U.S. Chemical Safety and Hazard Investigation Board

Popcorn Polymer Accumulation, Pipe Rupture, Explosions, and Fires at TPC Group Chemical Plant Butadiene Unit

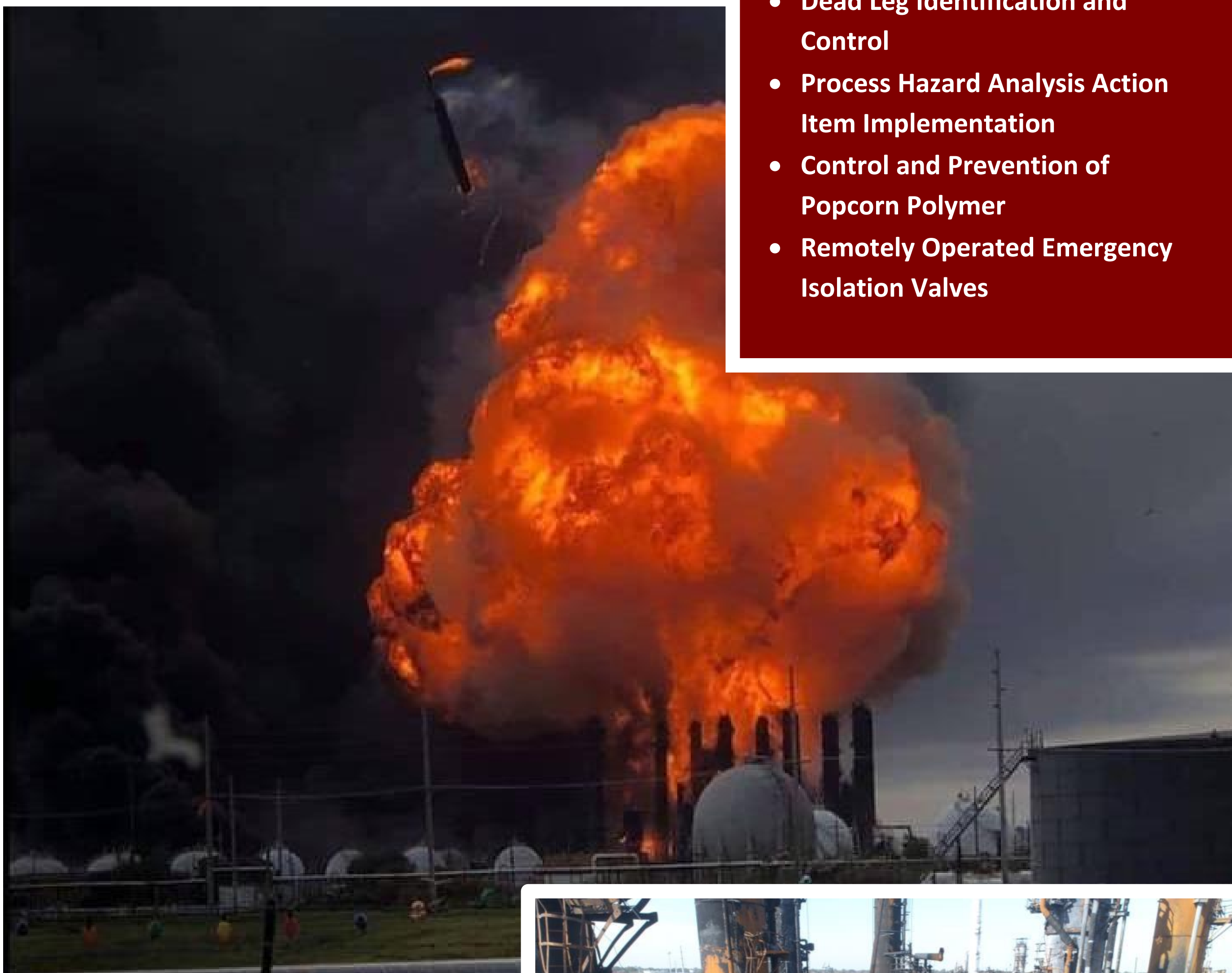
Port Neches, Texas | *Incident Date: November 27, 2019* | **No. 2020-02-I-TX**

Investigation Report

Published: December 2022

Safety Issues:

- **Dead Leg Identification and Control**
- **Process Hazard Analysis Action Item Implementation**
- **Control and Prevention of Popcorn Polymer**
- **Remotely Operated Emergency Isolation Valves**



U.S. Chemical Safety and
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ABBREVIATIONS

ACC	American Chemistry Council
ACGIH	American Conference on Governmental Industrial Hygienists
API	American Petroleum Institute
CCPS	Center for Chemical Process Safety
CDR	Chemical Data Reporting
CSB	U.S. Chemical Safety and Hazard Investigation Board
DCS	Distributed control system
DEHA	Diethyl hydroxylamine
DIB	Diisobutylene
EBV	Emergency block valve
EEPC	European Ethylene Producers Committee
EPA	U.S. Environmental Protection Agency
FCCU	Fluidized catalytic cracking unit
GEMS	General Engineering and Maintenance Standards
GPD	Gallons per day
HF	Hydrofluoric acid
HSE	Health and Safety Executive
IARC	International Agency for Research on Cancer
MOC	Management of change
MSU	Marine Safety Unit
MTBE	Methyl tertiary butyl ether
NIOSH	National Institute for Occupational Safety and Health
NTP	National Toxicology Program

OSH	Occupational Safety and Health
OSHA	U.S. Occupational Safety and Health Administration
P&ID	Piping and Instrumentation Diagram
PES	Philadelphia Energy Solutions
PHA	Process Hazard Analysis
PNO	Port Neches Operations
PSM	Process Safety Management
RAGAGEP	Recognized and generally accepted good engineering practices
RMP	Risk Management Plan
ROEIV	Remotely operated emergency isolation valve
TBC	Tertiary butyl catechol
TSCA	Toxic Substances Control Act
USCG	U.S. Coast Guard

EXECUTIVE SUMMARY

On November 27, 2019, a series of explosions occurred at the TPC Group (TPC) Port Neches Operations (PNO) facility, located in Port Neches, Texas, after highly flammable butadiene released from the process unit. The explosions caused a process tower to propel through the air and land within the facility, other process towers to fall within the unit, extensive facility damage, and fires that burned for more than a month within the facility. The butadiene unit was destroyed, forcing the facility to cease butadiene production operations indefinitely. As of the date of this report, the butadiene production operations remain shut down. Two TPC PNO employees and a contractor reported minor injuries, and according to media reports, at least five local residents reported injuries. Officials in Jefferson County, Texas declared the county to be in a state of disaster and issued a mandatory four-mile radius evacuation order that affected people in the cities of Port Neches, Groves, Nederland, and a portion of Port Arthur. The explosion also led to reduced usage of the Sabine-Neches Waterway, the nation's third largest waterway by cargo volume and a major economic driver in the U.S. The incident caused $450 million in on-site property damage and $153 million in off-site property damage to nearby homes and businesses. Media reports indicated that the blast was felt up to 30 miles away [1]. On June 1, 2022, TPC filed for Chapter 11 bankruptcy.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) investigated the incident and found that a dangerous substance known as popcorn polymer, which is prone to forming in processes with high-purity butadiene, accumulated in a temporary dead leg[a] that was created when a process pump was taken out of service for maintenance. Popcorn polymer is dangerous because once it forms, its continued growth and expansion can generate high pressures that may ultimately rupture equipment. The pump that was taken out of service remained offline for a period of 114 days. During this extensive offline period, popcorn polymer developed and exponentially expanded in the dead leg piping section until the internal piping pressure increased to the point that the piping ruptured, releasing butadiene from the process unit.

TPC PNO's fire team, along with the Port Neches Fire Department and the Sabine-Neches Chiefs Association, responded to the incident. Federal agencies that investigated the incident included the Occupational Safety and Health Administration (OSHA) and the CSB.

SAFETY ISSUES

The CSB's investigation identified the safety issues below:

- **Dead Leg Identification and Control.** TPC PNO had a procedure in place to minimize popcorn polymer hazards associated with dead legs. However, the CSB found no evidence that the inability to implement some of the procedure's requirements when the pump was taken out of service triggered any type of safety evaluation of the temporary dead leg associated with the offline pump. TPC PNO did not have an effective safety management system in place to identify when the safety-critical procedure could not be conducted as intended, or to identify the associated safety implications when the procedure could not be implemented. In addition, TPC PNO's dead leg procedure did not identify all potential temporary dead legs within the unit, which likely contributed to personnel not taking action to prevent

[a] A dead leg is a piping segment that is open to the process but does not have flow through it (for example, due to a closed valve in the segment, preventing flow) [47].

popcorn polymer formation and accumulation in the dead leg created by the out-of-service pump. Further, the American Chemistry Council's (ACC's) *Butadiene Product Stewardship Guidance Manual* does not contain information on the potential consequences of dead legs or how companies should identify, control, or prevent them. (Section 4.1)

- **Process Hazard Analysis (PHA) Action Item Implementation.** TPC PNO's 2016 PHA team recommended that TPC PNO ensure that piping associated with out-of-service equipment in high-purity butadiene service be flushed monthly. The implementation of the 2016 PHA recommendation could have helped prevent the incident by requiring personnel to flush the piping associated with the out-of-service pump, which could have prevented the buildup of popcorn polymer within the dead leg. The 2016 PHA recommendation was never implemented, and the dead leg conditions leading to the incident were not mitigated. (Section 4.2)

- **Control and Prevention of Popcorn Polymer.** TPC PNO was conducting operational trials leading up to the incident. After these trials began, an increase in popcorn polymer formation occurred throughout the butadiene unit. The CSB determined that TPC PNO did not have sufficient internal policies to lead employees to shut down and clean the butadiene unit after it experienced exceedingly high levels of hazardous popcorn polymer. The CSB also determined that additional guidance in ACC's *Butadiene Product Stewardship Guidance Manual* providing mitigation strategies that owner/operators should follow when popcorn polymer is identified could help prevent future popcorn polymer-induced loss of containment events. (Section 4.3)

- **Remotely Operated Emergency Isolation Valves.** The TPC PNO butadiene process was not equipped with remotely operated emergency isolation valves (ROEIVs)[a] designed to mitigate process releases remotely from a safe location. The TPC PNO incident demonstrates what can happen when portions of a chemical processing facility cannot be remotely isolated during a release and fire. Severe explosions caused a process tower to propel through the air and land within the facility, other process towers to fall within the unit, extensive facility damage, and fires that burned for more than a month within the facility. Manual and locally controlled emergency block valves (EBVs) are unreliable in this type of catastrophic incident; since the valves cannot be safely accessed, the equipment cannot be isolated. Had the TPC PNO butadiene process been equipped with ROEIVs, it is possible that (1) the feed to the column upstream of the release could have been stopped shortly after the release began, minimizing the size of the initial vapor cloud, and (2) any secondary releases caused by the initial explosion could have been mitigated early in the incident. Stopping the release(s) by using ROEIVs could have prevented some of the subsequent explosions and fires, thereby minimizing the damage caused by the incident. (Section 4.4)

Probable Cause

The CSB determined that the probable cause of the incident was TPC PNO's failure to identify that an out-of-service pump within the butadiene unit caused a hazardous temporary dead leg, which allowed popcorn polymer to develop and exponentially expand in the piping section until the piping ruptured. The pipe rupture caused

[a] This report references remotely operated emergency isolation valves (ROEIVs) and remotely operated EBVs. Because both TPC and the American Petroleum Institute (API) use the term "EBV," the CSB retained the term in this report to maintain consistency with their terminology. However, for the purposes of this report, an ROEIV is equivalent to a remotely operated EBV.

highly flammable butadiene to release into the unit, which ignited and caused an explosion, followed by multiple subsequent explosions. Contributing to the incident was TPC PNO's inadequate prevention and control of popcorn polymer within its process units and its inadequate implementation of the 2016 PHA action item. Contributing to the severity of the incident was the lack of ROEIVs within the butadiene process unit.

RECOMMENDATIONS

To TPC Group

For all TPC PNO terminal operations in high-purity butadiene service (e.g., greater than 80 percent butadiene concentration),[a] develop and implement a program to identify and control, or eliminate, dead legs. At a minimum, this program must require:

a) a comprehensive review of equipment configurations in high-purity butadiene service using both Piping and Instrumentation Diagrams (P&IDs) and field evaluations to identify all permanent dead legs. Implement a process to identify changes in operating conditions in high-purity butadiene service that could result in the formation of temporary or new permanent dead legs, such as when primary or spare pumps are temporarily or permanently out of service. Ensure this review is conducted at least every five years;

b) evaluation and implementation of design strategies, where practical, to prevent dead legs in areas susceptible to popcorn polymer formation;

c) mitigation, control, or prevention of hazardous popcorn polymer buildup in all identified dead legs in high-purity butadiene service, such as through increased monitoring, flushing of equipment, use of inhibitor(s), or planning maintenance activities to minimize the amount of time that a temporary dead leg is present; and

d) periodic continual auditing (at a minimum annually) by TPC PNO management to ensure that the process is being implemented.

For all TPC PNO terminal operations, passivate all storage vessels, fixed equipment, and associated piping systems in high-purity butadiene service consistent with industry good practice guidance.

At the TPC PNO facility, incorporate the recording of any paper-based process performance information into TPC PNO's existing electronic records management system so that the information can be reliably retained, retrieved, and analyzed in the event of a catastrophic incident. At a minimum, those records shall include Dead Leg Inspection check sheets, Spare Pump Rotation check sheets, and handwritten logs documenting the performance of all critical process instrumentation (e.g., the oxygen analyzer).

[a] The ACC states popcorn polymer is most likely to form in equipment containing butadiene concentrations greater than 80 percent purity [7, p. 32].

To American Chemistry Council

Revise the *Butadiene Product Stewardship Guidance Manual* to include guidance on identifying and controlling or eliminating dead legs in high-purity butadiene service. Specifically, provide guidance on the potential for dead legs to be formed when equipment, such as primary or spare pumps, is out of service. In the Manual, also provide guidance on method(s) to identify dead legs that could be formed when equipment, such as primary or spare pumps, is temporarily or permanently out of service. Recommend actions to mitigate, control, and prevent hazardous popcorn polymer buildup in these in-process or temporary dead legs, such as through monitoring, use of inhibitor(s), or conducting maintenance activities to minimize the presence of dead legs.

Revise the *Butadiene Product Stewardship Guidance Manual* to provide guidance on a methodology to help identify what should be considered excessive or dangerous amounts of popcorn polymer in a unit. Provide mitigation strategies that describe the actions that owner/operators should take during those polymer excursions to control or eliminate the popcorn polymer to reduce the likelihood of popcorn polymer-induced process loss of containment.

1 BACKGROUND

1.1 TPC GROUP

Based in Houston, Texas, TPC Group (TPC),[a] formerly Texas Petrochemicals, is a petrochemicals manufacturing company with facilities located in Lake Charles, Louisiana;[b] Houston, Texas; and Port Neches, Texas [2]. TPC describes itself as a "leading producer of value-added products derived from petrochemical raw materials [2]." At the time of the incident, all of its manufacturing facilities were certified by the American Chemistry Council (ACC) under the Responsible Care Management System program [3].[c]

1.2 PORT NECHES OPERATIONS FACILITY

The incident occurred in the South Processing Unit of the TPC Port Neches Operations (PNO) facility in Port Neches, Texas (**Figure 1**). This unit primarily manufactured 1,3-butadiene[d] (hereafter referred to as "butadiene").[e] Butadiene, which was released during the incident, is mainly used as a building block in the production of a wide range of polymers and copolymers, with synthetic rubber as the predominant end-use product [4, p. 4]. At the time of the incident, TPC PNO employed more than 175 personnel and 50 contractors.

Because butadiene was manufactured and stored at the TPC PNO facility as a flammable liquid with a flashpoint below 100 °F,[f] and because the TPC PNO facility maintained an on-site quantity of butadiene greater than 10,000 pounds, the TPC PNO facility was covered by the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) standard, 29 C.F.R. § 1910.119 [5]. Additionally, due to exceeding

[a] In 2012, TPC was acquired by two private equity firms, First Reserve and SK Capital [49].

[b] The Lake Charles facility is a terminal with no manufacturing capability [44].

[c] TPC is a manufacturer member company of the American Chemistry Council (ACC) [50]. The ACC requires all member companies to participate in its Responsible Care program as a condition of membership [50].

[d] TPC also manufactures butadiene at its Houston Operations facility [45].

[e] A separate unit within the facility also produced raffinate-1, which is a mixed C4 byproduct of butadiene and is a chemical building block used in the manufacture of methyl tertiary butyl ether (MTBE) and diisobutylene (DIB) [3].

[f] The flashpoint of butadiene is –105 °F [48, p. 239].

the 10,000-pound butadiene threshold quantity, the TPC PNO facility was also covered by the Environmental Protection Agency's (EPA's) Risk Management Plan (RMP) Rule, found at 40 C.F.R. Part 68 [6].

Figure 1. Aerial photo of the TPC PNO facility. South Unit is circled. (Credit: TPC, annotated by CSB)

1.3 THE TPC PNO BUTADIENE PROCESS

The TPC PNO butadiene production process is depicted in **Figure 2** below. Crude butadiene ranging from 35–75% purity was fed to the process, then underwent numerous production phases to increase its purity. After the final process phase, called final fractionation, the finished butadiene product specification was 99.8% purity. The November 27, 2019, incident occurred in the final fractionation phase.

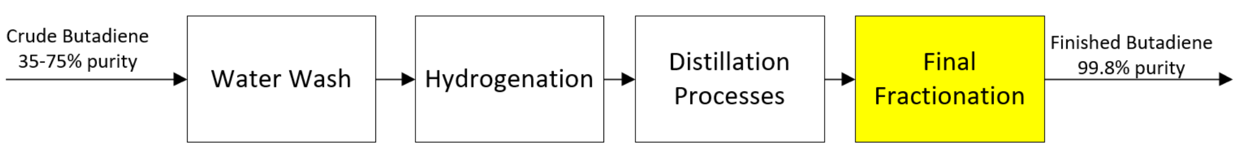

Figure 2. Block flow diagram of the TPC PNO butadiene production process. The November 27, 2019, incident occurred in the final fractionation phase (highlighted in yellow). (Credit: CSB)

Within the final fractionation section of the butadiene production process were Final Fractionator A and Final Fractionator B. TPC PNO design specifications include butadiene feeding Final Fractionator B at 98.16% purity, with the butadiene overhead product from Fractionator A at 99.8% purity. TPC PNO used a Primary Pump and a Spare Pump to transfer liquid hydrocarbons from the bottom of Final Fractionator A into the top of Final Fractionator B (**Figure 3**).

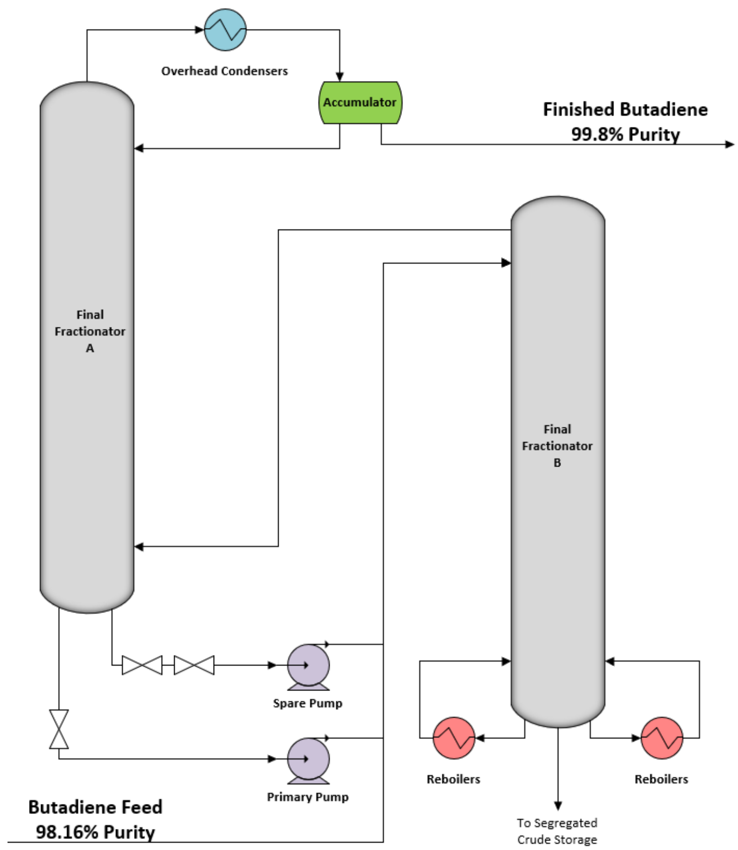

Figure 3. Depiction of Final Fractionators A and B with TPC PNO product specifications. (Credit: CSB)

1.4 Butadiene Health and Environmental Effects

Butadiene is a hazardous chemical due to its flammability, toxicity, and reactivity. With regard to toxicity, high concentrations of butadiene vapor can affect the central nervous system, as evidenced by giddiness, headache, dizziness, and nausea; in extreme cases, unconsciousness, respiratory depression, and death may occur. In confined spaces, high concentrations of butadiene may cause an oxygen-deficient atmosphere, resulting in loss of consciousness and potentially death. Several governmental entities classify butadiene as carcinogenic, with the respective classifications listed in **Table 1** [7, pp. 14-15].

