Fluid Mechanics

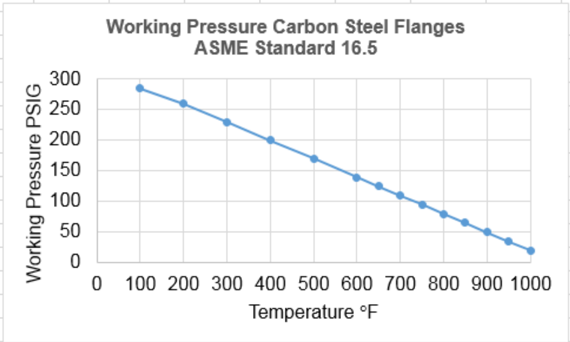
[1]**Safety Module 4:** *Praxair Incident Rocketing Cylinders, Praxair Flammable Gas Cylinder Fire and Explosion in St. Louis, MO* on *June 24, 2005*

Problem Statement: It was a hot day in St. Louis, 96°F (35.9°C), where Praxair had set cylinders with flammable gases on hot black asphalt pavement. Direct sunlight and radiant heat from the asphalt pavement heated the propylene cylinders.[2†]

The vapor pressure in a liquid propylene cylinder exceeded the faulty set pressure on the cylinder's relief valve that was too low, as a result propylene escaped into the yard. The resulting vapor plume found an ignition source and a fire started. The fire heated nearby acetylene and liquefied petroleum gas (LPG) cylinders and they in turn released more flammable gases, which enlarged the fire.

The escaping gas also caused the cylinders to be rocketed as projectiles, one of which created a hole in the wall of a building several hundred feet away as shown in the following figure.

Once the propylene gas escaped and the fire heated nearby cylinders softening the steel as shown in the following figure.



Softened steel coupled with the high internal pressure caused a hole to form in the cylinder. It can be speculated localized heating caused a rupture hole and that the superheated liquid instantaneously vaporized. This vaporization caused an explosive pressure increase, rocketing the cylinder hundreds of feet. This phenomenon is known as BLEVE, **B**oiling **L**iquid **E**xpanding **V**apor **E**xplosion.

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[1]In Collaboration with Kshitiz Parihar, Indian Institute of Technology Bombay

[2†] Katharine K. Guan, "Surface and ambient air temperatures associated with different ground material: a case study at the University of California, Berkeley," *Surface and Air Temperatures of Ground Material* Spring 2011.

Watch the Video: (*https://www.youtube.com/watch?v=-_ZLQkn7X-k*)

Incident Report Available At: (*https://www.csb.gov/file.aspx?DocumentId=5642*) (Pages 1-10)

(a) It is important that chemical engineers understand 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 Praxair incident with rocketing cylinders, the Praxair flammable gas fires and explosion and fill out the following algorithm. See definitions on the last page. If necessary, view 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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Additional Information:

The air temperature reached 96°F (36.9°C) at 2 p.m. and the asphalt surface was approximately 140°F (333 K) causing the cylinder temperature, T, to rise up to 135°F (330 K).

Cylinder dimensions:

-$Height, H = 1.07\ m$

-$Diameter, D = 0.31\ m$

-$Average\ Weight\ of\ Cylinder, M_C = 21.8\ kg$

-$Maximum\ gas\ capacity = 4.05\ m^3$

-$Diameter\ of\ the\ hole, d = 0.06\ m$

-Mass of Propylene kept in cylinder, M_P = 91.61 kg.

For Propylene[3]:

$$Cp = 70.04\ \frac{J}{mol.K};\ \Delta H_{vap} = 18.4\frac{kJ}{mol.K};\ T_{sat} = 225.6\ K;\ P_{sat} = 0.101\ MPa$$

Drag Coefficient[4], $C_D = 0.82$; Density of Air, $\rho_{air} = 1.225\ kgm^{-3}$

(b) Assume that due to nearby exploding cylinders, one of the fully filled cylinders was dislodged from its position and ended up lying in a tilted position making an angle of $\emptyset(\leq 90°)$ with the ground, with its head (where pressure relief valve is situated) towards the ground as shown in the figure below. Due to impact, the pressure relief valve is dislodged and the propylene inside the cylinder began to escape. Calculate the minimum value of $\emptyset$ above which the cylinder would take off and the initial velocity of the cylinder as it takes off.

