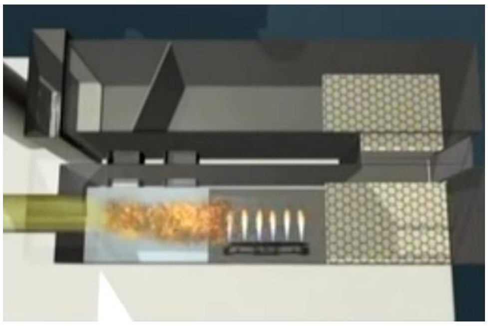
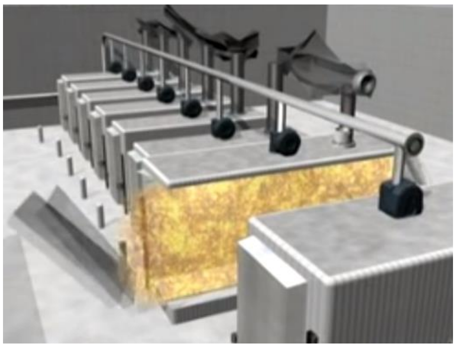
Separation Processes

Safety Module 2: *Sterigenics Ethylene Oxide Explosion, Ontario, California, 19 August 2004*

Problem Statement: Sterigenics International uses ethylene oxide (EO) to sterilize medical products such as syringes, catheters, and bandages at their facility in Ontario, California. The incident occurred during one of the test cycles, when a maintenance personnel skipped the critical gas washing step and advanced the cycle to chamber ventilation step. This resulted in the explosive mixture of EO to be evacuated to the open-flame catalytic oxidizer in the chamber ventilation system. When the EO reached the oxidizer, it ignited, and the flame quickly travelled back through the ducting to the sterilizer where approximately 50 pounds of the remaining EO ignited and exploded.





Watch the Video: (*https://www.youtube.com/watch?time_continue=1&v=_2UnKLm2Eag*)

Incident Report Available At: (*https://www.csb.gov/assets/1/20/sterigenics_report.pdf?13828*)
(Relevant Pages: Pg. 7-9, 21-23, 25-28)

(a) It is important that chemical engineers understand what the accident was, why it happened and how it could have been prevented to ensure similar accidents may be prevented. Applying a safety algorithm to the accident will help achieve this goal. In order to become familiar with a strategy for accident awareness and prevention, view the Chemical Safety Board video on the explosion at the Sterigenics Facility and fill out the following algorithm. See definitions on the last page. If necessary, view the incident report.

Safety Analysis of the Incident

Activity: ____

____

Hazard: ____

Incident: ______

Initiating Event: ______

Preventative Actions and Safeguards: ______

______

Contingency Plan/ Mitigating Actions: ______

______

Lessons Learned: ______

______

(b) Multiple steps were used to remove the EO from the chamber during normal procedures -these were all effectively based on fluid mechanics and material balances. Could you identify properties of EO that would give us alternatives to make the sterilization process safer than the existing procedures?

(c) The management is prospecting the installation of an absorption unit before sending the chamber gas into the back vent, using water as the absorbing liquid. Estimate the number of stages in a counter-current absorber that should be installed to reduce concentration of EO to 25% of its Lower Flammability Limit (LFL), and the water flow rate that would be required in the unit. For the sake of simplicity, assume that the concentration of EO in the inlet gas to the absorption tower (y_{N+1}) does not vary with time.

Additional Information:
Assume that the air flow rate into the absorber is 100 dm^3/s.
Operation is such that the ratio of the water-to-air flow rate is 1.55 times the minimum possible value of the ratio; ($(S/G) = \alpha \times (S/G)_{min}$) (α=1.55).
Henry's Law constant for EO-water system = 9.22 atm[1].
M_w of Ethylene Oxide[2] = 44.05 g/mol.

