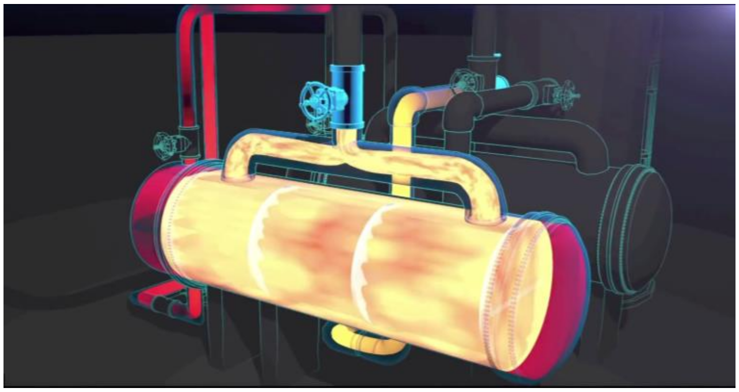
ChE 330 - Chemical and Engineering Thermodynamics

[i]**Safety Module 2:** *Williams Owens Olefin Plant Explosion, June 13, 2013 in Geismar, LA*

Problem Statement: The Williams Owens Plant in Geismar, LA produces ethylene and propylene. The heat exchanger is attached to a fractionation column. Hot water on the tube side heats the propane and propylene on the shell side.



Workers understood that oily tar had a tendency to build up on the inside of the reboiler tubes, requiring periodic shut down for cleaning. The plant manager observed a significant decrease in flow rate over the past day and attributed it to tar build up on the tube walls. Workers decided to switch to the stand-by exchanger, which had not been in use for 16 months. Unknown to workers, this stand-by heat exchanger was detached from its pressure relief valve and contained liquid propane. When hot water was introduced into this heat exchanger, it violently ruptured and exploded within three minutes. The incident killed two workers and injured 167.

Watch the Video: (*https://www.youtube.com/watch?v=Z1KaykPaF8M*)

Incident Report Available At: (*https://www.csb.gov/file.aspx?DocumentId=6004*)
(Pages 5, 9, 11, 14, 15, 56)

(a) It is important that chemical engineers have an understanding of what the accident was, why it happened and how it could have been prevented in order 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 Williams Owens Olefin plant explosion and fill out the following algorithm. See definitions on the last page. If necessary, view pages 5, 9, 11, 14, 15, and 56 of the incident report.

Safety Analysis of the Incident

Activity: ____

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Hazard: ____

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Incident: ____

Initiating Event: ____

Preventative Actions and Safeguards: ______________________________

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Contingency Plan/ Mitigating Actions: ______________________________

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Lessons Learned: ______________________________

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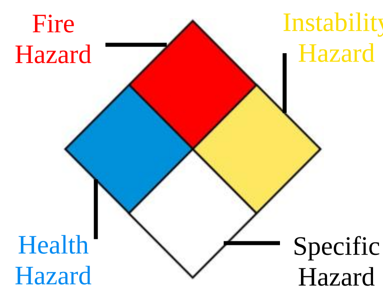

(b) Calculate the increase in pressure in the liquid propane shell side of the heat exchanger using the Clausius-Clapeyron equation when hot water flows through the tube side of the heat exchanger.

(c) Review the information in the NFPA Diamond tutorial. After reviewing the information, visit the CAMEOChemicals website and fill out the blank NFPA Diamond to the right for propane.

(d) Review the explanation of the components of a bow-tie diagrams found here. After reviewing the information, create a bow-tie diagram for the Williams Owen Olefin Plant incident.

(e) Describe what was the most unsettling to you about the incident.

Wolfram

Click here to download Wolfram CDF Player for free.

Click here to view CDF installation tutorial.

Click here to download Wolfram code for this module.