Table 1. Butadiene Carcinogenicity Classifications. (Credit: American Chemistry Council)

Organization	Classification
International Agency for Research on Cancer (IARC)	Group 1 – Carcinogenic to Humans
Environmental Protection Agency (EPA)	Carcinogenic to Humans by Inhalation
National Toxicology Program (NTP)	Known Human Carcinogen
National Institute for Occupational Safety and Health (NIOSH)	Carcinogen, with No Further Categorization
American Conference on Governmental Industrial Hygienists (ACGIH)	Group A2 – Suspected Human Carcinogen

1.5 Popcorn Polymer

Equipment that handles high-purity butadiene (typically > 80% purity) is highly susceptible to the development of a potentially hazardous substance called "popcorn polymer" [4, p. 32].[a] Popcorn polymer can be hazardous because when popcorn polymer accumulates inside equipment, its continued growth and expansion can generate high pressures that may ultimately rupture equipment [4, p. 32]. The physical appearance of popcorn polymer resembles "cauliflower or popcorn [7, p. 32]." Popcorn polymer can also "take the form of glassy, friable crystals; fluffy, needle-like crystals; or hard, clear gel [4, p. 32]." **Figure 4** shows an example of popcorn polymer from an undisclosed facility.[b]

Popcorn polymer formation involves two phases: the initiation phase (seed formation) and the propagation phase to polymer chains (seed growth to polymer chains) [9, p. 830]. **Figure 5** illustrates the popcorn polymer formation process.

During the initiation phase, oxygen (for example, from air, water, or rust) reacts with butadiene to form peroxide radicals. In the presence of a high concentration of butadiene, these butadiene peroxide radicals react with the butadiene to form active popcorn polymer seeds [10, pp. 8-9]. Though the growth mechanism is not completely

Figure 4. Popcorn polymer in a manway from an undisclosed facility (Credit: International Institute of Synthetic Rubber Producers Inc. [8, p. 261])

[a] As stated by the ACC, other conjugated dienes and vinyl aromatics, such as styrene and isoprene, can also produce popcorn polymer [7, p. 32].

[b] The popcorn polymer shown in **Figure 4** is not from a TPC facility.

understood, one commonly accepted explanation states that newly formed popcorn polymer seeds react with butadiene to form highly cross-linked popcorn polymer chains [11]. These polymer chains eventually rupture due to internal strain, forming more active popcorn seeds, thereby increasing the total volume of popcorn polymer as the process repeats [10, pp. 8-9]. The resulting increase in popcorn polymer volume can produce excessive pressures sufficient to rupture piping and equipment [12]. **Appendix D** provides examples of historical incidents caused by popcorn polymer, all of which occurred after popcorn polymer formed in what is known as a “dead leg”: a portion of piping or equipment in which the process fluid does not continuously flow.

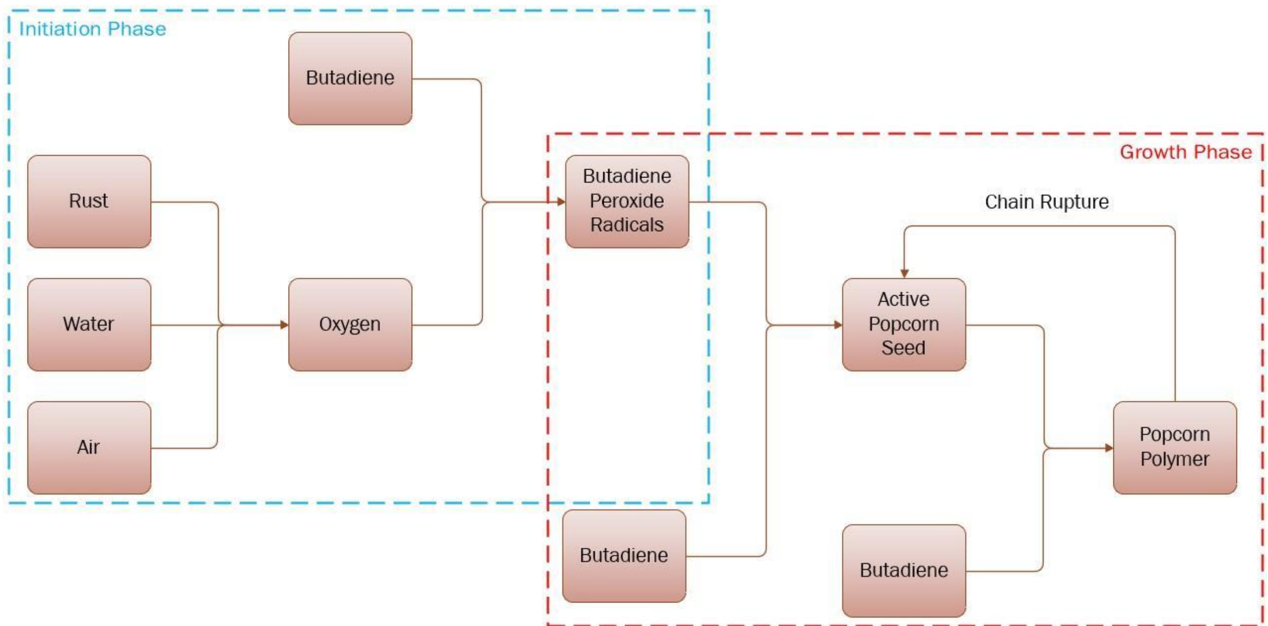

Figure 5. Mechanism for popcorn polymer formation. (Credit: CSB, derived from [10, p. 8])

Popcorn polymer growth rate also increases exponentially over time. **Figure 6** illustrates how quickly popcorn polymer can grow [10, p. 9].

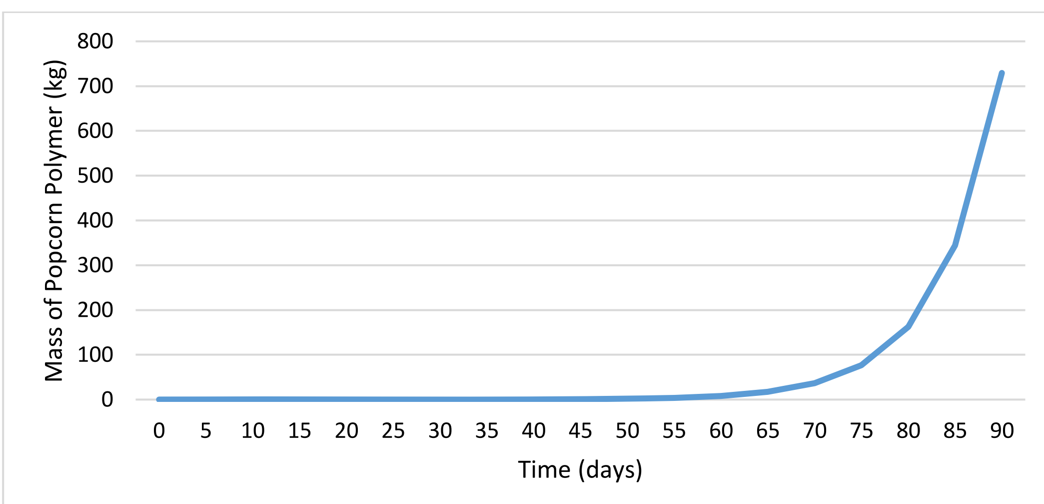

Figure 6. Growth of uninhibited popcorn polymer over time. (Credit: CSB, derived from [10, pp. 8-9])

Certain chemicals called "inhibitors" can be used in butadiene production processes to slow the growth of popcorn polymer. These inhibitors are used to "reduce the growth rate of popcorn polymer to very low levels" [4, p. 33]. Once the inhibitor is no longer present, the popcorn polymer seeds can grow at their previously uninhibited rate [4, p. 33]. TPC PNO had contracts with experts in butadiene process chemistry to help support and provide advice with respect to its butadiene production and storage processes. TPC PNO used three chemical inhibitors: sodium nitrite, tertiary butyl catechol (TBC), and diethyl hydroxylamine (DEHA).

Popcorn polymer is prone to forming in dead legs and other areas with low or lack of flow.[a] According to TPC PNO's Butadiene Knowledge Book:[b]

> Dead leg areas of lines that are in high-purity butadiene service are subject to popcorn polymer formation. Popcorn polymer, when growing, has unlimited expansion qualities and can open valve bonnets, crush tube bundles, expand lines and exchanger shells to the point of metal failure. […] Historically we have found that popcorn polymer forms in lines, valves and vessels where [there is] a lack of flow, combined with high ambient temperature, and butadiene concentrations above 90-95%.

[a] The European Ethylene Producers Committee document titled *Recommendations for Preventing Popcorn in Steam Crackers and Butadiene Plants* states, "The commonest areas for popcorn [polymer] formation are dead legs, or areas of low flow" [26, p. 26].

[b] TPC PNO's Butadiene Knowledge Book is a compilation of information regarding butadiene and how it is manufactured and stored at the PNO facility. The CSB is unaware if any of the content of this document was adopted as part of its butadiene process safety information or Recognized and Generally Accepted Good Engineering Practices (RAGAGEP).

1.6 Butadiene Production in the U.S.

In 2020, the EPA reported that butadiene was domestically manufactured in at least nine locations, all within the coastal regions of the Gulf of Mexico (see **Figure 7**).[a] Since 2011, the U.S. has consistently manufactured between one billion and five billion pounds of butadiene annually [13].

Figure 7. Approximate locations in the U.S. where butadiene is produced. (Credit: EPA; Google Earth)

1.7 Description of Surrounding Area

Figure 8 shows the TPC PNO facility and depicts the area within one, three, and five miles of the facility boundary. Summarized demographic data for the approximately one-mile vicinity of the TPC PNO facility is shown below in **Table 2**. There are over 18,000 people residing in over 7,600 housing units, most of which are single units, within one mile of the TPC PNO facility. Detailed demographic data is included in **Appendix B**.

[a] Information on chemical production is reported to the EPA under the Chemical Data Reporting Rule (CDR). "The CDR rule, under the Toxic Substances Control Act (TSCA), requires manufacturers (including importers) to provide EPA with information on the production and use of chemicals in commerce [13]."

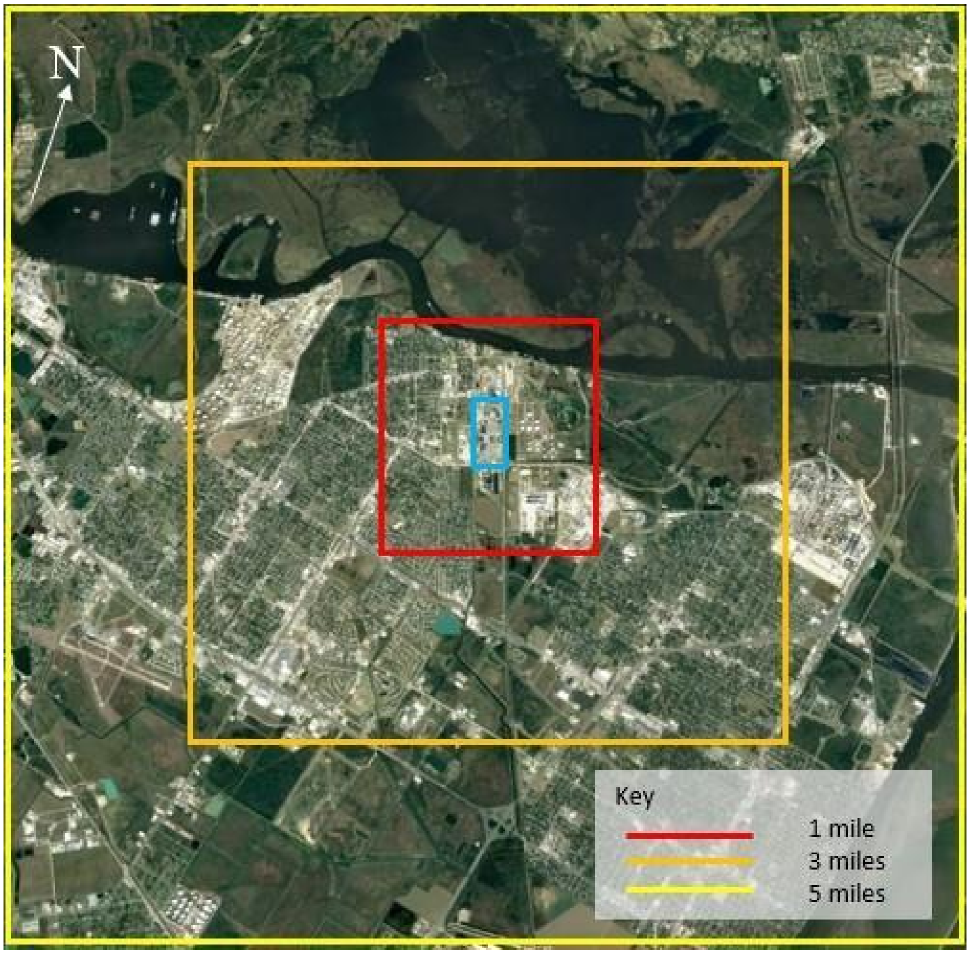

Figure 8. Overhead satellite image of the TPC PNO facility (blue) and the surrounding area (Credit: Google, annotated by CSB)

Table 2. Summarized Demographic Data for Approximately One-Mile Vicinity of TPC PNO Facility (Credit: CSB using data obtained from Census Reporter)

Population	Race and Ethnicity		Per Capita Income	Percent Poverty[a]	Number of Housing Units	Types of Housing Units	
18,377	White	80%	$38,094[b]	9.8%	7,656	Single Unit	85%
	Hispanic	9%				Multi-Unit	12%
	Asian	4%				Mobile Home	3%
	Two+	4%					
	Black	2%					

[a] The "Percent Poverty" figure represents the number of persons below the poverty line in the city of Port Neches, Texas [51].

[b] Census Reporter reports that Port Neches' per capita income was $38,626 [51]. The Census Bureau reports that the overall Per Capita Income for the United States from 2016-2020 was $35,384 [52].

2 Incident Description

2.1 Final Fractionator A/B Primary Pump Failure

Throughout 2019, TPC PNO experienced troubles with popcorn polymer developing in the unit (see Section 4.3 for information on popcorn polymer development at TPC PNO). On August 4, 2019, a worker was performing an operation in the butadiene unit to temporarily run the Final Fractionator A/B Spare Pump[a] (**Figure 3**) as part of a pump rotation procedure[b] regularly performed in the unit. During this pump rotation procedure, the worker shut down the Final Fractionator A/B Primary Pump. When the worker tried to restart the Final Fractionator A/B Primary Pump, the pump did not operate. After employees submitted a pump repair service request, TPC PNO initiated repair work by sending the pump to a third-party repair shop with expertise in refurbishing pumps. The pump remained out of service through the date of the incident—a period of 114 days (see Section 4.1 for additional information on the pump repair request).

During this 114-day period, the process piping between Final Fractionator A and the manual isolation valve upstream of the Primary Pump was a dead leg, as the pump could not initiate flow through the line. The portion of dead leg piping was 16 inches in diameter and approximately 35 feet long (**Figure 9**). During this 114-day period, TPC PNO continued to experience popcorn polymer formation and plugging in the unit (see Section 4.3). The U.S. Chemical Safety and Hazard Investigation Board (CSB) did not find that anyone at the TPC PNO facility realized the potential popcorn polymer and rupture hazard in the dead leg that was created when the Primary Pump became nonoperational.

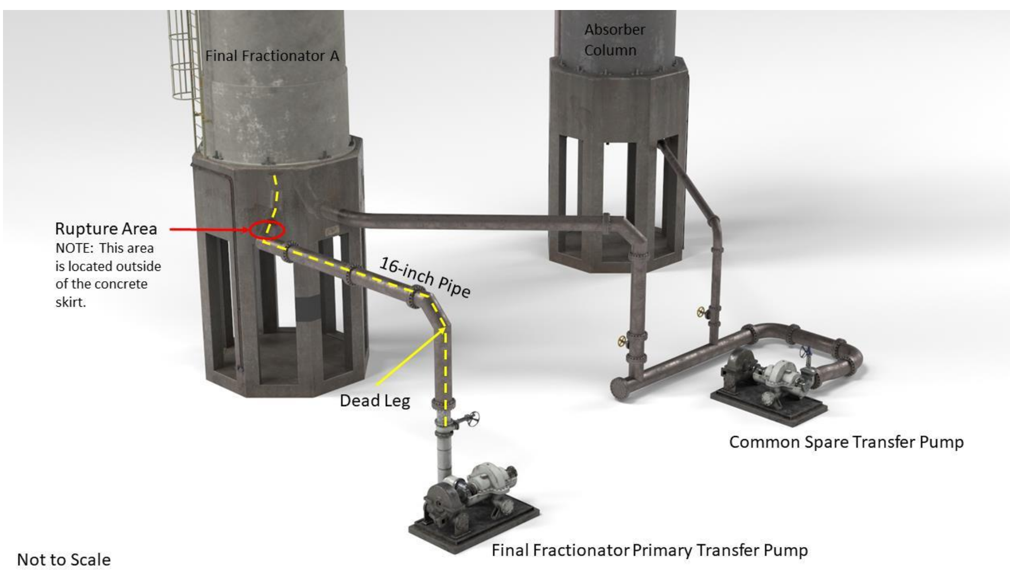

Figure 9. Schematic showing dead leg location when Primary Pump was nonoperational. (Credit: CSB)

[a] TPC PNO used a Primary Pump and a Spare Pump to transfer liquid hydrocarbons from the bottom of Final Fractionator A into the top of Final Fractionator B (see **Figure 3**). The Final Fractionator Spare Pump also served as a common spare transfer pump for an adjacent absorber column as shown in **Figure 9**.

[b] TPC PNO's "Dead Legs in High Purity Butadiene Service" procedure stated that spare pumps were to be run at least twice per month to flush identified dead legs associated with spare pumps. Workers told the CSB that the normal practice was to execute the Spare Pump flushing procedure once per week during the day shift.

2.2 The Incident

During the night shift[a] that began on Tuesday, November 26, 2019, one of the workers on the shift (which consisted of 30 workers) told the CSB the "night was quiet." Evidence indicates that, at 12:54 a.m. on November 27, 2019,[b] the dead leg between the Final Fractionator A and the manual isolation valve upstream of the offline Primary Pump suddenly ruptured.[c] The CSB determined this rupture was likely caused by the buildup and growth of popcorn polymer over the 114-day period the Primary Pump was out of service.

A loss of containment event then occurred as a result of the rupture, causing the liquid level in the Final Fractionator A to drop rapidly from its operating level. The CSB calculated the Final Fractionator A liquid volume at the time of the initial level drop to be approximately 6,000 gallons.[d] Process data indicate that the liquid, which was primarily butadiene, fully emptied from the Final Fractionator A in less than a minute (**Figure 10**). The liquid butadiene vaporized upon release[e] and formed a flammable vapor cloud.

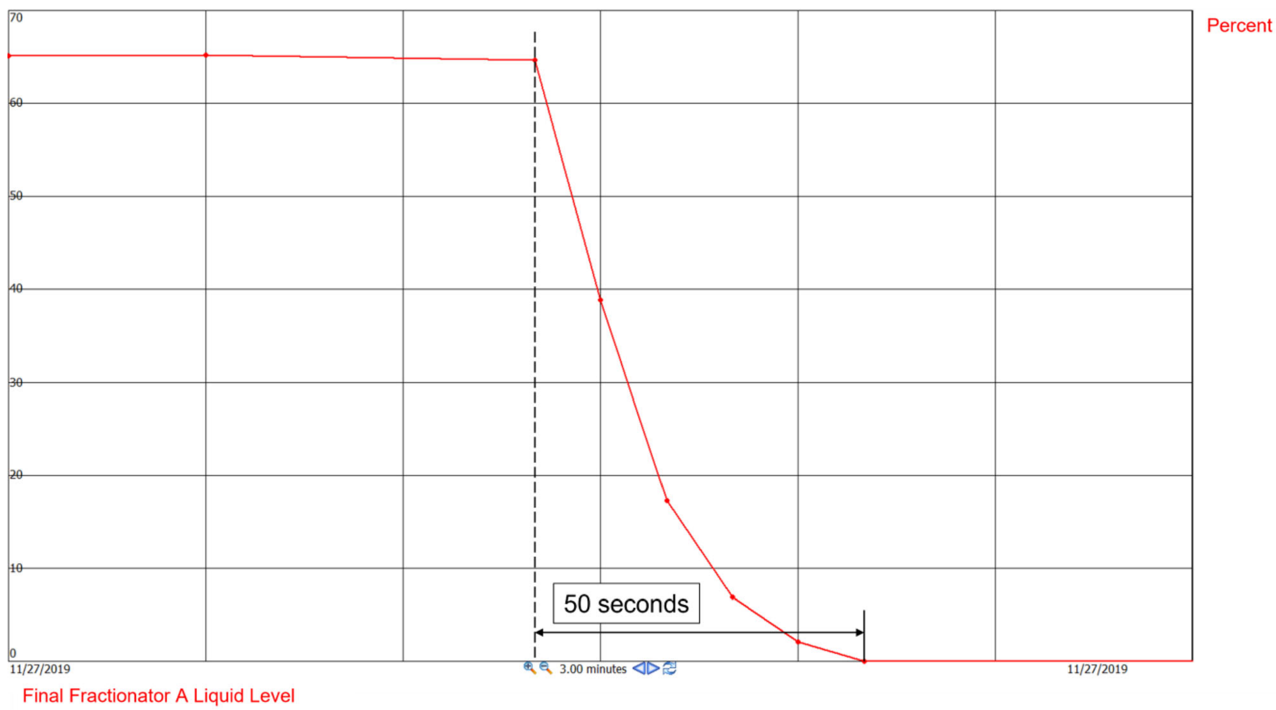

Figure 10. Process data trend showing the liquid level (in percent) in the Final Fractionator A at the time of the incident. (Credit: CSB)

[a] TPC PNO operated using two twelve-hour shifts.

