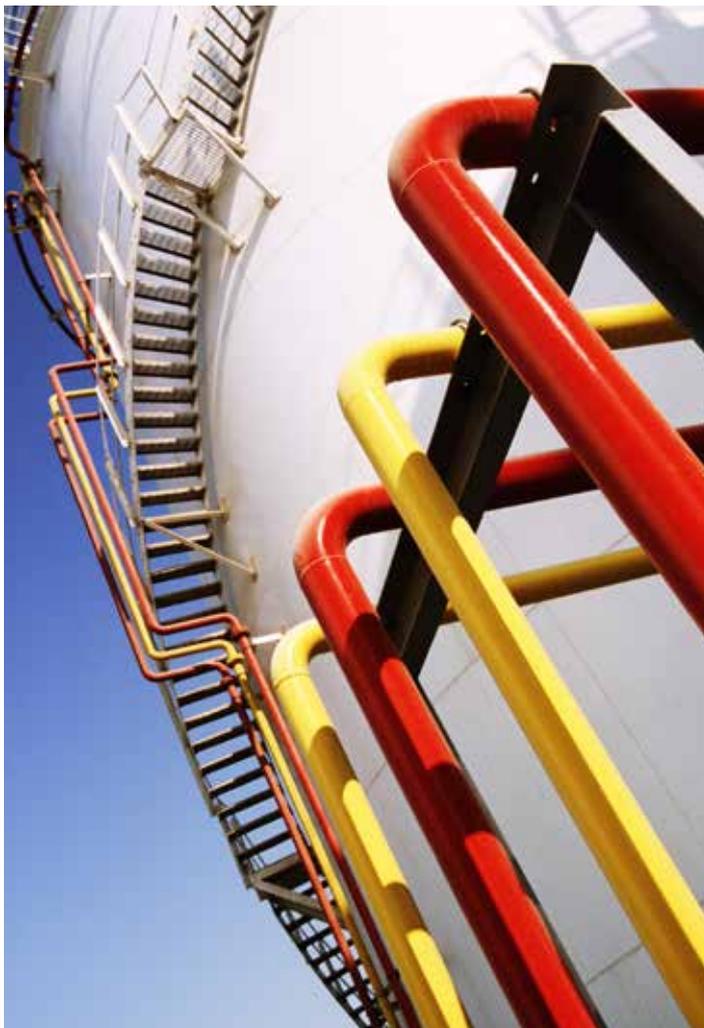


Shell Global Solutions



ENHANCEMENTS IN ETHYLENE OXIDE/ETHYLENE GLYCOL MANUFACTURING TECHNOLOGY

WHITE PAPER



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ENHANCEMENTS IN ETHYLENE OXIDE/ ETHYLENE GLYCOL MANUFACTURING TECHNOLOGY

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The markets for ethylene oxide (EO) and ethylene glycol (EG) continue to see attractive growth. This means that at least one or two new plants will need to be constructed every year if the industry is to meet the forecast demand. To unlock capacity increases economically, new capital-efficient processes, higher-performance catalysts and continuous process optimisation will be paramount. We review these aspects in this paper, beginning with a look at the innovations and technological achievements that got the industry to where it is today.

BACKGROUND AND EARLY HISTORY OF EO CATALYSTS

EO is produced by reacting ethylene with oxygen over a silver-based catalyst. These EO catalysts are characterised by several performance factors, including selectivity, activity, productivity and stability. One of the most important measures of an EO catalyst's performance is its selectivity, which is the ratio of ethylene converted to EO to the total amount of ethylene reacted.

In the early days of EO production, the typical start-of-cycle selectivity for EO catalysts ranged from 68 to 70%, i.e., 30% or more of the ethylene feed to the process was lost to the complete combustion side reaction. Then, in 1971, Shell identified an improvement to the catalyst formulation that helped to boost catalyst selectivity to over 80%. Over the next 15 years, the selectivity of EO catalysts seemingly plateaued, with only minor improvements to selectivity performance being realised. There were those in the industry who believed that EO catalyst advances had reached the theoretical limits of what was achievable. Since then, however, there has been an incredible journey of continuous improvement for EO catalyst performance, including substantial increases in catalyst selectivity, stability and productivity.