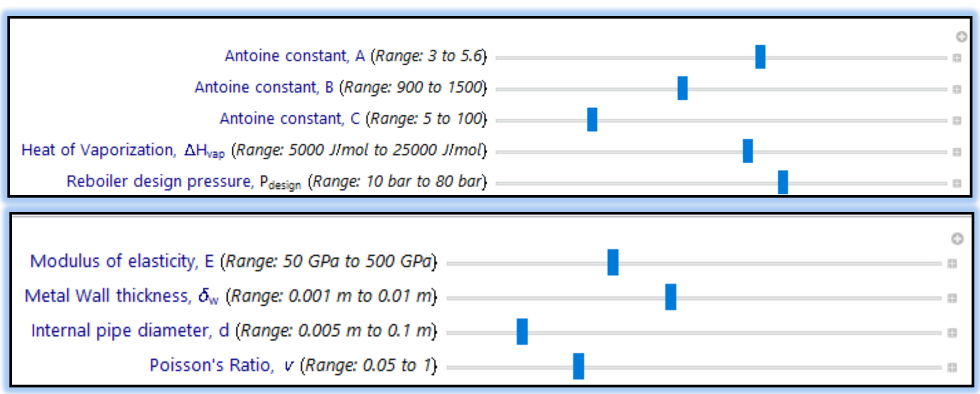

Fig 2.1 Wolfram sliders

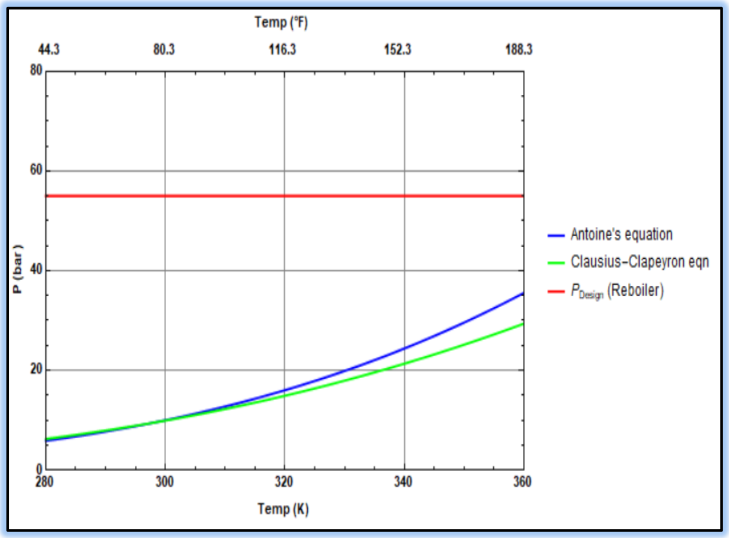

Fig 2.2 Vapor pressure vs. temperature

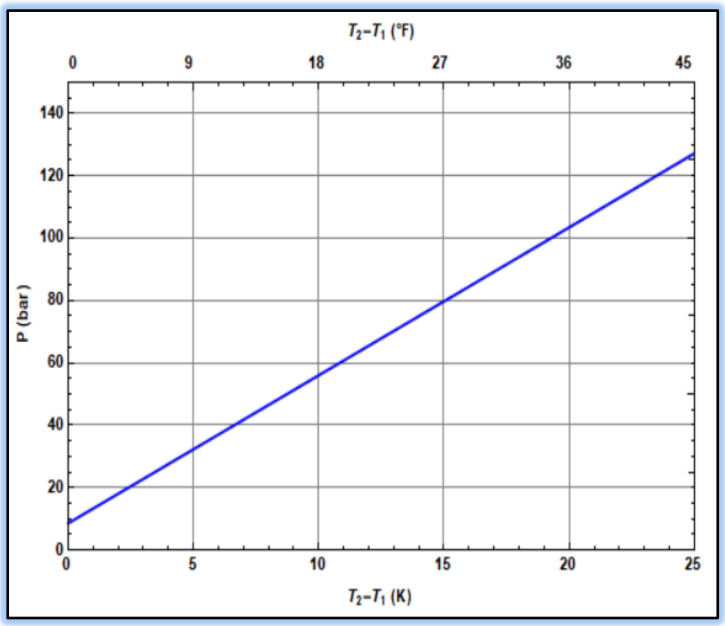

Fig 2.3 Pressure inside reboiler vs. change in temperature (final-initial)

(i) One of the reasons for explosion could have been the over-pressurization of the heat exchanger due to the equilibrium vapor pressure at the quench water inlet temperature of 360 K. From the Wolfram plot, estimate the pressure that was exerted by propane vapor, using the Antoine Equation. Do you think that equilibrium vapor pressure was a major reason for the rupture? Assume the reboiler rupture pressure to be 55 bar.

(ii) Describe how the vapor pressure obtained using the Clausius-Clapeyron Equation is different than that obtained using the Antoine equation. Find the value of ΔH_{vap} at which the pressures calculated using the Clausius-Clapeyron Equation and the Antoine Equation agree with each other (within 3%). Can you give an explanation for the discrepancy between the pressures calculated by the two equations?

