Overpressure Analysis of Girard Point Refinery Accident

Boiling-Liquid Expanding-Vapor Explosion

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0.1 Introduction

On June 21, 2019, an fire and explosion occurred at the Girard Point Refinery owned by Philadelphia Energy Solutions[1]. One of the three explosions observed was from an a treater-feed-surge-drum tank in the alkylation unit. The tank was propelled approximately 2,000 ft from the blast seat. The Philadelphia Fire Department requested ATF estimate the blast overpressure generated when the tank exploded.

It is hypothesized that a boiling-liquid expanding-vapor explosion (BLEVE) event provided the energy to generate the blast wave. This paper is an engineering analysis to estimate the blast overpressure. The analysis is based upon an adiabatic and isentropic energy analysis developed by the Center for Chemical Process Safety[2].

0.2 Background

The Girard Point Refinery is located in southwest Philadelphia, Pennsylvania, on the Schuylkill River, see fig. 0.1. The refinery produces 335,000 bpd of gasoline and is the largest on the East Coast. The treater-feed-surge-drum involved in the explosion is part of the alkylation process used in the production of gasoline.

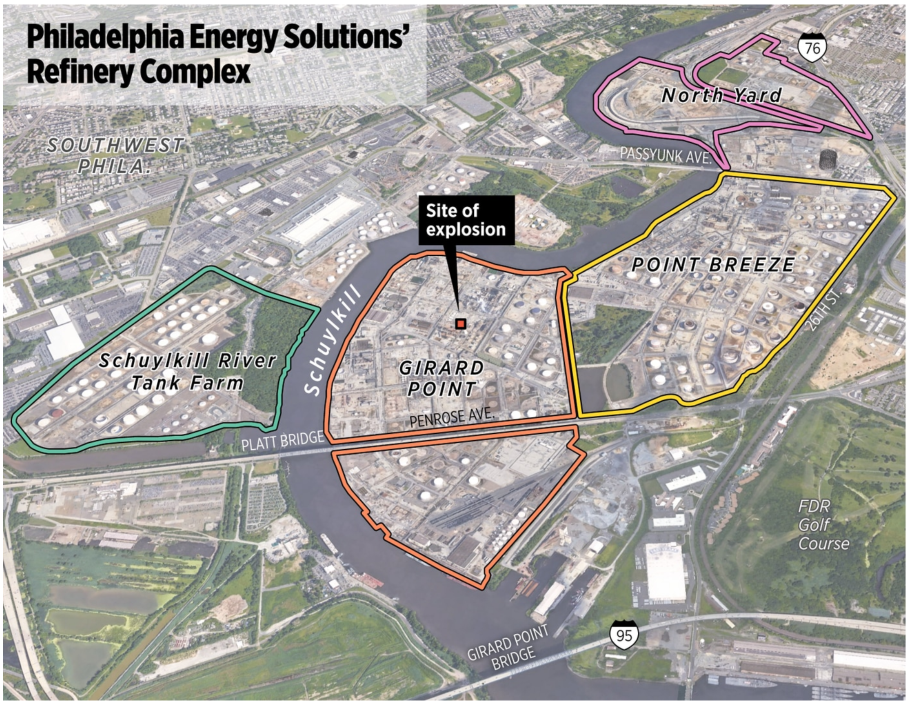


Figure 0.1: Map of Girard Point Refinery show the blast location[3].

The alkylaition process converts propylene (C_3H_6), butylene (C_4H_8), pentene (C_5H_{10}), and isobutane (C_3H_{10}) to alkane liquids such as isoheptane (C_7H_{16}) and isooctane (C_8H_{16}). These Alkylates are a highly valued component in the production of gasoline because of there high octane and low vapor pressure[4]. The treater-feed-surge-drum provides a temporary storage location for feed material during the production process or during maintenance.

The tank weighed 74,660 lb and contained 98,874 lb of butane (50%) and butene (40%) and other lesser constituients, see Table table 0.1.