THE INTRODUCTION OF HIGH-SELECTIVITY (HS) CATALYSTS

In 1986, Shell made a discovery in EO catalyst technology that significantly changed the industry. As a result, it was able to offer new catalysts to the market: HS catalysts. This discovery increased initial selectivity values by more than six percentage points to give start-of-cycle selectivity values of 86% or greater. The impact of this selectivity increase was huge, as it could save customers millions of dollars in ethylene feedstock costs.

Although HS catalysts provided great value with this selectivity boost, their activity and stability were lower compared with traditional catalysts, so they had to be changed out more frequently. Traditional EO catalysts were changed out after three to four years of service. HS catalysts had a life approximately half this.

Over time, both process and catalyst improvements extended the life and selectivity of HS catalysts. On the process side, new plants were designed with less-severe operating conditions in order to cope with HS catalysts' lower inherent activity. Most notably, the new designs were based on lower volumetric production rates (referred to as the catalyst work rate) and lower reactor inlet carbon dioxide (CO₂) concentrations. On the catalyst side, incremental advances in HS catalyst development led to initial selectivities of 90% or more, and greater stability.

Consequently, by the turn of the century, new plants were benefiting from excellent selectivity and achieving a catalyst life of three years or more. However, these benefits came with a compromise: increased capital costs. Larger reactors were necessary to compensate for the lower catalyst work rate and larger CO₂ removal units were installed to achieve low inlet CO₂ concentrations, both of which resulted in increased capital requirements. As the size of the new world-scale EO production plants increased, the associated reactors became a significant capital (equipment) cost.

THE INTRODUCTION OF HIGH-PERFORMANCE (HP) CATALYSTS

Fast forward to 2010, when yet another breakthrough in catalyst development provided an opportunity to address these capital costs. CRI Catalyst Company (CRI), the global catalyst technology company of the Shell Group and part of CRI/Criterion, Inc., developed a fundamental understanding of the catalyst ageing process through focused research and development. This discovery led to new technologies that significantly inhibit catalyst ageing and resulted in the HP catalyst family. HP catalysts are characterised by a high initial selectivity (comparable to that of HS catalysts), but with a significantly slower performance decline (see Figure 1). In addition, the HP catalyst family proved able to operate at significantly higher work rates and to be tolerant of higher CO₂ concentrations. These performance characteristics provided valuable opportunities for cost-saving changes to the process design.

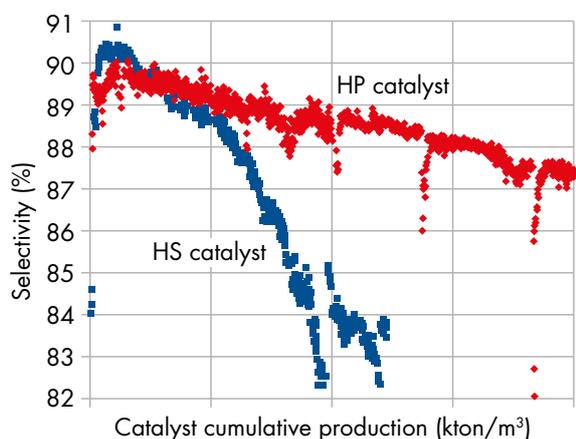


Figure 1: Example of selectivity curves comparing HS and HP catalysts over their lives at the same operating conditions.

THE EO/EG MANUFACTURING PROCESS

Producing EO over a catalyst is the first step in the overall EO/EG manufacturing process. In the reaction section, EO is produced by catalysed, direct partial oxidation of ethylene. Additionally, a portion of the ethylene fully oxidises to form CO₂ and water. These reactions take place in an isothermal (tubular) reactor at temperatures of 230–270°C. The reaction is moderated/optimised using an organic chloride. EO is recovered from the reactor product gas by absorption in water. Co-produced CO₂ and water are removed, and, after the addition of fresh ethylene and oxygen, the gas mixture is returned to the EO reactor as feed. The EO–water mixture can be routed to a purification section for recovery of high-purity EO and/or to a reaction section where EO and water are converted into glycols.

