

Overpressure Analysis of Girard Point Refinery Accident

Boiling-Liquid Expanding-Vapor Explosion

Author:

S. Kevin McNeill

shonn.mcneill@atf.gov

National Center for Explosives Training and Research
Explosives Research and Development Division

August 25, 2019

Contents

1	Introduction	3
2	Background	4
2.1	Refinery	4
2.2	Treater Feed Surge Tank	4
2.3	Pressure Relief Valve	7
2.4	Recovered Drum Debris	7
2.5	Boiling-Liquid Expanding-Vapor Explosion (BLEVE)	9
3	Calculation of Air Blast from a BLEVE	11
3.1	Data Collection	11
3.2	Pressure at State 1 (Pre-failure State)	11
3.3	Pressure at State 2 (Final Expanded State)	11
3.4	Internal Energy at State 2	13
4	The Specific Work	14
5	The Explosion Energy	15
5.1	Nondimensional Side-on Pressure and Impulse	15
6	References	16

1 Introduction

On June 21, 2019, at approximately 4:22 AM, a fire and explosion, see fig. 1.1, occurred at the Girard Point Refinery owned by Philadelphia Energy Solutions¹. One of the three explosions observed that day was from the V1 treater-feed-surge-drum in the refineries pretreatment unit. The explosion propelled the largest piece (estimated: $41809.6lb$ ($18964.5kg$)) of the drum approximately $2100ft$ ($640m$) from the blast seat, see ^{??}. It is hypothesized that a boiling-liquid expanding-vapor explosion (BLEVE) event provided the energy to generate the blast wave. The Philadelphia Fire Department requested ATF estimate the blast overpressure generated when the tank exploded. This paper is an engineering analysis to estimate the blast overpressure assuming a BLEVE occurred. The analysis is based upon an adiabatic and isentropic energy analysis developed by the Center for Chemical Process Safety².



Figure 1.1: A view of the Philadelphia Energy Solutions Inc's oil refinery while on fire³.

2 Background

2.1 Refinery

The Girard Point Refinery is located in southwest Philadelphia, PA, on the Schuylkill River, see fig. 2.1. The refinery produced approximately 335,000 bpd of gasoline, and was the largest on the East Coast⁴. The treater-feed-surge-drum, involved in the explosion, is part of the pretreatment process of alkylation used in the production of gasoline.