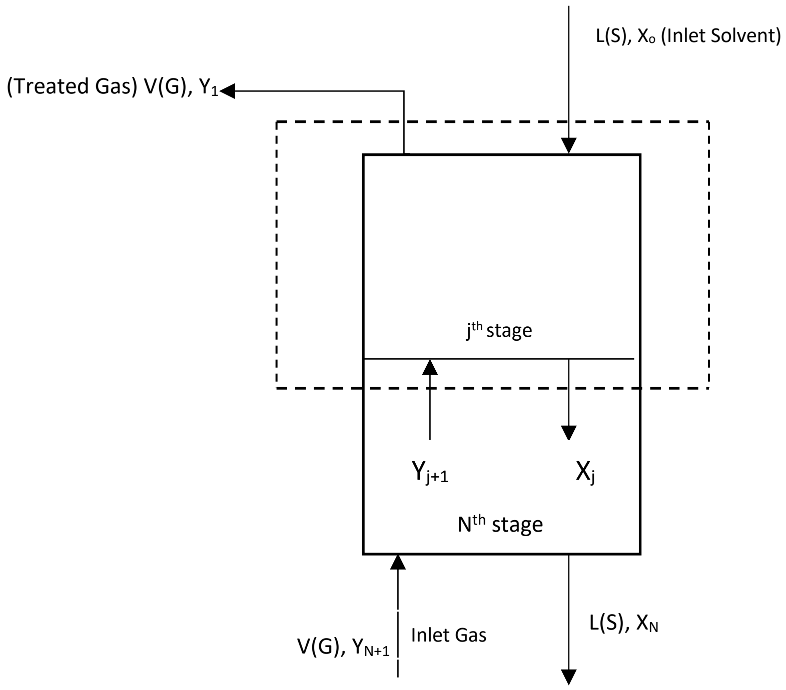
The following data has been obtained from the incident report:
125 lb. (56.7 kg) of EO is added to the chamber initially.
The sterilization process takes place at 310.15K.
LFL for EO = 2.6%[3]
Pressure in the chamber during sterilization = 20inches Hg (67.72 kPa)
50 lb. (22.68 kg) of EO remained in the chamber after the first evacuation step.

Hint:
As the air entering the absorber comes in contact with the water, EO in the air is absorbed into the water and concentration of EO in the air reduces. At each stage, the vapor exiting the tray is in equilibrium with the liquid exiting the tray.

The equation for equilibrium line is given using Henry's Law:

$$P_S = H_S \times x_S \qquad (1)$$

where P_S is the partial pressure of the solute in the vapor, H_S is the Henrys law constant for the solute and x_S is the concentration of the solute in the liquid.
The equation of the operating line can be obtained by applying mass balance around the envelope, as in the figure:



V: flow rate of vapor in the absorber
L: flow rate of liquid in the absorber
G: flow rate of carrier gas in absorber
S: flow rate of non-volatile solvent in the absorber
Y_{j+1}: mol ratio of EO in the gas phase, entering the j^{th} stage
X_j: mol ratio of EO in the liquid phase, exiting the j^{th} stage

Figure 1.1 Gas Absorber

Because the concentration in the mixture is high, the liquid flow rate(L) and vapor flow rate(V) will not be constant, and so the operating line in terms of mol fractions will not be a straight line. Therefore, we define variables S and G, and use mol ratios to obtain a straight operating line.
S: flow rate of non-volatile solvent in the absorber
G: flow rate of carrier gas in absorber

Mole Ratios

Mole ratios are defined as follows:

$$Y = \frac{mol\ of\ solute\ in\ gas}{mol\ of\ pure\ carrier\ gas}$$

$$X = \frac{mol\ of\ solute\ in\ liquid}{mol\ of\ pure\ solvent}$$

They can be related to mol fractions as follows:

$$Y = \frac{y}{1-y} \qquad (2)$$

$$X = \frac{x}{1-x} \qquad (3)$$

Where, x and y are the mol fraction of EO in the liquid and vapor phase respectively.

[1] https://pubchem.ncbi.nlm.nih.gov/compound/Ethylene-oxide#section=Octanol-Water-Partition-Coefficient (after adjusting the units)
[2] https://pubchem.ncbi.nlm.nih.gov/compound/Oxirane
[3] https://www.csb.gov/assets/1/20/sterigenics_report.pdf?13828

Obtaining the operating line:
Applying a solute mass balance on the envelope shown in Figure-1:

$$Y_{j+1}G + X_oS = Y_1G + X_jS$$

Rearranging the terms,

$$\boxed{Y_{j+1} = (\frac{S}{G})X_j + [Y_1 - (\frac{S}{G})X_o]} \qquad (4)$$

The minimum value for $\frac{S}{G}$ is obtained when it is assumed that at the exit (of the water stream), EO in the water is in equilibrium with EO in the incoming vapors.

