Factual Update

October 29, 2020

Incident Summary

- On November 27, 2019, a major loss of containment event occurred, resulting in multiple fires and explosions at the TPC Group (TPC) Port Neches Operations (PNO) facility in Port Neches, TX. The TPC PNO facility manufactured 1,3-butadiene and raffinate-1 [1].[a] The incident occurred in the facility's South Unit (**Figure 1**). The initial explosion resulted in injuries to two TPC employees and a security contractor and caused significant damage to the facility. Following the incident, county officials issued a mandatory four-mile radius evacuation order [2] which remained in effect until 10:00 a.m. on November 29, 2019.

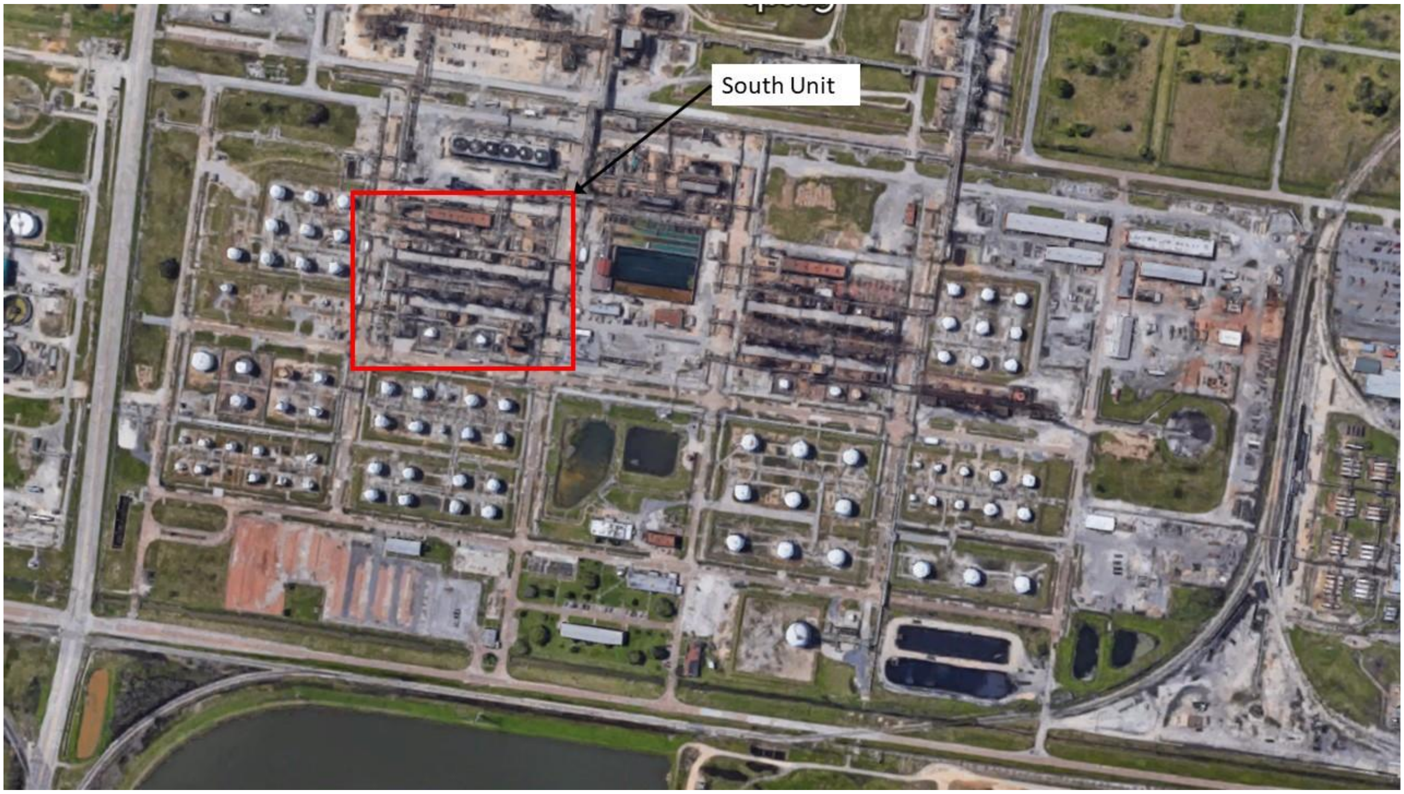

Figure 1. TPC PNO facility prior to the incident. (Credit: Google Maps)

- Because of the incident, TPC has decided to transition to a "terminal and services" operation while they evaluate and plan to rebuild [3]. As part of this transition, TPC terminated the employment of multiple workers and

[a] Raffinate-1 is a byproduct of 1,3-butadiene and is a chemical building block used in the manufacture of methyl tertiary butyl ether (MTBE) and diisobutylene (DIB) [15].

supervisors. Marsh JLT Specialty reported the property damage loss resulting from the incident to be $500 million [4].