[b] The time was obtained from correlating external time-stamped video to TPC PNO process data, using the initial multiple alarms as the time of the explosion. Since the TPC PNO timestamp from its process control system was found to be four minutes and thirteen seconds ahead of the time stamp from the video, the CSB subtracted four minutes and thirteen seconds from the TPC PNO time stamp.

[c] After the incident, OSHA inspected the facility. As a result of the inspection, OSHA issued Willful citations relating to dead leg procedures and mechanical integrity deficiencies, which were contested by TPC and remain under appeal. Details of relevant OSHA citations are in **Appendix C.**

[d] The volume was calculated based on the Final Fractionator A dimensions and liquid level of six feet. The weight in pounds was calculated using an assumed density of 38.75 pounds per cubic feet liquid butadiene.

[e] The normal boiling point of butadiene is 24.1 °F [4, p. 7].

Three workers were present in the unit at the time of rupture, two of which were facing directly toward the Final Fractionator A. Both of these workers told the CSB after the incident that they witnessed a pipe rupture. One of the two workers identified the release point to be on the suction piping between the Final Fractionator A and the Primary Pump. The third worker, who turned toward the sound of the rupture after it occurred, also believed the release point to be the suction piping between the Final Fractionator A and the Primary Pump. The workers' observations were consistent with the unit's recorded distributed control system (DCS) data shown in **Figure 10**. Immediately following the loss of containment, the three workers quickly departed the unit. **Figure 11** shows their locations during the event.

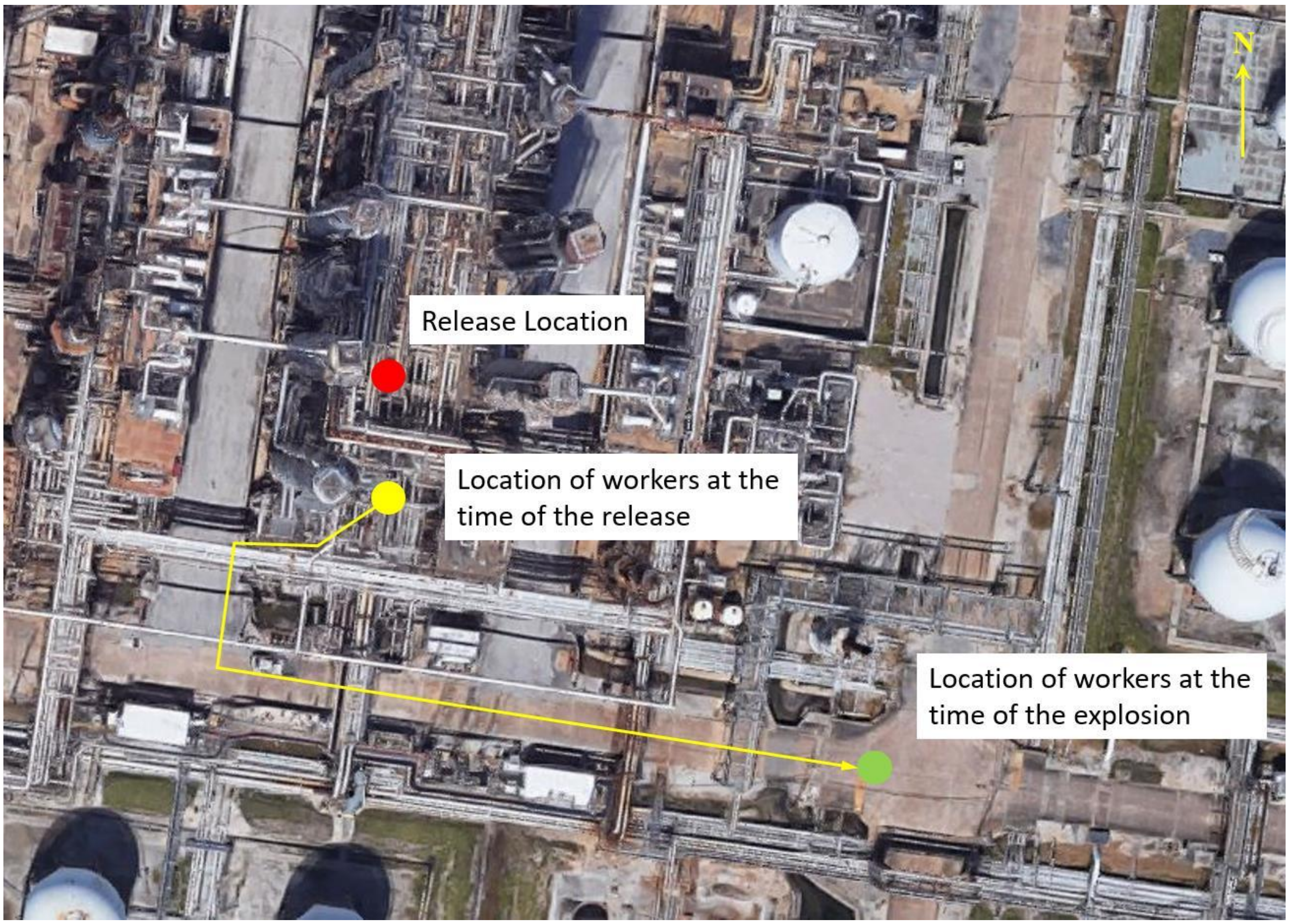

Figure 11. Worker locations during the incident. (Source: Google Maps; CSB)

At 12:56 a.m., the butadiene vapor cloud ignited,[a] causing an explosion that heavily damaged the site. Thermal imagery (**Figure 12**)[b] provided by TPC shows multiple fires within the TPC PNO facility that ignited following the explosion.

[a] Due to the post-incident condition of the site and the extensive number of possible ignition sources, the CSB was unable to determine the ignition source for this incident.

[b] Thermal imaging devices measure infrared (thermal) radiation and translate the data to images. In this instance, the colors progress from black (least amount of radiation) to white (greatest amount of radiation).

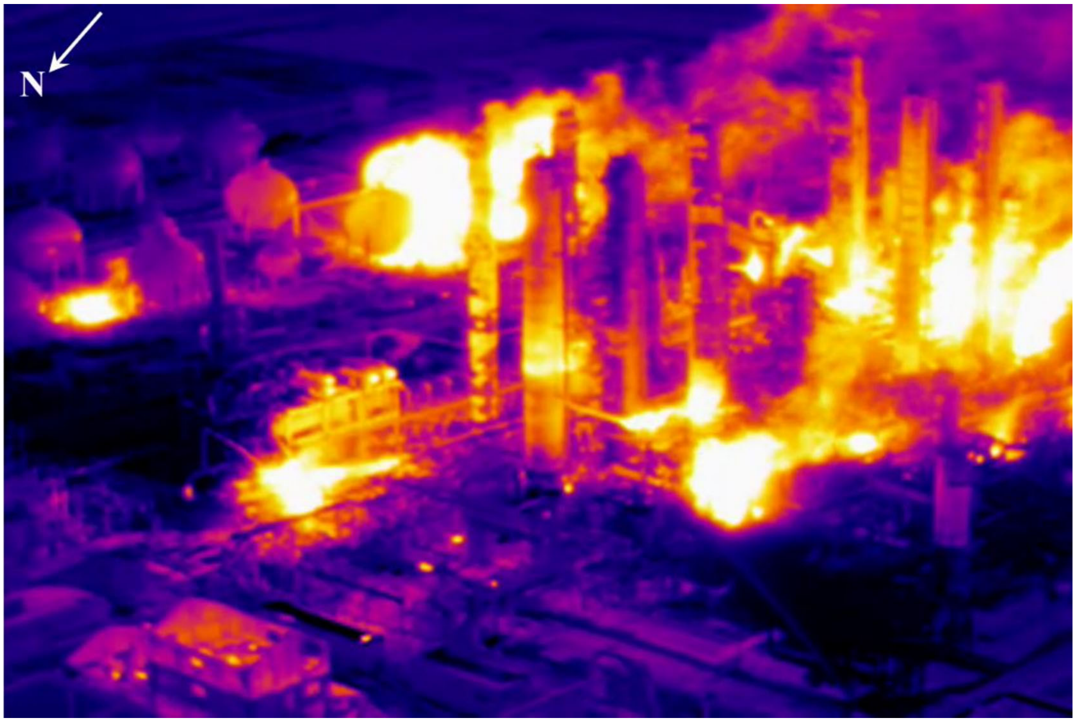

Figure 12. Thermal drone imagery of the TPC PNO facility South Unit taken the morning after the initial explosion. (Credit: TPC)

At least two additional explosions occurred following the initial blast. At 2:40 a.m., a cell phone recording captured one of the explosions (**Figure 13**). That afternoon, at 1:48 p.m., another explosion occurred, which caused one of the facility's towers to propel into the air (**Figure 14**). The tower landed within the confines of the TPC PNO facility.

The explosions and fires heavily damaged piping and equipment in the unit, much of which could not be remotely isolated. Most of the process equipment, including the Final Fractionator A, was not equipped with remotely operated emergency isolation valves (ROEIVs).

Figure 13. Explosion at 2:40 a.m. on November 27, 2019 captured by cell phone video. (Credit: TPC)

Figure 14. Explosion at 1:48 p.m. on November 27, 2019 which propelled one of the unit towers into the air. (Credit: Huntsman Corporation)

Following the incident, workers tried to manually isolate areas of the facility. After the initial fires were contained, smaller contained fires burned for more than a month while isolation efforts were underway. Over a month after the release began, at 10:09 a.m. on January 4, 2020, the TPC PNO Incident Command confirmed that all fires were out.

2.3 Incident Consequences

2.3.1 Incident Scene

The incident caused significant damage to piping and equipment (**Figure 15**). At least four columns fell as a result of the explosions and fires: the Final Fractionator A, an extractive distillation absorber, an out-of-service water wash tower, and the depentanizer (**Figure 16**).

Figure 15. Damaged piping and equipment in the South Unit. (Credit: TPC)

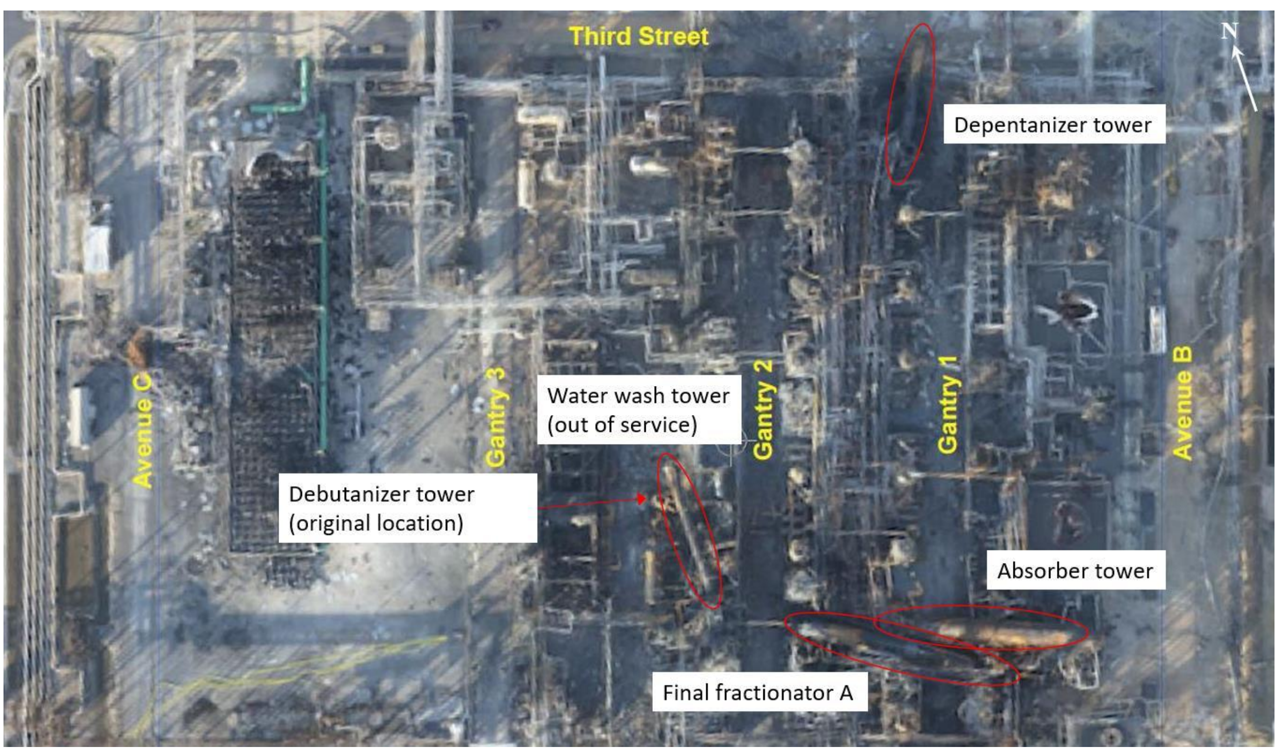

Figure 16. Overhead photograph of TPC PNO South Unit showing the locations of the fallen towers. (Credit: TPC)

2.3.2 Injuries

The initial explosion resulted in non-life-threatening injuries to two TPC PNO employees and a security contractor. All three individuals were treated and released. In addition, according to media reports, Jefferson County officials stated that five residents reported minor injuries [1].

2.3.3 Community Impact

The blast damaged nearby homes and buildings, and media reports indicate that the blast was felt up to 30 miles away [1].

On November 27, 2019, "because of the extreme hazard potential that exist[ed] as a result of the explosion at the TPC PNO facility," Jefferson County officials declared the county to be in a state of disaster [14]. At 3:28 p.m. on November 27, 2019, county officials issued a mandatory evacuation order for areas within a four-mile radius of the TPC PNO facility that affected people in the cities of Port Neches, Groves, Nederland, and a portion of Port Arthur [15]. In addition, on November 27, 2019, county officials issued a mandatory curfew order for a four-mile radius around the TPC PNO facility between 10:00 p.m. and 6:00 a.m. [16]. Jefferson County officials lifted the evacuation and curfew orders at 10:00 a.m. on November 29, 2019 [14].

When the evacuation and curfew orders were lifted, several "gas-pressured" fires at the TPC PNO facility were still burning but were "contained," and county officials cautioned the public that equipment that exploded "could have blown asbestos debris over the neighborhoods and into some yards" [17]. A TPC official cautioned residents to treat any foreign debris on their property as "potentially contaminated debris" and warned that they should not touch it [17]. The official encouraged residents to contact TPC about the debris and made them aware of the TPC-established process by which TPC would "test it, remove it, and dispose of it properly" [17].

Port Neches schools were also impacted. Although Port Neches schools were closed for Thanksgiving break on November 27, 2019, schools did not reopen as scheduled on December 2, 2019, because school officials needed additional time to clean debris, complete structural inspections, and repair school buildings [18] [19]. The Port Neches schools ultimately reopened on December 9, 2019.

In addition, the explosion led to reduced usage of a portion of the Sabine-Neches Waterway, the nation's third largest waterway by cargo volume and a major economic driver in the U.S. [20]. The U.S. Coast Guard (USCG) Marine Safety Unit (MSU) Port Arthur, Texas, issued a Marine Safety Information Bulletin on November 27, 2019, at 9:00 a.m., establishing a safety zone on the Neches River between Light 20 and Light 29 (see **Figure 17**). The bulletin stated that no persons or vessels may enter, transit through, or remain in the safety zone without the permission of the Captain of the Port. USCG MSU Port Arthur issued an updated bulletin on November 29, 2019, at 11:00 a.m., where the Captain of the Port began allowing vessels to transit through the safety zone without the need to obtain permission.

At 6:08 p.m. on Wednesday, December 4, 2019, the Port Neches Fire Chief issued a shelter-in-place for the city of Port Neches "out of an abundance of caution" [21]. At 10:00 p.m. that evening, the Jefferson County Judge issued a voluntary evacuation order for the city of Port Neches. On the early afternoon of Thursday, December 5, 2019, the Jefferson County Office of Emergency Management lifted the shelter-in-place and evacuation orders.

Figure 17. U.S. Coast Guard-established safety zone following the incident. (Source: Google Maps; CSB)

2.3.4 TPC PNO Facility Impact

As a result of the incident, the butadiene unit at the TPC PNO facility was completely destroyed, forcing the facility to cease butadiene production operations indefinitely. As of the date of this report, the butadiene production operations remain shut down. Because of the incident, TPC PNO decided to transition to a "terminal and services" operation while it evaluated and planned to rebuild the butadiene unit [22]. The incident caused $450 million in on-site property damage[a] and $153 million in off-site property damage. On June 1, 2022, TPC filed for Chapter 11 bankruptcy.

[a] It is worth noting that in April 2016, BakerRisk performed an insurance risk assessment, which included an estimate of the worst-case maximum loss scenario for the PNO facility. The worst-case scenario determined by BakerRisk was a six-inch release of butadiene mixture from the Final Fractionator "resulting in a [vapor cloud explosion] event."

3 Post-Incident Metallurgical Testing

The dead leg piping between Final Fractionator A and the manual isolation valve upstream of the Primary Pump was recovered after the incident. As shown in **Figure 18**, a rupture is visible within the piping segment. A CSB-commissioned metallurgical examination of the rupture concluded that the longitudinal rupture was consistent with internal pressure that exceeded the rupture strength of the pipe.

Figure 18. Photos of the recovered Final Fractionator A/B Primary Pump suction piping. (Credit: CSB)

4 SAFETY ISSUES

The following sections discuss the safety issues contributing to the incident, which include:

- Dead Leg Identification and Control (Section 4.1)
- PHA Action Item Implementation (Section 4.2)
- Control and Prevention of Popcorn Polymer (Section 4.3)
- Remotely Operated Emergency Isolation Valves (Section 4.4)

The graphical causal analysis (AcciMap) is in **Appendix A**.

4.1 DEAD LEG IDENTIFICATION AND CONTROL

4.1.1 FACTUAL INFORMATION

4.1.1.1 TPC PNO Procedure: Dead Legs in High Purity Butadiene Service

The TPC PNO facility had an operating procedure called "Dead Legs in High-Purity Butadiene Service," which had the purpose "to specify procedures for dealing with dead legs in high-purity butadiene service so as to minimize the hazards due to the formation of popcorn polymer." The procedure specifically identified "Spare Pump Dead Legs" within the unit and required that "spare pumps are to be ran at least twice a month as specified in the standing orders or as directed by supervision. Documentation of running these pumps must be made on the Spare Pump Rotation check sheet[a] or Intelatrac." The procedure also specifically mentioned the Final Fractionator A/B Spare Pump, stating to "[r]un [Final Fractionator A/B Spare Pump]… as part of the regular spare pump rotation." However, the procedure did not identify the dead leg that would be formed when the Final Fractionator A/B Primary Pump was offline and as such did not discuss any specific dead leg mitigation requirements for situations in which the Final Fractionator A/B Primary Pump was offline (**Figure 19**).

[a] TPC PNO also used Dead Leg Inspection check sheets for identified dead legs other than those associated with spare pumps. According to TPC PNO, any hard copy Spare Pump Rotation and Dead Leg Inspection check sheets were most likely maintained in a building that was destroyed in the incident.