Table 0.1: Sample of Chemical Contents in the Treater-Feed-Surge-Drum Closest to the Time of the Explosion

Chemical	Percent by Volume
methane	0.01
ethylene	0.00
ethane	0.01
propane	0.90
propylene	0.10
isobutane	37.28
nbutane	12.81
butens	40.41
neopentane	0.00
isopentane	3.94
npentane	0.25
butadiene	0.33
benzene	0.00
C5 olefins	3.54
C6 sats	0.33
C7+	0.04

The treater-feed-surge-drum tank that exploded is part of the refineries alkylation unit. T This analysis calculates the pressure of the blastwave generated from the BLEVE by finding the ### Boiling-Liquid Expanding-Vapor Explosion A BLEVE results from the sudden failure of a tank containing a compressed vapor (head space) and a super-heated liquid (a liquid heated above it's boiling point but without boiling). The magnitude of the blast depends on how super-heated the liquid was at failure. As the level of super-heat rises, the portion of liquid that flash-boils rises, thus increasing the energy released. Once containment failure occurs the energy is distributed into four forms:

1. Overpressure wave
2. Kinetic energy of fragments
3. Deformation and failure of the containment material
4. Heat transferred to environment

The distribution of the energy into the these four forms depends on the specifics of the explosion. Casal et al. found that a *fragile* failure releases 80% of the energy into the blastwave, while a *ductile* failure releases 40% of the energy into the blastwave. The remaining energy becomes kinetic energy of the fragments. The heat transfer to the environment is relatively small.[2] In practice most pressure vessels are designed with materials that are ductile rather than brittle to avoid sudden and catastrophic brittle (fragile) failures [3].

0.3 First Law of Thermodynamics

The 1st Law of Thermodynamics is a restatement of the conservation of energy (energy cannot be created or destroyed). A way of stating the first law of thermodynamics is the internal energy (ΔU) of a system is given by the sum of the heat (Q) that flows into and out-of the system and the work (W) done on the system:

$$\Delta U = Q + W \tag{0.1}$$

Therefore, there are only two ways to change the internal energy ΔU of the system:

- Add or remove heat from the system, Q.
- Perform or extract work from the system, W.

It is assumed for this analysis the BLEVE expansion of the super-heated liquid (initial state) to atmospheric conditions (final state) occurs so quickly there is no time for heat to be added or removed from the system. When heat cannot be added or removed from a system it is called an adiabatic process. During an adiabatic process the heat (Q) is zero and the 1st Law of Thermodynamics can be rewritten to:

$$\Delta U = W \tag{0.2}$$

Work The work W of an expanding gas is given by,

$$W = P_0 \Delta V \tag{0.3}$$

Where P_0 is the initial pressure and ΔV is the difference in the final and initial volumes. In the case of the BLEVE the change in volume is due to the conversion of the super-heated liquid to a gas. We know the initial volume of the system, V_i in this case, the tank volume. However, the final volume, V_f, is an unknown. We can however transform the final volume into terms we do know. If we rewrite the final volume (V_f) in terms of the specific volume (volume divided by mass) times the mass we can transform our change in final volume into a change in final mass,

$$\Delta V = V_f - V_i \tag{0.4}$$

$$\Delta V = (\nu_G m_G + \nu_L m_L)_f - V_i \tag{0.5}$$

Therefore,

$$W = P_0 \left[(\nu_G m_G + \nu_L m_L)_f - V_i \right] \tag{0.6}$$

The quality of a gas-liquid mixture is defined as the fraction of the total mass (gas + liquid) that is saturated vapor,

$$\chi = \frac{m_G}{m_T} \tag{0.7}$$

Where m_G is the mass of the gas and m_T is the total mass. Solving for the mass of the gas,

$$m_G = m_T \chi \tag{0.8}$$

The mass of the liquid is then given by,

$$m_T = m_G + m_L \tag{0.9}$$

$$m_L = m_T - m_G \tag{0.10}$$

$$m_L = m_T - m_T \chi \tag{0.11}$$

Substituting equations (7) and (10) back into (5) we have,

$$W = P_0 \left[(\nu_G m_T \chi + \nu_L (m_T - m_T \chi))_f - V_i \right] \tag{0.12}$$

$$W = P_0 \left[(\nu_G m_T \chi + \nu_L m_T - \nu_L m_T \chi)_f - V_i \right] \tag{0.13}$$

$$W = P_0 \left[((\nu_G - \nu_L)\, m_T \chi + \nu_L m_T)_f - V_i \right] \tag{0.14}$$

0.4 Internal Energy

The internal energy is the energy of atomic motion. It is the sum of the molecular kinetic and potential energies in a system (in our case, the tank filled with fluid). The molecular kinetic energy is made up of three types of molecular motion:

- translational,
- rotational, and
- vibrational.