The number of stages can be obtained by plotting the McCabe-Thiele plot for concentrated systems:

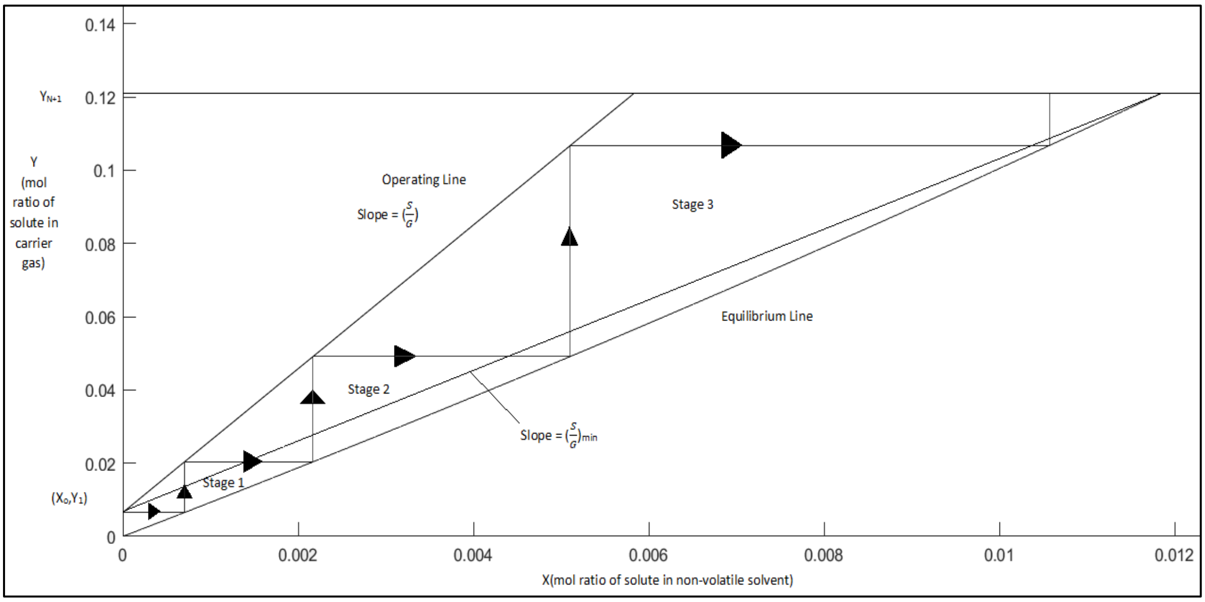


Figure 1.2 McCabe Thiele plot

(d) Ethylene Oxide has a Lower Flammability Limit (LFL) of 2.6% and an Upper Flammability Limit (UFL) of 100% hence even small amounts of EO escape into the back vent may be harmful. Installing an adsorption unit in the vent prior to the oxidizer could act as an extra safety unit. FeO has been used as an adsorbent.
Estimate the minimum amount of adsorbent that must be placed in the vent, assuming the gas wash step has been skipped.

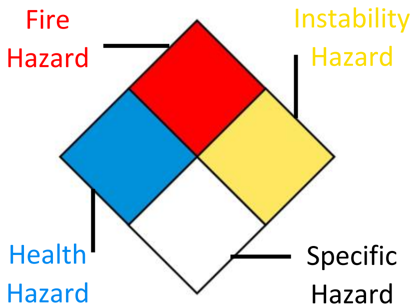
Additional Information:
Maximum EO that can be adsorbed on 1kg FeO = 36.12kg
Adsorption Equilibrium Constant for FeO-EO = 2.1×10^{-3}kPa
Hint:
The Langmuir Isotherm equation is given by:

$$q_A = q_{A,max} \times \frac{K_{A,p} \times p_A}{1 + K_{A,p} \times p_A} \qquad (13)$$

where,
q_A is the amount of species A (here, EO) adsorbed on the solid (here, FeO) (kg/kg adsorbent)
$q_{A,max}$ is the maximum amount of species A that can be adsorbed(kg adsorbed/kg adsorbent)
p_A is the partial pressure of species A over the solid (in atm)
K_A is the adsorption equilibrium constant

(e) On the basis of the values obtained about, which do you think will be a better option? Installation of an absorber, or an absorption unit? Justify.

