

Ethylene Oxide

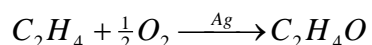
Reactor Design

1. General Information

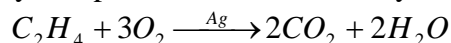
Ethylene oxide [75-21-8] was first prepared in 1859 by Wurtz from 2-chloroethanol (ethylene chlorohydrin) and aqueous potassium hydroxide. He later attempted to produce ethylene oxide by direct oxidation but did not succeed. Many other researchers were also unsuccessful. In 1931, Lefort achieved direct oxidation of ethylene to ethylene oxide using a silver catalyst. Although early manufacture of ethylene oxide was accomplished by the chlorohydrin process, the direct oxidation process has been used almost exclusively since 1940. The primary use for ethylene oxide is in the manufacture of derivatives such as ethylene glycol, surfactants, and ethanolamines.

Direct Oxidation Processes

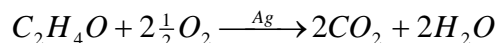
All ethylene oxide direct-oxidation plants are based on the original process chemistry discovered by Lefort in 1931. The main reaction is as follows:



The only significant by-products are carbon dioxide and water, which are formed either by complete combustion of ethylene:



or by further oxidation of ethylene oxide:



To prevent further oxidation of ethylene oxide, the ethylene conversion of the commercial processes is typically between 10 and 20%.

In addition to ethylene oxide, carbon dioxide, and water, small quantities of acetaldehyde and traces of formaldehyde are also produced in the process. They generally total less than 0.2% of the ethylene oxide formed. Acetaldehyde is most likely formed by isomerization of ethylene oxide, whereas formaldehyde is most likely formed by direct oxidation of ethylene.

A large amount of heat is released by the ethylene oxidation reactions. At 600 K, each kg of ethylene converted to ethylene oxide releases 3.756 MJ (3564 Btu); each kg of ethylene converted to carbon dioxide and water releases 50.68 MJ (48,083 Btu).

Commercial processes operate under recycle conditions in a packed-bed, multitubular reactor. Reaction temperatures of 200–300°C are typical, and operating pressures of 1–3 MPa (10–30 atm) have been reported. The reactor is of the shell and tube type comprised of several thousand mild steel or stainless steel tubes, 20–50 mm inside diameter. The reactor can be either oil or boiling water cooled. Figure 1 is a schematic diagram of an oil-cooled reactor. Based on published information regarding catalyst productivities and space velocities, the reactor tube lengths are 6–12 m. These tubes are filled with a silver-based catalyst ca 3–10 mm dia supported on a carrier material with a surface area usually. The yield (moles of product produced per moles of ethylene consumed in the process) is normally 70–80% depending on catalyst type, per pass conversion, reactor design, and a large number of process operating variables.