Antoine Equation parameters for propane:

$$\log_{10}(\boldsymbol{P}^{sat}) = \boldsymbol{A} - \frac{\boldsymbol{B}}{\boldsymbol{T}(\boldsymbol{K}) + \boldsymbol{C}}$$

A= 4.54
B= 1149
C= 24.9

(iii) Vary the parameters A, B, and C of the Antoine Equation and comment on the sensitivity of these parameters.

(iv) Next consider the possibility of a **boiling liquid expanding vapor explosion (BLEVE)**[1]**.** The expansion of the liquid with temperature can ultimately lead to over-pressurization and rupture of the container. From the Wolfram plot, find the BLEVE pressure buildup, and determine whether it exceeded the maximum pressure which the reboiler could handle. Is the BLEVE pressure buildup more or less than the pressure buildup due to heating of propane vapor obtained in part (i)?

The pressure buildup in the confined space inside the reboiler is due to the pressure rise due to simultaneous heating of the pipe and blocked-in liquid in the confined space of the container (BLEVE) , and can be calculated using the following equation (CCPS[2] and Karcher[3]**)** :

$$\boldsymbol{P}_2 = \boldsymbol{P}_1 + \frac{(\boldsymbol{T}_2 - \boldsymbol{T}_1)(\alpha_v - 3\alpha_l)}{\chi + (\frac{\boldsymbol{d}}{2\boldsymbol{E}\delta_w})(2.5 - 2\nu)}$$

(v) Vary parameters *E*, δ_w, *d*, *v* on the sliders and observe how the pressure in the confined space inside the reboiler changes, and how the explosion could have been prevented.

(vi) Write a set of conclusions based on your experiments (i) through (v).

Additional Information:
Quench water temperature= 360 K
Ambient temperature= 300 K
Total volume available between closed valves= 8.2 m^3
Density at ambient temperature = 495 kg/m^3
Density at Quench water inlet temperature = 324 kg/m^3

BLEVE nomenclature:
P_2 is the final gauge pressure of blocked-in, liquid-full equipment
P_1 is the initial gauge pressure of blocked-in, liquid-full equipment= 854.95 kPa (vapor pressure of liquid at ambient temp)

T_2 is the maximum temperature of blocked-in, liquid-full equipment= 311 K (At this temperature, the reboiler exploded due to over-pressurization)
T_1 is the initial temperature of blocked-in, liquid-full equipment= 300 K
α_v is the cubic expansion coefficient of the liquid= 0.003 /K
α_l is the linear expansion coefficient of metal wall= $13*10^{-6}$ /K
χ is the isothermal compressibility coefficient of the liquid= 6.22 $*10^{-9}$/Pa
d is the internal pipe diameter, expressed in inches= 0.01905m
E is the modulus of elasticity for the metal wall at T_2, expressed in psi= 200 GPa
δ_w is the metal wall thickness of tube, expressed in inches= 0.00508 m
ν is Poisson's ratio= 0.3

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 the property, to the environment, or asset/business.
Initiating Event:	The event that triggers the incident, (e.g. failure of equipment, instrumentation, human actions, flammable release, etc.). It could also include precursor events that precede the initiating event (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

Module Specific To Williams Owens Olefin Plant Explosion

Boiling Liquid Expanding Vapor Explosion (BLEVE)†	A BLEVE occurs when a vessel containing a liquid at a temperature above its atmospheric boiling point ruptures. The subsequent BLEVE is an explosive vaporization of a large fraction of the vessel content that can be followed by combustion or explosion of the vaporized cloud. BLEVE is typically caused when an external heat source heats the concenters of the vessel thereby causing an increase in the vapor pressure of the vessel, reducing its structural integrity.
Fouling	Fouling is the accumulation of unwanted material on solid surfaces to the detriment of function.

Table 1.1: Nomenclature

Symbol	Description	Unit
P^{sat}	Saturation pressure	bar
ΔH_{vap}	Enthalpy of vaporization	kJ/mol

References:
[1] https://inspectapedia.com/plumbing/BLEVE-Explosions.php
[2] CCPS, Guidelines for pressure relief and effluent handling systems, 1998, ISBN 0-8169-0476-6
[3]G.C Karcher , Pressure changes in liquid filled vessles or piping due to temperature changes, ExonMobil Research and Engineering Mechanical Newsletter EE.84E.76 , August 1976

[1] In collaboration with Kara Steshetz, University of Michigan, Devosmita Sen: Indian Institute of Technology Bombay, and Professor Andrej Lenert: University of Michigan

† From Crowl, D. A. and J.F. Louvar, *Chemical Process Safety with Applications*, Prentice Hall, Upper Saddle River, NJ.