# Process Design for Annual Output of 60,000 Tons of Ethylene Oxide

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## Abstract

**Ethylene oxide is a kind of ethylene derivative, which is a very important basic organic chemical raw material. The preparation of ethylene oxide by direct oxidation of ethylene with silver as catalyst was studied. The temperature in the reactor is about 182 °C, and the pressure is about 2.1 MPa. Then the absorption of the product, carbon dioxide removal and other operations were designed, and finally mainly for the design of the distillation tower. Design results: 12 theoretical trays and 21 actual trays are needed for the distillation tower. The diameter of the tower is designed to be 2.6m and the height of the tower is required to be 23.6 m.**

## Keywords

**Ethylene Oxide; Direct Oxidation; Distillation Tower Design.**

## 1. Introduction

Ethylene oxide opens the ring easily and releases more energy, making it chemically more reactive. When ethylene oxide encounters alkali, alkali metal, iron, tin, aluminum and other catalysts with high activity, disproportionation, self-polymerization, decomposition reactions will occur, releasing more heat [1].

AreEthylene oxide (EO) has a wide range of applications due to its active chemical properties. Ethylene oxide is an important organic chemical product second only to polyethylene and polyvinyl chloride in ethylene industrial derivatives [2]. Most ethylene oxide is directly used to produce ethylene glycol, and refined ethylene oxide can be used to produce ethoxy compounds, ethanolamine, glycol ether, etc. [3].

Ethylene oxide is also a toxic carcinogen with bactericidal effect. Human exposure to ethylene oxide (ETO) is mainly through inhaling occupational air pollution and tobacco smoke. ETO can react with DNA and protein to produce some molecular adducts [4]. Ethylene oxide (EO), a metabolite of ethylene also present in cigarette smoke, is a carcinogen in rodents [5]. Poolej [6] found that the risk of human cancers caused by ethylene oxide is very low, especially at the level of occupational exposure that has occurred in the United Kingdom in recent decades.

Ethylene oxide has bactericidal effect, high osmotic pressure, no corrosion to metals and no residual odor, so it can be used as a gaseous fungicide for some articles and materials that cannot withstand high temperature disinfection. The future of ethylene oxide (EO) sterilization has been questioned due to its associated toxicity. EO has existed for more than 60 years, mainly because of its recognized reliability and effectiveness, combined with process flexibility, and compatibility with most mechanical equipment [7]. EO sterilization may reduce the biological performance of osteo-induced implants and reduce cell penetration to bulk materials [8].

As for the production of ethylene oxide, the earlier method was chloroalcohol, but with the development of technology, people found a better and easier method, that is the direct oxidation of ethylene. In addition, the research team at the University of Toronto, Canada, with the premise of green development, is studying a new and green production method, renewable electricity-based electrochemical process, which reduces $CO_2$ emission and pollution compared with common methods.

Ethylene direct oxidation method is: with silver as a catalyst, ethylene and oxygen in a certain reaction conditions, will react, in the appropriate temperature, pressure, $CH_2=CH_2$ and $O_2$ reaction, preparation of ethylene oxide, and is an exothermic reaction. Direct oxidation method can be divided into two

oxidation methods of air type and oxygen type according to the different oxidant selection of ethylene. The UCC used the air type method back in the 1980s. American SD Company, Shell Company and United Carbon Company have all mastered the method of producing ethylene oxide by directly reacting $CH_2=CH_2$ and $O_2$ to produce ethylene oxide by oxidation method [9].

As an oxidant of air oxidation method, it has a certain purification effect on harmful impurities. Due to the high inert gas content in the system, ethylene consumption is high and energy consumption is high, so the cost is high. As times have changed, the advantages of direct air oxidation have diminished, so it is rarely used today.