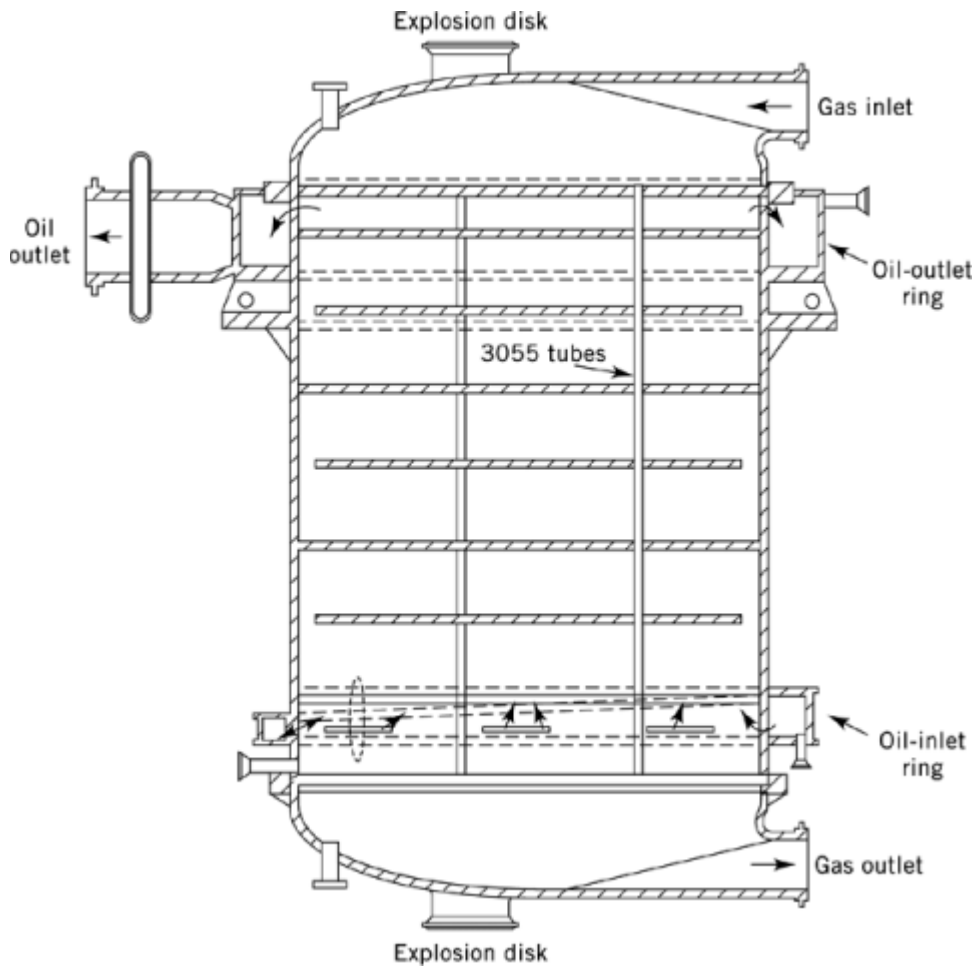


Figure 1. Oil-cooled reactor for the oxidation of ethylene to ethylene oxide.

Air-Based Direct Oxidation Process

A schematic flow diagram of the air-based ethylene oxide process is shown in Figure 2. The process can be conveniently divided into three primary sections: reaction system, oxide recovery, and oxide purification.

