PERP Program – Ethylene Oxide/Ethylene Glycol

New Report Alert

February 2006

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Ethylene Oxide/Ethylene Glycol (04/05-5)***. To view the table of contents or order this report, please click on the link below:
http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

TECHNOLOGY

Ethylene Oxide

Ethylene oxide is produced commercially by the vapor phase oxidation of ethylene over a silver based catalyst. The reaction proceeds at 200-300°C (390-570°F) and 10-30 atmospheres of pressure. Selectivity to ethylene oxide is 80-86 mole percent depending on the catalyst employed. New catalyst development is aimed at developing selective silver based catalysts to minimize combustion of ethylene to carbon dioxide, carbon monoxide, and water.

The exotherm of the desired reaction is less than 10 percent of the heat of combustion of ethylene. Temperature control is enhanced by the use of a ballast gas or diluent that is added to the recycle stream.

Selectivity depends not only on kinetic factors (e.g. pressure, temperature, and ethylene and oxygen concentrations) but also on other factors such as the concentration of other gases (e.g. ethane and carbon dioxide). Small amounts (ppm concentrations in the reactor feed) of halogenated compounds (e.g. ethylene dichloride or ethyl chloride) are used as inhibitors to the undesirable combustion reaction.

To prevent the oxidation of ethylene oxide, the ethylene conversion per reactor pass is typically limited to between 10 and 20 percent in commercial processes.

Acetaldehyde is formed by the isomerization of ethylene oxide. Normally, several hundred to 1,000 ppm of acetaldehyde remain in the unrefined ethylene oxide; specifications for purified oxide require less than 30 ppm.

Direct oxidation processes can be designed using either air or pure oxygen as the oxygen source. Current plant design is predominantly based on pure oxygen feed since it is generally more economical than air based plants. Oxygen has an inherent overall yield advantage over air, since the volume of ethylene-containing recycle gas is less and the reactor selectivity is normally higher than in an air based plant.

Air based plants are higher in capital cost compared to oxygen based plants to which oxygen is supplied at the battery limit. Currently operating air based plants are uniquely cost effective due to their large size, energy recovery/heat conservation schemes, and plant integration/synergy, which reduce utility costs and partly compensate for the lower yield. Approximately 97 percent of current ethylene oxide global capacity is oxygen based.

The small purge gas stream flow in an oxygen based process makes it economically feasible to use cycle gas diluents (ballast gas) other than nitrogen. The benefit of methane ballast gas over nitrogen comes from its higher heat capacity and thermal conductivity. This allows a higher safe oxygen concentration in the cycle gas and helps moderate the peak reaction temperature. The result is a higher yield of ethylene oxide at a fixed productivity, or a higher productivity with the same reactor volume.

All catalysts employed in the oxidation of ethylene to ethylene oxide are based on silver. Almost all reported catalysts are supported on a low surface area alumina.

The activity, selectivity, and life of an ethylene oxide catalyst depend on many factors, including the support surface area, shape, porosity, pore size, and chemical composition. The particle size and distribution of the silver on the support affect performance. Typical catalyst life is two to four years.

The major licensors of EO process technology are Scientific Design and Shell. Dow is also offering the former Union Carbide EO process called the Meteor EO/EG process.

Ethylene Glycol

Ethylene glycol is commercially produced by the liquid phase non-catalytic hydrolysis of ethylene oxide, as an integrated product of an ethylene oxide plant. The process is carried out with greater than 20 times molar excess of water in order to minimize higher glycol by-products. The reaction proceeds at 140-230°C (285-445°F).

Higher glycols (primarily diethylene glycol and triethylene glycol) form by the interaction of ethylene oxide with ethylene glycol; the oxide is more reactive with glycol than with water.

The formation of the higher glycols can be minimized by employing an excess of water in the reaction, about 22 moles of water per mole of ethylene oxide. Despite this large excess, which reflects itself in energy and equipment costs, ethylene glycol is only about 90 to 90.5 percent of the total product. Diethylene glycol constitutes about 9 percent, whereas triethylene and higher glycols account for 0.5 to 1 percent. This product distribution corresponds to a selectivity of ethylene oxide to ethylene glycol of about 89 mole percent.