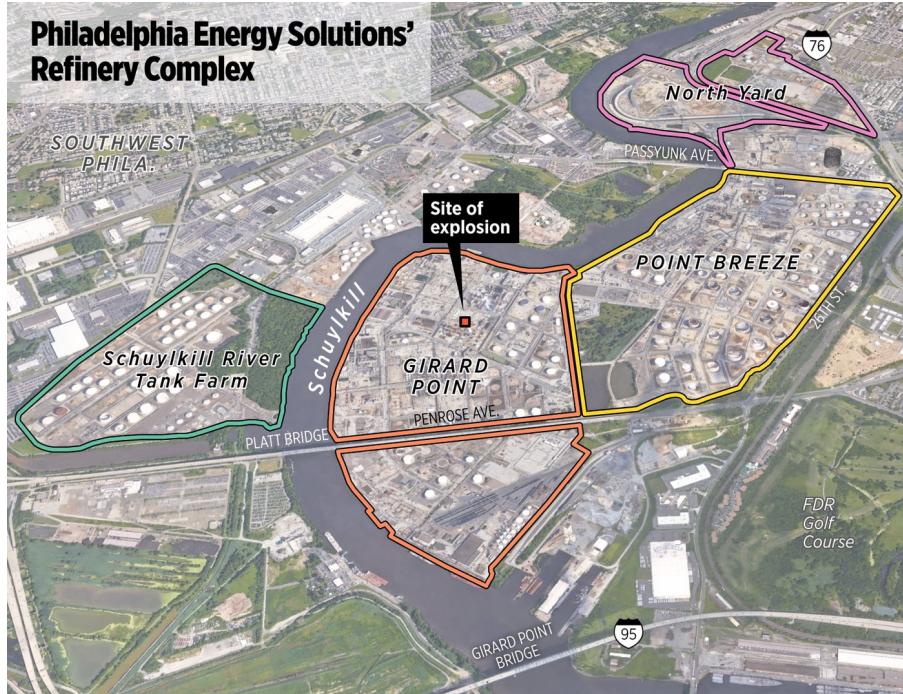


Figure 2.1: Map of Girard Point Refinery showing the blast seat location⁵.

2.2 Treater Feed Surge Tank

Alkylation generally 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 their high octane and low vapor pressure⁶. The treater-feed-surge-drum (TFSD) was located between the fluid catalytic cracker and the alkylation unit. The purpose of a surge drum is to stabilize fluctuations in the overall system flow rate. The TFSD was part of the pretreatment process for alkylation, see fig. 2.2. During pretreatment, also referred to as sweetening, sulfur compounds (hydrogen sulfide, thiophene and mercaptan) are removed to improve color, odor, and oxidation stability.

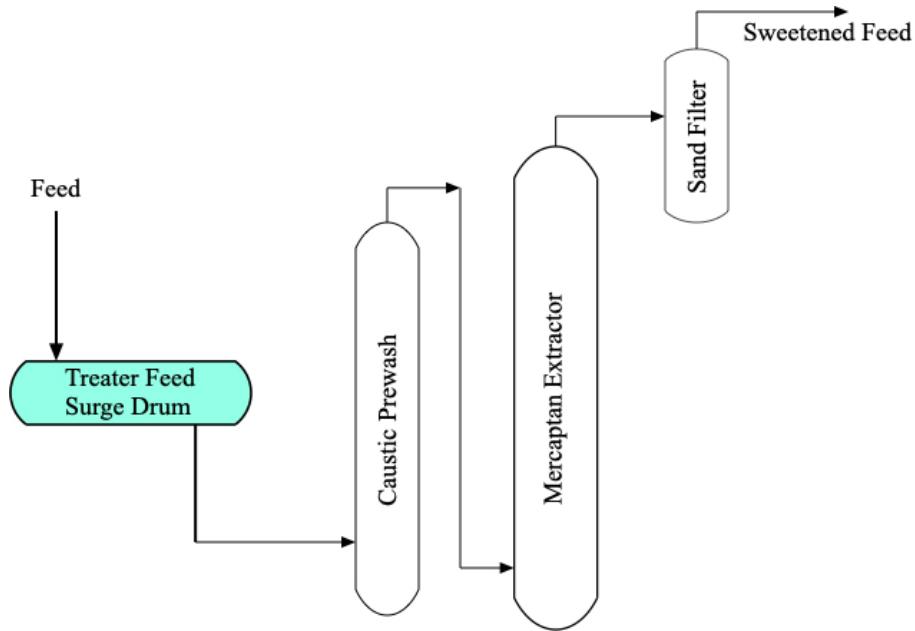


Figure 2.2: Simple flow diagram of the sweetening and treating process where the TFSD was located at the time of the explosion.^{7,8}

The TFSD tank measured 39'-8" in length, not including the heads, see table 2.4 and fig. 2.3 for construction details⁹. At the time of the explosion, the TFSD contained 20160 gal (76.3m³) of butane (50% by volume) and butene (40% by volume) and other lesser constituents, see table 2.2.