The advanced technology of oxygen direct oxidation provides a greater possibility for mass production of ethylene oxide. The production process consumes less raw materials, and the generated products contain less impurities, and the purity can even reach 99.99 %. The production scale of oxygen direct oxidation method is small, the investment is small, but the utilization rate of ethylene in the production process is high, the loss is less, and the exhaust gas emission is reduced. Compared with air oxidation, this method uses pure oxygen oxidant, which has the advantages of lower cost, higher feed concentration, higher selectivity, lower reaction temperature and longer catalyst life. Comparatively speaking, the use of oxygen direct oxidation method is better, so this design uses oxygen type method, using ethylene direct oxidation method to produce ethylene oxide.
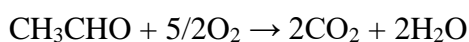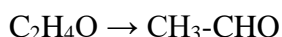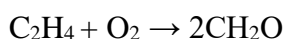
## 2. Reaction principle

### 2.1 Oxidation principle
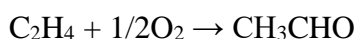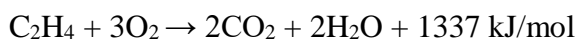
Broccoli Ethylene oxidation can be divided into partial oxidation and complete oxidation. In the reaction process, the C=C double bond of $CH_2=CH_2$ is activated, and some of the C=C double bond is oxidized to form $C_2H_4O$. Because the $CH_2=CH_2$ molecule has poor structural stability, the $CH_2=CH_2$ skeleton is likely to be damaged if oxidized normally. Therefore, when ethylene oxide is produced, carbon dioxide and water will also be generated, which will affect the reaction. As the product is not pure, the reaction result is not only EO, but also by-products.

Silver catalyst technology occupies an important position in the development of ethylene oxide - ethylene glycol - polyester industrial chain.

The main reaction: $C_2H_4 + 1/2O_2 \rightarrow C_2H_4O + 105$ kJ/mol

In the reaction of ethylene oxidation to ethylene oxide, Ag acts as the main catalytic component of the catalyst. However, the single-component Ag catalyst can only have about 50% selectivity, and the selectivity of Ag catalyst can be significantly improved by adding extremely small amount of cesium component [10].

In addition, carbon dioxide and water are by-products of the direct oxidation of ethylene. The effect of $CO_2$ on catalyst selectivity can be divided into three stages: when $C(CO_2) < 1\%$, the catalyst selectivity ranges from 85.2% to 53.9%; When $1\% < C(CO_2) < 2\%$, the selectivity of catalysts ranged from 83.6% to 90.9%. When $C(CO_2) > 2\%$, the selectivity of the catalyst is 80.1 % ~70.2 % [11]. The by-products are formed in two main ways. The first is the main reaction:

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O + 1337$ kJ/mol

$C_2H_4 + 1/2O_2 \rightarrow CH_3CHO$

$C_2H_4 + O_2 \rightarrow 2CH_2O$

$C_2H_4O \rightarrow CH_3\text{-}CHO$

$CH_3CHO + 5/2O_2 \rightarrow 2CO_2 + 2H_2O$

### 2.2 Principles of carbon dioxide removal

$CO_2$ is a by-product of oxidation reaction, so the by-product elimination reaction is also needed. The thermal $K_2CO_3$ method can be used to remove $CO_2$. This method belongs to the chemical method:

$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3 + 267.8912$ kJ/mol

## 3. Process flow

The Ethylene oxide production is mainly divided into: reaction absorption →$CO_2$ removal→ reabsorption stripping→refining EO.

The overview of technological process shows that the reaction system is operated in a cyclic process. The reaction raw materials include ethylene and oxygen. In order to maintain the stability of the process, methane can be added to it.

## 4. Material balance

### 4.1 Physical and chemical properties

Table 1. Physical properties

| No | Component | Molecular | Molecular | Boiling point/°C |
|----|-----------|-----------|-----------|------------------|
| 1 | Nitrogen | $N_2$ | 28.0000 | -196.0 |
| 2 | Oxygen | $O_2$ | 32.0000 | -183.0 |
| 3 | Argon | Ar | 40.0000 | -186.0 |
| 4 | Methane | $CH_4$ | 16.0000 | -162.0 |
| 5 | Ethane | $C_2H_6$ | 30.0000 | -89.0 |
| 6 | Ethylene | $C_2H_4$ | 28.0000 | -104.0 |
| 7 | Epoxy ethane | $C_2H_4O$ | 44.0000 | 10.0 |
| 8 | Carbon dioxide | $CO_2$ | 44.0000 | -78.0 |
| 9 | Acetaldehyde | $CH_3CHO$ | 44.0000 | 20.0 |
| 10 | Ethylene glycol | $(CH_2OH)_2$ | 62.0000 | 197.0 |
| 11 | Water | $H_2O$ | 18.0000 | 100 |