Shell OMEGA (Only MEG Advanced) Process

As described earlier, about 9 percent of the EO gets converted to diethylene glycol (DEG) during the hydrolysis process to make EG. While this quantity of DEG can be a boon to the economics of EG production if the market for DEG is good, it does complicate the EG plant design and requires sales and marketing effort for a material that goes into markets much different in application and scale than EG.

Shell Chemicals, in order to obviate the complications associated with DEG by-production, is licensing a new EG process termed OMEGA (Only MEG Advanced). The heart of this new process, developed by Mitsubishi Chemical and acquired by Shell in 2002, is a method that eliminates the production of DEG via a two-step process.

- Conversion of EO to ethylene carbonate by reaction with carbon dioxide
- Catalytic hydrolysis of the ethylene carbonate to EG, liberating carbon dioxide

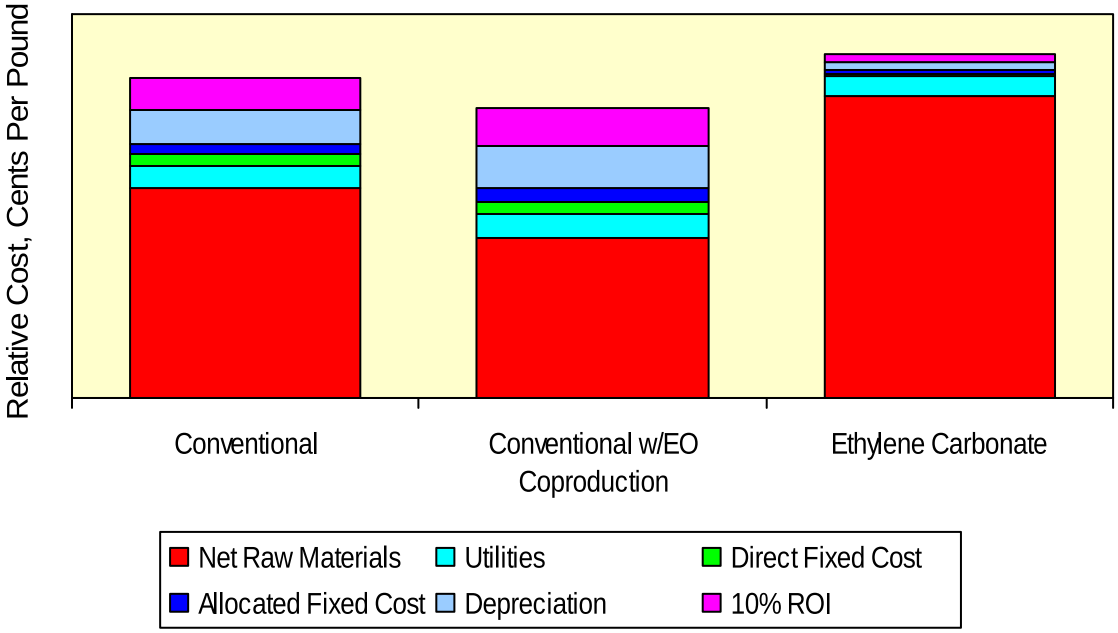
Recent work in this area disclosed by Mitsubishi involves a simplified process in which ethylene oxide is absorbed in a solution containing carbon dioxide. Reaction to ethylene carbonate takes place, followed by hydrolysis of the carbonate to ethylene glycol. Simplification occurs by combining the ethylene oxide absorption step and the carbonation step. Energy savings compared to the conventional process result from avoiding stripping of ethylene oxide from absorption water and separation of a large excess of water following ethylene glycol production.