Table 2.1: Treater-Feed-Surge-Drum Construction Parameters⁹

Parameter	Value	Units
Type	horizontal	NA
Year Built	1972	NA
Construction Material	A516 Type 70 Steel	NA
Tank Wall Thickness	0.8125	in
Volume	372228	gal
Percent Filled	53.3	%
Mass	74660	lb
Safety Valve Set	155	psig

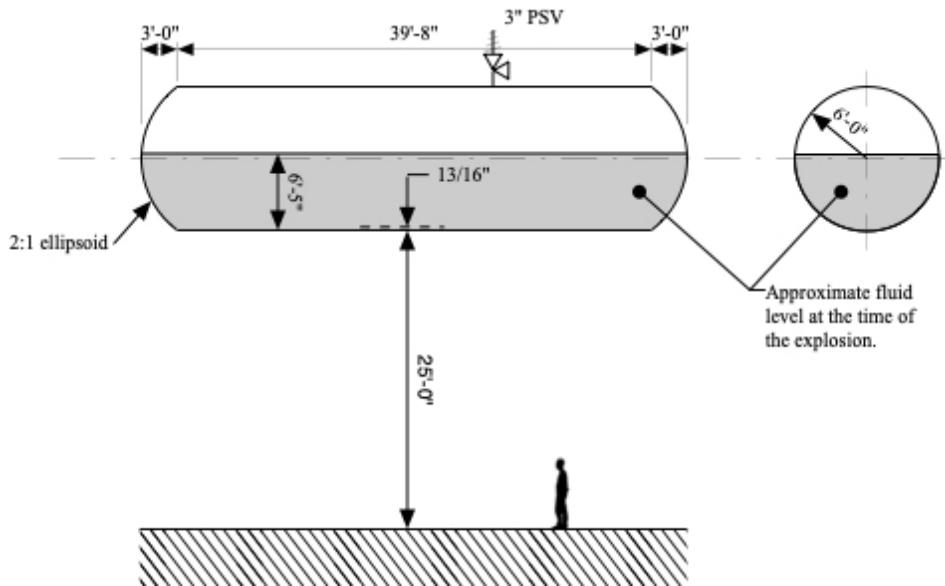


Figure 2.3: Diagram depicting the dimensions of the TFSD tank. The tank was positioned 25 ft above ground level and estimated to contain 20160 gal (53.3% filled) of butane (50% by volume) and butene (40% by volume) at the time of the explosion.⁹

Table 2.2: Chemical Contents in the Treater-Feed-Surge-Drum Nearest to the Time of the Explosion⁹

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
butene	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

For this analysis it will be assumed that the entire mixture is butane. This assumption greatly simplifies the analysis, avoiding partial pressures and multiple energy calculations with different vapor qualities. The assumption is reasonable because butane and butene make up more than 90% of the fluid volume and butane and butene are chemically similar, see table 2.3. The boiling temperatures for butene and butane are 20.66 °F (-6.3 °C) and 31.1 °F (-1.0 °C) respectively; both are well above the tank temperature when exposed to fire so a BLEVE assumption is reasonable.

Table 2.3: Chemical Properties of Butene and Butane^{10;11}

Property	Butene	Butane
Molecular Formula	C_4H_8	C_4H_{10}

Property	Butene	Butane
Molecular Weight	$56.108 \frac{g}{mol}$	$58.12 g \frac{g}{mol}$
Boiling Point at 760mm Hg	$20.6^{\circ}F$	$31.1^{\circ}F$
Flash Point	$-110.0^{\circ}F$	$-76.0^{\circ}F$
Density at $25^{\circ}C$, 1 atm	$0.588 \frac{g}{cc}$	$0.573 \frac{g}{cc}$
$\frac{C_p}{C_V}$ Ratio γ	1.13	1.12

2.3 Pressure Relief Valve

The TSFD was fitted with a Consolidated (1906-30LC-1-CC-MS-31-RF-1) 3" x 4" pressure relief valve (PRV). The relief pressure was set to 155psig (1068.7kPa) and the relief temperature was set to $183.5^{\circ}F$ ($84.3^{\circ}C$). The PRV was positioned on the top of the TRFD, see fig. 2.3.