The molecular potential energy is derived from the electromagnetic force that exists between the atoms in individual molecules and the intermolecular forces between molecules. The internal energy is directly proportional to the temperature of the system (higher temperatures mean more internal energy and lower temperatures mean lower internal energy).

The change in internal energy can be changed similarly to how we change the volume in the Work section. The change in internal energy can be rewritten in terms of the specific internal energy (internal energy divided by the mass) and the quality,

$$\Delta U = U_f - U_i \tag{0.15}$$

$$\Delta U = (u_G m_G + u_L m_L)_f - U_i \tag{0.16}$$

Substituting equations (7) and (10) into the internal energy equation (15) we have,

$$\Delta U = \left(u_G m_T \chi + u_L (m_T - m_T \chi)\right)_f - U_i \tag{0.17}$$

$$\Delta U = \left(u_G m_T \chi + u_L m_T - u_L m_T \chi\right)_f - U_i \tag{0.18}$$

$$\Delta U = \left((u_G - u_L)\, m_T \chi + u_L m_T\right)_f - U_i \tag{0.19}$$

Referring back to equation (3) and substituting equations (14) and (19) we can solve for the quality χ,

$$\chi = \frac{m_T P_0 \nu_L - V_i P_0 + m_T u_L - U_i}{\left[(u_L - u_G) - (\nu_G - \nu_L) P_0\right] m_T} \tag{0.20}$$

By substituting χ back into equation (19) we can solve for the internal energy, ΔU. Once we know the change in internal energy due to the flash-boiling we can calculate the equivalent weight of TNT that will produce the same change in internal energy.

0.5 Conversion to TNT Equivalent Weight

The equation for the conversion to equivalent TNT weight in kilograms is,

$$W_{TNT} = \beta\, 0.2136 \Delta U \tag{0.21}$$

Where: - β is the fraction of the energy released converted to the blast wave (fragile = 80% and ductile = 40%) - 0.2136$\frac{kg}{MJ}$ is the inverse of blast energy of TNT $(4680\ J/g_{TNT})$4 - ΔU is the internal energy of the flash boiling liquid in $bar\ m^3$.

With the weight of TNT known it is a simple matter to calculate the overpressure at a specific distance from the BLEVE using the Kingery Bulmash equations [5].

1 Notebook Imports

2 Thermodynamic Data

2.1 Pressure at State 1 (Pre-failure State)

The drum (tank) is assumed to fail at 1.21 times the opening pressure of the pressure relief valve (PRV)[5]. The PRV was set to open at 15 MPa therefore, the absolute pressure at state 1 (failure state) is given by,

$$p_1 = 1.21\left(p_{PRV} + p_{atm}\right) \tag{2.1}$$

$$p_1 = 1.21\left(1500000 + 101325\right) \tag{2.2}$$

$$p_1 = 1.916\, MPa \tag{2.3}$$

2.2 Pressure at State 2 (Final Expanded State)

The pressure at state 2 (final expanded state) is standard atmospheric pressure or 0.101 MPa. The other state variables can be determined based on the "saturated" state of the propane inside the tank and the known pressures. The thermodynamic data for states 1 and 2 is summarized in Table (table 2.1).

Table 2.1: Propane Thermodynamic Data for Inital (1) and Final (2) States

State	$P\,(kPa)$	$h_f\left(\frac{kJ}{kg}\right)$	$h_g\left(\frac{kJ}{kg}\right)$	$v_f\left(\frac{m^3}{kg}\right)$	$v_g\left(\frac{m^3}{kg}\right)$	$u_f\left(\frac{kJ}{kg\,K}\right)$	$u_g\left(\frac{kJ}{kg\,K}\right)$	$s_f\left(\frac{kJ}{kg\,K}\right)$	$s_g\left(\frac{kJ}{kg\,K}\right)$
1	1937.60325	354584.413136	625197.730383	0.002287	0.022459	350.152477	581.681515	1.503188	2.325970
2	101.32500	100356.292970	525947.893053	0.001722	0.413884	100.181860	484.011098	0.607045	2.449144

