Ethylene oxide (EO) and ethylene glycol (EG) are widely used industrial organic intermediates. In 1995, their production volumes ranked them among the top 20 organic chemicals in the United States. Monoethylene glycol (MEG) accounts for more than 90% of the market for EG. More than one-half of all MEG produced goes into polyester fibers, resins, and films. Most of the rest goes into antifreeze for automotive applications. Nearly all EG is made from EO by thermal hydration.

The largest application for EO is EG production, but EO is also used for making ethanolamines, glycol ethers, polyethylene glycols, and surfactants. The primary EO manufacturing process is direct oxidation of ethylene over a supported Ag catalyst. Small amounts of a chlorinated moderator suppress the complete oxidation of ethylene to CO\textsubscript{2}, thereby increasing selectivity to the desired EO. Much development work in recent years has sought to maximize selectivity, usually by adding traces of other metals to the Ag catalyst.

The report summarizes recent patents on the direct oxidation process, particularly those on new catalysts. We describe the main commercial process in detail, and evaluate an integrated plant for making EO and converting 50% of it to EG. (The rest of the EO is purified for sales.) Our evaluation indicates that the sale of EO at its current market price significantly subsidizes the manufacture of EG. As might be expected, the main determinant of the cost is the price of ethylene. On a molar basis, purified EO and fiber-grade MEG sell for about the same price, but the price of a pound of EO is higher because of its lower molecular weight.

We also evaluate variants in which all of the EO is converted to EG, with none of the EO purified for sales. Costs for making EG are higher in this case. In addition, we examine a variant in which all of the EO is higher because of its lower molecular weight.

Modern plants use oxygen to oxidize ethylene. Some older plants use air as the oxidant, but doing so is less efficient and costs are higher as a result. The report evaluates several variants of air processes.

Other routes to EG have been proposed, but none is commercial. We evaluate routes from EO via ethylene carbonate, and from ethylene by direct hydroxylation with water and oxygen. Proposed routes from ethylene that we describe, but do not evaluate, include those via glycol esters and via 1,2-dichloroethane. We also describe a route that uses organic peroxides, along with an old route via ethylene chlorohydrin.

Other inexpensive raw materials have also been considered for making EG. From our evaluation of a process for making EG from syngas (mixtures of CO and hydrogen), we conclude that selectivity to EG is too low and that the pressures required are too high. We also evaluate a two-step process for making EG from formaldehyde by hydroformylation to glycolaldehyde. We
describe four other processes that start with formaldehyde, along with two from methanol and one from CO via oxalate esters.

This report is of special interest to current and potential producers of EO or EG, and to consumers of these chemicals. Process development chemists and catalyst specialists will be interested in the summaries of the more than 350 patents that have been issued in the last 15 years.
ETHYLENE OXIDE AND ETHYLENE GLYCOL
SUPPLEMENT F

by ROBERT H. SCHWAAR

January 1997

A private report by the
PROCESS ECONOMICS PROGRAM

Menlo Park, California 94025
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