2.4 Recovered Drum Debris

Three major pieces of the TSFD were identified after the explosion. They were thrown a maximum of 2100ft (640m), see fig. 2.4. The largest piece (Large End Cap) was approximately 22ft (6.7m) in length, see fig. 2.5, or a little more than half the original tank length. The other end of the TSFD (Small End Cap) was recovered 1761ft (536m) from the blast seat. It was approximately 5ft (1.5m) in length, see fig. 2.6. The piece thrown the shortest distance (fillet) was 819ft (249m) from the blast seat. The fillet piece was heavily damaged and a photographic analysis of the length was not possible. However, based on the original length of the tank and removing the large and small end cap lengths the fillet length is approximately 12ft (3.6m), see fig. 2.7.

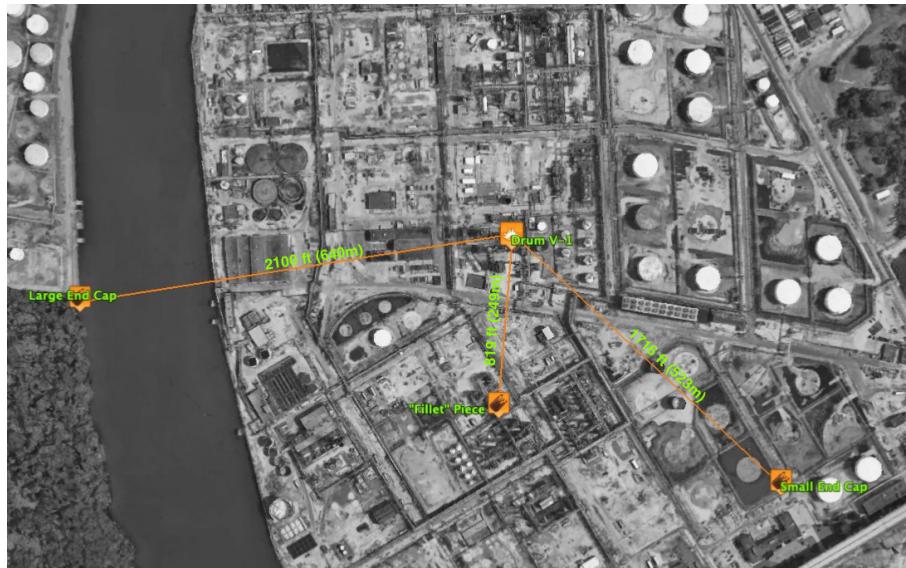


Figure 2.4: Map of Girard Point showing the blast seat and locations of the three main pieces of the TSFD (V-1).¹²



Figure 2.5: Photograph of the large end cap, estimated to be 22ft (6.7m) in length based on photographic analysis. In this photograph the tank has been moved from it's original landing location.¹²



Figure 2.6: Photograph of the small end cap, estimated to be 5ft (1.5m) in length based on photographic analysis.¹²



Figure 2.7: Photograph of the fish fillet piece, calculated to be 12ft (3.6m) in length based on the total length of the drum less the lengths of the large and small end caps.¹²

The estimated mass of each piece of the TFSD is summarized in table 2.4. The mass calculations are based on the refinery recorded mass of the vessel, 74660lb (33865kg), multiplied by the percent mass calculated using the following equations,

Ellipsoidal Head:

$$V_{eh} = \frac{\pi D^2(D/4)}{6} \quad (2.1)$$

Cylinder:

$$V_c = \frac{\pi D^2 l}{4} \quad (2.2)$$

where the drum wall thickness is 0.83in (2.1cm), the tank diameter is 12ft (3.7m), and the material density for A516 steel is 7.8g/cc⁸. The difference in calculated and refinery recorded mass is likely due to appurtenances attached to the tank not accounted for in the calculated mass.