ETHYLENE GLYCOL – ECONOMIC COMPARISON

Nexant compared the cost of production for various routes to ethylene glycol. On a cash cost basis (which excludes depreciation and ROI), the co-production plant making both EG and EO has a huge net raw material advantage when crediting the ethylene oxide co-product at its cost of production plus 10 percent return on investment. The lower utilities cost and lower fixed costs (related to the lower capital) for the ethylene carbonate route do not overcome the raw material cost disadvantage. On a cost of production plus ROI comparison basis (Figure 1), the ethylene carbonate route improves its position, but remains the laggard. However, when compared to conventional EG technology, the cost of the ethylene carbonate route is only about 7 percent higher, and it avoids the problem of sales of the byproduct diethylene and triethylene glycols, which can be viewed as a business advantage for certain producers.

In the United States over the last twenty years, DEG prices have ranged from a low of 14 cents per pound to a high of 41 cents per pound. At about 9 percent of the EG product produced, the fluctuation in DEG price can have a large effect on EG production cost. In order to assess the competitiveness of the ethylene carbonate route, Nexant compared that route's cost to conventional EG technology over a range of DEG prices (including fuel value).

Figure 1
EG Cost of Production plus ROI Comparison



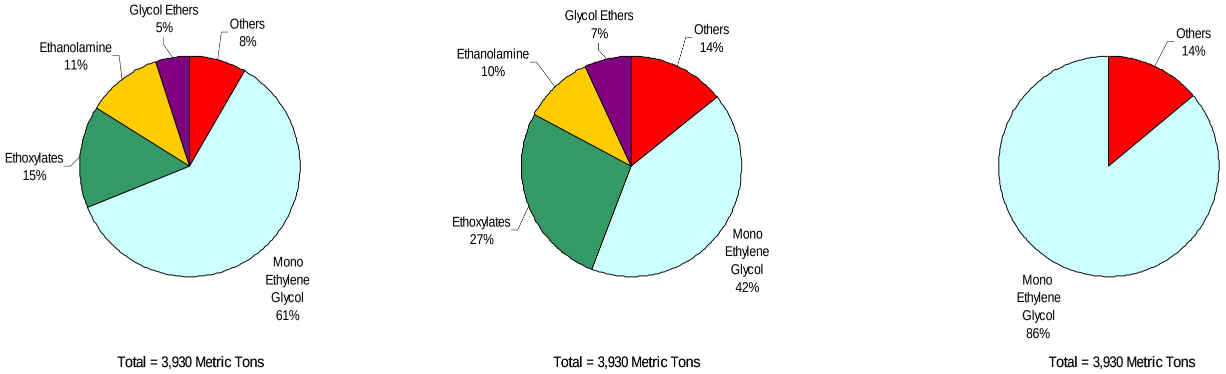
COMMERCIAL ANALYSIS

Figure 2 shows the estimated distribution of EO consumption by end use for the United States, Western Europe, and Asia Pacific.

The proportion of EO consumption for MEG production is highest in Asia pacific, followed by the United States and then Western Europe. Conversely, EO derivatives other than MEG are much more important in Western Europe (about 60%) and the United States (about 40%) than in Asia Pacific (about 14%).

In the United States, MEG consumption is dominated (about 60%) by polyester (fiber, bottle, film) with growth driven by PET bottle grade production. United States consumption for antifreeze, the second largest application, fluctuates from year to year depending on the severity of winter weather. MEG use for antifreeze has been gradually declining due to antifreeze recycling, extended-life formulations, and smaller engines. Industrial uses for MEG include specialty heat transfer fluids and coolants, hydraulic fluids, and latex surface coatings.

Figure 2
Tri-regional EO Consumption by End Use, 2005



In Western Europe, the proportion of MEG consumption for PET is higher than the United States, at about 70%, while antifreeze is correspondingly lower.

These trends hold for Asia Pacific, where MEG consumption for PET climbs to almost 90%.

The report includes 2005 EO and EG capacities by producer and location for the United States, Western Europe, and Asia Pacific.

The report further provides tri-regional supply, demand by end use, and trade data for 2000 to 2004, with estimates for 2005 and 2010.

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