In the standard thermal glycol reaction process, EO and water are reacted at an elevated temperature (about 200°C) and pressure without catalyst. This process typically yields about 90–92% monoethylene glycol (MEG) and 8–10% heavier glycol products, mainly diethylene glycol (DEG) and triethylene glycol (TEG). The proportion of the higher glycols is limited by using excess water to minimise the reaction between the EO and glycols. The resultant water–glycol mixture from the reactor is then fed to multiple evaporators where the excess water is recovered and largely recycled. Finally, the water-free glycol mixture is separated by distillation into MEG and the higher glycols.

A more modern technology is to react EO with CO₂ to form ethylene carbonate (EC) and subsequently react the EC with water to form MEG, both reactions being catalysed. In this two-step process, most of the MEG forms in an EO-free environment, which minimises the co-production of heavier glycols and results in a MEG yield of more than 99%. Figure 2 shows a basic overview of the EO/EG process.

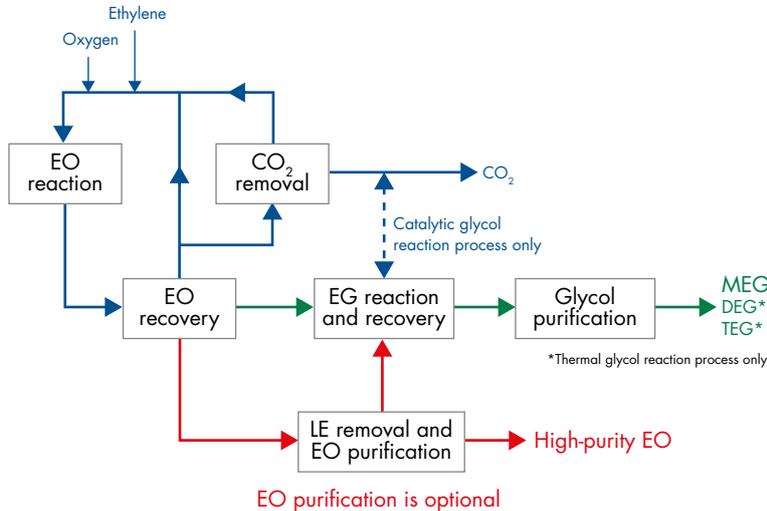


Figure 2: Block scheme showing the major sections of the EO/EG process.

EO/EG PROCESS OPTIMISATION

When designing an EO/EG plant, it is essential to take the owner’s priorities and business objectives into account. Experience shows that substantial value can be captured through process optimisation. However, this involves a highly complex evaluation owing to the many parameters that influence the project economics. It requires intimate knowledge of how specific operating parameters, such as feed gas composition and operating conditions (pressure, temperature, gas flow rate and catalyst work rate), influence key variables such as EO catalyst performance, capital investment and energy consumption. Examples of questions that the designer must answer include:

- How high should the gas flow through the reactor be? Increasing the flow enhances catalyst performance but increases capital and energy costs.
- At what pressure should the EO reactor be operated? At higher pressure, the gas volume that is circulated through the reactor and in the recycle gas loop will be lower, which reduces energy consumption and equipment sizes. However, the operating conditions become less favourable for catalyst selectivity, thereby increasing feedstock consumption.
- How low should the CO₂ concentration be in the EO reactor feed gas? Reducing it will enhance catalyst performance but will increase the capital and variable cost of the CO₂ removal equipment system.

Table 1 shows how various operational parameters can have conflicting effects on feedstock use (related to catalyst selectivity), capital expenditure and energy use.

	Desired change in parameters to...		
	...minimise feedstock consumption	...minimise capital expenditure	...minimise energy consumption
Catalyst work rate	▼	▲	▲
Total gas flow	▲	▼	▼
System pressure	▼	▲	▲
CO ₂ removal capacity	▲	▼	▼

Table 1: The trade-offs in key process design parameters. This shows, for example, that to minimise feedstock consumption the catalyst work rate should be reduced, whereas minimising capital expenditure requires the catalyst work rate to be increased.