(f) Review the information in the [NFPA Diamond tutorial.](#) After reviewing the information, visit the [CAMEO Chemicals website](#) and fill out the blank NFPA Diamond to the right for ethylene oxide.

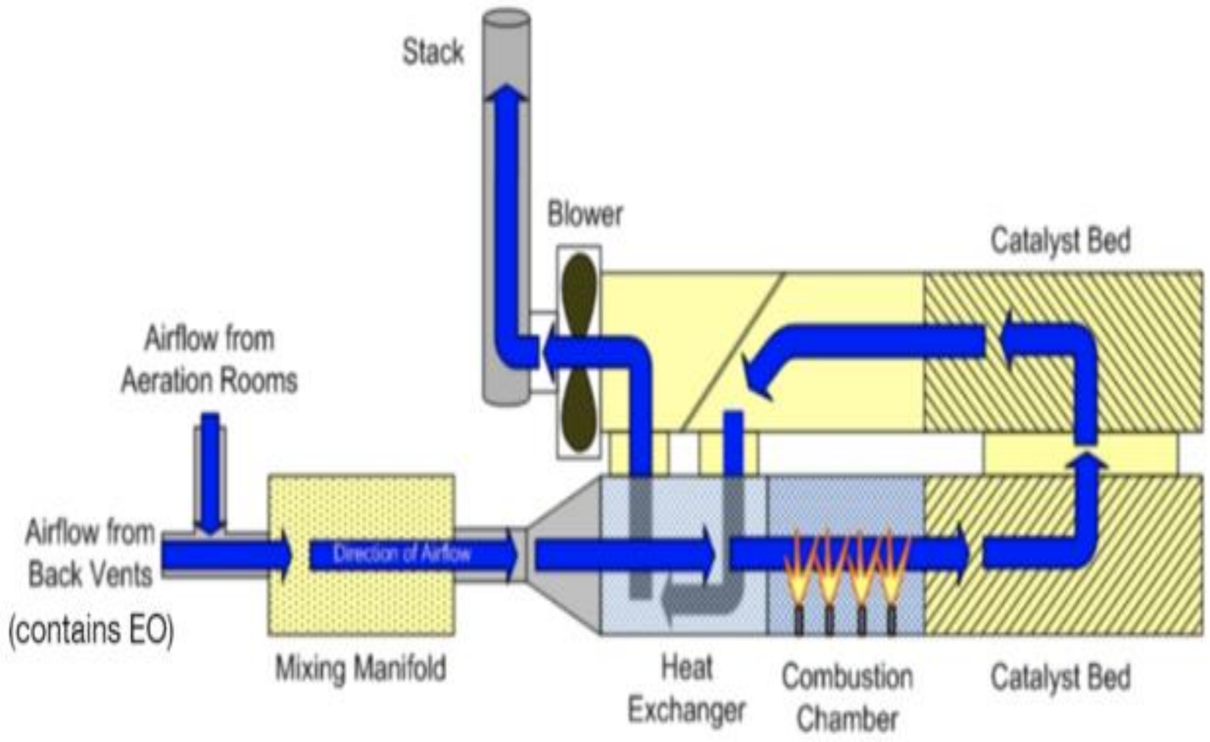


Parts (g)-(i) are based on industry practices used to assess process safety. For more information on process safety and its importance in chemical engineering, please visit the University of Michigan SafeChE website [here](#). *It is recommended that professors only assign 1-2 of the following parts due to the similar nature of the questions.*

(g) Review the explanation of the components of a BowTie diagram found [here](#). After reviewing the information, create a BowTie diagram for the Sterigenics Incident.

