



Review

Thermal reactivity of ethylene oxide in contact with contaminants: A review



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ABSTRACT

A review on the experimental studies of the reactivity of ethylene oxide (EO) with various contaminants including water, different kinds of iron oxides and alkalis are presented. It is shown that: (1) Pure EO is not prone to initiate a runaway reaction under 200 °C under adiabatic conditions. (2) The possibility of EO aqueous solution to experience an exothermic reaction depends strongly on the EO concentration, and the onset temperatures could be predicted well by a fourth order reaction rate model. (3) EO exhibits different sensitivities to various kinds of iron oxides. Although γ -Fe₂O₃ is the most active iron oxide to EO, its runaway reaction consequence is less severe. The reactivity for EO with iron oxides could be: γ -Fe₂O₃ > α -Fe₃O₄ > hydrated α -Fe₂O₃ > α -Fe₂O₃. (4) Alkalis could reduce the initial reaction temperature of EO to room temperature with sufficient concentrations, and the proposed hazard potentiality for alkalis is NH₄OH > KOH > NaOH.

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Nomenclature

Notation

A	Pre-exponential factor, $[(\text{m}^3)^3 \text{kmol}^{-3} \text{s}^{-1}]$
C_b	Specific heat of the bomb, $[\text{J}(\text{kg}^\circ\text{C})^{-1}]$
C_s	Specific heat of the sample, $[\text{J}(\text{kg}^\circ\text{C})^{-1}]$
dT/dt_{max}	Maximum temperature rise rate, $[\text{C}^\circ \text{min}^{-1}]$
dP/dt_{max}	Maximum pressurization rate, $[\text{kPa} \text{min}^{-1}]$
E	Activation energy, $[\text{J}/\text{mol}^{-1}]$
H	Heat of polymerization, $[\text{kJ} \text{mol}^{-1}]$
k	Rate constant, $[(\text{m}^3)^2 \text{kmol}^{-2} \text{s}^{-1}]$
K	Equilibrium constant
M_b	Mass of testing cell, $[\text{g}]$
M_{EO}	Mass of EO, $[\text{g}]$
M_S	Mass sample, $[\text{g}]$
M_{total}	Total mass of sample and cell, $[\text{g}]$
P_{max}	Maximum pressure, $[\text{kPa}]$
r_1	Rate constant of EO with water, $[\text{kmol} \text{m}^{-3} \text{s}^{-1}]$
r_2	Rate constant of EO with glycols, $[\text{kmol} \text{m}^{-3} \text{s}^{-1}]$
r_{EG}	The formation rate of EG, $[\text{kmol} \text{m}^{-3} \text{s}^{-1}]$
r_{DEG}	The formation rate of DEG, $[\text{kmol} \text{m}^{-3} \text{s}^{-1}]$
t	Time, $[\text{s}]$
T_f	Final temperature, $[\text{C}^\circ]$
T_{max}	Maximum temperature, $[\text{C}^\circ]$
T_{mp}	Temperature at maximum pressure, $[\text{C}^\circ]$
T_{MR}	Time to maximum reaction rate, $[\text{min}]$
T_{on}	Onset temperature, $[\text{C}^\circ]$
W	Mass fraction of EO aqueous solution, $[\%]$

Greek letters

ΔT_c	Adiabatic temperature rise, $[\text{C}^\circ]$
Φ	Thermal inertia factor

1. Introduction

Ethylene oxide (EO) is one of the most versatile chemical intermediates because its highly strained ring can be opened easily to produce varieties of fine chemicals [1,2]. Besides its direct use as disinfectant, sterilizing agent, and fumigant, EO is frequently applied in the production of many important surfactants, solvents, polyesters, and antifreezes such as ethylene glycol (EG), ethanolamine, ethylene glycol ethers etc. Important as EO is in the chemical industry, it is an extremely hazardous material due to the high reaction sensitivity—it is susceptible to contaminants such as alkalis, iron oxides and water, which could lead to runaway reactions or even spontaneous decomposition [3].