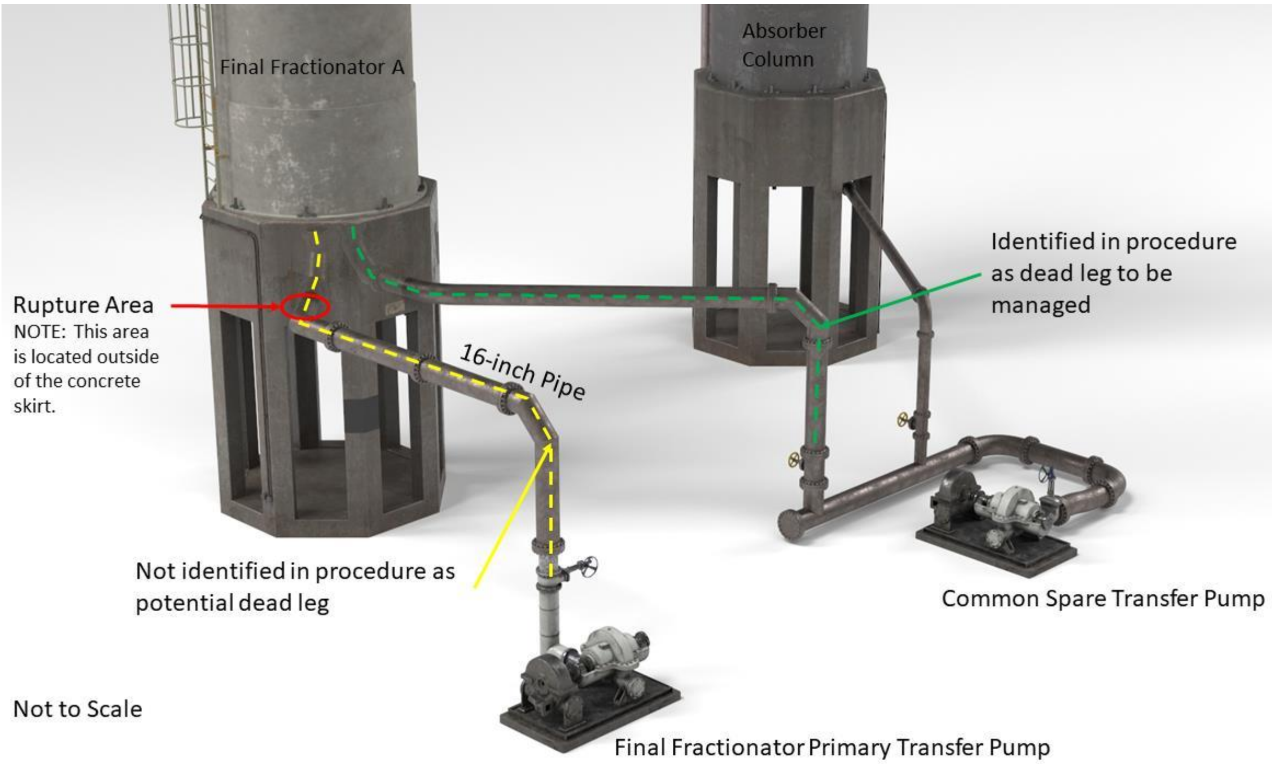

Figure 19. Primary Pump dead leg not identified in TPC PNO procedure. (Credit: CSB)

4.1.1.2 Primary Pump Maintenance Priority

TPC PNO classified equipment service request priority as "Emergency," "Urgent," or "Routine," as defined in **Figure 20** below.

PRIORITY: Service Request & Work Order

❖ *Prioritization of Work*

Value	Description	Definition
E	Emergency	High likelihood of immediate safety, environmental, economical, or production impacts. <u>Actions to be taken</u> [redacted]
1	Urgent	High likelihood of impacts to safety, environmental, economic, or production if not completed within 7 days. <u>Actions to be taken</u> [redacted]
2	Routine	All other work that is not "E" or "1" priority. Routine, Preventive, and Predictive work falls under this category <u>Actions to be taken</u> [redacted]

Figure 20. TPC PNO service request and work order priority definitions. (Credit: TPC)

The CSB found that although TPC PNO originally established the maintenance priority for the out-of-service Primary Pump as "urgent," on August 5, 2019, TPC PNO changed the priority of the pump repair to "routine." TPC PNO indicated to CSB investigators that the Primary Pump repair was not classified as "emergency" or "urgent" due to the existence of the Spare Pump. One TPC PNO employee stated that the repair urgency was not elevated because TPC PNO did not "have the…parts to repair it." The employee also stated the following about the operation of the spare pump while the primary pump was out of service: "If you lost the common spare [i.e., the Final Fractionator A/B Spare Pump, which was also a spare for an adjacent absorber column], then the whole unit's down. Then your production's down. Then you know, every…everything is down." The timeline of the Final Fractionator A/B Primary Pump maintenance activities is depicted below in **Figure 21**.

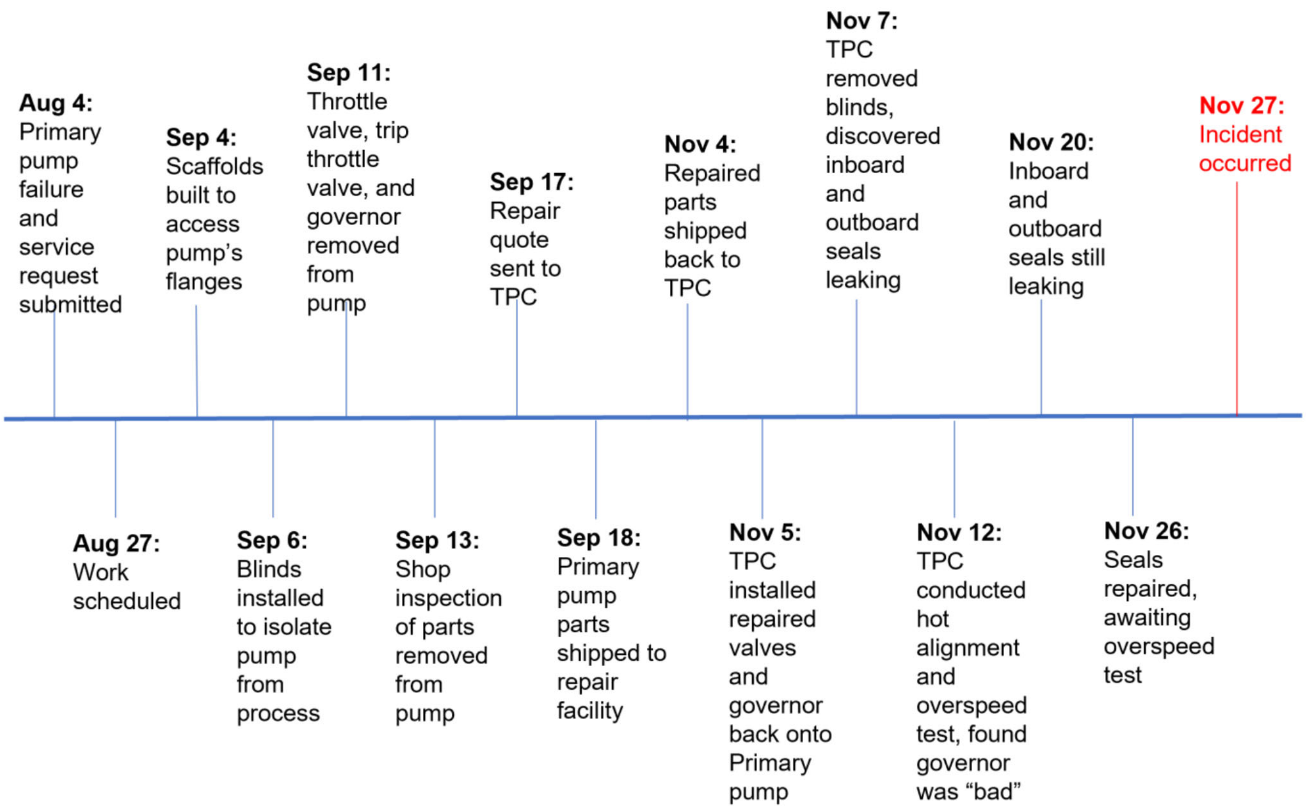

Figure 21. Primary Pump repair timeline. (Credit: CSB)

4.1.2 Analysis

4.1.2.1 Gaps in TPC PNO's Safety Management System

The CSB concludes that a significant temporary dead leg (~35 feet of 16-inch diameter pipe),[a] was created in piping containing over 98% high-purity butadiene when the Final Fractionator A/B Primary Pump became inoperable. The dead leg existed for at least 114 days, allowing dangerous levels of popcorn polymer to form and grow. While TPC PNO had a procedure in place to minimize the popcorn polymer hazards associated with dead legs, the procedure, and TPC PNO's associated management system, did not prevent the incident. For instance, with the Primary Pump nonoperational and the Spare Pump in continuous operation, TPC PNO

[a] Additional information on prior CSB recommendations concerning dead legs can be found in **Appendix F**. Also, as mentioned in **Appendix F**, the American Petroleum Institute (API) Recommended Practice (RP) 2001, *Fire Protection in Refineries*, provides guidance on how companies can address dead legs in their facilities.

personnel were unable to implement the procedure requirements that "spare pumps are to be ran at least twice a month" and "[d]ocumentation of running these pumps must be made on the spare pump rotation check sheet or Intelatrac," as the pump was *already running*. The CSB found no evidence that the inability to conduct the normal Spare Pump operation triggered any type of TPC PNO safety evaluation of the temporary dead leg associated with the Primary Pump. The CSB concludes that TPC PNO did not have an effective safety management system in place to identify when the safety-critical "Dead Legs in High-Purity Butadiene Service" procedure could not be conducted as intended, or to identify the associated safety implications when the procedure could not be implemented.

In addition, the CSB concludes that TPC PNO's dead leg procedure did not identify all potential dead legs within the unit, which may have contributed to personnel not taking action to prevent popcorn polymer formation and accumulation in the dead leg created by the nonoperational Primary Pump. Had the dead leg procedure specifically identified the potential for a hazardous temporary dead leg formation when the Primary Pump was nonoperational, TPC PNO personnel may have taken action to mitigate the hazard, for example by prioritizing the pump repair, purging the piping, or adding popcorn polymer inhibitor to the dead leg. Instead, TPC PNO appeared to consider the offline pump as primarily a threat to maintaining unit operation and not a threat to process safety.

While TPC PNO has suspended process operations indefinitely and plans to conduct business solely as a terminal, the facility will still be handling butadiene and may be at risk of popcorn polymer formation within equipment. The CSB issues a recommendation to TPC PNO to develop and implement a process to identify and control, or eliminate, dead legs in high-purity butadiene service, which must include requirements for identifying potential dead legs, implementing preventive design strategies, preventing popcorn polymer buildup in any identified dead legs, and effective management oversight.

4.1.2.2 Gaps in Industry Guidance: ACC's Butadiene Product Stewardship Guidance Manual

The ACC is a trade organization in the United States that represents more than 190 chemical companies [23]. In 1994, the ACC formed a panel specializing in olefins ("Olefins Panel") to "provide health and safety information to customers and government agencies and to promote scientifically sound government regulatory action for olefins" [24]. The ACC Olefins Panel is one of more than 100 chemical-specific groups represented by the ACC, all of which are focused on issues relevant to their manufacturers and users [25].

KEY LESSON

Companies should establish a process to identify, control, or eliminate dead legs in operations susceptible to popcorn polymer formation. This process must include identifying potential temporary or in-process dead legs, such as those that could be formed when equipment (e.g., primary or spare pumps) is out of service. The process should also include a method to flag equipment that when offline could create temporary or in-process dead legs and establish a method to prevent hazardous popcorn polymer buildup in these dead legs, such as through flushing piping, prioritizing maintenance activities to bring the equipment back online quickly, or the additional use of inhibitor. Companies must support this process with an effective safety management system that can identify when an operating deviation, such as a prolonged equipment outage, could result in a hazardous condition.

The ACC Olefins Panel has developed a guidance document called the *Butadiene Product Stewardship Guidance Manual* [4]. The Guidance Manual "is intended to provide general information to persons who may handle or store butadiene" [4]. Within the document is a subsection called "Butadiene Popcorn Polymer Formation," which provides a general description of popcorn polymer appearance, formation conditions, and recommendations for prevention and control of butadiene popcorn polymer. One of these recommendations in the guidance document is to "minimiz[e] low points and 'dead' legs in the piping systems" [4, p. 34]. The Manual does not, however, contain information on the potential consequences of dead legs or how companies should identify, control, or prevent dead legs. The CSB concludes that such additional guidance in ACC's *Butadiene Product Stewardship Guidance Manual* on how to effectively identify, control, or prevent dead legs—including dead legs created when equipment is temporarily out of service —could have helped to prevent this incident and could help to prevent future similar incidents. The CSB issues a recommendation to ACC to provide additional such guidance in its *Butadiene Product Stewardship Guidance Manual*.

4.2 PHA Action Item Implementation

4.2.1 Factual Information

The CSB reviewed the two previous Process Hazard Analysis (PHA) revalidations for TPC PNO's butadiene process (performed in 2011 and 2016), which included the final fractionation process. TPC PNO defined an analysis section, or node, that extended from the Final Fractionator A outlet to the Final Fractionator B inlet (see **Figure 22**). This node included both the Primary Pump and the Spare Pump. The PHA teams analyzed "no/low flow" as a potential deviation caused by Primary Pump failure. The consequence identified for this deviation was "possible unit upset causing off-test product resulting in economic impact," and one of the claimed safeguards was the existence of a Spare Pump (see **Figure 23**). Neither PHA team identified the potential consequence of popcorn polymer accumulation, piping failure, and release to atmosphere for the no/low flow deviation for this node.

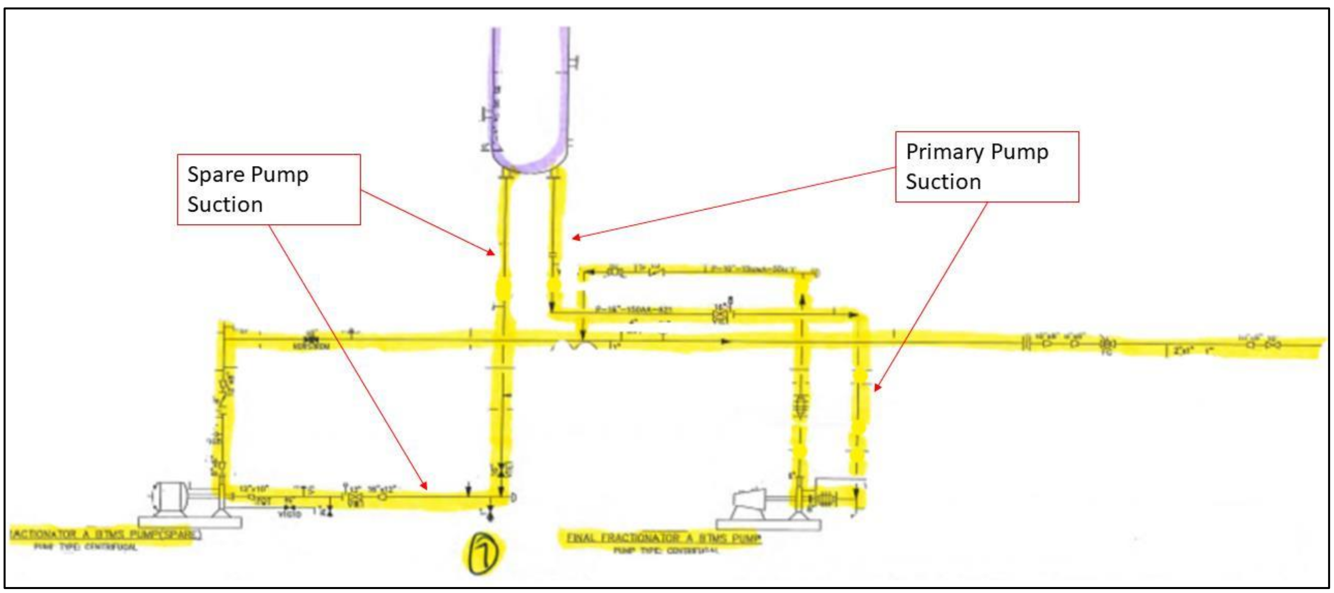

Figure 22. Excerpt from TPC PNO's 2016 PHA revalidation of the butadiene process depicting the node encompassing the Primary Pump and the Spare Pump. (Credit: TPC, annotated by CSB)

Node Name: 7. Final Fractionator A Bottoms Pump
Drawing:
Equipment Number(s):
Design Intent & Process Control Method(s): To transfer bottoms from Final Fractionator A to Final Fractionator B

Deviation	Cause	Consequence	Safeguards	S			E			C			B			Recommendations (PHA)	Comment
				S	L	RR	S	L	RR	S	L	RR	S	L	RR		
1. No/Low Flow	1. Pump failure	1. Possible unit upset causing off-test product resulting in economic impact.	1. High level alarm										1	D	1D		
			2. Low flow alarm														
			3. Low level alarm														
			4. Spare pump available.														

Figure 23. Excerpt from the 2016 PHA worksheet for the node encompassing the Primary Pump and the Spare Pump. (Credit: TPC, annotated by CSB)

Despite not identifying the pipe rupture consequence for the node shown in **Figure 22**, in an earlier node analyzed during the PHA, the PHA team found that no/low flow could be caused by popcorn polymer formation, resulting in "possible line rupture with hydrocarbon release to atmosphere … resulting in potential environmental/economic impact/personnel exposure and/or fire." Based on this analysis, the PHA team made a recommendation that TPC PNO "assure that when equipment in high-purity [butadiene] service is [out of service] for maintenance, the lines are still flushed monthly" (see **Figure 24**). The PHA team felt this needed to be emphasized in the existing "Dead Legs in High Purity Butadiene Service" procedure. As the PHA acknowledges, this procedure was originally implemented in response to a popcorn polymer rupture incident that occurred at the site in 1999.[a] TPC PNO accepted this recommendation and assigned a targeted due date for implementation of December 7, 2016, almost three years before the incident. TPC PNO did not implement this recommendation, however.

3. Assure that when equipment in high purity BD service is OOS for maintenance, the lines are still flushed monthly. The team felt this needed to be emphasized in the existing procedure #106-0.2.30., Dead Legs in High Purity Butadiene Service.	Consequence: 2.1.2.1	SF3	Resolution: Accept, assigned to [redacted] with a targeted due date of 12/7/2016.

Figure 24. Excerpt from the 2016 PHA recommendations. (Credit: TPC, annotated by CSB)

TPC PNO provided the CSB with its "Dead Legs in High Purity Butadiene Service" procedure in effect on the day of the incident, which was last revised in 2012. Since the latest revision to this procedure was *before* the 2016 PHA recommendation, TPC PNO did not yet address the 2016 recommendation at the time of the incident. TPC PNO documentation also indicates that the 2016 PHA recommendation action item was completed on April 4, 2019, but the documentation also indicates it was never validated.

4.2.2 Analysis

The CSB concludes that the 2016 PHA recommendation to assure flushing of piping associated with out-of-service equipment was never implemented, and the dead leg conditions leading to the incident were not mitigated. The CSB concludes that the implementation of the 2016 PHA recommendation could have helped

[a] In 1999, the PNO facility was under the ownership of Huntsman Corporation.

prevent the incident by requiring personnel to flush the piping associated with the out-of-service Primary Pump, which could have prevented the buildup of popcorn polymer within the dead leg.

4.3 Control and Prevention of Popcorn Polymer

4.3.1 Factual Information

4.3.1.1 Industry Guidance on Methods to Prevent/Control Popcorn Polymer

The ACC *Butadiene Product Stewardship Guidance Manual* provides the following guidance regarding the prevention and control of popcorn polymer:

> Inhibitors such as hydroquinone, tertiary butyl catechol (TBC), certain hydroxylamines, and mercaptans, as well as proprietary inhibitors sold by specialty chemical companies, can be used to reduce the growth rate of popcorn polymer to very low levels. Sodium nitrite has been used to passivate[a] metal surfaces as these surfaces can play a role in popcorn polymer formation. The inhibitors are presumed to react with the free radicals being generated. However, these inhibitors do not permanently deactivate polymerization, for when they are removed, the polymer seed will eventually attain its former uninhibited growth rate. […]
>
> Thorough removal of popcorn polymer found in equipment will minimize the potential for seeds to initiate further growth when the equipment is returned to service. Popcorn polymer is most often removed by mechanical means, such as chipping or hydroblasting. If the equipment can be safely and conveniently exposed to high temperatures (e.g., heat exchanger bundles), the polymer may be burned off in an oven.
>
> New equipment or equipment being returned to service are purged to remove oxygen … and can be acid-cleaned and then treated with a hot sodium nitrite solution… to remove rust and “passivate” the metal surface in order to reduce the tendency to form diene polymers. Treating with amines will also passivate the metal surface. Advanced passivation procedures sold by specialty chemical companies call for both metal passivation and popcorn seed deactivation at start up. The popcorn seed passivation is conducted with proprietary inhibitors.
>
> Once back in service, adoption of procedures that exclude oxygen from the process will minimize the potential for initiating the growth of new popcorn polymer seeds or forming butadiene peroxides. For example, periodic, controlled venting of all high points in vapor spaces will minimize oxygen accumulation. Other preventive measures include minimizing “dead” vapor spaces, keeping

[a] The *Encyclopedia and Handbook of Materials, Parts, and Finishes (3rd Edition)* defines passivation as “the changing of a chemically active surface of a metal to a much less reactive state [46].”

> peroxide levels low, and minimizing low points and "dead" legs in the piping systems [4, pp. 33-34].

The sections below detail the TPC PNO butadiene unit events and conditions leading to the incident that could have affected popcorn polymer formation.