It is important to understand how these and other trade-offs affect the overall cost of EO/EG production for a customer’s specific set of economic conditions. The process licensor should be able to help the owner to select the design solution that offers owner the highest value, taking into account the owner’s specific circumstances and constraints.

To arrive at the preferred design solution, Shell Global Solutions and CRI have developed and applied three proprietary models:

- a **catalyst performance model** that takes into account the EO reaction kinetics and calculates the catalyst performance profile for a defined set of process conditions;
- a **capital expenditure (capex) model** that calculates the investment costs for equipment and plant construction; and
- an **operational expenditure (opex) model** that takes into account variable costs such as ethylene, oxygen, catalysts, chemicals and utilities, and the costs associated with changing out the EO catalyst, to arrive at the total variable cost of EO/EG production.

These models have been integrated to create a tool that helps plant designers to predict the total EO production cost (Figure 3) for a given catalyst and plant design. The data from the three models enable examination of the operating space to identify catalyst operating conditions that help to minimise the total cost of producing EO. One lesson learned from applying the tool is that optimising the design conditions could easily save tens of US dollars per ton in EO manufacturing costs

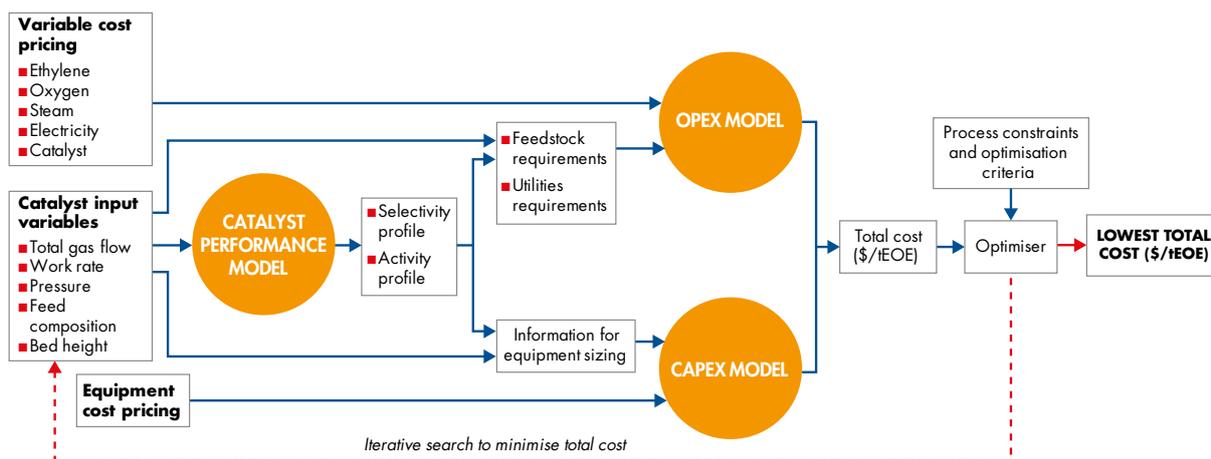


Figure 3: The optimisation tool leverages data from the three models and searches the operating space for the best set of conditions for minimising the total EO production cost.

OPTIMISED PROCESS OPTIONS

With both HS and HP catalysts available, Shell has been able to develop and optimise manufacturing processes around each catalyst family. As well as the type of catalyst, the key differences between the two processes reside in the EO reaction system design. Compared with the HS process, the HP process enables 30% fewer reactor tubes, 20% shorter catalyst bed lengths and significantly higher work rates. Consequently, the reactor volume can be roughly halved. Depending on the overall plant capacity target, this reduction in volume may mean the elimination of one reactor from the line-up (Figure 4). As the reactor(s) typically represent a significant portion of capital required for new plants, the elimination of one reactor can substantially reduce capital investment costs.

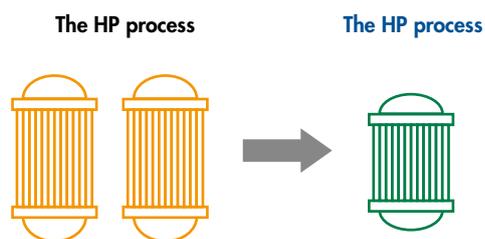


Figure 4: Because HP catalysts can operate at higher work rates, a reactor can be eliminated from the lineup for certain capacity ranges with the HP process.