### 4.2 Design basis

1) Design tasks: annual output of 60,000 tons of ethylene oxide process design;

2) Assumed annual factory work: 7,800 hours;

3) Assume that the yield of EO in the factory is 0.3;

4) Assume the conversion rate of plant $C_2H_4$ in one direction: 0.1;

5) Assume that the selectivity of EO of the factory is 0.8;

6) Assume $CO_2$ selectivity: 0.2;

7) Assuming the selectivity of $C_2H_4O$: 0.002;

8) Assumed absorption rate of EO: 0.996;

9) Assume the exhaust air ratio: 0.0018.

### 4.3 Design basis
### 4.3.1 Calculation basis

1) $O_2$: $x(N_2) = 0.00005$; $x(Ar) = 0.00195$; $x(O_2) = 0.9980$

2) $C_2H_4$: $x(CH_4) = 0.0005$; $x(C_2H_4) = 0.9985$; $x(C_2H_6) = 0.0010$

3) CH4: $x(N_2) = 0.0200$; $x(CH_4) = 0.9690$; $x(C_2H_4) = 0.0050$; $x(CO_2) = 0.0060$

4) Absorption tower: L/V = 2.000

5) The absorption rate of CO2:0.1800

### 4.3.2 Mixer

$C_2H_4$:$F_2 = F(C_2H_4)$ = task/(time × molar mass of EO × yield of EO) = (6 × 10000 × 1000)/(7800 × 44.0524×0.3) = 582.0574 Kmol/h

$F_2(CH_4) = 582.0574/0.998 \times 0.0005 = 0.2916$ Kmol/h

$F_2(C_2H_6) = 582.0574/0.998 \times 0.00100 = 0.5832$ Kmol/h

$F_2 = F_2(C_2H_4) + F_2(CH_4) + F_2(C_2H_6) = 582.0574 + 0.2916 + 0.5210 = 582.8700$ Kmol/h

$F_2$ = 582.8700 Kmol/h

### 4.3.3 Reactor

RF ($C_2H_4$) =MF ×y($C_2H_4$) ×(One-way conversion of ethylene) =19024.4818 ×0.3 ×0.9

=5136.6101 kmol/h

$R_F$ (EO) = $M_F$ × y($C_2H_4$) × (One-way conversion of ethylene) × (Selectivity of ethylene oxide) + $M_F$ × $y_{EO}$ = 19024.4818 × 0.3 × 0.1 × 0.8 + 19024.4818 × 0.0001 = 458.4900 kmol/h

$R_F$($CO_2$) = $M_F$ × y($C_2H_4$) × (One-way conversion of ethylene) × (Carbon dioxide selectivity) × 2 + $M_F$ × y($CO_2$) = 19024.4818 × 0.3 × 0.1 × 0.2 × 2 + 19024.4818 × 0.05 = 1179.5179 kmol/h

$R_F$($C_2H_4O$) = $M_F$ × y($C_2H_4$) × (One-way conversion of ethylene) × (Selectivity of acetaldehyde) = 19024.4818 × 0.3 × 0.1 × 0.002 = 1.1415 kmol/h

$R_F$ ($H_2O$) = $M_F$ × y($H_2O$) + $M_F$ × y($C_2H_4$) × (One-way conversion of ethylene) × (Carbon dioxide selectivity) × 2 = 19024.4818 × 0.0063 + 19024.4818 × 0.3 × 0.1 × 0.2 × 2 = 348.1480 kmolh

$R_F$ ($O_2$) = 19024.4818 × 0.0832 - 19024.4818 × 0.3 × 0.1 × 0.8 × 0.5 -19024.4818 × 0.3 × 0.1 × 0.002 × 0.5 - 19024.4818 × 0.3 × 0.1 × 0.2 × 3 = 1012.0000 kmo/h
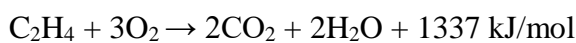
### 4.3.4 Absorption of carbon dioxide

Preheat first, better absorption effect. Among them, the absorption and desorption of $CO_2$ are chemical reaction processes.