4.3.1.2 TPC PNO Equipment Passivation

Passivation is one of the methods described above used to reduce the likelihood of popcorn polymer formation. In *Recommendations for Preventing Popcorn in Steam Crackers and Butadiene Plants,* the European Ethylene Producers Committee (EEPC) recommends passivation of process equipment "after each time it is exposed to air [26, p. 32]." Much of the equipment in the TPC PNO butadiene process was not passivated. One employee assigned to TPC's corporate office communicated to the CSB:

> [O]ne of the best practices in the industry [to control popcorn polymer] is to passivate all your equipment when you use it in a finished butadiene service. The Port Neches facility had not passivated any equipment, I think, in over 25 years. One of the reasons why we use so little inhibitor in [our other facility] and we … don't have the problems [there] that Port Neches does, is we're very aggressive when it comes to passivating our equipment.

TPC PNO told the CSB that the TPC PNO facility began passivating equipment called butadiene finish tanks in May 2019. TPC PNO also completed passivating the overhead condensers for Final Fractionator A in June 2019. However, other equipment within the unit were not yet passivated, including both the Final Fractionator A and B columns and the Final Fractionator A overhead accumulator, which were scheduled to be passivated during the next outage. **Figure 25** shows photos of the Final Fractionator A, and **Figure 26** shows photos of the Final Fractionator A overhead accumulator, both taken during TPC PNO's 2017 turnaround. Both figures show rust formed on the steel equipment walls, which is known to contribute to the formation of popcorn polymer. **Figure 27** shows photos of passivation coupons that were used to determine the efficacy of the passivation operation for the Final Fractionator A overhead condensers. This figure also illustrates how effective passivation can be for neutralizing rust.

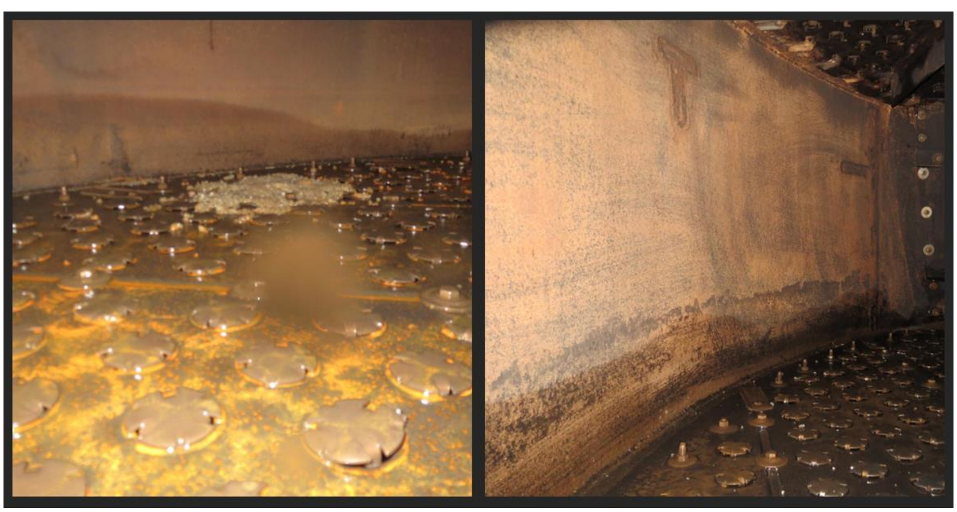

Figure 25. Photos of Final Fractionator A column taken during TPC PNO's 2017 turnaround. (Credit: TPC)

Figure 26. Photos of the Final Fractionator Overhead Accumulator taken during TPC PNO's 2017 turnaround. (Credit: TPC)

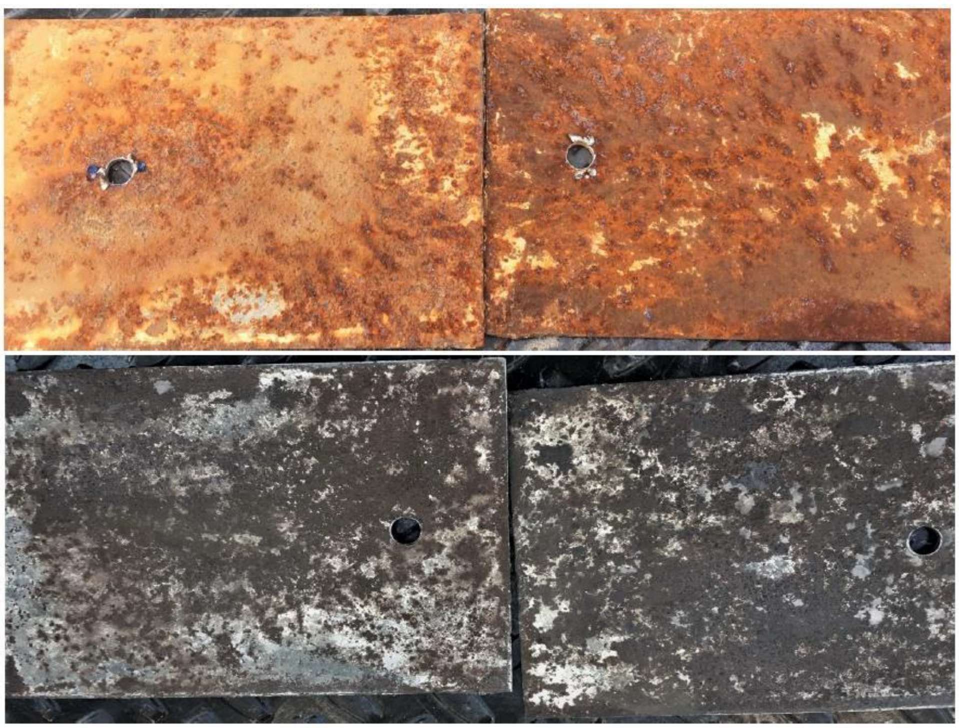

Figure 27. Photos showing passivation coupons that were used to determine the efficacy of the passivation operation for the Final Fractionator A overhead condensers. Before passivation (top) and 19 hours after passivation (bottom). (Credit: TPC)

4.3.1.3 Oxygen Presence in the Process Stream

As stated in Section 1.5, oxygen in the presence of high-purity butadiene can lead to popcorn polymer formation. The importance of controlling oxygen in the process stream is specifically discussed in the ACC *Butadiene Product Stewardship Guidance Manual* [5, p. 30], which states, "Butadiene and oxygen readily react to form thermally unstable butadiene peroxide. […] Butadiene peroxide is believed to play a primary role in the formation of butadiene popcorn polymer." Oxygen can be controlled, for example, through venting operations and by using certain inhibitors, such as DEHA, which act as oxygen scavengers.

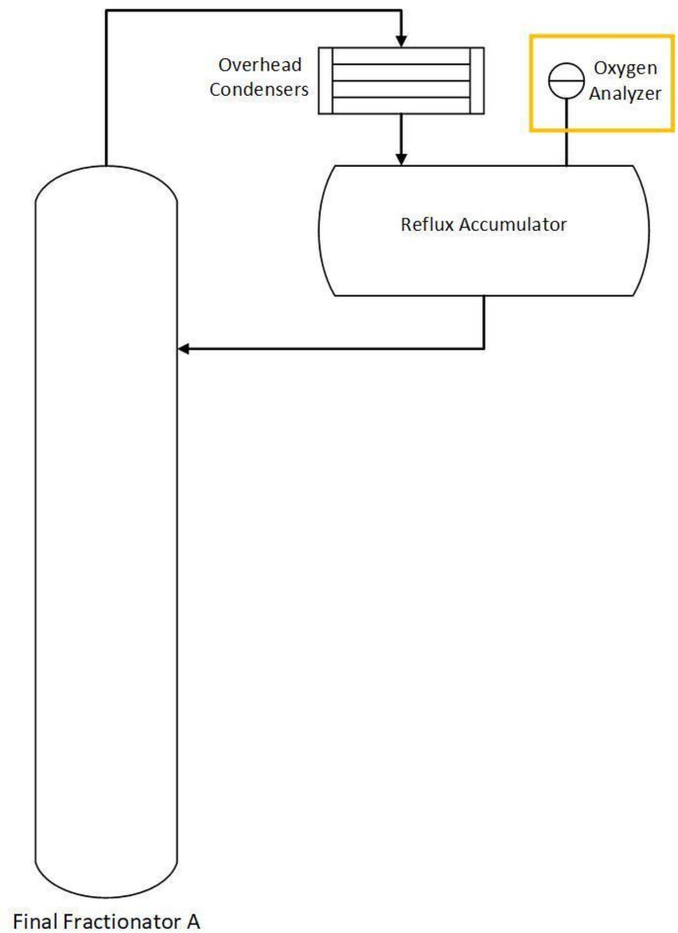

Figure 28. Schematic showing the location of the Final Fractionator overhead oxygen analyzer. (Credit: CSB)

TPC PNO measured the oxygen concentration in the Final Fractionator using an analyzer attached to the vapor space of its reflux accumulator (**Figure 28**). The TPC PNO Tower Profile procedure specified a maximum oxygen concentration of 5 ppm.[a] This procedure further stated that manually venting the reflux accumulator "can be used if [oxygen] content is high in the overhead [accumulator]," though TPC PNO relied on continuous condenser venting to ensure oxygen removal. Between September 1, 2019, and the time of the incident, this analyzer indicated elevated oxygen concentration levels greatly exceeding the 5 ppm maximum, at some points reaching over 90 ppm, during three separate long-term periods (**Figure 29**).

TPC PNO communicated to the CSB that Final Fractionator A accumulator oxygen concentration was also recorded using offline field samples taken twice per day. The laboratory analysis results of these samples are provided in **Figure 30**. These results indicate the oxygen level never exceeded 2.5 ppm in the samples. The CSB was not able to determine the reason for the large disparity between the analyzer readings and the laboratory analysis results. TPC PNO communicated that during the first two time periods indicated in **Figure 29**, the high oxygen readings were due to water in the analyzers, but TPC PNO communicated to the CSB that written evidence of this water content was not available, as it was maintained in a building that was destroyed during the incident, and the CSB was unable to confirm the validity of this statement.

[a] TPC PNO did not include this maximum oxygen concentration as part of its PSM safe operating limits.

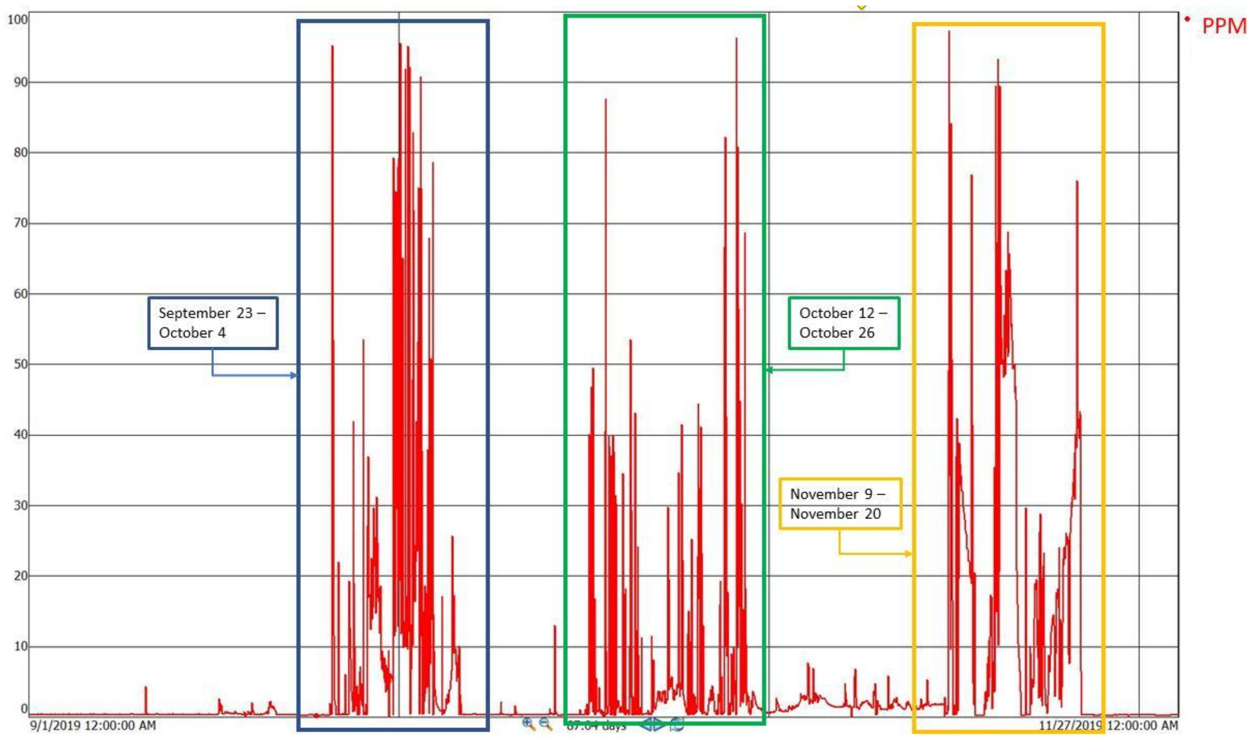

Figure 29. Process trend data graph showing the oxygen concentration levels (in ppm) in the Final Fractionator reflux accumulator from September 1, 2019, until the time of the incident. (Credit: CSB)

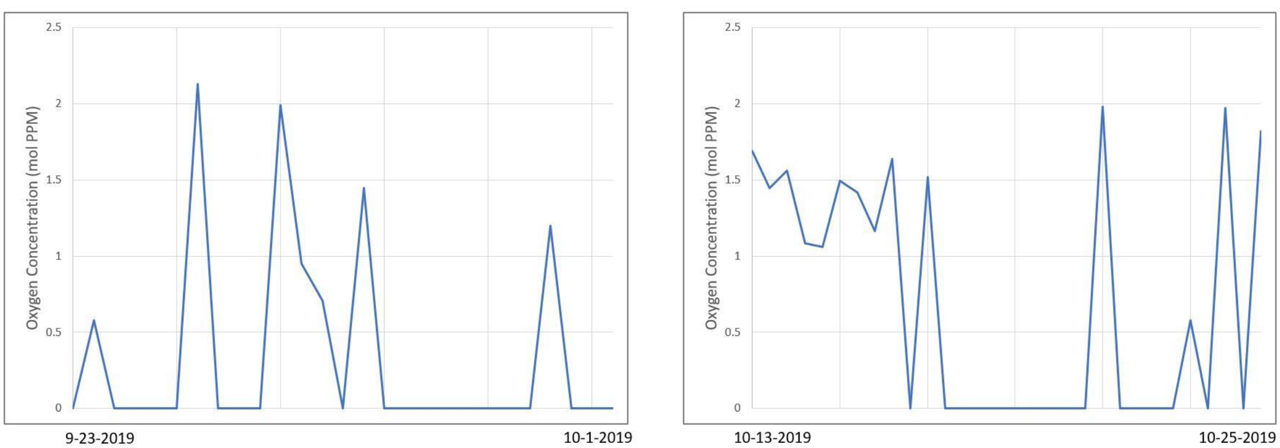

Figure 30. Oxygen concentration in finished butadiene from September 23, 2019, through October 1, 2019, (left) and from October 13, 2019, through October 25, 2019. (Credit: CSB)

4.3.1.4 Popcorn Polymer Plugging at TPC PNO

The TPC PNO site has historically experienced popcorn polymer formation at its facility. With some rare exception,[a] the bulk of the facility's popcorn polymer was removed from the equipment depicted in **Figure 31**, which included the butadiene water wash tower and its associated equipment (filter and coalescer), the waste

[a] From January 2011 to May 2019, TPC PNO's outbound drum inventory records indicate only 4.5 out of 180 tons (2.5%) of popcorn polymer were removed from the South Unit.

water stripper, and the finished butadiene storage tanks (also called "rundown" tanks). Since 2011, 95.6%[a] of all disposed popcorn polymer, nearly 20 tons annually, came from the areas shown in **Figure 31**.

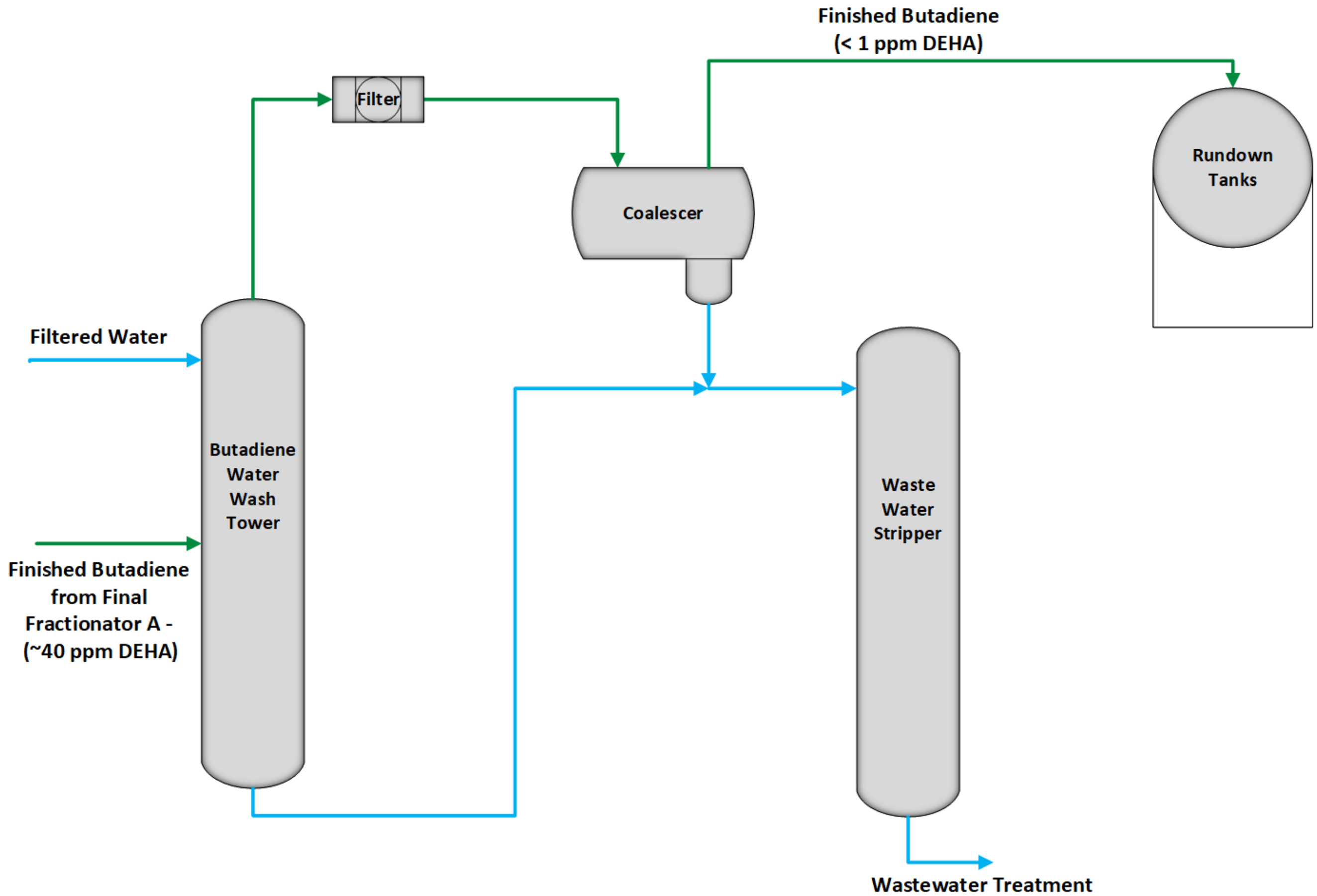

Figure 31. Flow diagram depicting the butadiene process flow through the butadiene water wash tower to the rundown tanks (until April 2019). (Credit: CSB)

The purpose of the butadiene water wash tower was to remove DEHA and carbonyls from the finished butadiene to meet TPC PNO's customer specifications. In April 2019, TPC PNO initiated a trial to permanently[b] bypass the butadiene water wash tower[c] while maintaining less than 10 ppm DEHA in the final butadiene product. To meet the 10 ppm DEHA concentration requirement in the final product without the use of the water wash tower, in March 2019, TPC PNO installed an atomizing quill to inject DEHA into the Final Fractionator A condensers on a trial basis. The quill was intended to allow for better disbursement of the DEHA, thereby

[a] This figure was calculated by adding the total popcorn from these areas and dividing it by the total popcorn shipped from the entire plant.

[b] The butadiene water wash tower was historically temporarily bypassed every two years pursuant to procedure.

[c] TPC PNO authorized the Management of Change (MOC) for the tower bypass on May 28, 2019. Trend data show the water feed ("Filtered Water" in **Figure 31**) to the butadiene water wash tower stopped on April 16, 2019.

theoretically allowing TPC PNO to use less DEHA and eliminating the need for the water wash tower.[a] In consultation with its contracted butadiene process chemistry expert,[b] TPC PNO decreased its overall DEHA usage from 83 gallons per day (GPD) to 23 GPD. TPC PNO also changed its DEHA injection configuration. Prior to the quill installation, DEHA was injected into the Final Fractionator overhead condensers as depicted in green in **Figure 32**. Once the quill was operational, TPC PNO stopped the injections to the individual condensers, instead injecting DEHA at the location indicated by the red arrow. To monitor how the TPC PNO unit responded to these changes, the trial included "[Final Fractionator] tower/exchanger performance and fouling" as a key performance indicator. TPC PNO also worked with its process chemistry expert on these changes.