(Hint: Minimum value of $\emptyset$ will be when upward thrust by the escaping gas balances the gravitational force. Initial velocity can be evaluated by doing an impulse balance at t = 0 using a small-time interval, Δt = 0.1 sec)

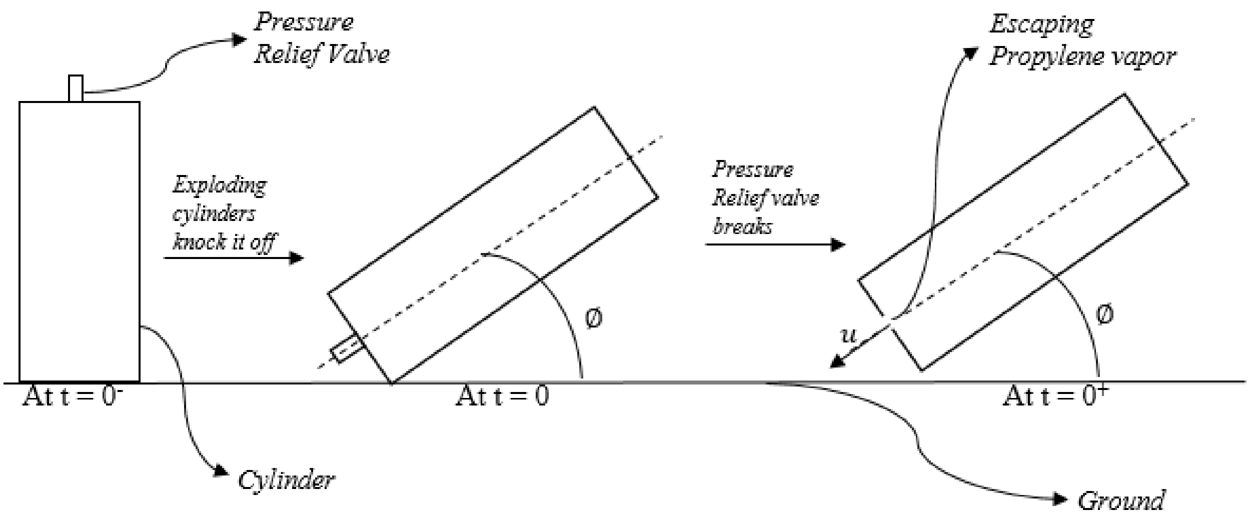

Figure 1: Above images depict the events just before the cylinder takes off

Mass flow rate, $\dot{m}$, and discharge velocity, u, of the exiting propylene vapor from the hole are required to evaluate the minimum value of $\emptyset$ and initial velocity.

For calculating $\dot{m}$ and u:

Assume ideal gas and constant specific heats, C_P and C_V, for propylene vapor in the cylinder.

The hole will cause BLEVE. And the exiting propylene vapor will undergo expansion as it flows from high pressure, in the cylinder to much lower pressure, i.e. atmospheric pressure. Assuming that the flow is frictionless and adiabatic, the expansion will then be isentropic, i.e. there will be no change in entropy.

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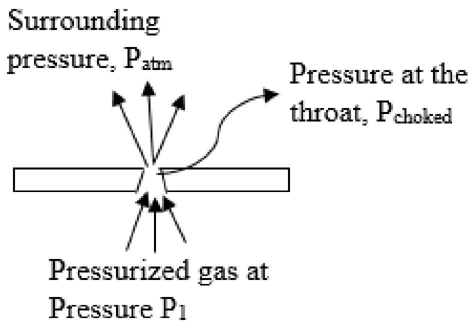
[3] From https://webbook.nist.gov/cgi/cbook.cgi?ID=115-07-1

[42] From Center for Chemical Process Safety (CCPS), *Guidelines for Process Safety Fundamentals in General Plant Operations*, (John Wiley & Sons), p. 322

Mass flow rate for vapor, m, during isentropic expansion, is given by[5]*,*

$$\dot{m} = A_h \sqrt{\frac{2\gamma}{\gamma - 1} P_1 \rho_1 \left[1 - \left(\frac{P}{P_1}\right)\right]^{\frac{\gamma-1}{\gamma}} \left(\frac{P}{P_1}\right)^{\frac{2}{\gamma}}} \qquad (b\text{-}1)$$

where, A_h is the area of the hole, γ is the ratio of specific heats, P_1 is the upstream pressure (inside the cylinder), ρ_1 is the density of vapor at conditions inside the cylinder, P is the pressure downstream where m has to be calculated.