3 Internal Energy at States 1 and 2

3.1 Internal Energy at State 1

The internal energy at at state 1 (saturated) is calculated from,

$$h = u + pv \tag{3.1}$$

where h is the enthalpy, p is the pressure, and v is the specific volume. Therefore, for state 1 (fluid and gas) we have,

$$u = h - pv \tag{3.2}$$

$$u_{1f} = h_{1f} - p_1 v_{1f} \tag{3.3}$$
$$u_{1f} = 354584.4 - (1937.603\,kPa)(0.002287\,m^3/kg) \tag{3.4}$$
$$u_{1f} = 350.15\,kJ/kg \tag{3.5}$$

$$u_{1g} = h_{1g} - p_1 v_{1g} \tag{3.6}$$
$$u_{1g} = 100356.29 - (101.325\,kPa)(0.001722\,m^3/kg) \tag{3.7}$$
$$u_{1g} = 581.68\,kJ/kg \tag{3.8}$$

and similarly for state 2,

$$u_{2f} = 100.18\,kJ/kg \tag{3.9}$$
$$u_{2g} = 484.01\,kJ/kg \tag{3.10}$$

3.2 Internal Energy at State 2

When the drum breaks and the propane at state 1 expands to state 2 (atmospheric pressure) some of the liquid propane vaporizes and some of the gaseous propane condenses. Therefore unlike at the saturated state 1, there is both vapor and fluid present. We can calculate the vapor present using the vapor quality (χ), from,

$$\chi = \frac{\nu_{tot} - \nu_f}{\nu_g - \nu_f} \tag{3.11}$$

where ν is the specific gravity. This equation is also true for the entropy (s), internal energy (u), and enthalpy (h). Using the entropy (s) we can calculate the quality of the saturated liquid and vapor as the propane transitions from state 1 to state 2. Therefore, the liquid vapor quality at state 2 is given by s

$$\chi_f = \frac{s_{f1} - s_{f2}}{s_{g2} - s_{f2}} \tag{3.12}$$

$$\chi_f = \frac{1.503188 - 0.607045}{2.449144 - 0.607045} \tag{3.13}$$

$$\chi_f = 0.4865 \tag{3.14}$$

and for the vapor at state 2,

$$\chi_g = \frac{s_{g2} - s_{g1}}{s_{g2} - s_{f2}} \tag{3.15}$$

$$\chi_g = \frac{2.449144 - 2.325970}{2.449144 - 0.607045} \tag{3.16}$$

$$\chi_g = 0.06687 \tag{3.17}$$

We can then calculate the internal energy at state 2 using,

$$u_{2-fluid} = (1 - \chi_f)u_{f2} + \chi_f u_{g2} \tag{3.18}$$

$$u_{2-vapor} = (1 - \chi_g)u_{g2} + \chi_g u_{f2} \tag{3.19}$$

$$u_{2-fluid} = (1 - 0.4865)100.1818 + (0.4865)(484.0111) \tag{3.20}$$

$$u_{2-vapor} = (1 - 0.0668)484.0111 + (0.0668)(100.1818) \tag{3.21}$$

$$u_{2-fluid} = 286.9068\, kJ/kg \tag{3.22}$$

$$u_{2-vapor} = 458.3459\, kJ/kg \tag{3.23}$$

4 The Specific Work

The work that the expanding vapor and fluid can perform is the difference between the initial (1) and final (2) states,

$$e_{ex} = u_1 - u_2 \tag{4.1}$$

for the saturated fluid we have,

$$e_{exf} = u_{f1} - u_{2-fluid} \tag{4.2}$$
$$e_{exf} = 350.15 - 286.91 \tag{4.3}$$
$$e_{exf} = 63.25\, kJ/kg \tag{4.4}$$

and for the vapor,

$$e_{exg} = u_{g1} - u_{2-vapor} \tag{4.5}$$
$$e_{exg} = 581.68 - 458.35 \tag{4.6}$$
$$e_{exg} = 123.34\, kJ/kg \tag{4.7}$$

```
(8743.821988545078, 222.63002781996232)
```