Background

- The South Unit is used to produce 1,3-butadiene, which is primarily used to manufacture synthetic rubber and resins [5, p. 4]. Because 1,3-butadiene is a flammable liquid with a flashpoint below 100 °F,[a] and because the TPC PNO facility maintains an onsite quantity of 1,3-butadiene greater than 10,000 pounds, the production of 1,3-butadiene at the TPC PNO facility is regulated by the requirements of the Occupational Safety and Health Administration's (OSHA) Process Safety Management (PSM) standard, 29 CFR 1910.119 [6]. Also, 1,3-butadiene is a regulated substance under section 112(r) of the Clean Air Act; as such, the process is subject to the Environmental Protection Agency's (EPA) Risk Management Plan (RMP) Rule [7].

- In addition to its flammability, 1,3-butadiene is also highly reactive, with several undesirable reactions. In the presence of oxygen, butadiene readily reacts to form a butadiene peroxide. Butadiene peroxides, which are denser than 1,3-butadiene, will separate out and form a second liquid phase. If enough butadiene peroxides become concentrated, a critical mass is achieved which can initiate a fire or explosion [5, p. 30]. Another potential undesirable reaction that can occur between oxygen and 1,3-butadiene is the formation of popcorn polymer. Popcorn polymer, if left uninhibited, grows exponentially [8, p. 4]. When popcorn polymer growth is left unabated inside process equipment, the accumulated material can generate very high pressure inside the equipment and can ultimately lead to equipment rupture [9, p. 240].

- **Figure 2** shows a block flow diagram of the butadiene production process at TPC PNO. Crude butadiene ranging from 35 to 75 percent purity proceeds through multiple production phases. After the final fractionation phase, the 1,3-butadiene is at 99.8 percent purity, where it is sent to storage tanks for shipping. The loss of containment occurred in the final fractionation phase.

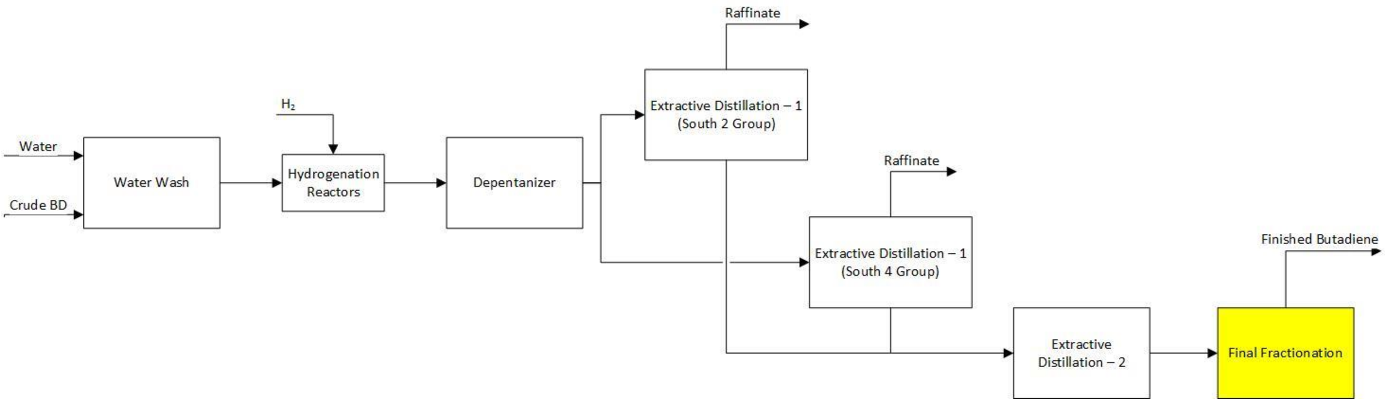

Figure 2. Block flow diagram of the butadiene production process at TPC PNO. The highlighted area shows where the loss of containment occurred. (Credit: CSB)

[a] The flashpoint of 1,3-butadiene is –105 °F [9, p. 239].