P/P_1 ratio resulting in maximum flow rate through the hole, calculated by differentiating Eqn. (b-1) with respect to (P/P_1) and equating the derivative to zero, is given by[6]

$$\left(\frac{P_{Choked}}{P_1}\right) = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma-1}} \qquad (b\text{-}2)$$

where P_{choked} is the choked pressure which is the maximum downstream pressure resulting in maximum flow through the hole.

If the downstream pressure is less than or equal to P_{choked}, then[7]

(i) The velocity of the fluid at the throat of the leak (hole) is equal to the velocity of sound at the prevailing conditions.

(ii) The mass flow rate cannot be increased further by reducing the downstream pressure; it is independent of the downstream conditions.

This type of flow is called choked or critical flow.

The maximum flow, obtained by substituting Eqn. (b-2) in Eqn. (b-1), is given by[4]

$$\dot{m} = A_h \sqrt{\gamma P_1 \rho_1 \left[\frac{2}{\gamma + 1}\right]^{\frac{\gamma+1}{\gamma-1}}} \qquad (b\text{-}3)$$

Before we can evaluate mass flow rate through the hole, we need to check whether it is a choked flow or not. For this we should compare P_{choked} and atmospheric pressure, P_{atm} (= 14.7 psi) , because the discharge pressure for the gas is P_{atm} in this problem.

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[5] From J. O. Wilkes , *Fluid Mechanics for Chemical Engineers,* 3rd ed. (Prentice Hall), p. 161

[6] Ibid, p. 162

[7] From D. A. Crowl and J. F. Louvar, *Chemical Process Safety: Fundamentals with Applications,* 1st ed. (Englewood Cliffs, N. J.: Prentice Hall), p. 100

P_{choked} can be calculated as follows:
(i) And γ is given by

$$\gamma = \frac{C_P}{C_V} \qquad \text{(b-4)}$$

(ii) P_1 can be calculated using Clausius - Clapeyron equation, assuming vapor liquid equilibrium in the cylinder at P_1 and temperature, T.

$$ln\, ln\, \left(\frac{P}{P_{sat}}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_{sat}}\right) \qquad \text{(b-5)}$$

(iii) Substitute the values obtained from Eqn. (b-4) and Eqn. (b-5) in Eqn. (b-2).

If $P_{choked} \geq P_{atm}$, then there is choked flow, and mass flow rate will be calculated using Eqn. (b-3). Else, no choked flow, and mass flow rate will be calculated using Eqn. (b-1) by putting $P = P_{atm}$.

The propylene gas in the cylinder is at an absolute pressure P_1 and has a densityρ_1. The final discharge is to the atmosphere, P_{atm}. The discharge velocity for the gas is obtained using,

$$\dot{m} = \rho A_h u \qquad \text{(b-6)}$$

where, u is the discharge velocity and ρ in the density of propylene at discharge pressure, P_{atm}.

For calculating ρ, we can use [8]

$$\frac{P}{\rho^{\gamma}} = c = \frac{P_1}{\rho_1^{\gamma}}$$

Substituting $P = P_{atm}$ in above equation, one obtains

$$\rho = \rho_1 \left(\frac{P_{atm}}{P_1}\right)^{\frac{1}{\gamma}} \qquad \text{(b-7)}$$

Discharge velocity is calculated by substituting Eqn. (b-7) in Eqn. (b-6),

$$u = \frac{\dot{m}}{\rho A_h} \qquad \text{(b-8)}$$

[8] From J. O. Wilkes , *Fluid Mechanics for Chemical Engineers,* 3rd ed. (Prentice Hall), p. 160

(c) Taking $\emptyset = 60°$, solve for

1) Velocity of the cylinder, v

2) Angle made by the cylinder with the horizontal (x axis), θ

3) Total mass of the cylinder, M (propylene mass + cylinder mass)

4) Distance travelled by the cylinder in x and y direction, i.e. cylinder's trajectory

Assume that mass flow rate, $\dot{m}$, and corresponding discharge velocity, u calculated in part (b) to be remain constant until gas is present in the cylinder.

(Hint: Apply mass and momentum balance for $t < t_{empty}$ and $t \geq t_{empty}$ separately, where t_{empty} is the time at which all gas has exited the cylinder.)

The angle with which the cylinder takes-off, θ_i,will not be equal to $\emptyset$ because the downward force due to gravity will make the θ_i less than $\emptyset$. This angle can be calculated using the y component, v_{yi}, and the x component, v_{xi}, of the initial velocity which were calculated in part (b).