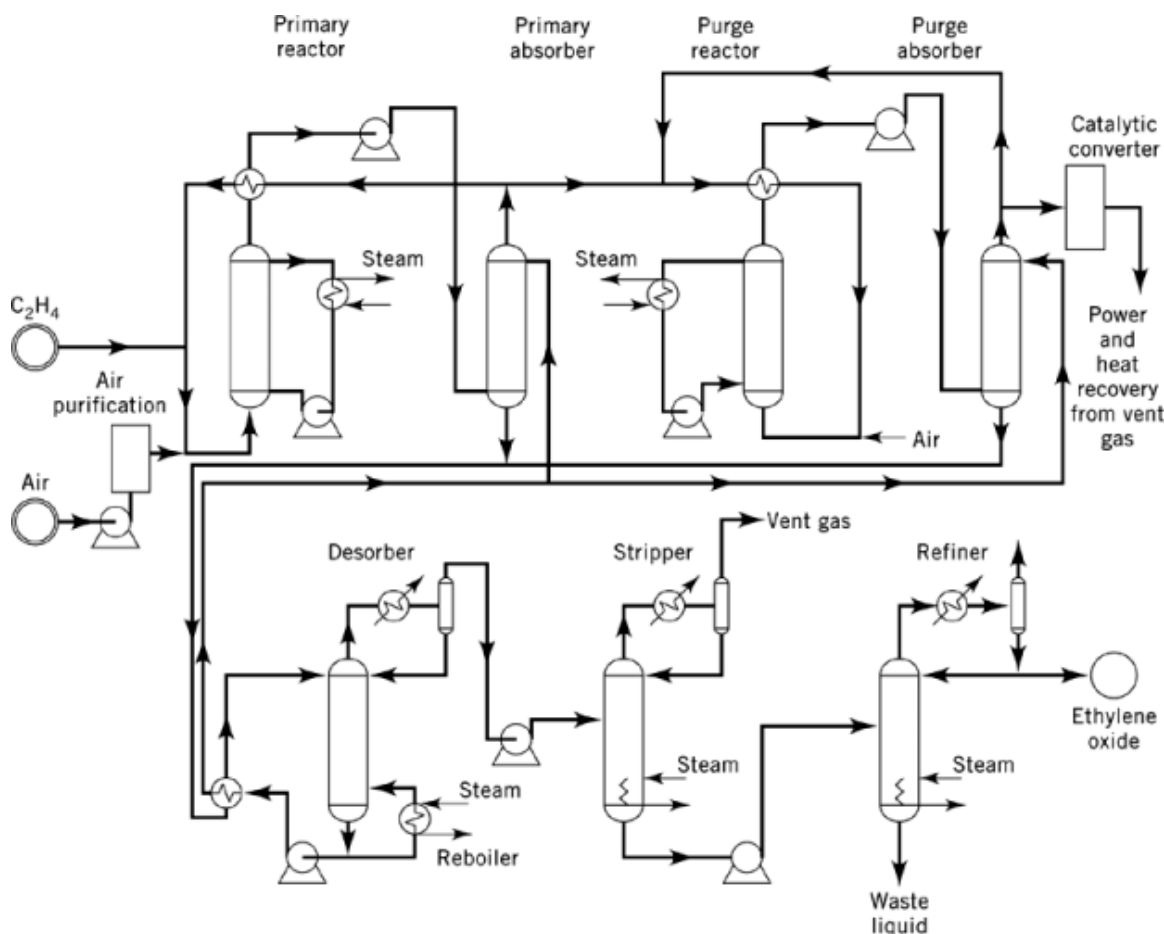


Figure 2. Air-based direct oxidation process for ethylene oxide.

In the first section, compressed air is filtered, purified (if necessary), and fed separately with ethylene into a recycle gas stream. This recycle stream feeds a bank of one or more primary multitubular reactors that operate in parallel. The number of primary reactors used depends chiefly on the plant capacity, size of the individual reactors, and the activity and the selectivity of the catalyst used. The ethylene is oxidized to ethylene oxide, carbon dioxide, and water in the packed-bed converters, and the heat of reaction is removed by circulating or boiling an organic oil on the shell side, eg, Dowtherm, Tetralin, or other high boiling materials. The hot oil is cooled in a steam generator, producing considerable amounts of high pressure steam for the ethylene oxide and other processes at the plant site. The per pass ethylene conversion in the primary reactors is maintained at 20–30% in order to ensure catalyst selectivities of 70–80%. Vapor-phase oxidation inhibitors such as ethylene dichloride or vinyl chloride or other halogenated compounds are added to the inlet of the reactors in ppm concentrations to retard carbon dioxide formation. The process stream exiting the reactor may contain 1–3 mol % ethylene oxide. This hot effluent gas is then cooled in a shell-and-tube heat exchanger to around 35–40°C by using the cold recycle reactor feed stream gas from the primary absorber. The cooled crude product gas is then compressed in a centrifugal blower before entering the primary absorber.

The second important step of the process is ethylene oxide recovery from the crude product gas. This is accomplished in the primary absorber by countercurrent scrubbing with cold water in a column ca 18–20 m high. The ethylene oxide produced in the reactor is dissolved in the absorber water along with some nitrogen and carbon dioxide, and traces of ethylene, ethane, and aldehydes. The aqueous stream is removed from the base of the absorber and sent to a desorber. The unabsorbed gas from the main absorber overhead is split into two portions. The largest portion is recycled to the primary reactor after it cools the hot product gas in the shell-and-tube heat exchanger, and the circulation cycle is repeated. A much smaller fraction of the primary adsorber overhead gas stream is heat-exchanged to raise its temperature, and it is then fed as the main stream to the secondary or purge reactor system. In the purge reactor, more air may be added to increase the oxygen content of the feed gas. The gases leaving the purge reactor are heat-exchanged against the feed gas to the same reactor, and then enter a purge absorber. In the purge absorber, ethylene oxide is removed with water in the same manner as in the main absorber.

The third key section of the process deals with ethylene oxide purification. In this section of the process, a variety of column sequences have been practiced. The scheme shown in Figure 2 is typical. The ethylene oxide-rich water streams from both the main and purge absorbers are combined, and after heat exchange are fed to the top section of a desorber where the absorbate is steam stripped. The lean water from the lower section of the desorber is virtually free of oxide, and is recirculated to the main and purge absorbers. The concentrated ethylene oxide vapor overhead is fed to the ensuing stripper for further purification. If the desorber is operated under vacuum, a compressor is required. The ethylene oxide recovered in the desorber contains some carbon dioxide, nitrogen, aldehydes, and traces of ethylene and ethane. In the stripper the light gases are separated overhead and vented, and the partially purified ethylene oxide is sent from the bottom of the stripper to the mid-section of a final refining column. The ethylene oxide from the refining section should have a purity of . The final product is usually stored as a liquid under an inert atmosphere.

The overall economics of the process are strongly dictated by the design of the reaction system and the actual operating conditions used. The catalyst properties, as they influence reactor design and operating variables are, therefore, of the greatest significance. Specific information on actual conditions employed in the manufacture is not disclosed. However, the general ranges suggested by literature and patent reviews are summarized in Table 1.