Table 2.4: Estimated Treater-Feed-Surge-Drum Debris Mass⁹

TFSD ID	Cylinder (ft)	Calculated Debris Mass (lb)	Percent Mass Calculated	Refinery Recorded Mass (lb)
Large End Cap	22.0	31541.8	0.56	41809.6
Small End Cap	5.0	10078.5	0.18	13438.8
Fillet	12.0	15150.5	0.26	19411.6
Total	39.0	56770.8	1.00	74660.0

2.5 Boiling-Liquid Expanding-Vapor Explosion (BLEVE)

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 its 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 these four forms depends on the specifics of the explosion. Planas-Cuchi 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 small¹³. In practice most pressure vessels are designed with materials that are ductile rather than brittle to avoid sudden and catastrophic brittle (fragile) failures¹⁴.

3 Calculation of Air Blast from a BLEVE

There is a seven step process for calculating the air blast from a BLEVE:

1. Data Collection
 - a. Vessel internal pressure, p_1
 - b. Ambient air pressure, p_2
 - c. Vessel volume
 - d. Ratio of specific heats of gas in the vessel
 - e. Distance from the center of the tank to the receptor
 - f. Shape of the vessel (spherical or cylindrical)
 - g. Speed of sound of air
 - h. Ratio of specific heats of air
2. Calculate the Vessel-Gas Energy Using Brodes Equation ¹⁵
3. Calculate the Vessel Burst Pressure Ratio p_1/p_2 and Select Blast Curves
4. Calculate the Scaled Standoff Distance \bar{R} of the Receptor ¹⁶
5. Determine the Scaled Positive Overpressure and Impulse
6. Adjust for Elevated Temperatures and Vessel Geometry
7. Calculate Overpressure and Impulse

3.1 Data Collection

For this analysis the following data will be used:

1. Ambient air pressure, 14.7psi (0.101MPa)
2. Vessel volume, 372228gal (1409.0m^3)
3. Ratio of specific heats of butane (1.12)
4. Distance from the center of the tank to the receptor, 25ft (7.62m)
5. Shape of the vessel is cylindrical ($L/D = 3.3$)
6. Speed of sound of air, 1115.49ft/s (340m/s)

3.2 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) ¹⁷. This pressure is based on the American Petroleum Institutes Standard 521 which, requires that pressure relief valves on pressure vessels achieve rated flow at 1.21 times the maximum allowable working pressure. The PRV was set to 155psig (1.07MPa) therefore, the absolute pressure at state 1 (failure state) is given by,

$$p_1 = 1.21 (p_{PRV} + p_{atm}) \quad (3.1)$$

$$p_1 = 1.21 (14.70 + 155.00) \quad (3.2)$$

$$p_1 = 205.33\text{psia} (1.42\text{ MPa}) \quad (3.3)$$

3.3 Pressure at State 2 (Final Expanded State)

The pressure at state 2 (final expanded state) is standard atmospheric pressure or 14.7psi (0.101MPa). ## Internal Energy at States 1 and 2 Th internal energy u can be used to estimate the energy released in an explosion. With the gases in the saturated state and knowing the pressures at state 1 (explosion) and state 2 (atmospheric) we can use lookup tables determine the specific volume v , and the enthalpy h . Combining these two properties with the pressure we can calculate the internal energy u using,

$$h = u + pv \quad (3.4)$$

where h is the enthalpy, p is the pressure, and v is the specific volume. Therefore, solving for the internal energy u we have,

$$u = h - pv \quad (3.5)$$

The internal energy at state 1 for butane in the liquid state is,

$$u_{1f-butane} = h_{1f-butane} - (p_{1-butane})(v_{1f-butane}) \quad (3.6)$$

$$u_{1f-butane} = 451.46 - (1415.72 \text{ kPa})(0.002261 \text{ m}^3/\text{kg}) \quad (3.7)$$