Both processes provide low total costs for producing EO. The best choice of process option depends on relative capital expenditure and raw material costs, which can vary geographically, and on considerations such as plant capacity and desired cycle time.

DEBOTTLENECKING EXISTING PLANTS

Importantly, there are also opportunities for existing producers; many have significantly increased their output without major capital expenditure by simply upgrading to the latest-generation catalysts.

For example, Figure 5 shows the catalyst selectivity performance over the life of three different generations of catalysts at one plant. In this example, the selectivity and life of the catalysts are shown (each point representing about one month of operation). The first-generation HS catalyst gave an average lifetime selectivity of 84% during its one and a half years of operation. Performance significantly improved with use the newer-generation HS catalyst, which gave an average lifetime selectivity of greater than 85% while operating at a higher work rate and for significantly longer.

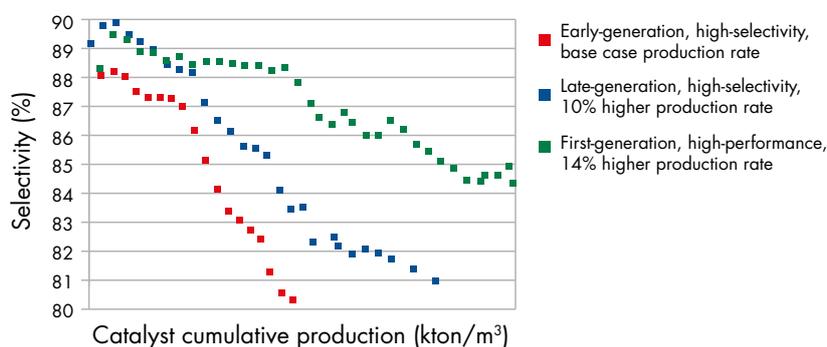


Figure 5: Real-world data showing how one EO producer benefited by upgrading to latest-generation catalysts.

The producer captured even greater benefits, however, when it upgraded to HP catalyst. Now, with HP catalyst, the average selectivity is significantly higher, currently averaging about 87%, and catalyst life is much longer. This has all been achieved with the plant operating at record production rates: a work rate that is 14% higher than the average work rate of the previous-generation HS catalyst.

KEY TAKEAWAYS

The markets for EO and EG continue to see attractive growth, and there is a continuous drive to improve EO/EG manufacturing economics.

Advances in EO catalyst performance have been key factors in these improvements and provided higher work rate operations while improving selectivity and stability. EO/EG manufacturing processes have been optimised to take advantage of the catalyst performance enhancements. These developments help to increase yields and reduce the capital expenditure or running costs of grassroots projects. Existing plants can also benefit. Facilities around the world that have replaced older catalysts with latest-generation catalysts have captured substantial value.

Latest-generation processes that feature a HP EO catalyst enable the EO reactors to be significantly smaller (up to 50%). As the reactor(s) typically represent a significant portion of capital required for new plants, the elimination of one reactor can substantially reduce capital investment costs. For some producers, especially those in areas where feedstock costs are high while capital is relatively inexpensive, leading-edge processes that feature HS EO catalysts may still be preferred.

Experience shows that substantial value can be captured by optimising the process design conditions. This optimisation is complex because there are many design variables that can influence the capital and operating costs in competing ways. In Shell, a dedicated optimisation tool has been developed to identify the preferred EO reactor operating conditions for each customer, taking into account local economics and constraints.