Table 1. Ranges of Reaction System Variables in the Direct Oxidation Process for Ethylene Oxide

Variable	Air oxidation	Oxygen oxidation
ethylene, mol %	2–10	20–35
oxygen, mol %	4–8	4–8
carbon dioxide, mol %	5–10	5–10
ethane, mol %	0–1.0	0–1.0
temperature, °C	220–277	220–235
pressure, MPa	1–3	2–3
space velocity, h ⁻¹	2000–4500	2000–4500
pressure drop, kPa	41–152	41–152
conversion, %	20–65	8–12
selectivity or yield (mol basis, %)	63–75	75–82

Oxygen-Based Direct Oxidation Process

Even though the fundamental reaction and the ultimate results are the same, there are substantial differences in detail between air- and oxygen-based processes. Virtually all the differences arise from the change in the oxidizing agent from air (ca 20 mol % O₂) to pure oxygen (O₂). Due to the low per pass conversion, the need for complete removal of ethylene oxide by absorption, and the accumulation of nitrogen in the cycle, the air process requires a substantial purge stream. As a direct consequence of this purge stream, the air-based process requires the staged reaction–absorption system described earlier. The oxygen-based process uses substantially pure oxygen, reduces the quantities of inert gases introduced into the cycle, and thereby results in almost complete recycle of the unconverted ethylene. This eliminates the need for a purge reactor system in an oxygen-based process. However, as in the air-based process, the volume of carbon dioxide formed is about half the volume of ethylene that reacts at a catalyst selectivity of 70–80%. This CO₂ must be eliminated on a continuous basis in order to control its concentration at a fixed acceptable level in the cycle. Concentrations of CO₂ much in excess of 15 mol % adversely influence catalyst activity. Therefore, in an oxygen-based system, part of the recycle gas leaving the absorber must be treated in a CO₂ removal unit before it is sent back to the main reaction cycle.

In addition to the CO₂ removal unit purge stream, an additional process vent is required to prevent accumulation of argon in the cycle. Argon is a significant impurity in the oxygen supply, and can build up to 30–40 mol % in the cycle gas if no deliberate purge is used. When this happens, because of the lower heat capacity of the argon, the cycle gas may enter the flammable region, and as a result the oxygen concentration in the cycle has to be lowered. Consequently, the selectivity of the process is substantially lower. In spite

of this additional purge, the total vent stream in an oxygen-based process is much smaller than in an air-based unit. The operation of the main reactor can be at much higher ethylene concentration than that possible in air-based process due to the smaller purge flow. The high ethylene concentration improves the catalyst selectivity because the per pass conversions are lower for a given ethylene oxide production. The small purge rates in an oxygen-based system operated with very high purity oxygen (99.0–99.5 mol %) make it possible to use cycle diluents of improved heat capacity other than nitrogen. These diluents facilitate the use of higher oxygen concentrations in the cycle and, therefore, improve selectivity.

Figure 3 shows a simple schematic diagram of an oxygen-based process. Ethylene, oxygen, and the recycle gas stream are combined before entering the tubular reactors. The basic equipment for the reaction system is identical to that described for the air-based process, with one exception: the purge reactor system is absent and a carbon dioxide removal unit is incorporated. The CO₂ removal scheme illustrated is based on a patent by Shell Oil Co., and minimizes the loss of valuable ethylene in the process.