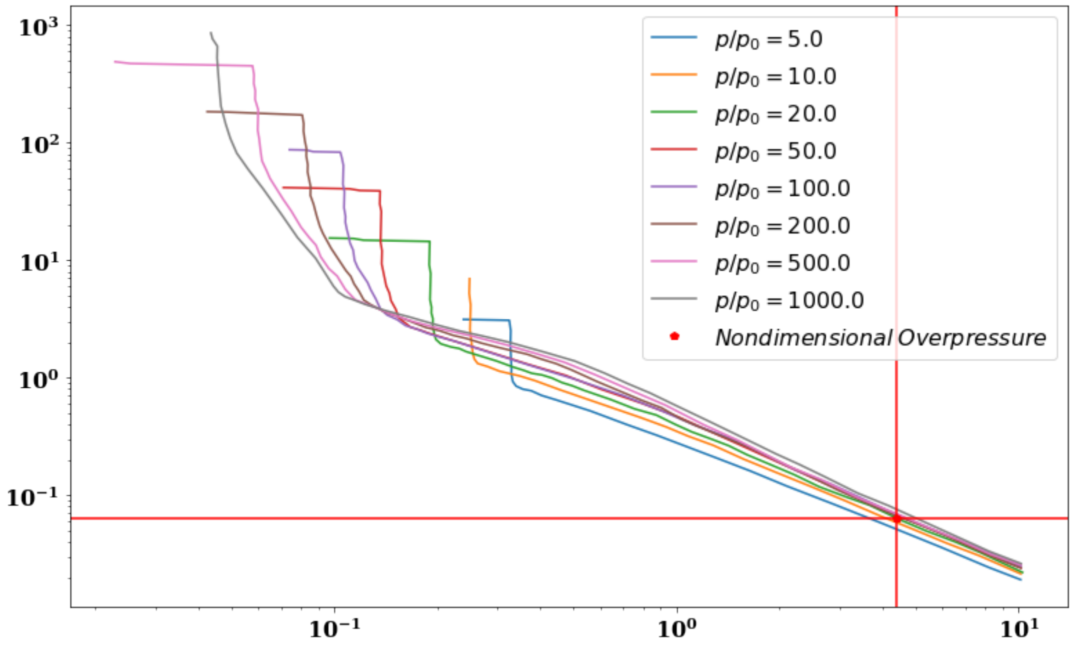
```
(1106018.0441464642, 54916.43853777208)
```

```
1160934.4826842363
```

```
(4.441950730199333, 19.12265729089563)
```

	P	R	w	z
0	3.128611	0.238936	5.0	$p/p_0 = 5.0$
1	3.118639	0.252979	5.0	$p/p_0 = 5.0$
2	3.106715	0.270923	5.0	$p/p_0 = 5.0$
3	3.094836	0.290141	5.0	$p/p_0 = 5.0$
4	3.086942	0.303704	5.0	$p/p_0 = 5.0$

```
array(0.06403677)
```




```
(5876.85, 9.40580773951352)
```

5 Cleanup Data

Like families, tidy datasets are all alike but every messy dataset is messy in its own way. Tidy datasets provide a standardized way to link the structure of a dataset (its physical layout) with its semantics (its meaning). In this section, I'll provide some standard vocabulary for describing the structure and semantics of a dataset, and then use those definitions to define tidy data. tidyr

6 Analysis/Modeling

7 Results

- Focus on main analysis steps and findings
- Remove intermediate results or move to supplement

8 Conclusion

9 References

[1] Jarrett Renshaw and Jessica DiNapoli. Unit at Philadelphia refinery completely destroyed in fire, 2019. URL https://www.reuters.com/article/us-usa-refinery-blast/unit-at-philadelphia-refinery-completely-destroyed-in-fire-sources-idUSKCN1TO0SZ.

[2] Safety Center for Chemical Process. *Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE, and Flash Fire Hazards*. John Wiley & Sons, Ltd, Hoboken, 2nd edition, 2010. ISBN 978-0-470-25147-8.

[3] John Duchneskie. Image From: Philadelphia Energy Solutions to close refinery damaged by fire; gas prices spike, jun 2019. URL https://www.inquirer.com/business/philadelphia-refinery-fire-plan-to-close-20190626.html.

[4] Flowserve Corporation. Refinery Processes Industry Guide, 2000. URL https://pro-quip.com/images/proquip/PDFs/RefiningIndustryGuide.pdf.

[5] American Society of Mechanical Engineers. *Boiler and Pressure Vessel Code, Section III, Rules for Construction of Pressure Vessels*. ASME, New York, NY, 2013.