Traditionally, EO is produced by the direct oxidation of ethylene with oxygen by metallic silver [4,5]. Due to the deflagration and explosion risk of the process, some other inherent safer processes have been proposed to reduce risk, such as silver-catalyzed oxidation of ethylene to EO in micro-reactor, or homogeneous liquid phase oxidation with catalyst (methyltriox-orhenium), oxidant (H_2O_2) and reaction medium (methanol/water) [6,7]. Also, some researchers conducted optimization of the reaction concept and design parameters of EO process in order to save energy and reduce emission [8–10]. The industrial production technologies for EO based on direct oxidation process over silver catalyst are mainly patented and licensed by Shell, Scientific Design (SD) and DOW Chemical. As shown in Fig. 1, the direct oxidation process consists of oxidation reaction unit, carbon dioxide removal unit, EO purification unit, EO storage/transportation unit and possible ethylene glycol production unit. A recycle gas stream containing ethylene and oxygen is first circulated through the fixed bed reactor, partially oxidizing ethylene into EO over sphere or ring shaped silver cata-

lyst at about 200°C and 2.0 MPa. The process parameters of direct oxidation technology has been summarized in Table 1, depending on catalysts performance and production technology. The recycle gas containing EO and byproduct such as carbon dioxide, water and acetaldehyde is then transported into scrubbers to absorb EO and to remove carbon dioxide. The residual recycle gas is reloaded with oxygen and ethylene through oxygen mixer and returned to the reactor. In the liquid phase, the resulting aqueous EO solution is passed to the EO purification unit to collect pure EO product through a series of stripping towers and distillation towers, where low-boiling components are stripped of at the same time. Depending on the design of the EO plant, the EO product can be refrigerated and transported to the storage tank or subsequently reacted with water to produce ethylene glycol.

The process hazards of EO production lie mainly in the oxidation reaction and EO purification process [13] (Fig. 1). In the oxidation reaction unit, a significant amount of flammable gases including ethylene and methane mixes and reacts with oxygen. The flammable gases concentration has to pass through the flammable region when diluted down by oxygen to the operating level, requiring a fairly complicated control scheme to assure safety therefore. The oxidation reaction of ethylene is extremely exothermic especially when the complete oxidation of EO to carbon dioxide takes place. As a result, the heat removal system must be sufficiently reliable to cope with the heat release in the reactor, otherwise runaway reactions may be induced and the accumulated heat could result in damage to assets, human health or the environment [14]. Typical incidents in the oxidation reaction are pre-ignition, temperature runaway and explosion of flammable cyclic gases. In the EO purification unit, high purity EO is combustible and sensitive to various impurities, prone to cause fires and deflagrations [15–17]. The consequence of incidents in the EO purification unit is often much more severe than that in other units in the EO production process because of the strong exothermic effect. The disastrous explosion was usually initiated by the exothermic reaction of EO with inobservant impurities. Looking through the history of EO industry, it is not difficult to name a few incidents caused by the existing impurities in the EO purification unit.

On July 3rd, 1987, a purification distillation column of BP Chemicals' EO plant in Antwerp exploded. It was concluded after accident investigation that EO leaked from the manhole flange and was trapped inside the insulation where it started to react in the presence of rust, water and the insulation. The temperature gradually increased because of heat released in the exothermic reactions until it reached a critical level, where there was an acceleration in the rate of the exothermic reactions, resulting in a rapid release of heat. The temperature of the resultant hot metal surface was sufficient to ignite the EO vapor internally [18]. An EO plant of BASF licensed by Shell in Antwerp also experienced severe fire and explosion damage in the EO distillation section on March 7th, 1989. It is believed that polyethylene glycols (PEG) were formed by escaped EO and accu-

Table 1
Process parameters in the oxygen-based production of EO [11,12].

Parameters	Value range
C_2H_4 concentration, vol%	15–40
O_2 concentration, vol%	5–9
CO_2 concentration, vol%	5–15
C_2H_6 concentration, vol%	0–2
CH_4 concentration, vol%	1–60
Inlet gas temperature, $^\circ\text{C}$	30–40
Reaction temperature, $^\circ\text{C}$	220–275
Pressure, MPa	1–2.2
space velocity, h^{-1}	2000–4000
C_2H_4 conversion, %	7–15
Selectivity, %	80–90

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