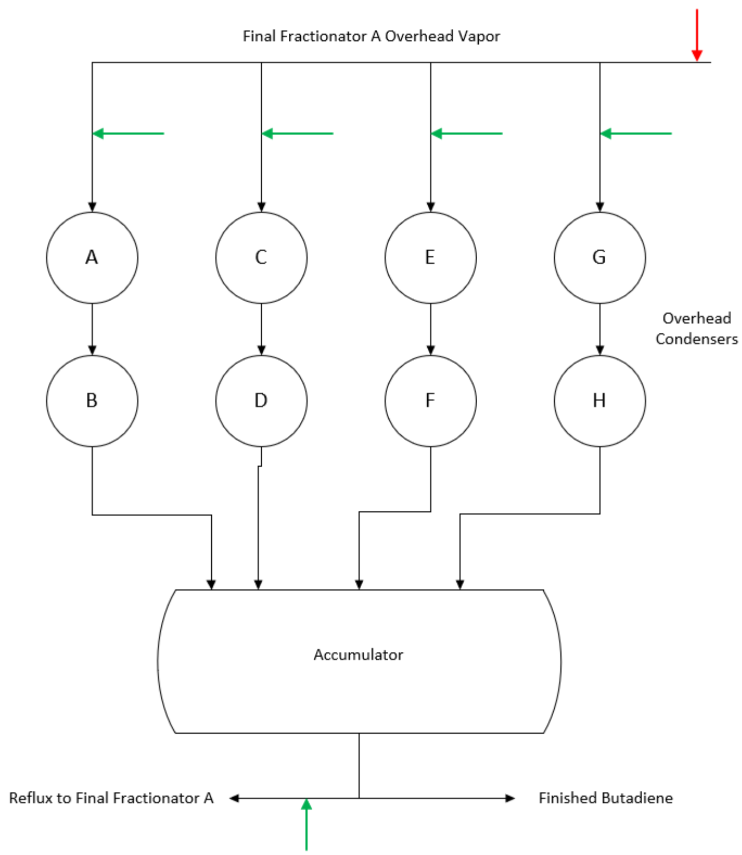

Figure 32. Final Fractionator DEHA injection locations prior to (green) and following quill installation (red). (Credit: CSB)

In May 2019, TPC PNO noted an increase in strainer cleanings in the rundown tanks just downstream of the bypassed butadiene water wash tower (**Figure 31**). In a document titled "Current Fouling Threats," an employee wrote:

[a] One TPC PNO employee told the CSB that TPC PNO wanted to remove the water wash tower from service because it was "a problematic tower to run. And it's one tower that the Houston operation does not have. They do not run a water wash tower like [the TPC PNO facility does]." The employee indicated that he believed the water wash tower was problematic because he was concerned the water was adding oxygen to the process and promoting popcorn polymer formation, in addition to the tower requiring shut down for cleaning every two years.

[b] TPC PNO consulted with Nalco Company LLC on these trial process changes.

> The frequent cleaning of tank strainers [in the finished butadiene equipment] suggests that there may be popcorn polymer growing in the finished [butadiene] rundown tanks. … This places these tanks at elevated risk for a potential runaway popcorn polymerization reaction that can result in broken valves, burst pipes, over pressurize the tank, and [butadiene] releases.

The TPC employee recommended that TPC PNO assemble a team to investigate the popcorn polymer formation, which TPC PNO formally put into place in August 2019. Nevertheless, after making this observation, TPC PNO continued operating the butadiene unit, continuing the trial in which the water wash tower was bypassed.

At the end of June 2019,[a] still during the trial in which the water wash tower was permanently bypassed and the amount of DEHA used in the unit was reduced, TPC PNO began to observe popcorn polymer plugging downstream of the Final Fractionator B bottoms, in the segregated crude pumps and the Butadiene Tower A (see **Figure 33**). TPC PNO also experienced popcorn polymer plugging in the bottom of the heavy ends removal tower (see **Figure 33**). The shift handover logs showed multiple popcorn polymer plugging incidents involving the Butadiene Tower B and the heavy ends removal tower throughout the months of July and August.

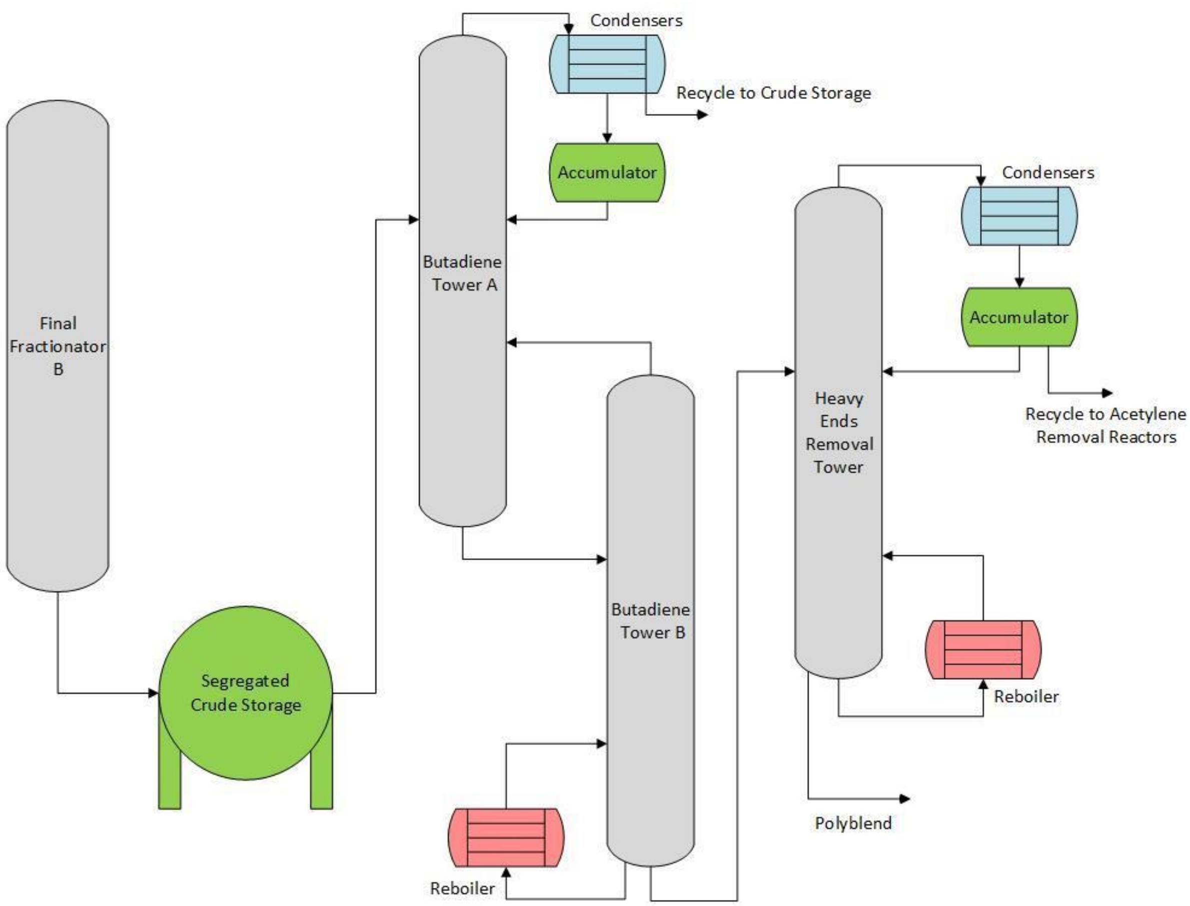

Figure 33. TPC PNO segregated crude unit. (Credit: CSB)

[a] The shift handover log mentions the pump and regulator issues on June 28, 2019.

TPC PNO continued to experience popcorn polymer and equipment plugging in the butadiene process throughout the remainder of 2019. Circled in red in **Figure 34** below are locations where the TPC PNO facility had experienced popcorn polymer blockage in equipment between June and October 2019.[a]

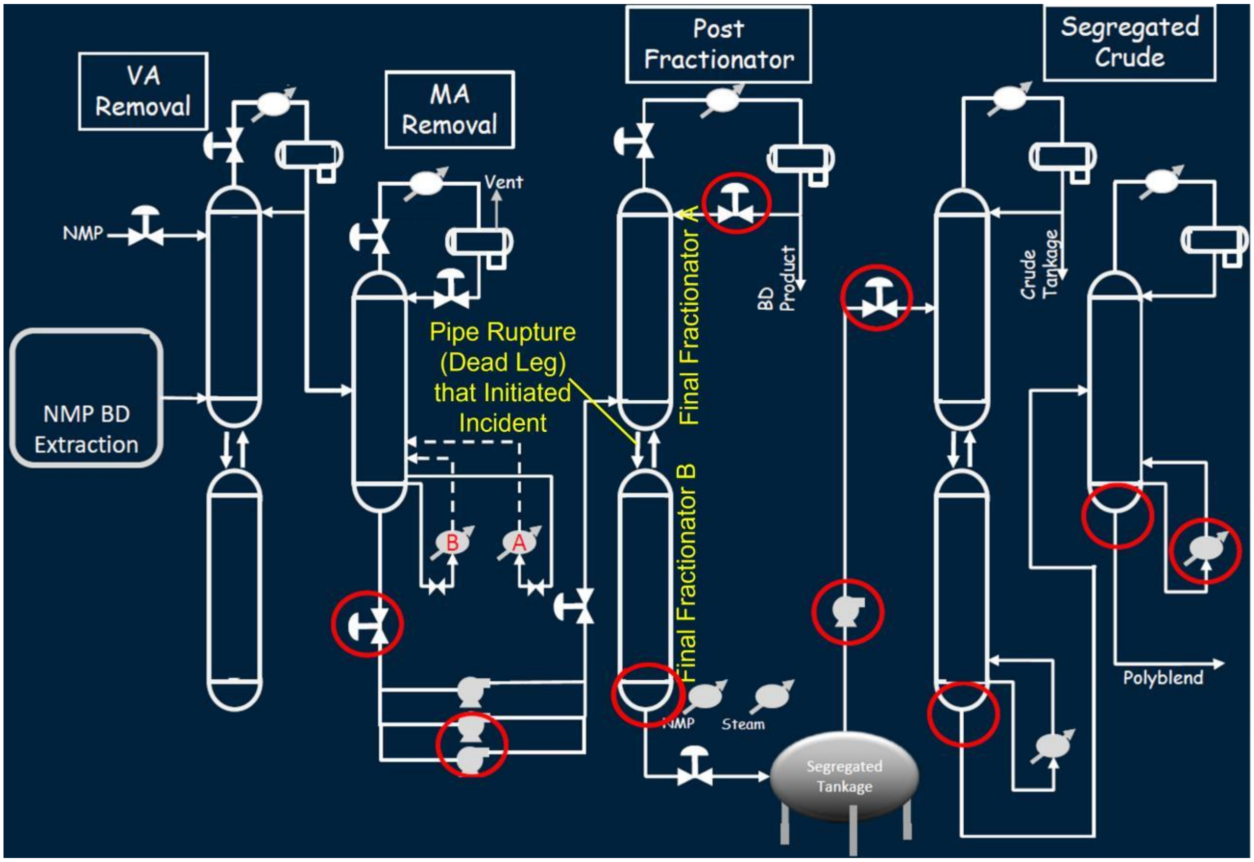

Figure 34. Locations of popcorn polymer blockages or fouling between June and October 2019. (Credit: TPC with text added by CSB)

TPC PNO then experienced two significant outages in September 2019; the first was a steam outage forcing the butadiene unit to shut down and the second was a power outage due to Tropical Storm Imelda. A TPC employee communicated to the CSB that unit upsets are particularly concerning in butadiene units, as rapid temperature changes occur and oxygen—which contributes to popcorn polymer formation—can ingress into the system. TPC PNO suspected these outages contributed to a subsequent popcorn polymer plugging event, which occurred in the Final Fractionator A reflux piping and began on September 24, 2019. TPC PNO employees tried to use steam to clear the reflux plugging[b] but then eventually used untreated fire protection water, which likely contained dissolved oxygen, to clear the plugging.

In early October 2019, a TPC PNO employee expressed concerns to their senior leadership about popcorn polymer plugging:

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[a] These blockages were presented to TPC staff by a TPC employee in October 2019.

[b] This water was used to clear plugging at the Final Fractionator A reflux valve.

> We have been fighting suspected polymer plugging for a couple of weeks on [the Final Fractionator A/B Towers]. We are having issues with level transmitters, level gauge glass, pressure transmitters, and the reflux line continuing to plug off resulting in loss of control parameters. … [W]e are struggling to maintain the minimum level indication to allow us to continue to operate with sufficient confidence to ensure no operational or environmental consequence.

TPC PNO employees considered shutting down the unit for an unscheduled "mini-outage" in the next 20 to 45 days to "clean up the polymer" and "make necessary modifications/improvements[a] to bring [the unit] up to polymer minimization best practice standards." These upgrades included installing nitrogen sweeps, filters, block valves, and magnetic level gauges. TPC PNO was also planning to passivate Final Fractionator A and B during this outage.

During October 2019, after the concerns above were raised, the Final Fractionator A/B performance began to improve after several polymer blockages were cleared. TPC PNO employees then recommended that the proposed shut down be rescheduled until early 2020, "contingent on [the] installation of temporary/permanent [filters] at [the] earliest possible moment." Based on the recommendation, on November 22, 2019, a filter skid (**Figure 35**) was installed at the Final Fractionator B bottoms, in addition to filters installed at other locations (**Figure 36**), to filter popcorn polymer from the process stream.[b] Shortly after installation, the filters at the Final Fractionator B bottoms started plugging. On November 22, 2019, a TPC PNO employee sent the following email to his colleagues:

> All:
>
> We were able to get the [Final Fractionator B bottoms] filters freed up this morning and have the line moving again. However, the filters fill with popcorn within 30 seconds of putting them online. As it stands, [we are] constantly changing filters as they plug. We're going to need to make sure that the warehouse is stocked with plenty of filters.

Figure 35. Temporary filter skid – exemplar. (Credit: TPC)

[a] One TPC employee told the CSB they were planning to address one of the control valves, replace level transmitters and gauges, and install nitrogen sweeps in the nozzles.

[b] This filter skid was previously installed on the same line further downstream.

Figure 36. Photos of filter skids located elsewhere on the TPC PNO facility. (Credit: CSB)

One worker described their experience with the filter changes:

> And we could stay out there…and you open up a valve, poof, you hear it, they fill up. So you go back to change it, do the second bank, fill up. And then, as the next shift came on…they were changing [filters] throughout the [shift]. We couldn't stop it. I mean it was…it was getting everywhere. So we [were] out there shoveling it up, put[ting] it in barrels…because we didn't want it blowing…all over the place.

By November 27, 2019 (the day of the incident), TPC PNO was changing the filters every 12 hours (once per shift). Some employees told the CSB that the filters were not filling up as fast, but others told the CSB the filters were still filling up quickly after the filter change frequency was decreased.

4.3.2 Analysis

Bypass of Water Wash Tower and Reduction of DEHA

As discussed above, in April 2019, TPC PNO began a trial to permanently bypass its water wash tower that removed DEHA from the butadiene. Additionally, in consultation with its process chemistry expert, TPC PNO simultaneously reduced the quantity of DEHA injected into the unit while making other process chemistry changes (i.e., installation of an injection quill). Then, in May and June 2019, TPC PNO began noticing increased popcorn polymer formation, both downstream of the bypassed butadiene water wash tower and downstream of Final Fractionator B. This observed popcorn polymer formation occurred before other polymer-inducing events occurred at TPC PNO, including the unit outages and the introduction of untreated fire water. This suggests that the increased popcorn polymer formation may have been triggered by TPC PNO's reduction of DEHA in the unit.

DEHA is used as an oxygen/free-radical scavenger in numerous applications, including anti-polymerization [27]. The amount of DEHA required for effective oxygen scavenging is dependent upon the amount of oxygen in the process. For example, one user calculated a ratio of 3:1 DEHA to oxygen [28].[a] The CSB found, however, that TPC PNO determined its DEHA dosing in the Final Fractionator A/B based solely on the quantity of residual DEHA remaining in the finished butadiene and not on oxygen levels or other conditions within the unit. As a comparison, residual DEHA concentration in the finished butadiene leaving the Final Fractionator accumulator prior to the bypass of the butadiene water wash tower averaged around 32 ppm; the residual DEHA specification after the bypass was 5 to 7 ppm, and the average DEHA concentration was around 5 ppm. The CSB concludes that the reduction in DEHA dosing may have contributed to the extensive growth of popcorn polymer experienced at the TPC PNO facility in the months before the incident.

Limited Equipment Passivation

As described above, much of the equipment in the TPC PNO butadiene unit was not passivated, including the Final Fractionator A and B towers. The rust evident inside the unit process equipment may have contributed to the formation of popcorn polymer. The CSB concludes that TPC PNO's limited equipment passivation was not in keeping with industry good practice guidance regarding the prevention and control of popcorn polymer. Had TPC PNO passivated more of its equipment, it could have mitigated a source of popcorn polymer formation that may have contributed to the incident. The CSB recommends that TPC PNO passivate all equipment that could be susceptible to popcorn polymer formation as needed to ensure compliance with industry good practice guidance.

Delay of Unit Shutdown

In October 2019, TPC PNO considered an unscheduled "mini-unit" shutdown of the butadiene unit after "fighting suspected polymer plugging for a couple of weeks on [the Final Fractionator A/B Towers]." It planned to "clean up the polymer" and "make necessary modifications/improvements to bring [the unit] up to polymer minimization best practice standards"; install nitrogen sweeps, filters, block valves, and magnetic level gauges; and passivate the Final Fractionator A and B. TPC PNO ultimately decided to delay this shutdown and repairs until early 2020 after the Final Fractionator A/B performance began to improve after several polymer blockages were

KEY LESSON

Popcorn polymer excursions in butadiene facilities are highly hazardous events. If there are any process vulnerabilities, like unknown dead legs or unknown regions in which popcorn polymer is accumulating, popcorn polymer can accumulate to the point of rupturing piping or other equipment and can lead to material releases, explosions, and fires. Butadiene facilities should develop robust policies to prevent and control popcorn polymer development and growth based on industry guidance, such as through equipment passivation, controlling oxygen levels, through chemical inhibitors, and other best practice methods. Butadiene facilities should also establish processes that require unit shutdowns and popcorn polymer incident investigations after threshold quantities of popcorn polymer are observed within the unit.

[a] The example provided was calculated for boiler feedwater applications, not for popcorn polymer inhibition.

cleared. The CSB concludes that TPC PNO's decision to delay the butadiene unit shutdown allowed the unit to continue operating with large quantities of popcorn polymer present and allowed additional time for the popcorn polymer in the dead leg to continue accumulating and ultimately rupture the piping.

In addition, TPC PNO had no internal formal procedures or guidance documents specifying when TPC PNO should shut down and clean the unit to prevent a popcorn polymer-induced loss of containment event, instead leaving such decisions solely to site employees. The CSB also found that ACC's *Butadiene Product Stewardship Guidance Manual* also contains no guidance on process conditions, such as oxygen levels or quantities of popcorn polymer formation, that could justify shutting down and cleaning a butadiene unit. The CSB concludes that TPC PNO did not have sufficient internal policies to lead employees to shut down and clean the butadiene unit after it experienced high levels of hazardous popcorn polymer formation. The CSB also concludes that the development and publication of additional guidance in ACC's *Butadiene Product Stewardship Guidance Manual* regarding process conditions, such as oxygen concentration levels or quantities of popcorn polymer formation that could justify shutting down and cleaning a butadiene unit, could help prevent future popcorn polymer-induced loss of containment events. The CSB recommends that the American Chemical Council revise the *Butadiene Product Stewardship Guidance Manual* to provide guidance on what should be considered excessive or dangerous amounts of popcorn polymer in a unit and describe the actions owner/operators should take during those polymer excursion events to control or eliminate the popcorn polymer to reduce the likelihood of a popcorn polymer-induced process loss of containment.

Records Retention for Data Reliability

As stated in Section 4.3.1.3, between September 1, 2019, and the time of the incident, an analyzer associated with the Final Fractionator A equipment indicated elevated oxygen concentration levels greatly exceeding TPC's 5 ppm maximum, at some points reaching over 90 ppm, during three separate long-term periods. TPC PNO communicated to the CSB that during the first two time periods the instrument measured high oxygen content, the high oxygen readings were due to water in the analyzers. TPC PNO, however, communicated to the CSB that written evidence of this water content was not available as it was maintained in a building that was destroyed during the incident, and the CSB was unable to confirm the validity of this statement. Also, as discussed in Section 4.1.1.1, TPC PNO likely maintained paper-based copies of Spare Pump Rotation and Dead Leg Inspection check sheets in a building that was destroyed during the incident.

The CSB concludes that had TPC electronically stored information regarding its analyzer data accuracy, both Government and TPC investigators could have better evaluated the process conditions leading to the incident, which is critical for conducting a high-quality incident investigation and identifying incident causes. The CSB recommends to TPC PNO to incorporate the recording of any paper-based process performance information into TPC PNO's existing electronic records management system so that the information can be reliably retained, retrieved, and analyzed in the event of a catastrophic incident.