$$u_{1f-butane} = 271.68 \text{ kJ/kg} \quad (3.8)$$

and for the gaseous butene we have,

$$u_{1g-butene} = h_{1g-butene} - (p_{1-butene})(v_{1g-butene}) \quad (3.9)$$

$$u_{1g-butene} = 515.58 - (1937.60 \text{ kPa})(0.0021 \text{ m}^3/\text{kg}) \quad (3.10)$$

$$u_{1g-butene} = 477.49 \text{ kJ/kg} \quad (3.11)$$

and similarly for butene at state 2,

$$u_{2f-butene} = -0.16 \text{ kJ/kg} \quad (3.12)$$

$$u_{2g-butene} = 354.35 \text{ kJ/kg} \quad (3.13)$$

and for states 1 and 2 for butane we have,

$$u_{1f-butane} = 498.49 \text{ kJ/kg} \quad (3.14)$$

$$u_{1g-butane} = 697.31 \text{ kJ/kg} \quad (3.15)$$

$$u_{2f-butane} = 198.70 \text{ kJ/kg} \quad (3.16)$$

$$u_{2g-butane} = 547.18 \text{ kJ/kg} \quad (3.17)$$

All the gas properties are summarized in ??

3.4 Internal Energy at State 2

When the drum breaks and the butane and butene at state 1 expands to state 2 (atmospheric pressure) some of the liquid vaporizes and some of the gases condense. Therefore, unlike at the saturated state 1, there is both vapor and fluid present at state 2. We can use the quality of the vapor and liquid to calculate the internal energy at state 2. The vapor quality (χ), can be calculated from,

$$\chi = \frac{s - s_f}{s_{g2} - s_{f2}} \quad (3.18)$$

where s is the entropy of the butane or butene. For the saturated liquid expanding from state 1 to state 2 we have,

$$\chi_f = \frac{s_{f1} - s_{f2}}{s_{g2} - s_{f2}} \quad (3.19)$$

$$\chi_f = \frac{1.503188 - 0.607045}{2.449144 - 0.607045} \quad (3.20)$$

$$\chi_f = 0.4865 \quad (3.21)$$

and for the vapor at state 2,

$$\chi_g = \frac{s_{g2} - s_{g1}}{s_{g2} - s_{f2}} \quad (3.22)$$

$$\chi_g = \frac{2.449144 - 2.325970}{2.449144 - 0.607045} \quad (3.23)$$

$$\chi_g = 0.06687 \quad (3.24)$$

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

$$u_{2-fluid} = (1 - \chi_f)u_{f2} + \chi_f u_{g2} \quad (3.25)$$

$$u_{2-vapor} = (1 - \chi_g)u_{g2} + \chi_g u_{f2} \quad (3.26)$$

$$u_{2-fluid} = (1 - 0.4865)100.1818 + (0.4865)(484.0111) \quad (3.27)$$

$$u_{2-vapor} = (1 - 0.0668)484.0111 + (0.0668)(100.1818) \quad (3.28)$$

$$u_{2-fluid} = 286.9068 \text{ kJ/kg} \quad (3.29)$$

$$u_{2-vapor} = 458.3459 \text{ kJ/kg} \quad (3.30)$$

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,

$$e_{ex} = u_1 - u_2 \quad (4.1)$$

for the saturated fluid we have,

$$e_{exf} = u_{f1} - u_{2-fluid} \quad (4.2)$$

$$e_{exf} = 350.15 - 286.91 \quad (4.3)$$

$$e_{exf} = 63.25 \text{ kJ/kg} \quad (4.4)$$

and for the vapor,

$$e_{exg} = u_{g1} - u_{2-vapor} \quad (4.5)$$

$$e_{exg} = 581.68 - 458.35 \quad (4.6)$$

$$e_{exg} = 123.34 \text{ kJ/kg} \quad (4.7)$$

5 The Explosion Energy

The explosion energy is calcu

5.1 Nondimensional Side-on Pressure and Impulse

The nondimenstional side-on pressure can be calculated from Figure X and gives a $\bar{P}_s = 0.064$ for an $\bar{R} = 4.4$ and a $p/p_0 = 19.12$. The nondimensional side-on impulse can be calculated from Figure Y and gives a $\bar{i}_s = 0.013$ for an $\bar{R} = 4.4$ and a $p/p_0 = 19.12$.