$CO_2$(suction) = $CO_2$(enter) × $CO_2$(absorption rate) = 1179.5179 × 0.2 = 235.9036 kmol/h

F(cycle)($CO_2$) = 1179.5179 - 235.9036 = 943.6144 kmol/h

## 5. Heat balance

$C_2H_4$ + 1/2$O_2$ → $C_2H_4O$ + 105 kJ/mol

$C_2H_4$ + 3$O_2$ → 2$CO_2$ + 2$H_2O$ + 1337 kJ/mol

T(benchmark) = $T_0$ = 25 °C(298.15 K)

The reactor: Tfeed = T1 = 151 °C (424.15 K),

Treaction = T = 235 °C(508.15 K);

Tdischarge= T2 = 235 °C(508.15K);

Conversion rate: 0.1, selectivity: 0.8, airspeed: 4000 /h, gas phase is the reference phase.

Table 2. Specific heat at constant pressure

| Component | A | B | C | D×108 |
|-----------|-----------|-----------|--------------|---------|
| O2 | 26.0082 | 0.01174 | -0.000002341 | -0.0562 |
| N2 | 29.4717 | -0.00476 | 0.000012706 | -0.4794 |
| CO2 | 23.0566 | 0.05687 | -0.000031828 | 0.6388 |
| H2O | 32.4150 | 0.00034 | 0.000012851 | -0.4408 |
| C2H4 | 5.7037 | 0.143894 | -0.000067284 | 1.1800 |
| C2H4O | -7.5911 | 0.22238 | -0.000126044 | 2.6122 |

Table 3. $CP^0$ value of feed gas (J/(mol·K))

| Component | $C_2H_4$ | $O_2$ | $CO_2$ | $N_2$ |
|-----------|----------|---------|---------|---------|
| Feed gas | 63.6358 | 30.5237 | 41.9395 | 29.3728 |

Table 4. $CP^0$ value of oxidation gas(J/(mol·K))

| Component | $C_2H_4$ | $O_2$ | $CO_2$ | $N_2$ | $H_2O$ | $C_2H_4O$ |
|-----------|----------|---------|---------|---------|---------|-----------|
| | 61.6044 | 31.2957 | 44.5748 | 29.7048 | 35.3277 | 73.2075 |

Table 5. Correction parameters of feed gas pressure

| Component | $C_2H_4$ | $O_2$ | $CO_2$ | $N_2$ |
|---|---|---|---|---|
| Tc/K | 282.4000 | 154.6000 | 304.2000 | 126.2000 |
| Pc/MPa | 5.0360 | 5.0460 | 7.3760 | 3.3940 |
| Tr | 1.7110 | 3.1250 | 1.5880 | 3.8280 |
| Pr | 0.1990 | 0.1980 | 0.1360 | 0.2950 |
| $\omega$ | 0.0850 | 0.0210 | 0.2250 | 0.0400 |
| $\Delta Cp0$/ (J/(mol·K)) | 0.6700 | 0.1590 | 0.5440 | 0.1380 |
| $\Delta Cp1$/ (J/(mol·K)) | 0.6280 | 0.0380 | 0.5860 | 0.0000 |
| Cp/ (J/(mol·K)) | 61.5230 | 31.2600 | 44.4760 | 29.7380 |

Table 6. Oxide gas pressure correction parameters

| Component | $C_2H_4$ | $O_2$ | $CO_2$ | $N_2$ | $H_2O$ | $C_2H_4O$ |
|---|---|---|---|---|---|---|
| Tc | 282.4000 | 154.6000 | 304.2000 | 126.2000 | 647.3000 | 469.0000 |
| Pc | 5.0360 | 5.0460 | 7.3760 | 3.3940 | 22.050 | 7.1940 |
| Tr | 1.8530 | 3.3840 | 1.7200 | 4.1450 | 0.8080 | 1.1150 |
| Pr | 0.1990 | 0.1980 | 0.1360 | 0.2950 | 0.0450 | 0.1390 |
| $\omega$ | 0.0850 | 0.0210 | 0.2250 | 0.0400 | 0.3440 | 0.2000 |
| $\Delta Cp0$ | 0.5440 | 0.1340 | 0.4190 | 0.1260 | 1.3810 | 2.0930 |
| $\Delta Cp1$ | 0.5020 | 0.00840 | 0.5020 | 0.0000 | 4.1860 | 5.0230 |
| Cp | 64.8870 | 31.5340 | 45.532 | 29.926 | 38.3210 | 81.0980 |