4.4 Remotely Operated Emergency Isolation Valves

4.4.1 Factual Information

4.4.1.1 TPC PNO Policy: Emergency Block Valves

At the time of the incident, the TPC General Engineering & Manufacturing Specifications (GEMS) included a document titled *Emergency Block Valves* that "define[s] TPC Group requirements for the location and design of valves used for emergency isolation of process equipment to be installed on new facilities." It includes American Petroleum Institute (API) Recommended Practice (RP) 553 *Refinery Valves and Accessories for Control and Safety Instrumented* Systems as a reference.

The *Emergency Block Valves* document classifies TPC PNO emergency block valves (EBVs) into four types:

- Type A: Manually operated fire-safe block valve used when ignition is not expected in the event of a leak.
- Type B: Manually operated fire-safe block valve used when ignition is expected in the event of a leak.
- Type C: Same as type B EBV, but with locally controlled powered operation.
- Type D: Remotely operated EBV.

For pumps, the TPC *Emergency Block Valve* document required a Type C (locally powered) or Type D (remotely operated) EBV if the upstream vessel "contains greater than 4000 gallons of liquid hydrocarbons" and is less than 50 feet from the suction vessel. The *Emergency Block Valves* document applied to new facilities only and was developed after the butadiene unit was constructed.

For new vessels, the TPC *Emergency Block Valve* document requires a Type A (manual) or Type B (manual) EBV on all connected piping two-inch diameter or larger connected below the top of the working liquid level range.[a] For new large piping exceeding 10 inches in diameter, the TPC *Emergency Block Valve* document requires a Type C (locally powered) or Type D (remotely operated) EBV. Again, the *Emergency Block Valves* document applied to new facilities only and was developed after the butadiene unit was constructed.

4.4.1.2 2016 FM Global Audit

In April 2016, as part of a facility visit by a large group of insurers to review recommendations and plant changes, FM Global observed that the butadiene process unit was not equipped with ROEIVs:

> This large C4 Processing Plant [where butadiene is produced] has a large single area where crude C4 products are distilled, extracted, reacted, and distilled again into different products streams. Across the units, the plant reports there are no emergency motorized shutoff valves except for a few within the Tank Farm. Engineering has estimated depressurization to take up to 10 to 12 hr. in some sections of the process unit. Due to the minimal distance between process blocks

[a] This applies if liquid inventory is over 1,000 but less than 10,000 gallons. For vessels containing greater than 10,000 gallons, all lines below the top of the liquid working level require EBVs. According to TPC, liquid inventory includes tray and reboiler holdup.

> across the Gantry ways, access for manual firefighting is fair, at best. Emergency isolation will help limit the size of a release. This could greatly aid in manual firefighting efforts and prevent more processing areas getting involved. Also, by reducing the fire area, property damage and the time to complete repairs will also be reduced.

Based on this finding, FM Global recommended that TPC PNO "improve remote isolation capabilities within the tank farm and within the process units." The FM Global report stated that TPC PNO should "[i]solate the incoming and outgoing lines of columns, exchangers, tanks, and vessels with holdups in excess of 1,500 gal. (roughly 10,000 lb[s].)."

The FM Global audit also recommended the following:

> The plant should conduct an audit of the [butadiene] process units … for the location and installation of emergency block valves…. This should include design for the valves to be remotely shut off from the control room and a local station away from any fire exposure. Also, the valve design should include the ability to withstand a 15-minute fire exposure and still activate. …
>
> A major factor in the escalation of fires in the chemical industry is the lack of remote isolation capabilities where ignitable liquids and LPGs are processed. This plant has applied a standard at 10,000 gal. FM Global recommends that a small threshold be used.

After issuing this recommendation, FM Global observed the following:

> [A TPC PNO employee] indicated that … [o]ther emergency block valves will be considered if they are identified in process hazard reviews, for there is currently no corporate desire to go back retroactively and apply the TPC GEMS standard for the emergency block valves. … No additional emergency block valves have been identified during revalidation process hazard analyses.

4.4.1.3 Industry Guidance: API RP 553

API RP 553 *Refinery Valves and Accessories for Control and Safety Instrumented Systems*[a] provides, among other subjects, recommendations for EBVs [29, p. 1]. It defines EBVs as "a means of isolating flammable or toxic substances in the event of a leak or fire [29, p. 94]." API RP 553 classifies EBVs into four types (the same type classifications used by TPC):

- Type A: "A manually operated fire-safe block valve installed at the equipment. This type of valve is installed when ignition is not expected in the event of a leak."

[a] While the title of this recommended practice is "Refinery Valves," TPC used this document as a RAGAGEP for its operations.

- Type B: "This fire-safe block valve should be installed at a minimum of 7.6 m (25 ft) from the leak source when ignition is expected. The Type B valve is manually operated and is limited to sizes up to and including [8 inches in diameter] …."
- Type C: "The Type C valve is a power-operated Type B valve. The valve should be power-operated if larger than [8 inches in diameter]. … Controls are accessible from the valve location."
- Type D: "This is an EBV with remote controls. There is no restriction as to where the valve may be located, but the controls should be a minimum of 12 m (40 ft) from the leak source and should be out of the fire zone [30, p. 7]."

For pumps, API RP 553 requires the following:

- An EBV is typically required for pumps having seals where the upstream vessel contains greater than 7.6 m^3 (2,000 gallons) of light ends or hydrocarbons above the auto ignition point or above 316 °C (600 °F).
- An EBV is needed where the upstream vessel contains greater than 15 m^3 (4,000 gallons) of liquid hydrocarbons.
- Pumps with high discharge pressures shall have an EBV at its discharge (i.e., downstream of pump spillback) for reverse flow overpressure protection [30, p. 95].

For vessels, API RP 553 requires the following:

- An EBV is needed for vessels containing light ends or toxic material. The flow from these vessels should be isolated from potential leak sources such as pumps, compressors, and heat exchangers and fired equipment. Any branch connection between the vessel and the EBV should have its own EBV.
- An EBV is needed for vessels containing liquids heavier than light ends, but above the flash point [30, p. 95].

API RP 553 does not detail conditions at which a Type D (remotely operated) EBV is required.

4.4.2 Analysis

Various recognized industry process safety sources recommend using ROEIVs on equipment containing large inventories of flammable and toxic material:

- The Center for Chemical Process Safety (CCPS) states that "[r]emote isolation of equipment containing hazardous material is necessary to mitigate a release of hazardous material when there has been loss of containment. Isolation can be accomplished with the appropriate location of remotely operated…EBVs. Remotely operated EBVs should be located such that major process equipment or unit operations can be isolated in the event of a loss of containment [31]."

- The Health and Safety Executive (HSE)[a] states that "appropriate means of isolation, which may include [Remotely Operated Shutoff Valves], should be provided between individual inventory units to limit the quantity of substance that can be released from any single failure." [32, p. 26].

The TPC PNO incident demonstrates what can happen when portions of a chemical processing facility cannot be remotely isolated during a release and fire. Severe explosions caused a process tower to propel through the air and land within the facility, other process towers to fall within the unit, extensive facility damage, and fires that burned for more than a month within the facility. Manual and locally controlled EBVs ("Type A," "Type B," and "Type C," as defined by both TPC and API RP 553) are unreliable in this type of catastrophic incident. Since the valves cannot be safely accessed, the equipment cannot be isolated. The CSB concludes that had the TPC PNO facility been equipped with "Type D" EBVs (as defined by both TPC and API RP 553), the feed to the Final Fractionator A column could have been stopped shortly after the release began, potentially minimizing the size of the initial vapor cloud, and any secondary releases caused by the initial explosion could have been stopped early in the incident. Stopping the release(s) by using ROEIVs could have prevented some of the subsequent explosions, thereby minimizing the damage caused by the incident.

The TPC PNO incident is not the only incident in recent years in which the absence of remote emergency isolation capability allowed a release and fire to cause subsequent explosions and destruction of the facility. On June 21, 2019, a pipe elbow in the Philadelphia Energy Solutions (PES) hydrofluoric acid (HF) alkylation unit ruptured. A large vapor cloud—composed of about 95% propane, 2.5% HF, and other hydrocarbons—engulfed part of the unit. The vapor cloud ignited two minutes after the start of the release, causing a large fire. The CSB investigated this incident and found that the release location could not be isolated from the rest of the process. Three subsequent explosions occurred in the unit. The third explosion was the largest and occurred when a vessel, called V-1, containing primarily butylene, isobutane, and butane, violently ruptured. A fragment of the V-1 vessel weighing approximately 38,000 pounds flew across the Schuylkill River and landed on the other side, and two other fragments, one weighing about 23,000 pounds and the other 15,500 pounds, landed in the PES refinery. The HF alkylation unit was severely damaged by the fire and explosions. Marsh Specialty reported that the incident resulted in an estimated property damage loss of $750 million, and the 2020 Marsh Specialty report ranked the PES incident as the third-largest refinery loss to occur worldwide since 1974 [33]. On June 26,

KEY LESSON

Companies that handle large inventories of flammable or toxic material should assess their capability to remotely isolate these inventories in the event of a loss of process containment. Manual and locally controlled emergency block valves ("Type A," "Type B," and "Type C," as defined by API RP 553) serve no reliable function in catastrophic incidents, since the valves often cannot be safely accessed during these events, thereby preventing the ability to isolate equipment and stop releases. Equipment that handles large inventories of flammable or toxic material should be equipped with "Type D" remotely operated emergency isolation valves so that hazardous releases can be quickly and remotely stopped from a safe location.

2019, PES announced that the refining complex would be shutting down permanently [34]. Additional incidents involving remote isolation are described in **Appendix E**.

The CSB concludes that both the 2019 PES incident and the TPC PNO incident—in which prolonged releases and fires, multiple subsequent explosions, and facility destruction occurred—demonstrate the catastrophic consequences that can occur when facilities processing hazardous materials are not equipped with ROEIVs. After investigating the PES incident, the CSB recommended that API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* be amended to require the installation of ROEIVs on the inlet(s) and outlet(s) of all hydrofluoric acid containing vessels, and all hydrocarbon containing vessels meeting defined threshold quantities. The CSB concludes that improved requirements in both industry guidance documents and federal regulations are necessary to help prevent the recurrence of these highly destructive and dangerous events involving the release of highly flammable or toxic materials that cannot be isolated. The CSB intends to conduct further analyses of incidents involving lack of remote isolation capability to determine the appropriate course(s) of action to recommend to industry groups and regulatory agencies.

[a] HSE is the "independent regulator for work-related health and safety in Great Britain."

5 CONCLUSIONS

5.1 FINDINGS

Dead Leg Identification and Control

1. A significant temporary dead leg (~35 feet of 16-inch diameter pipe) was created in piping containing over 98% high-purity butadiene when the Final Fractionator A/B Primary Pump became inoperable. The dead leg existed for at least 114 days, allowing dangerous levels of popcorn polymer to form and grow.

2. TPC PNO did not have an effective safety management system in place to identify when the safety-critical "Dead Legs in High-Purity Butadiene Service" procedure could not be conducted as intended, or to identify the associated safety implications when the procedure could not be implemented.

3. TPC PNO's dead leg procedure did not identify all potential temporary dead legs within the unit, which may have contributed to personnel not taking action to prevent popcorn polymer formation and accumulation in the dead leg created by the nonoperational Primary Pump. Had the dead leg procedure specifically identified the potential for a hazardous temporary dead leg formation when the Primary Pump was nonoperational, TPC PNO personnel may have taken action to mitigate the hazard, for example by prioritizing the pump repair, purging the piping, or adding popcorn polymer inhibitor to the dead leg.

4. Additional guidance in ACC's *Butadiene Product Stewardship Guidance Manual* on how to effectively identify, control, or prevent dead legs—including dead legs created when equipment is temporarily out of service —could have helped to prevent this incident and could help to prevent future similar incidents.

PHA Action Item Implementation

5. The 2016 PHA recommendation to assure flushing of piping associated with out-of-service equipment was never implemented, and the dead leg conditions leading to the incident were not mitigated.

6. The implementation of the 2016 PHA recommendation could have helped prevent the incident by requiring personnel to flush the piping associated with the out-of-service Primary Pump, which could have prevented the buildup of popcorn polymer within the dead leg.

Control and Prevention of Popcorn Polymer

7. The reduction in DEHA dosing may have contributed to the extensive growth of popcorn polymer experienced at the TPC PNO facility in the months before the incident.

8. TPC PNO's limited equipment passivation was not in keeping with industry good practice guidance regarding the prevention and control of popcorn polymer. Had TPC PNO passivated more of its equipment, it could have mitigated a source of popcorn polymer formation that may have contributed to the incident.

9. TPC PNO's decision to delay the butadiene unit shutdown allowed the unit to continue operating with large quantities of popcorn polymer present and allowed additional time for the popcorn polymer in the dead leg to continue accumulating and ultimately rupture the piping.

10. TPC PNO did not have sufficient internal policies to lead employees to shut down and clean the butadiene unit after it experienced high levels of hazardous popcorn polymer formation.

11. The development and publication of additional guidance in ACC's *Butadiene Product Stewardship Guidance Manual* regarding process conditions, such as oxygen concentration levels or quantities of popcorn polymer formation that could justify shutting down and cleaning a butadiene unit, could help prevent future popcorn polymer-induced loss of containment events.

12. Had TPC electronically stored information regarding its analyzer data accuracy, both Government and TPC investigators could have better evaluated the process conditions leading to the incident, which is critical for conducting a high-quality incident investigation and identifying incident causes.

Remotely Operated Emergency Isolation Valves

13. Had the TPC PNO facility been equipped with "Type D" EBVs (as defined by both TPC and API RP 553), the feed to the Final Fractionator A column could have been stopped shortly after the release began, potentially minimizing the size of the initial vapor cloud, and any secondary releases caused by the initial explosion could have been stopped early in the incident. Stopping the release(s) by using ROEIVs could have prevented some of the subsequent explosions, thereby minimizing the damage caused by the incident.

14. Both the 2019 PES incident and the TPC PNO incident—in which prolonged releases and fires, multiple subsequent explosions, and facility destruction occurred—demonstrate the catastrophic consequences that can occur when facilities processing hazardous materials are not equipped with ROEIVs.

15. Improved requirements in both industry guidance documents and federal regulations are necessary to help prevent the recurrence of these highly destructive and dangerous events involving the release of highly flammable or toxic materials that cannot be isolated. The CSB intends to conduct further analyses of incidents involving lack of remote isolation capability to determine the appropriate course(s) of action to recommend to industry groups and regulatory agencies.

5.2 Probable Cause

The CSB determined that the probable cause of the incident was TPC PNO's failure to identify that an out-of-service pump within the butadiene unit caused a hazardous temporary dead leg, which allowed popcorn polymer to develop and exponentially expand in the piping section until the piping ruptured. The pipe rupture caused highly flammable butadiene to release into the unit, which ignited and caused an explosion, followed by multiple subsequent explosions. Contributing to the incident was TPC PNO's inadequate prevention and control of popcorn polymer within its process units and its inadequate implementation of the 2016 PHA action item. Contributing to the severity of the incident was the lack of ROEIVs within the butadiene process unit.

6 RECOMMENDATIONS

To prevent future chemical incidents, and in the interest of driving chemical safety change to protect people and the environment, the CSB makes the following safety recommendations:

6.1 TPC GROUP

2020-02-I-TX-R1

For all TPC PNO terminal operations in high-purity butadiene service (e.g., greater than 80 percent butadiene concentration), develop and implement a program to identify and control, or eliminate, dead legs. At a minimum, the program must require:

a) a comprehensive review of equipment configurations in high-purity butadiene service using both Piping and Instrumentation Diagrams (P&IDs) and field evaluations to identify all permanent dead legs. Implement a process to identify changes in operating conditions in high-purity butadiene service that could result in the formation of temporary or new permanent dead legs, such as when primary or spare pumps are temporarily or permanently out of service. Ensure this review is conducted at least every five years;

b) evaluation and implementation of design strategies, where practical, to prevent dead legs in areas susceptible to popcorn polymer formation;

c) mitigation, control, or prevention of hazardous popcorn polymer buildup in all identified dead legs in high-purity butadiene service, such as through increased monitoring, flushing of equipment, use of inhibitor(s), or planning maintenance activities to minimize the amount of time that a temporary dead leg is present; and

d) periodic continual auditing (at a minimum annually) by TPC PNO management to ensure that the process is being implemented.

2020-02-I-TX-R2

For all TPC PNO terminal operations, passivate all storage vessels, fixed equipment, and associated piping systems in high-purity butadiene service consistent with industry good practice guidance.

2020-02-I-TX-R3

At the TPC PNO facility, incorporate the recording of any paper-based process performance information into TPC PNO's existing electronic records management system so that the information can be reliably retained, retrieved, and analyzed in the event of a catastrophic incident. At a minimum, those records shall include Dead Leg Inspection check sheets, Spare Pump Rotation check sheets, and handwritten logs documenting the performance of all critical process instrumentation (e.g., the oxygen analyzer).

6.2 AMERICAN CHEMISTRY COUNCIL

2020-02-I-TX-R4

Revise the *Butadiene Product Stewardship Guidance Manual* to include guidance on identifying and controlling or eliminating dead legs in high-purity butadiene service. Specifically, provide guidance on the potential for dead legs to be formed when equipment, such as primary or spare pumps, is out of service. In the Manual, also provide guidance on method(s) to identify dead legs that could be formed when equipment, such as primary or spare pumps, is temporarily or permanently out of service. Recommend actions to mitigate, control, and prevent hazardous popcorn polymer buildup in these in-process or temporary dead legs, such as through monitoring, use of inhibitor(s), or conducting maintenance activities to minimize the presence of dead legs.

2020-02-I-TX-R5

Revise the *Butadiene Product Stewardship Guidance Manual* to provide guidance on a methodology to help identify what should be considered excessive or dangerous amounts of popcorn polymer in a unit. Provide mitigation strategies that describe the actions that owner/operators should take during those polymer excursions to control or eliminate the popcorn polymer to reduce the likelihood of popcorn polymer-induced process loss of containment.

7 KEY LESSONS FOR THE INDUSTRY

To prevent future chemical incidents, and in the interest of driving chemical safety change to protect people and the environment, the CSB urges companies to review these key lessons:

1. Companies should establish a process to identify, control, or eliminate dead legs in operations susceptible to popcorn polymer formation. This process must include identifying potential temporary or in-process dead legs, such as those that could be formed when equipment (e.g., primary or spare pumps) is out of service. The process should also include a method to flag equipment that when offline could create temporary or in-process dead legs and establish a method to prevent hazardous popcorn polymer buildup in these dead legs, such as through flushing piping, prioritizing maintenance activities to bring the equipment back online quickly, or the additional use of inhibitor. Companies must support this process with an effective safety management system that can identify when an operating deviation, such as a prolonged equipment outage, could result in a hazardous condition.

2. Popcorn polymer excursions in butadiene facilities are highly hazardous events. If there are any process vulnerabilities, like unknown dead legs or unknown regions in which popcorn polymer is accumulating, popcorn polymer can accumulate to the point of rupturing piping or other equipment and can lead to material releases, explosions, and fires. Butadiene facilities should develop robust policies to prevent and control popcorn polymer development and growth based on industry guidance, such as through equipment passivation, controlling oxygen levels, through chemical inhibitors, and other best practice methods. Butadiene facilities should also establish processes that require unit shutdowns and popcorn polymer incident investigations after threshold quantities of popcorn polymer are observed within the unit.

3. Companies that handle large inventories of flammable or toxic material should assess their capability to remotely isolate these inventories in the event of a loss of process containment. Manual and locally controlled emergency block valves ("Type A," "Type B," and "Type C," as defined by API RP 553) serve no reliable function in catastrophic incidents, since the valves often cannot be safely accessed during these events, thereby preventing the ability to isolate equipment and stop releases. Equipment that handles large inventories of flammable or toxic material should be equipped with "Type D" remotely operated emergency isolation valves so that hazardous releases can be quickly and remotely stopped from a safe location.