The side-on pressure and impulse can be calculated from the following:

$$\bar{P}_s - p_0 = (0.064)(101.325 \text{ kPa}) = 6.5 \text{ kPa} \quad (5.1)$$

$$i_s = \frac{(0.013)(101325 \text{ kPa})^{2/3}(1160.9E6 \text{ J})^{1/3}}{340 \text{ m/s}} = 86.31 \text{ Pa-s} \quad (5.2)$$

6 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-idUSKCN1T00SZ>.
- [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] Andrew Maykuth. Philadelphia Energy Solutions to close refinery damaged by fire ; gas prices spike. *Philadelphia Inquirer*, jun 2019.
- [4] Associated Press. Biggest oil refinery on the East Coast closes after explosive fire - MarketWatch, 2019. URL <https://www.marketwatch.com/story/biggest-oil-refinery-on-the-east-coast-closes-after-explosive-fire-2019-06-26>.
- [5] John Duchneskie. Image From: Philadelphia Energy Solutions to close refinery damaged by fire; gas prices spike, jun 2019. URL <https://www.inquirer.com/business/philly-refinery-fire-plan-to-close-20190626.html>.
- [6] Flowserve Corporation. Refinery Processes Industry Guide, 2000. URL <https://pro-quip.com/images/proquip/PDFs/RefiningIndustryGuide.pdf>.
- [7] T. Temur, E. Avcilar, E. Özinan, and M. Karakaya. Reduce LPG Sulfur with a 'rules of thumb' Checklist. *Gas Processing & LNG*, jun 2014.
- [8] Gary S. Malone. Email: Philadelphia Refinery Explosion (Tank Piece 2), 2019.
- [9] Philadelphia Energy Solutions. Letter: July 11, 2019 ATF Information Request, 2019.
- [10] National Center for Biotechnology Information. PubChem Database. Butane, CID = 7843, . URL <https://pubchem.ncbi.nlm.nih.gov/compound/Butane>.
- [11] National Center for Biotechnology Information. PubChem Database. Butene, CID=7844, . URL <https://pubchem.ncbi.nlm.nih.gov/compound/1-Butene>.
- [12] Gary S. Malone. Documents, Video, and Photographs (mailed thumb drive), 2019.
- [13] E. Planas-Cuchi, J. M. Salla, and J. Casal. Calculating overpressure from BLEVE explosions. *Journal of Loss Prevention in the Process Industries*, 17(6):431–436, 2004. ISSN 09504230. doi:[10.1016/j.jlp.2004.08.002](https://doi.org/10.1016/j.jlp.2004.08.002).
- [14] Daniel J. Benac, Nicholas Cherolis, and David Wood. Managing Cold Temperature and Brittle Fracture Hazards in Pressure Vessels. *Journal of Failure Analysis and Prevention*, 16(1):55–66, 2016. ISSN 15477029. doi:[10.1007/s11668-015-0052-3](https://doi.org/10.1007/s11668-015-0052-3).
- [15] Harold L. Brode. Blast wave from a spherical charge. *Physics of Fluids*, 2(2):217–229, nov 1959. ISSN 10706631. doi:[10.1063/1.1705911](https://doi.org/10.1063/1.1705911). URL <https://aip.scitation.org/doi/10.1063/1.1705911>.
- [16] Wilfred E. Baker. *Explosions in Air*. University of Texas Press, Austin, TX, 1973. ISBN 029272003.
- [17] American Society of Mechanical Engineers. *Boiler and Pressure Vessel Code, Section III, Rules for Construction of Pressure Vessels*. ASME, New York, NY, 2013.