THE AUTHORS

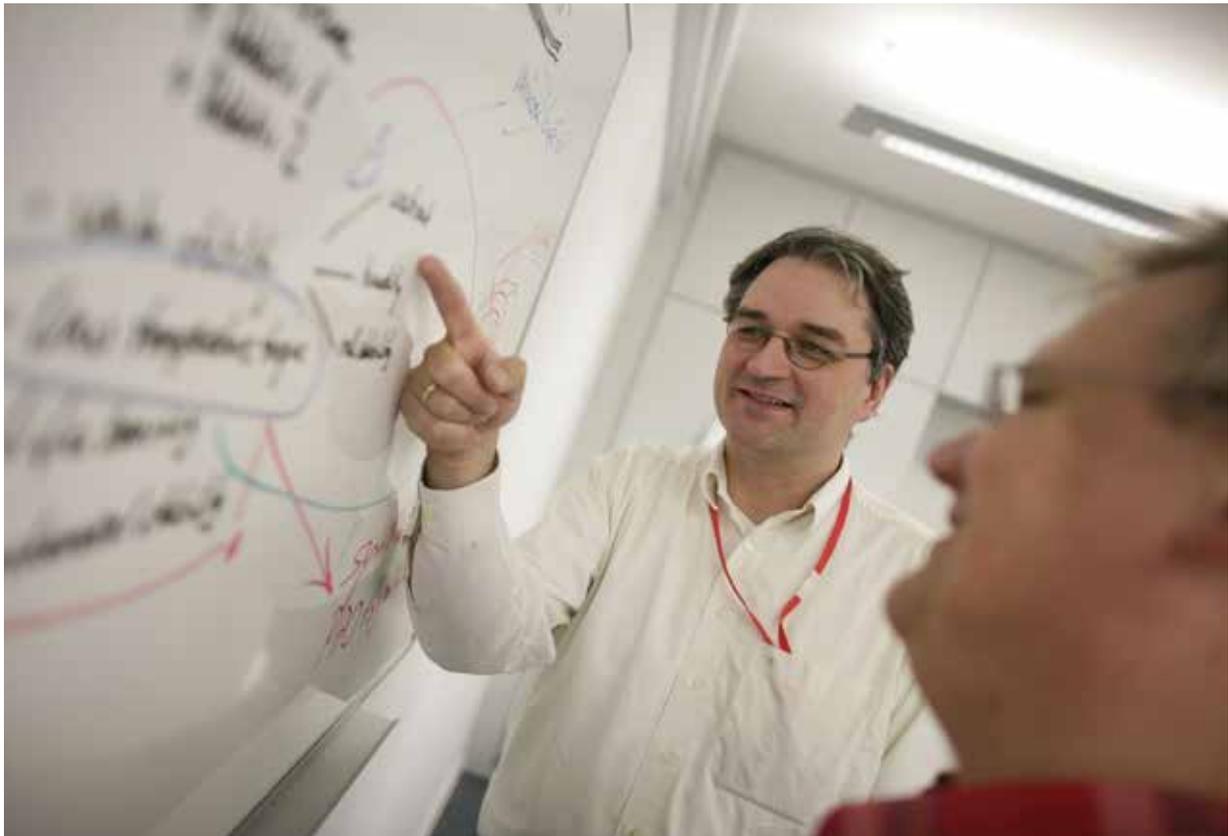
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Brian VanderWilp is the Business Director, Americas, EO Catalysts, CRI Catalyst Company. He graduated with a degree in chemical engineering from Michigan State University, USA, in 1985, and earned an MBA from the University of Houston–Victoria, USA, in 1990. Brian joined CRI in 1996 after spending the first part of his professional career as a production support engineer with Union Carbide and later The Upjohn Company. His initial role with CRI was as a technical service engineer for the EO catalyst and later on for the hydrogenation catalyst businesses. In 2006, he acquired sales and product management responsibilities for the hydrogenation and speciality catalyst business. In 2011, he returned to the EO business as business director.



Gary J. (Jimmy) Wells is a Principal Researcher in the EO catalyst research and development group, CRI Catalyst Company. Jimmy completed undergraduate studies in chemical engineering at Clemson University, USA, and earned a PhD in chemical engineering from the University of Wisconsin, USA. In 2003, he joined Shell in the EO/glycols process support group in Houston, USA, where he developed and deployed advanced process monitoring tools to manufacturing sites. Since 2007, Jimmy has worked as a catalyst performance modeler at CRI. He integrates research and development results into models for customer guidance, supports the deployment and performance monitoring of new catalysts, and leads a co-operative team with process design and licensing staff to co-optimize new catalysts with the EO/glycols process.



ABOUT US

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