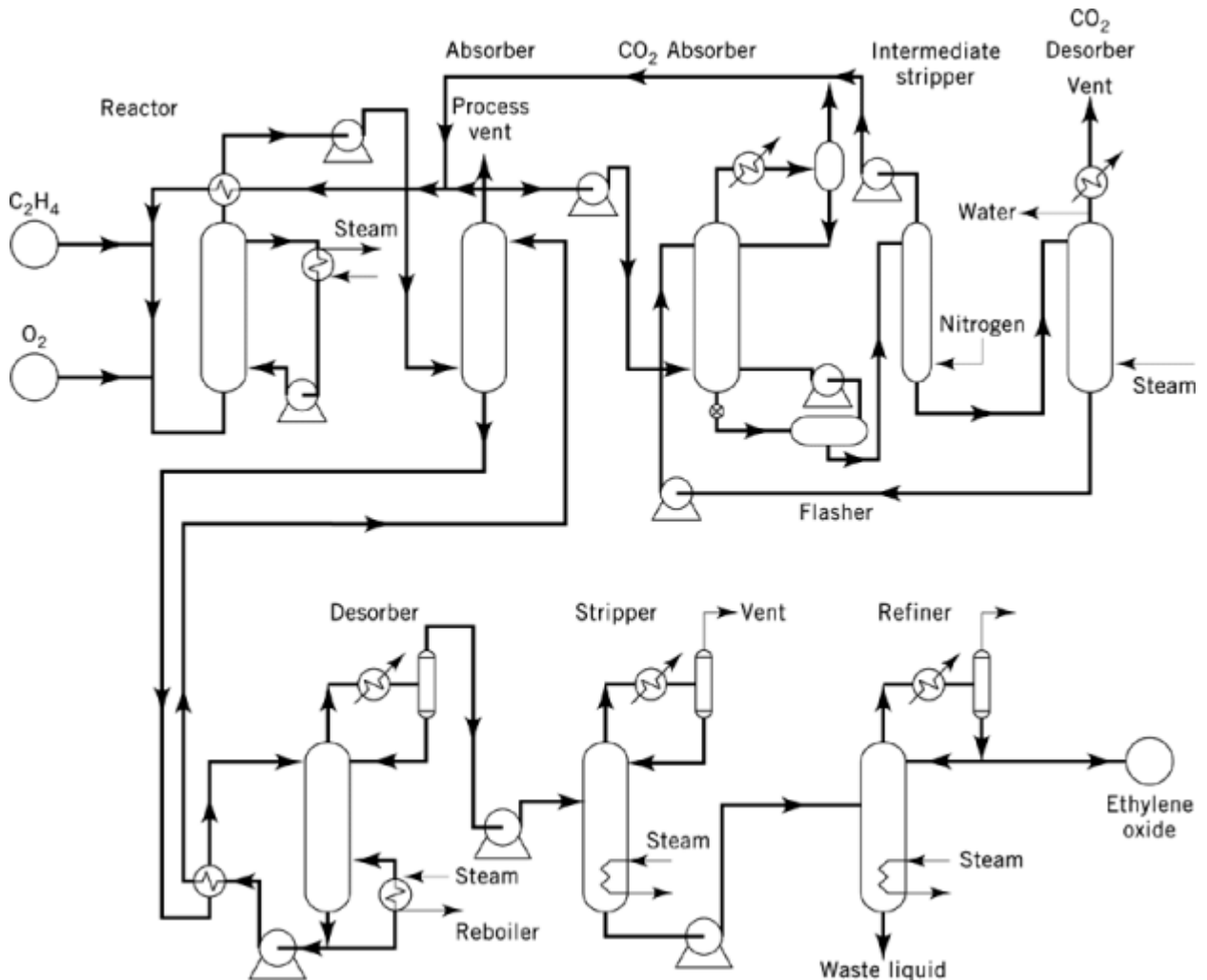


Figure 3. Oxygen-based direct oxidation process for ethylene oxide.

The main process vent stream generally contains a fairly high hydrocarbon concentration, particularly if the diluent is not nitrogen. In such cases, the purge stream can be readily used in a boiler or incinerated in a furnace without supplemental fuel. The ethylene oxide recovery and refining sections for both the air- and oxygen-based processes are almost identical. As with the air-based process, specific operating conditions for the reaction system are proprietary; however, the general ranges reported in the literature and patents are summarized in Table 1.

Temperature and Thermal Factors

Temperature is used to control two related aspects of the reaction: heat removal from the reactor bed and catalyst operating temperature. The reactor temperature is controlled through the use of a heat-transfer fluid on the reactor shell. The coolant used in most recent designs is boiling water. Boiling water provides good heat transfer and improved safety over previous reactor designs using either boiling or circulating organic heat-transfer fluids. Control of the catalyst operating temperature is necessary to prevent catalyst damage such as sintering or tube damage resulting from excessive temperatures in the catalyst bed. Localized hot spots of 100–300°C above the coolant temperature can form in the catalyst bed without adequate temperature control.