(h) A HAZOP study is structured analysis of process design to identify potential vulnerabilities in a facility. Review the background on how to conduct a HAZOP study [here](#) before completing one for the following system. It is important to note that not all guidewords and parameters will be relevant for different systems. Some information is given here for guidance:

System to consider: The catalytic oxidizer (includes combustion chamber and catalyst beds)



Process Parameters Related to air-EO Mixture Directly Entering Oxidizer: Flow Rate of Gas Entering Catalyst Bed, Temperature of Gas Entering Catalyst Bed, Concentration of EO in Gas Entering Combustion Chamber

(i) Fill out the HAZOP chart as shown in the tutorial. Some information has been filled out here for you.

Guideword + Parameter = Deviation	Causes	Consequences	Safeguards	Recommendations
More Flow Rate of Gas Entering Catalyst Bed	Failure of automatic opening of chamber doors			
More (Higher) Temperature of Gas Entering Catalyst Bed	Increased fuel supply to combustion chamber			
More (Higher) Temperature of Gas Entering Catalyst Bed				
More (Higher) Concentration of EO in Gas Entering Combustion Chamber				

(ii) When conducting a HAZOP, you will often find combinations of guidewords and parameters that describe a possible situation for the system that is not hazardous. For the given process parameters, give an example and explain why the situation is not hazardous.

(iii) Write a short conclusion on some takeaways from completing a HAZOP for this system and recommendations you would make.

(i) A Layers of Protection Analysis (LOPA) is a semi-quantitative study to identify available safeguards and determine if the safeguards sufficiently protect against a given risk. Review the background on how to conduct a LOPA study here before filling the table out for the system described in this module. Some information is given for guidance:

- Assume that the plant can only accept a moderate risk
- Assume that a maintenance cycle is required 25 times per year (i.e. number of opportunities per year)
- According to the CSB report, the incident caused 4 injuries and resulted in losses between $1-10 million

LOPA Study for EO Explosion at Sterigenics		
Initiating Event	Cause:	Operator error (in skipping the gas washing step during a maintenance cycle)
	Consequence:	A stream of air containing EO in large concentrations comes into contact with the catalytic oxidizer, leading to an explosion.
	FOIE:	
	Description of IPL_1, IPL_2, ...	

IPL(s)	$PFD = PFD_1 \times PFD_2 \times ...$	
MCF	$MCF = FOIE \times PFD$	
	Category of MCF:	
Severity	Impact:	4 severe injuries, and financial loss of $1 - 10 million.
	Category:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	
If risk evaluated above is unacceptable, please continue below:		
Proposed IPL(s) (P-IPL(s))	Description of $P\text{-}IPL_1$, $P\text{-}IPL_2$, ...	
	$P\text{-}PFD = P\text{-}PFD_1 \times P\text{-}PFD_2 \times ...$	
MCF	$MCF = FOIE \times PFD \times P\text{-}PFD$	
	Category of MCF:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	

(j) Describe what was most unsettling to you about this incident.

MATLAB

Click here to download the MATLAB file.
To run the code, you can download the latest version of MATLAB here.
Click here to download the MATLAB tutorial.