Table 7. Heat carried by feed gas

| Component | Cp/ (J/(mol·K)) | Xni | XniCpi |
|---|---|---|---|
| $C_2H_4$ | 61.5230 | 0.0340 | 2.0920 |
| $O_2$ | 31.2600 | 0.0560 | 1.7510 |
| $CO_2$ | 44.4760 | 0.0770 | 3.4250 |
| $N_2$ | 29.7380 | 0.8330 | 24.7720 |
| Total | | 1.0000 | 30.0400 |

Table 8. Heat carried out by oxidizing gas

| Component | Cp/ (J/(mol·K)) | Xni | XniCpi |
|---|---|---|---|
| $C_2H_4$ | 64.8870 | 0.0273 | 1.7710 |
| $O_2$ | 31.5340 | 0.04680 | 1.4750 |
| $CO_2$ | 45.5320 | 0.04690 | 2.1350 |
| $N_2$ | 29.9260 | 0.83490 | 24.9850 |
| $H_2O$ | 38.3210 | 0.00450 | 0.1720 |
| $C_2H_4O$ | 81.0980 | 0.00460 | 0.3730 |
| Tota | | 1.0000 | 30.9120 |

## 6. Equipment calculation

### 6.1 Theoretical plate number calculation

### 6.1.1 Operating line equation of rectification section

$Y_n = [R / (R + 1)] \times X_{n-1} + x_d / (R + 1) = 0.990 X_{n-1} + 0.050$

$L = R \times D = 178.30 \times 16.50 = 2941.95$ kmol/h

$V = (R + 1) \times D = 2958.45$ kmol/h

### 6.1.2 Operating line equation of stripping section

$Y'_{n+1} = L'/V' \times x_n + (Dx_D - Fx_F)/V' = [L'/(L' - W)] \times X'_n - [W/(L' - W)] \times X_w = 4.440 X'_n - 0.0140$

$L' = L + F = 11664.59$ kmol/h

$V' = V = 2958.45$ kmol/h

$y_1 = x_D$

$x_n = y_n / [\alpha - (\alpha - 1)y_n]$

$y_{n+1} = RX_n / (R + 1) + x_D / (R + 1)$

Number of theoretical trays in distillation section : $N_T = 7$;

The theoretical number of trays in the stripping section is (6-1) = 5.

The total number of theoretical boards is 7 + 5 = 12

### 6.2 Determination of actual plate number

$E_0 = N_T / N_P \times 100\%$, t = 59.5 °C

$E_0 = 0.584$, $N_P = N_T / E_0 \times 100\% = 12 / 0.584 \times 100\% = 20.5 = 21$

### 6.3 Calculation of tower diameter

#### 6.3.1 Rectifying section

L = 2941.95kmol/h = 0.8172 kmol/s; V = 2958.45kmol/h = 0.8218 kmol/s

$M_D = x_a M_a + x_b M_b = 42.80$ kg/kmol

$\rho g = pM_D/RT = (304 \times 42.80) / 319R = 4.906$ kg/m3; $\rho L = 849$ kg/m$^3$

$V_g = VM_D / \rho g = 7.90$ m$^3$/s; $V_L = LM_D / \rho L = 0.040$ m$^3$/s

Plate spacing:$H_T = 0.46$ m,$H_L = 0.12$ m;

The separation of space:$H = H_T - H_L = 0.46 - 0.12 = 0.34$ m

$u m\alpha_x = 1.9020$ m/s$u = 0.65um\alpha_n = 1.2363$ m/s

$D_T = 3.135$ m.