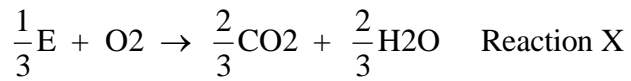
Heat removal from the reactor is necessary for stable operation. Heat is removed through two processes: sensible heat of the process gas and heat transfer to the coolant. Stable operation of the reactor requires balancing these removal processes with the heat generated in the reaction. The undesired complete oxidation of ethylene is the primary source of heat, with a heat of reaction of 1419.0 kJ/mol of ethylene compared with the partial oxidation heat of reaction of 105.2 kJ/mol (25 kcal/mol). Since the activation energy for complete combustion (16.8 kJ/mol) is greater than for partial oxidation (15.2 kJ/mol), and higher temperatures increase the rate of ethylene oxide combustion, the catalyst selectivity drops as temperature increases. This compounds the increased heat generation with increasing catalyst temperature. For example, 25 t/h of ethylene oxide production at 75% selectivity generates 91.3 MW; increasing the temperature to increase production to 30 t/h will decrease the catalyst selectivity, say to 70%, and the heat generated (135 MW) for this 20% increase in production is a 48% increase. Therefore, stable operation of the ethylene oxide reactor requires stability in the coolant temperature control.

The reactor stability is also affected by the internal temperature profile in the tubular catalyst bed. The highest reaction rate occurs near the inlet, where the partial pressure of the components is the highest. This results in the highest heat generation rate and therefore the maximum (bed temperature–coolant) temperature. Stable operation of the reactor requires keeping this peak temperature difference to less than 30–40°C. Several techniques have been proposed for resolving this problem. For example, a gradation in the catalyst activity down the length of the reactor could result in a uniform temperature profile and improved catalyst selectivity. Other solutions propose improving the reactor thermal conductivity.

Literally summarized from: Kirk-Othmer Encyclopedia of Chemical Technology, 2005 Published by John Wiley & Sons, Inc.

2. Reaction equations

In short notation the reaction equations are:



3. Kinetics

The reaction rate expressions reported in literature vary from completely empirical to complex equations of the Langmuir-Hinselwood type. In case of a large excess of ethylene as applied in oxygen based units, literature agrees that first order kinetics in oxygen concentration can be used. We selected the following rate expressions from literature data:

$$-R_p = k_p C_{\text{O}_2} = 35.2 e^{\frac{-7200}{T}} C_{\text{O}_2}, \quad \frac{\text{mol O}_2}{\text{kg}_{\text{cat}} \cdot \text{s}}$$

$$-R_x = k_x C_{\text{O}_2} = 74.1 \times 10^3 e^{\frac{-10800}{T}} C_{\text{O}_2}, \quad \frac{\text{mol O}_2}{\text{kg}_{\text{cat}} \cdot \text{s}}$$

With T in Kelvin.

4. Enthalpy of reaction

In table 2, the enthalpy of formation and the C_p of the components involved are listed.

The heat capacities are assumed to be constant.

Table 2: $H_f(298.2K)$ and C_p values

	$H_f(298.2K)$ [J/mol]	C_p [J/(mol.K)]
E	5.24×10^4	65
EO	-5.26×10^4	78
O ₂	0	30
CO ₂	-3.935×10^5	49
H ₂ O	-2.418×10^5	36

5. Maximal particle size of the catalyst

Bases on a single particle model it was derived that the size of the particles should be less than 3 mm in order to have no mass and energy limitations at particle level. In your design you should work with such small particles.

6. Reactor Model

Both 1-dimensional and 2-dimensional models are applied to describe wall cooled packed bed reactors. Obviously, 2D models provide more detail. However, for a ethylene oxide reactor with typically low d_t/d_p (reactor diameter over catalyst particle diameter) and a high gas load, the 1D plug-flow model is adequate to describe a single packed tube. Detailed information on packed bed models is available in “Chemical Reactor Design and Operation” by Westerterp, Van Swaaij and Beenackers, 2nd edition, page 622 and further.

A) Derive a 1D plug-flow model for an ethylene oxide reactor using oxygen. The following assumptions can be made:

- The feed contains only oxygen and ethylene oxide.

- In the energy balance the C_p of ethylene is representative for the whole mixture and C (mol/m³) can be taken as $P/(RT_{in})$
- The enthalpy of reaction is constant for both reactions:

$$\Delta H_p = -2.11 \times 10^5 \text{ J/mol O}_2$$

$$\Delta H_x = -4.42 \times 10^5 \text{ J/mol O}_2$$
- The inlet temperature equals the coolant temperature.
- The overall heat transfer coefficient is constant and evaluated at the inlet conditions.
- A proper particle size has been selected under 3 mm so that the effectiveness factor is larger than 0.90 under all conditions. For modeling purposes it is assumed that the effectiveness factor is 1, i.e. the reaction rate can be evaluated at the bulk conditions.