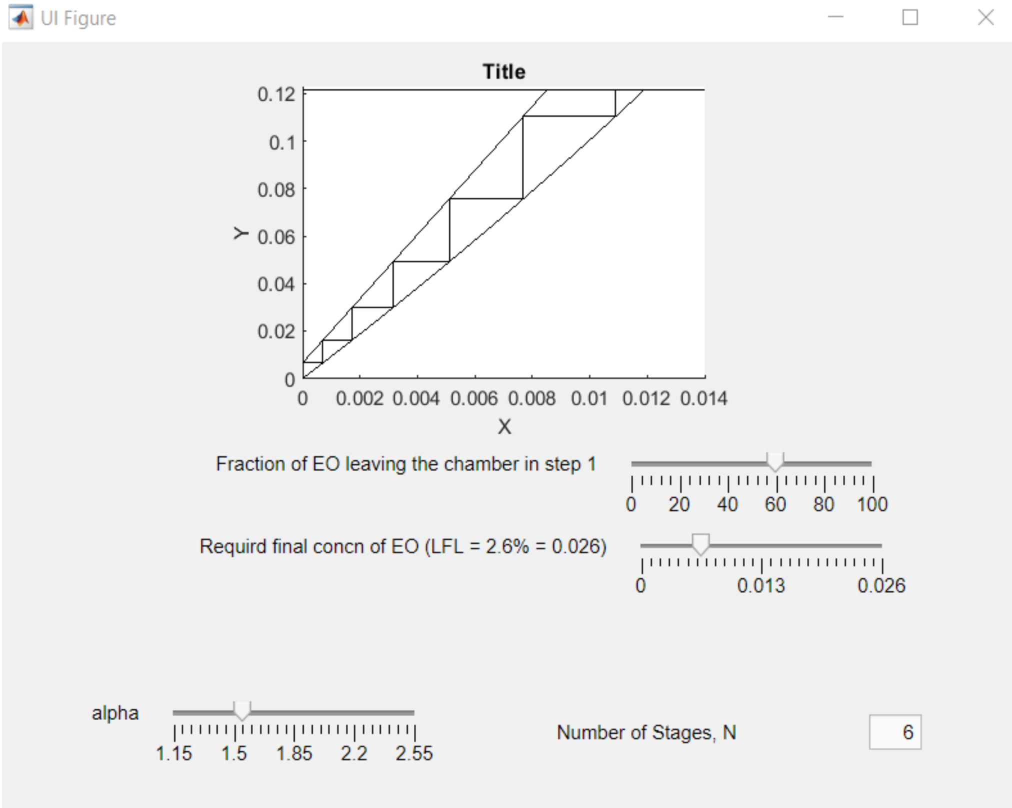


Figure 1. *Output of MATLAB code: McCabe Thiele plot*

(i) Vary the *fraction of EO leaving the chamber in step 1* and *required final concentration of EO*. How do these parameters effect the number of stages required?

(ii) Vary the parameter *alpha*. How does the parameter *alpha* effect the operating line and the number of stages required?

(iii) Write a set of conclusions based on your experiments in (i) and (ii).

Definitions

Activity: The process, situation, or activity for which risk to people, property or the environment is being evaluated.

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property, or the environment.

Incident: What happened? Description of the event or sum of the events along with the steps that lead to one or more undesirable consequences, such as harm to people, damage to property, harm to the environment, or asset/business losses.

Initiating Event: The event that triggers the incident, (e.g., failure of equipment, instrumentation, human actions, flammable release, etc.). Could also include precursor events, (e.g., no flow from pump, valve closed, inadvertent human action, ignition). The root cause of the sum events in causing the incident.

Preventative Actions and Safeguards: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property, or the environment. Brainstorm all problems that could go wrong and then actions that could be taken to prevent them from occurring.

Contingency Plan/ Mitigating Actions: These actions occur after the initiating event. They are steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring

BowTie Diagram: A qualitative hazard analysis tool through which potential problems and consequences associated with a hazard are studied through a pictorial representation. Necessary preventive and mitigating barriers are determined to reduce the process safety risk.

Hazard and Operability Study (HAZOP): A qualitative hazard analysis tool that uses a set of guide words to determine whether deviations from design or operating intent can lead to undesirable consequences. The existing safeguards are evaluated and if required, actions are recommended to mitigate the consequences.

Layer of Protection Analysis (LOPA): A semi-quantitative study that determines initiating event frequency, consequence severity, and likelihood of failure of independent protection layers (IPLs) to calculate the risk of a scenario. If the existing risk is intolerable, then additional IPLs are suggested to bring down risk to an acceptable level.

Table of nomenclature

Symbol	Name	Units
S	Liquid (water) flow rate	dm^3/s
G	Gas (air) flow rate	dm^3/s
α	Alpha – the factor multiplied to the minimum value of the ratio (S/G)	No units
y	Mole fraction of EO in air	mol/mol
x	Mole fraction of EO in water	mol/mol
N	Number of stages	No units
Y	Mole ratio of EO in air	mol/mol
X	Mole ratio of EO in water	mol/mol
P_s	Partial pressure of EO in air	atm
H_s	Henrys law constant	atm
x_s	Mole fraction of EO in water	mol/mol
q_A	Amount of EO adsorbed on FeO	kg/kg
$q_{A,max}$	Maximum amount of EO that can be adsorbed on FeO at the given temperature	kg/kg
$K_{A,p}$	Adsorption equilibrium constant	atm^{-1}
p_A	Partial pressure of EO	atm

[i] In collaboration with Triesha Singh, Indian Institute of Technology, Bombay