$D_T = 3.135 \approx 3.5$ m $\approx 4$

#### 6.3.2 Stripping section

L' = L + F = 11664.59 kmol/h = 3.240 kmol/s

V' = V = 2958.45 kmol/h = 0.8218 kmol/s

$M_D = x_a M_a + x_b M_b = 18.20$ kg/kmol

$\rho g = pM_D / R_T = 2.70$ kg/m$^3$;$\rho'L \approx 924$ kg /m$^3$

$V_g' = V'M_D /\rho'g = 6.50$ m$^2$/s; $V_L' = L'M_{D'} /\rho'L = 0.070$ m$^2$/s

Plate spacing: $H'_T = 0.46$ m, $H'_L = 0.12$ m

The separation of space:$H' = 0.46 - 0.12 = 0.34$ m

$V'L / V'g = 0.1992$

$C' = C_{20} / [(0.020/\sigma')0.2] = 0.13$

$u'm\alpha x = C' = 2.4000$ m/s

$u' = 0.65u'm\alpha_n = 1.56$ m/s

$D'T = 2.53$ m

Round design tower diameter: 2.6m

### 6.4 Tower height calculation

Rectifying section:$D_T = 3.1$ m $\approx 4$ m; Stripping section:$D'_T = 2.6$ m; $H_T = 0.46$ m; $H_B = 1.6$ m, $H_D = 3.6$ m, $H_q = 2.6$ m.

$Z = (N_p - 1)H_T + D_T + D'_T + H_D + H_B + H_q = 23.6$ m

## 7.  Conclusion

Ethylene oxide is an organic compound, is the simplest cyclic ether, one of the heterocyclic compounds, is an important petrochemical products. Using silver as catalyst, ethylene oxide was prepared by direct oxidation of ethylene. The temperature in the reactor is about 182°Cand the

pressure is about 2.1Mp. Then the absorption of the product, carbon dioxide removal and other operations were designed, and finally mainly for the rectification tower this equipment was calculated in detail. The calculation shows that the annual production of 60,000 tons of ethylene oxide, in the annual work of 7, 800 hours, the distillation tower needs 12 theoretical trays, the actual trays need 21, the tower height is 23.6 m.

## References

[1] Li C Q, Ruan L F, Yang J X. Synthesis of ethylene oxide by chemical process [J]. New Industrialization, 2020, 10 (5): 121-122, 133.

[2] Tan J, Zhong X H, Li W. Analysis on the market of ethylene oxide at home and abroad [J]. Contemporary Petroleum & Petrochemical, 2014, 22 (2): 30-35.

[3] Qian Y Y, Chen R l, Chen J H, et al. Market analysis of ethylene oxide in China [J]. Chemical Industry, 2016, 34 (2): 46-48.

[4] Vincenti M, Scursone E, Bono R, et al. Formation of N-(2-hydroxyethyl)valine due to exposure to ethylene oxide via tobacco smoke: A risk factor for onset of cancer [J]. Environmental Research. Section A, 1999, 81 (1): 62-71.

[5] Watson M, Fennell T R, Morris RW, et al. Hemoglobin adducts from acrylonitrile and ethylene oxide in cigarette smokers: effects of glutathione S-transferase T1-null and M1-null genotypes [J]. Cancer epidemiology, biomarkers and prevention: A publication of the American Association for Cancer Research, 2000, 9 (7) : 705-712.

[6] Poole J, Coggon D, Palmer K T, et al. Mortality of workers exposed to ethylene oxide: extended follow up of a British cohort [J]. Occupational and environmental medicine,2004,61(4):358-362.

[7] DA-CUNHA-MENDES GC, DA-SILVA-BRANDAO TR, MIRANDA-SILVA CL. Ethylene oxide potential toxicity [J]. Expert review of medical devices, 2008, 5 (3): 323-328.

[8] LINDQVIST SB, ASPENBERG P. Ethene oxide and bone induction. Controversy remains [J]. Acta orthopaedica Scandinavica., 1998, 69 (2): 173-176.

[9] Zhu J F, Qian B Z. Chemical Industry and Technology Market, 2007, 30 (7): 1-7.

[10] Ni L. Research progress on preparation of ethylene oxide from ethylene catalyzed by silver [J]. Liaoning Chemical Industry, 2020, 49 (9): 1151-1152, 1154.

[11] Liu X F. Effect of CO2 concentration in circulating gas of ethylene oxide plant on catalyst selectivity [J]. Petroleum & Chemical Equipment, 2020, 23 (2): 32-34.