The overall heat coefficient can be calculated with the model of Dixon (Chemical Engineering and Processing 35 (1996) p 323). The correlations of Schündler and co-workers are used for calculating the effective radial conductivity (λ_r) of the reactor (Chem. Ing. Techn. 38 (1966) p 967, Chem. Ing. Techn. 42 (1975) p 933).

$$\frac{1}{U} = \frac{1}{\alpha_w} + \frac{R_t}{3\lambda_r} \frac{Bi + 3}{Bi + 4}$$

$$Bi = \frac{\alpha_w R_t}{\lambda_r}$$

$$Re_p = \frac{\rho_g u d_p}{\mu_g}$$

$$Nu = \frac{\alpha_w d_p}{\lambda_r} = 1.5 Re_p^{-0.25}$$

$$\lambda_r = \lambda_o + \lambda_t$$

$$\lambda_t = \frac{\rho_g C_{p_g} u d_p}{8(2 - (1 - 2 \frac{d_p}{d_t})^2)}$$

$$\frac{\lambda_o}{\lambda_g} = 0.67 \varepsilon + (1 - \varepsilon)^{0.5} A$$

$$A = \frac{2}{(1 - B \frac{\lambda_g}{\lambda_c})} \left(\frac{(1 - \frac{\lambda_g}{\lambda_c}) B}{(1 - B \frac{\lambda_g}{\lambda_c})^2} \ln(\frac{\lambda_c}{B \lambda_g}) - \frac{B + 1}{2} - \frac{B - 1}{(1 - B \frac{\lambda_g}{\lambda_c})} \right)$$

$$B = 1.25 \left(\frac{(1 - \varepsilon)}{\varepsilon} \right)^{1.11}$$

Properties are listed in table 3.

Table 3. Properties

Parameter	Description	Unit	Value
C	Molar concentration	mole/m ³	
C _{p_g}	Specific heat of the bulk gas	J/kg/K	
C _{p_E}	Specific heat of ethylene	J/mol/K	65
D _g	Diffusion coefficient of the bulk gas	m ² /s	5.10 ⁻⁵
D _{eff}	Effective diffusion coefficient in the catalyst particle	m ² /s	4.10 ⁻⁷
d _t	Inner diameter of the reactor tube	m	1'' = 24.3.10 ⁻³ m 2'' = 49.3.10 ⁻³ m 3'' = 73.7.10 ⁻³ m
d _{to}	Outer diameter of the reactor tube	m	1'' = 25.4.10 ⁻³ m 2'' = 50.8.10 ⁻³ m

			$3'' = 76.2 \cdot 10^{-3} \text{ m}$
d_p	Diameter of the catalyst particles	m	
f_i	Volume fraction of component i in the bulk gas	-	
H_p	Reaction enthalpy of reaction p	J/mole O ₂	$-2.11 \cdot 10^5$
H_x	Reaction enthalpy of reaction x	J/mole O ₂	$-4.42 \cdot 10^5$
P	Pressure	Pa	
R	Gas constant	J/mol/K	8.314
R_t	Inner radius of the reactor tube	m	
r	Radius of the reactor tube	m	
T	Temperature	K	
T_{in}	Inlet temperature	K	
T_c	Coolant temperature	K	
T_{max}	Maximal temperature in the reactor	K	
T_m	Maximal allowable temperature	K	
u	Linear gas velocity in the reactor	m/s	
U	Overall heat transfer coefficient based on the inner reactor tube diameter	W/m ² /K	
α	Heat transfer coefficient from the bulk to the particle	W/m ² /K	
α_w	Heat transfer coefficient inner wall reactor tube	W/m ² /K	
ε	Porosity (gas fraction) of the packed bed	-	0.45
η_g	Viscosity of the bulk gas	Pa.s	$1.5 \cdot 10^{-5}$
λ_g	Conductivity of the bulk gas	W/m/K	0.04
λ_c	Conductivity (effective) of the catalyst	W/m/K	0.22
λ_r	Radial conductivity of the inside of the reactor tube	W/m/K	
λ_o	“No flow” contribution to λ_r	W/m/K	
λ_t	Convective contribution to λ_r	W/m/K	
ρ_c	Density of the catalyst based on the particle's volume	kg/m ³ _{cat}	1900
$\rho_{c,t}$	Density of the catalyst based on the reactor tube's volume	kg/m ³ _{tube}	850

B) Develop a MatLab code to solve the equations.

Input parameters for the model should be: the annual EO production, d_p , d_t , P, $T_{in}(T_c)$, u, composition of the feed (f_i) and the desired oxygen conversion.