- A simplified process flow diagram of the TPC PNO butadiene post-fractionation process is shown in **Figure 3**. Indicated on the process flow diagram by the red ellipse is the area of interest as the potential origin of the flammable vapor release.[a]

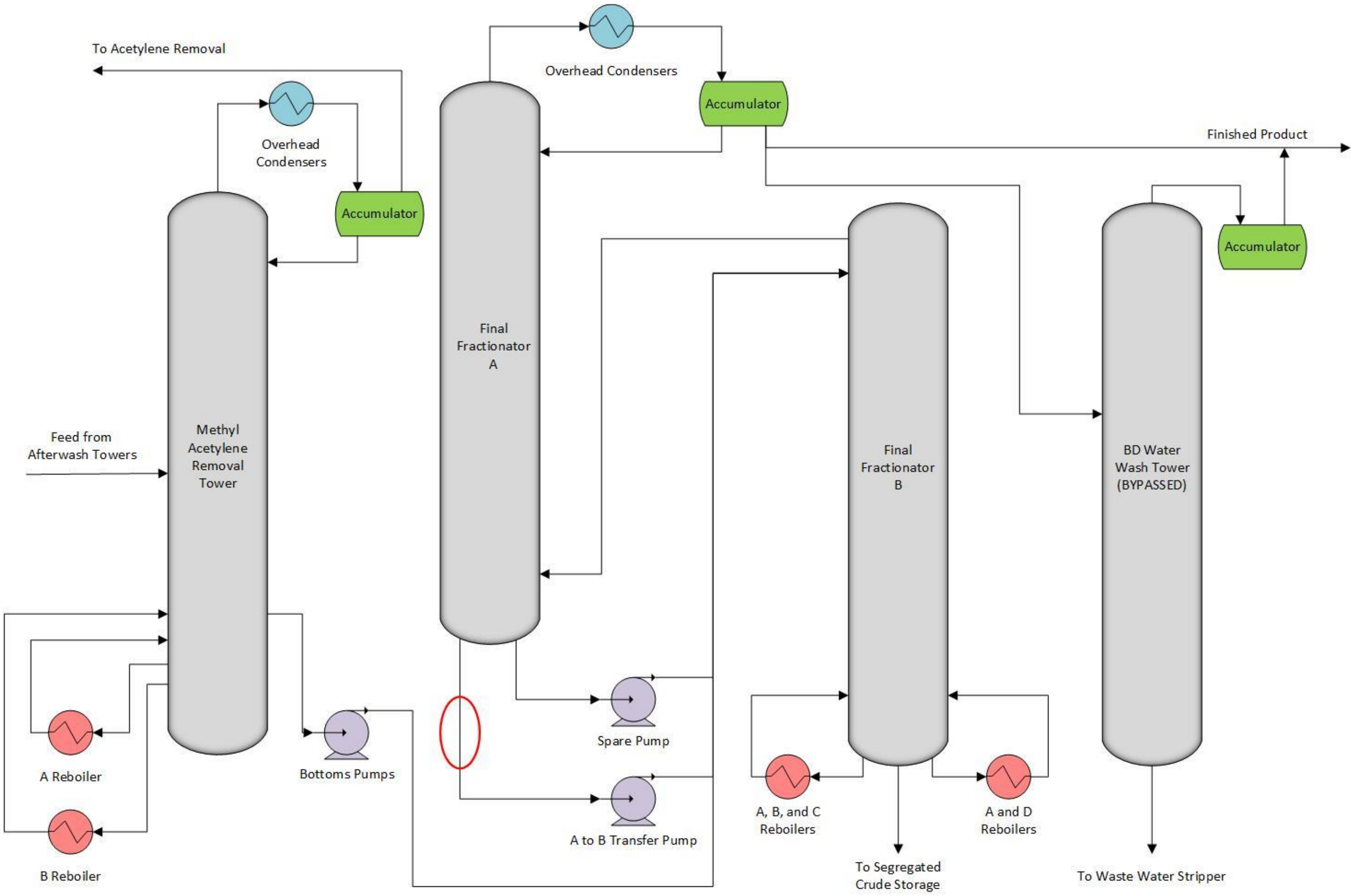

Figure 3. Simplified process flow diagram of the TPC PNO butadiene post-fractionation process at the time of the incident. (Credit: CSB)

Preliminary Incident Timeline

- During the night shift that began on Tuesday, November 26, 2019, the unit was reportedly operating normally.

- At 12:54 a.m.,[b] a loss of containment event occurred, causing the liquid level in the final fractionator A to drop rapidly from its operating level. The CSB calculated the liquid volume at the time of the initial level drop to be

[a] The likely location of release is based on data from the final fractionator A level controller and eyewitness accounts. As of this update, the CSB has not been able to visually confirm the failure location due to the extensive damage at the site.