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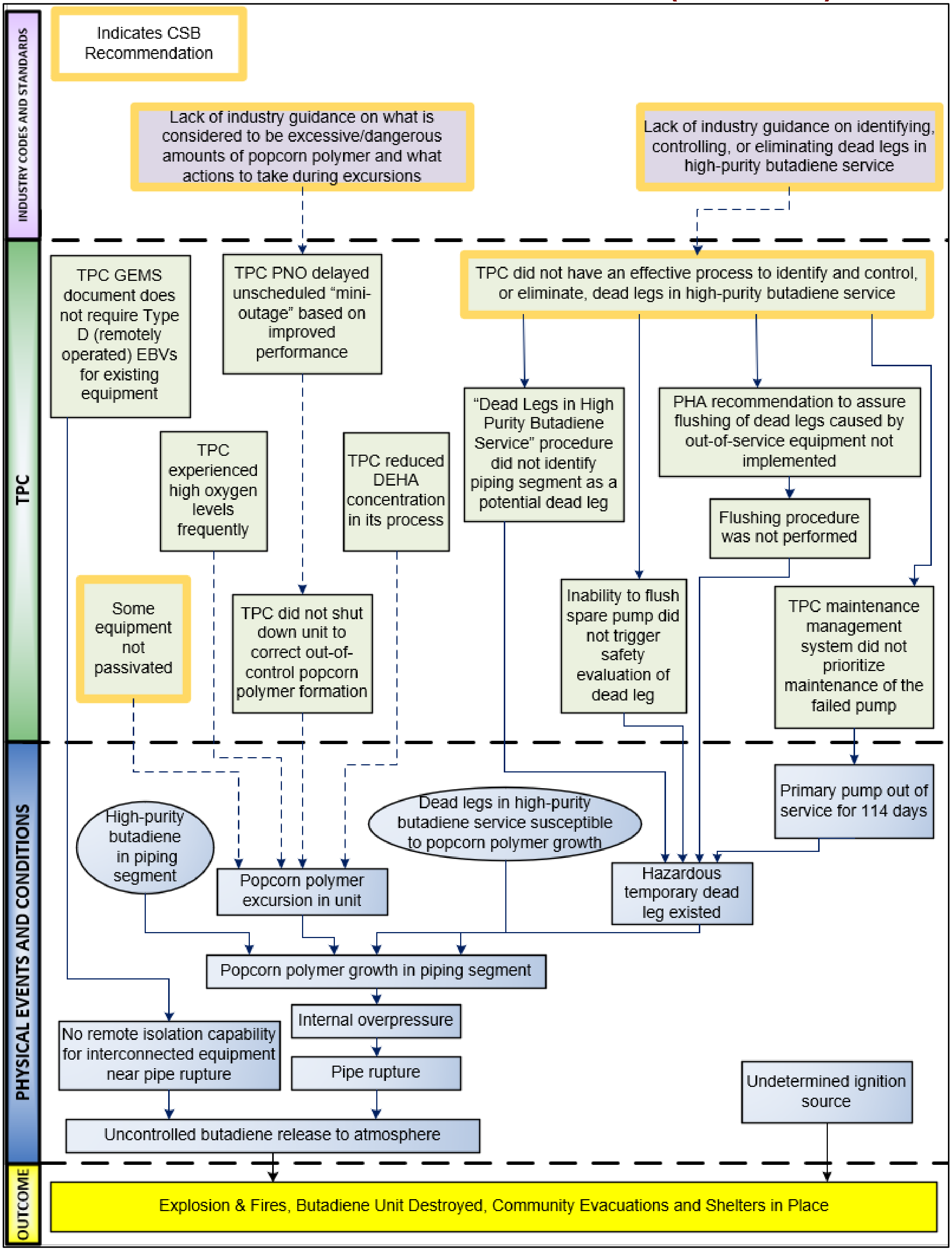
Appendix A—Causal Analysis (AcciMap)



APPENDIX B—DESCRIPTION OF SURROUNDING AREA

The demographic information of the population residing within about one mile of the TPC PNO facility fence line is contained below in **Figure 37** and **Table 3** below.

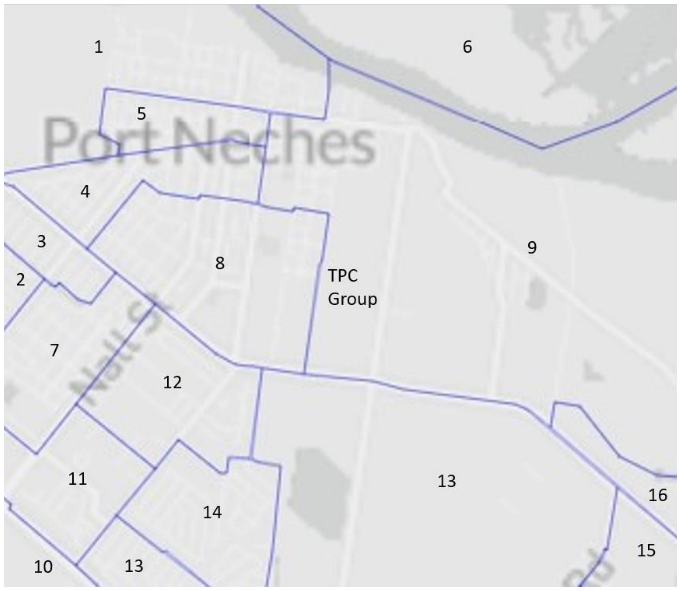


Figure 37. Census blocks in the approximately one-mile distance from the TPC PNO facility fence line. (Credit: Census Reporter with annotations by CSB)

Table 3. Demographic Data for Approximately One-Mile Vicinity of TPC PNO Facility. (Credit: CSB using data obtained from Census Reporter)

<table>
<tr><th>Tract Number</th><th>Population</th><th>Median Age</th><th colspan="2">Race and Ethnicity</th><th>Per Capita Income</th><th>Number of Housing Units</th><th colspan="2">Types of Structures</th></tr>
<tr><td rowspan="8">1</td><td rowspan="8">836</td><td rowspan="8">36.2</td><td>76.0%</td><td>White</td><td rowspan="8">$49,897</td><td rowspan="8">312</td><td>97%</td><td>Single Unit</td></tr>
<tr><td>0.0%</td><td>Black</td><td>0%</td><td>Multi-Unit</td></tr>
<tr><td>0.0%</td><td>Native</td><td>3%</td><td>Mobile Home</td></tr>
<tr><td>1.0%</td><td>Asian</td><td>0%</td><td>Boat, RV, van, etc.</td></tr>
<tr><td>1.0%</td><td>Islander</td><td colspan="2" rowspan="4"></td></tr>
<tr><td>0.0%</td><td>Other</td></tr>
<tr><td>5.0%</td><td>Two+</td></tr>
<tr><td>17.0%</td><td>Hispanic</td></tr>
<tr><td rowspan="4">2</td><td rowspan="4">1,410</td><td rowspan="4">49.1</td><td>86.0%</td><td>White</td><td rowspan="4">$41,374</td><td rowspan="4">565</td><td>100%</td><td>Single Unit</td></tr>
<tr><td>0.0%</td><td>Black</td><td>0%</td><td>Multi-Unit</td></tr>
<tr><td>0.0%</td><td>Native</td><td>0%</td><td>Mobile Home</td></tr>
<tr><td>0.0%</td><td>Asian</td><td>0%</td><td>Boat, RV, van, etc.</td></tr>
</table>

			0.0%	Islander				
			0.0%	Other				
			0.0%	Two+				
			14.0%	Hispanic				
3	616	38.6	96%	White	$31,352	241	100%	Single Unit
			0%	Black			0%	Multi-Unit
			0%	Native			0%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			0%	Two+				
			4%	Hispanic				
4	1,857	31.3	81%	White	$38,007	555	98%	Single Unit
			0%	Black			2%	Multi-Unit
			0%	Native			0%	Mobile Home
			2%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			12%	Two+				
			5%	Hispanic				
5	1,006	34.2	72%	White	$19,295	331	97%	Single Unit
			0%	Black			0%	Multi-Unit
			0%	Native			3%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			28%	Two+				
			0%	Hispanic				
6	1,960	34.1	89%	White	$43,486	893	89%	Single Unit
			0%	Black			0%	Multi-Unit
			0%	Native			11%	Mobile Home
			1%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			4%	Other				
			0%	Two+				
			6%	Hispanic				
7	1,183	49.9	92%	White	$39,418	573	100%	Single Unit
			0%	Black			0%	Multi-Unit
			0%	Native			0%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				

			0%	Other				
			1%	Two+				
			8%	Hispanic				
8	1,604	20.9	84%	White	$24,429	572	80%	Single Unit
			6%	Black			20%	Multi-Unit
			0%	Native			0%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			0%	Two+				
			10%	Hispanic				
9	473	41.9	95%	White	$34,026	248	94%	Single Unit
			0%	Black			6%	Multi-Unit
			0%	Native			0%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			0%	Two+				
			5%	Hispanic				
10	1,164	38.4	39%	White	$23,759	555	36%	Single Unit
			16%	Black			64%	Multi-Unit
			0%	Native			0%	Mobile Home
			36%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			5%	Two+				
			4%	Hispanic				
11	1,081	50.3	88%	White	$39,003	642	44%	Single Unit
			8%	Black			44%	Multi-Unit
			0%	Native			12%	Mobile Home
			1%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			0%	Two+				
			3%	Hispanic				
12	1,253	37	72%	White	$45,825	501	79%	Single Unit
			5%	Black			21%	Multi-Unit
			0%	Native			0%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				

			0%	Two+				
			24%	Hispanic				
13	1,431	43.1	71%	White	$39,832	508	94%	Single Unit
			0%	Black			2%	Multi-Unit
			0%	Native			4%	Mobile Home
			13%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			0%	Two+				
			16%	Hispanic				
14	1,395	48.4	85%	White	$58,982	698	100%	Single Unit
			0%	Black			0%	Multi-Unit
			0%	Native			0%	Mobile Home
			4%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			4%	Two+				
			7%	Hispanic				
15	959	40.9	77%	White	$33,341	351	100%	Single Unit
			1%	Black			0%	Multi-Unit
			0%	Native			0%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			5%	Two+				
			17%	Hispanic				
16	149	60.9	85%	White	$33,954	111	94%	Single Unit
			0%	Black			0%	Multi-Unit
			0%	Native			6%	Mobile Home
			0%	Asian			0%	Boat, RV, van, etc.
			0%	Islander				
			0%	Other				
			0%	Two+				
			15%	Hispanic				

Appendix C—OSHA Citations

After the incident, OSHA inspected the facility. In relation to incident causation, OSHA issued the following Willful citations relating to dead leg procedures and mechanical integrity deficiencies, which were contested by TPC and remain under appeal.[a]

- 29 C.F.R. 1910.119(f)(1): The employer failed to implement written operating procedures for safely conducting activities involved in each covered process:

  (a) On or about 11/27/2019 and times prior to, at the TPC Group Port Neches facility, the employer failed to implement its "Dead Legs in High Purity Butadiene Service" procedure to avoid a dead leg on the suction line of the [Primary] pump by flushing and/or by performing the required pump rotation, while the pump was down for maintenance.

- 29 C.F.R. 1910.119(j)(5): The employer did not correct deficiencies in equipment that were outside acceptable limits (defined by the process safety information on paragraph (d) of this section) before further use and did not take necessary means to assure safe operation:

  (a) On or about 11/27/2019 and times prior to, at the TPC Group Port Neches facility, employees operating the south 4 group and north unit distillation towers including [the Final Fractionator A and B] were exposed to fire and explosion hazards when operating the unit's equipment outside acceptable limits as a result of the presence of polymer including crystalline popcorn polymer.

  -In the Alternative-

  Occupational Safety and Health (OSH) Act of 1970 Section (5)(a)(1): The employer did not furnish employment and a place of employment which were free from recognized hazards that were causing or likely to cause death or serious physical harm to employees due to fire and explosion hazards:

  (a) On or about 11/27/2019 and times prior to, at the TPC Group Port Neches facility, employees operating the south 4 group and north group unit distillation towers including [the Final Fractionator A and B] were exposed to fire and explosion hazards following a release of highly hazardous chemical as a result of the presence of polymer including crystalline popcorn polymer.

  Among other methods, a feasible and acceptable abatement method to correct these hazards are to: 1. Follow the American Chemistry Council (2019) (Butadiene Popcorn Polymer Formation: Prevention/Control-Page 34) recommendations of ways to remove popcorn polymer from a unit to include: (i) Mechanical means such as Chipping or hydro-blasting.

[a] OSHA also issued other citations that were not related to the cause of the incident.

APPENDIX D—HISTORICAL INCIDENTS INVOLVING POPCORN POLYMER

The CSB reviewed numerous historical incidents involving popcorn polymer relevant to its investigation of the November 27, 2019, butadiene release incident at the TPC PNO facility.

Baytown, Texas (2019)

On July 31, 2019, a hydrocarbon release, explosion, and fire occurred at the ExxonMobil Baytown Olefins plant ("ExxonMobil") (**Figure 38**). Local media reported that the incident injured 37 people [35].[a] ExxonMobil's investigation of the incident found that butadiene popcorn polymer ruptured 20-inch (diameter) piping connected to a heat exchanger. The piping was in a part of the system that did not have material flowing through it. ExxonMobil described this dead leg piping as being in a "stagnant zone" of a depropanizer reboiler piping circuit. The report noted that, "Stagnant zones give popcorn polymer time to initiate seeds and grow."

Figure 38. July 31, 2019, Baytown Incident. This picture shows the fire following the rupture of a section of 20-inch piping attributed to butadiene popcorn polymer. (Credit: Houston Chronicle [35]).

ExxonMobil's incident investigation report said:

> Although the formation of popcorn polymer in services with high butadiene concentration has been recognized in the industry as a potential hazard and is incorporated into ExxonMobil practices at this site and globally, the

[a] ExxonMobil did not provide the CSB with information describing the number or extent of worker injuries.

> concentration of butadiene in [this system] is not considered to be high and is below that of the ExxonMobil site and global practices for popcorn polymer risk management. As such, all of the mitigation steps that could be taken to manage popcorn polymer formation were not applied.

Port Neches, Texas (2002)

On January 9, 2002, a butadiene release and fire occurred at the then Ameripol Synpol plant in Port Neches, Texas.[a] In a letter communicating the company's investigation to an OSHA official, the company asserted that the event was caused by "a form of butadiene peroxide" decomposition in the suction piping feeding a butadiene recycle pump. The company's corrective actions were aimed at preventing butadiene popcorn polymer formation and hazard concentrations of butadiene peroxides by "completely removing any quantity of butadiene from vessels idled for more than 30 days, and where contact with oxygen is possible [8, pp. 150-152]."

Victoria, Australia (2002)

Butadiene popcorn polymer was identified as the reason a one-meter section of piping ruptured, releasing ammonia and cuprous ammonium acetate on July 24, 2002, at the Qenos Olefins Pty Ltd facility in Victoria, Australia [36, p. 9]. An Australian government agency issued a summary report of the incident. The report noted that the failed piping was in a dead leg [36, p. 9]. The report also identified the following butadiene popcorn polymer lessons for industry:

> Oxygen ingress into a butadiene rich process and the scavenging of any free oxygen must be continuously managed. Changes to conditions can allow popcorn polymer to form in areas that do not usually experience this growth. Suspect polymer must be treated as popcorn until proven to be other species. Any buildup of butadiene (popcorn) polymer must be cleaned out at the earliest opportunity and must not be allowed to increase to the point of blocking piping [36, p. 9].

The report stated that, among other corrective actions, the company addressed dead leg piping by ensuring flow through piping segments, and they also employed a chemical treatment program to minimize the risk of growing polymer [36, p. 9].

Pasadena, Texas (2000)

On March 27, 2000, media reports show that one worker was killed and up to 69 other workers were injured following an explosion at the Phillips Petroleum plant in Pasadena, Texas [37]. The incident occurred in a unit that uses butadiene to produce a type of plastic. The company's investigation indicated that butadiene popcorn polymer reacted in an out-of-service tank and plugged purge lines, preventing an effective purge from taking place [38]. Media reports show that post-incident corrective actions focused on worker training. John Miles, an OSHA regional administrator at the time, provided an example of a worker training gap in one media interview. He said that "the site's engineers knew that a 'pinging' sound from a storage tank was an indicator that a

[a] CSB records show that the Port Neches plant has experienced several ownership changes since the January 2002 incident, but the site is now owned and operated by Lion Elastomers. TPC Group is a supplier of butadiene to Lion Elastomers.

potentially hazardous chemical reaction was taking place," and added that, "the engineers had not shared that information with the plant operators" [37].

Lavéra, France (2000)

According to a French government agency report, on December 14, 2000, about 15,000 pounds of butadiene released from a ruptured pipe at a chemical manufacturing facility in Lavéra, France [39]. The report shows that a butadiene vapor cloud formed, spread, and drifted beyond the plant boundaries [39, p. 2]. The butadiene vapor cloud did not ignite. There was no explosion and no fire. Plant workers initiated an emergency shutdown of the facility [39, p. 2]. Workers were able to isolate the equipment and an all-clear was issued about 90 minutes after the piping rupture occurred [39, p. 2]. The report shows that butadiene popcorn polymer created high pressure conditions inside the piping, causing the piping rupture [39, p. 3]. This piping was located at the outlet of a spare heat exchanger, a reboiler [39, p. 3]. Because steam was not flowing through this heat exchanger, butadiene in the piping was not flowing, and the ruptured piping was a dead leg [39, p. 3].

The report details several corrective actions, including:

Modifications were made to run both reboilers during normal operation to eliminate the dead leg;

Programs were established to passivate certain equipment before startups to prevent rust formation;

Changes were made to the chemical treatment program that was used to inhibit polymer formation and growth; and

A program was established to perform radiography every three months to detect accumulation of butadiene popcorn polymer inside equipment [39, pp. 3-4].

APPENDIX E—HISTORICAL INCIDENTS INVOLVING LACK OF REMOTE ISOLATION

The CSB reviewed numerous historical incidents involving remote isolation relevant to its investigation of the November 27, 2019, butadiene release incident at the TPC PNO facility.

Ellesmere Port, Cheshire (UK, 1994)

On February 1, 1994, a release of reactor solution occurred at the Associated Octel Company Limited facility due to mechanical failure downstream of a recirculating pump discharge port. The reactor solution, which was "highly flammable, corrosive and toxic," contained ethyl chloride, hydrogen chloride, and aluminum chloride. Despite attempts to isolate the leak, a pool of liquid formed and continued to collect near the base of the reactor. Flammable vapors from the release eventually ignited, resulting in a "major pool fire [40]."

The investigation report concluded that "the incident escalated rapidly because it was not possible to stop the initial release." One of the lessons learned from this incident was that companies should "critically review" EBV provisions at vessels containing large inventories of hazardous materials [32, pp. 4-5].

Grangemouth, Falkirk (UK, 2000)

On June 10, 2000, workers at the BP Grangemouth Refinery reported a leak of hydrocarbons from a debutanizer column during startup of a fluidized catalytic cracking unit (FCCU). As workers began to manually isolate valves and investigate the source of the leak, hydrocarbon vapor ignited, causing a serious fire in the vicinity of the debutanizer column. During the response, operators were able to close some manual valves and shut down pumps to minimize released inventories. However, the control room operator could not achieve complete isolation because the plant lacked remote isolation capability in key areas of the unit. The report recommended the "installation of remotely operated [EBVs] to allow rapid remote isolation of significant process inventories in order to minimi[z]e the consequences of an uncontrolled leak and allow remote emergency shutdown of ancillary equipment… [41, pp. 42-53]."

Point Comfort, Texas (2005)

On October 6, 2005, 16 employees were injured following a series of explosions that occurred at the Formosa Plastics Corporation facility in Point Comfort, Texas [42]. On the day of the incident, a towed trailer damaged a drain valve attached to a liquid propylene system, resulting in a release. The released liquid propylene "rapidly vaporized, forming a large flammable vapor cloud [42, p. 2]." Responding workers attempted to isolate the equipment but were unable to sufficiently isolate due to the advancing vapor cloud. The vapor cloud eventually ignited and subsequently exploded [42].

Investigators found the leak occurred downstream of propylene product pumps, and flow through those pumps was controlled by manual valves. As a result of the vapor cloud, workers could not reach the manual valves to isolate the leak, and they were unable to reach the local control station to shut down the pumps [42, p. 9]. Investigators concluded that remote isolation capability upstream of the pumps would likely have reduced the severity of the incident, possibly ending the incident prior to vapor cloud ignition [42].

APPENDIX F—PRIOR CSB RECOMMENDATIONS CONCERNING DEAD LEGS

In 2018, the CSB released a Safety Digest highlighting key safety lessons to help companies perform winterization in their facilities [43]. The digest summarizes three incidents where ineffective winterization practices were found to be causal to the incidents. In two of these incidents, the CSB determined the existence of dead legs to be a causal factor.

- ***Valero Refinery Propane Fire (February 16, 2007).*** A massive refinery fire occurred near Dumas, Texas, that seriously burned three people and shut down the refinery for two months. The CSB investigation revealed that the fire occurred when a release of propane gas ignited, injuring workers and causing more than $50 million in damage. The release was due to a crack in a dead leg section of piping after accumulated water froze and expanded.

- ***Bethlehem Steel Corporation Gas Condensate Fire (February 2, 2001).*** This incident occurred when a closed 10-inch valve cracked, releasing flammable liquid gas condensate, which subsequently ignited. The valve was at the end of a 25-foot pipe section that once supplied a furnace fueled by coke oven gas. The furnace was disconnected nine years earlier, but the pipe section and valve were left in place, creating a dead leg.

The CSB Safety Digest highlighted published guidance and resources for cold weather preparation, such as the API RP 2001, *Fire Protection in Refineries*. This guidance recommends that the freeze protection programs should (1) systematically conduct a careful review of out-of-service piping or units to identify potential problems to rectify; and (2) "design-out" dead legs, including process bypass piping. While this guidance pertains specifically to freeze protection, the above recommendations are applicable to any process where dead legs can result in potentially hazardous situations. The CSB Safety Digest further recommends that facilities systematically review process units and survey piping systems for dead legs and ensure they are properly isolated and/or removed [43].

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