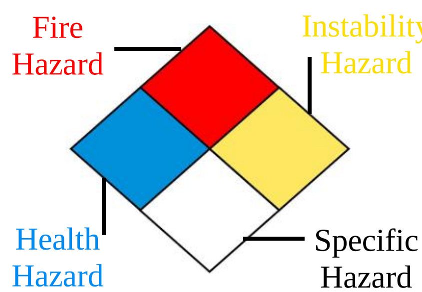
$$\theta_i = \left(\frac{v_{yi}}{v_{xi}}\right) \qquad \text{(c-1)}$$

Drag force (F_D) due to air on the cylinder is given by[9],

$$F_D = 0.5 C_D \rho_{air} A_p v^2 \qquad \text{(c-2)}$$

where C_D is drag coefficient, ρ_{air} is the density of air, A_p is the projected area of cylinder in the direction of motion and v is the velocity of the cylinder.

(d) 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 propylene.



Parts **(e)-(g)** 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.*

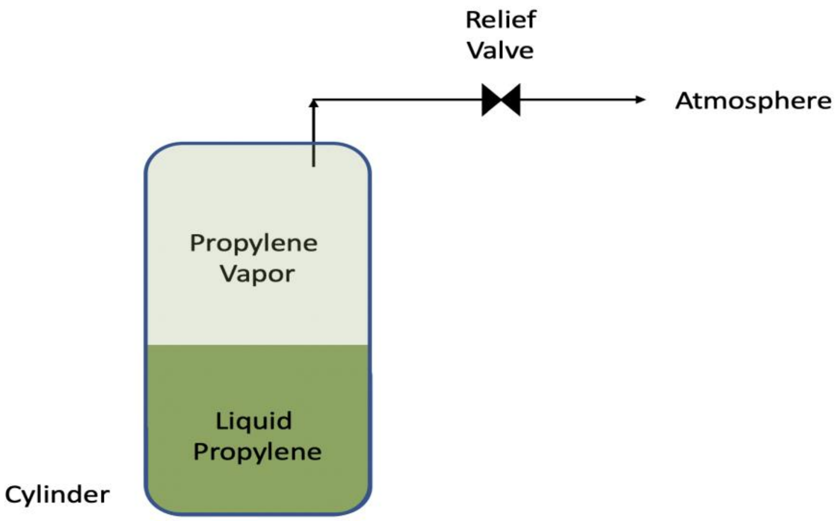
(e) Review the explanation of the components of a BowTie diagrams found here. After reviewing the information, create a BowTie diagram for the Praxair incident.

(f) 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

[9] From J. O. Wilkes , *Fluid Mechanics for Chemical Engineers,* 3rd ed. (Prentice Hall), p. 196

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: Praxair cylinder filled with propylene in vapor-liquid equilibrium



Process Parameters to Consider: Temperature, Pressure

(i) Fill out the HAZOP chart as shown in the tutorial. In this case, the consequences, safeguards, and recommendations will be the same for both deviations.

Guideword + Parameter = Deviation	**Causes**	**Consequences**	**Safeguards**	**Recommendations**
More (Higher) Temperature				
More (Higher) Pressure	Increase of temperature in cylinder			

(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.

(g) 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 minor risk
- The fire destroyed many cylinders and tanks, resulting in business losses of more than $100,000. Flying cylinders created the potential for severe injuries
- The ultimate cause of the incident was the heat wave, which can be expected to occur 1 time every year in St. Louis

LOPA Study for Praxair Fire and Explosion		
Initiating Event	Cause:	Heat wave
	Consequence:	Release of propylene vapor due to high pressure in cylinder and potential for ignition and explosion
	FOIE:	
IPL(s)	Description of IPL_1, IPL_2, ...	
	$PFD = PFD_1 \times PFD_2 \times ...$	
MCF	MCF = FOIE x PFD	
	Category of MCF:	
Severity	Impact:	Potential for severe injury and some business losses
	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-IPL_1, P-IPL_2, ...	
	P-PFD = P-PFD_1 x P-PFD_2 x ...	
MCF	MCF = FOIE x PFD x P-PFD	
	Category of MCF:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	

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

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.

Module Specific for Praxair Cylinder Fire and Explosion

Set Pressure: Pressure at which a relief valve begins to open
Relief Valve: A spring-operated valve designed to prevent damage to equipment due to high pressure