The outputs of the model should be:

- At the desired oxygen conversion: L (required length), X_E , X_{O_2} , $(\sigma_{EO})_E$, Y_E , and $T(=T_{out})$.
- The temperature at the hot-spot (T_{max}): the maximal temperature in the reactor.
- The number of tubes (n_{tubes}) required for the production of x ton ethylene oxide per year.
- The over heat transfer coefficient and the total required heat exchange area (based on the inner diameter of the tubes).
- Plots of axial profiles of X_{O_2} , $(\sigma_{EO})_E$ and T for the range $l = 0 - 20$ m.

7. Simulations

The model developed under section 6 has been thoroughly validated by comparison with experiments conducted in single tubes of equal sizes as foreseen for the commercial reactor. The positive results of the validation gives the reactor-engineers confidence in using the model for design calculations of a large commercial unit.

Here we will perform several simulations to investigate the effect of the operating conditions and the choice of tube diameter and catalyst size on the reactor performance and the required reactor volume. Plot the axial profiles of T, the oxygen conversion (X_{O_2}) and $(\sigma_{EO})_E$ for every considered case.

The design data are:

- 50×10^3 ton per year EO production (1 year = 8000 h).
- $T_{\max} = 500^\circ\text{C}$.
- $P_{\max} = 35$ bar.
- Tubes of 1, 2 or 3" can be used.
- Maximal height = 20 m
- $X_{O_2} > 0.35$.
- $(\sigma_{EO})_E > 0.70$.

T_{\max} and P_{\max} are material constraints. The required minimum values of X_{O_2} and $(\sigma_{EO})_E$ are dictated by an economic evaluation of the whole EO plant.

A) We will consider the following base-case:

$$d_p = 4 \text{ mm}, d_t = 2'', P = 1 \text{ MPa } T_c(T_{in}) = 225^\circ\text{C}, u = 1.3 \text{ m/s}, f_{O_2} = 0.07, f_E = 0.93, \\ X_{O_2} = 0.4$$

B) Base-case with $d_p = 2 \text{ mm}$

C) Base-case with $X_{O_2} = 0.5$

D) Base-case with $d_t = 3''$

E) Base-case with $f_{O_2} = 0.09, f_E = 0.92$

F) Base-case with $f_{O_2} = 0.12, f_E = 0.88$

These conditions will lead to “run-away” behavior (see answers).

We can also determine what the operation space is for near “run away” conditions. This region is important, because very small disturbances in the conditions can lead to a run away. In practice such disturbances are always present, e.g. the heat transfer coefficient drops due to fouling of the tubes. We can illustrate this by considering a feed with 10.5 vol% (others conditions = base case). This feed composition shows no run away. But if we decrease the heat transfer coefficient by only 5%, the system runs away. Check this.

With a mathematical model, as the one we developed, we can detect run away conditions. There are also criteria developed from theory for run away. However, they are always based on approximations and are only valid for specific cases. There are criteria for single reactions (Froment and co-workers, e.g. Chem. Eng.

Sci. 25 (1970), p1503) and first order parallel reactions (Westerterp and Ptasiński, Chemical Engineering Science, 39 (1984), p235-251).

The criterion of Westerterp, however, is based on a certain desired selectivity level and not especially on save operation.

The first criterion of Froment goes as follows;

$$\frac{RT_m}{E_{act}} \leq 0.5 \left[1 - \sqrt{1 - \frac{4RT_c}{E_{act}}} \right]$$

In this equation E_{act} is the activation energy of the reaction, T_c the coolant temperature and T_m the “maximal allowable temperature”. The exact physical of T_m is not quite clear. The second criterion of Froment is given by:

$$\frac{\Delta T_{ad}}{T_m - T_c} \leq 1 + \sqrt{\frac{N_c}{e}} + \frac{N_c}{e}$$

$$N_c = \frac{4U}{d_t k_v(T_c) \rho_g C_{p_g}}$$

$$e = 2.718281828$$

In this equation, k_v is the reaction rate constant (1/s) based on the reactor's volume and ΔT_{ad} the adiabatic temperature gradient.

Check if the criteria of Froment can predict the maximal oxygen fraction in the feed for base case conditions. Use in the analysis the kinetic data of the undesired reaction, X.

- G) Base-case with $T_{in} = 240^\circ\text{C}$
- H) Base-case with $u = 0.6 \text{ m/s}$
- I) Base case with $u = 1.9 \text{ m/s}$
- J) Base-case with $P = 30 \text{ MPa}$

8. Reactor

What would be your optimal design? Motivate your choices and final result by simulations.