[b] Time obtained from correlating external time-stamped video to TPC PNO process data, using the initial loss of multiple alarms as the time of the explosion. Since the TPC PNO timestamp from their 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 timestamp.

approximately 6,000 gallons. The liquid, which was primarily butadiene,[a] emptied from the fractionator in less than a minute (**Figure 4**). The liquid vaporized upon release[b] and formed a vapor cloud. Three workers were in the unit at that time. Two of them were facing toward the final fractionator A, and they both told the CSB after the incident that they saw a pipe rupture. Of these two workers, one of them identified the release point (circled in red in **Figure 3**) to be in the suction piping of the final fractionator A to B transfer pump. The third worker, who turned toward the sound of the release after the release occurred, also believed it was the suction piping into the final fractionator A to B transfer pump that failed. The workers' observations are consistent with the unit's recorded process data. The CSB has not yet visually confirmed the failure location due to the extensive damage and unstable structural conditions at the site.

- Immediately following the loss of containment, the three workers quickly departed the unit.
- At 12:56 a.m., the vapor cloud ignited, resulting in an explosion that created a pressure wave that heavily damaged the site and caused damage to buildings, including houses, offsite. Thermal imagery[c] provided by TPC shows multiple fires following the explosion **(Figure 5**).

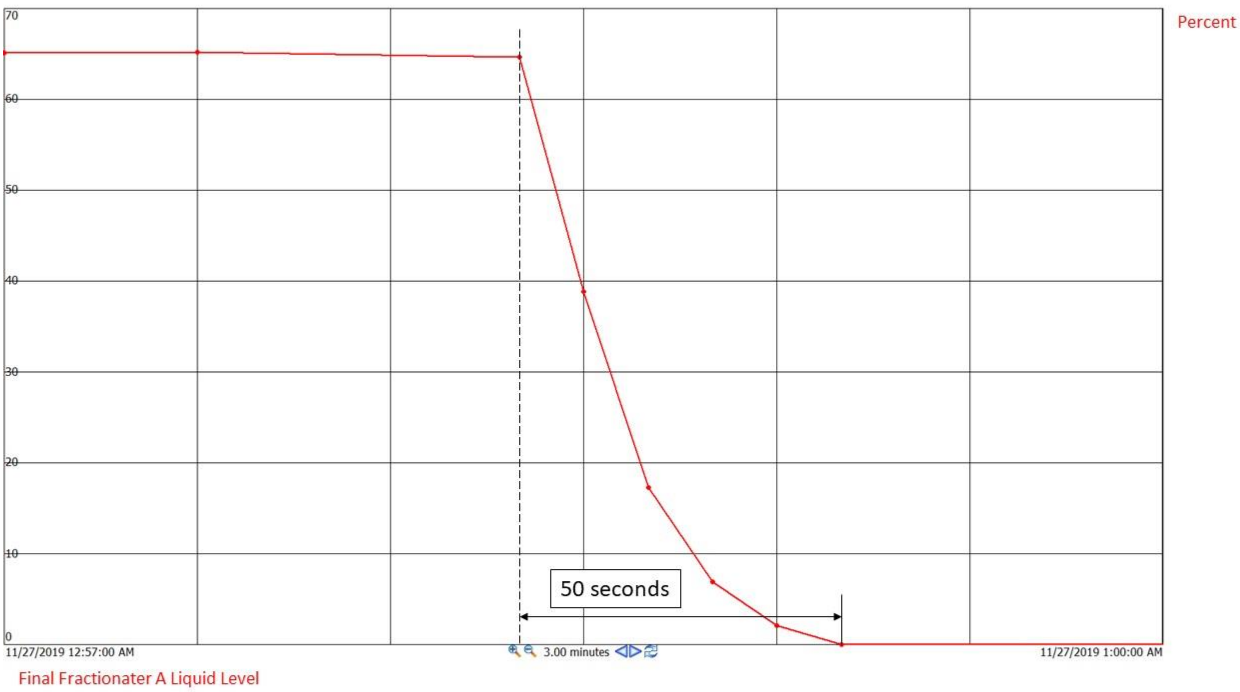

Figure 4. Process data trend graph showing the liquid level (in percent) in the final fractionator A dropping from its operating level to zero in less than a minute. The estimated liquid quantity in the fractionator at the time of the release was 6,000 gallons (30,000 pounds).[d] (Credit: CSB)

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[a] The composition of the contents at the bottom of the final fractionator A was not analyzed on-line; however, the design specification of the feed into the final fractionator from the methyl acetylene removal tower was 98.00 wt.% 1,3-butadiene minimum.

[b] The normal boiling point of 1,3-butadiene is 24.1 ^oF [5, p. 7].

[c] 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).

[d] Volume 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.

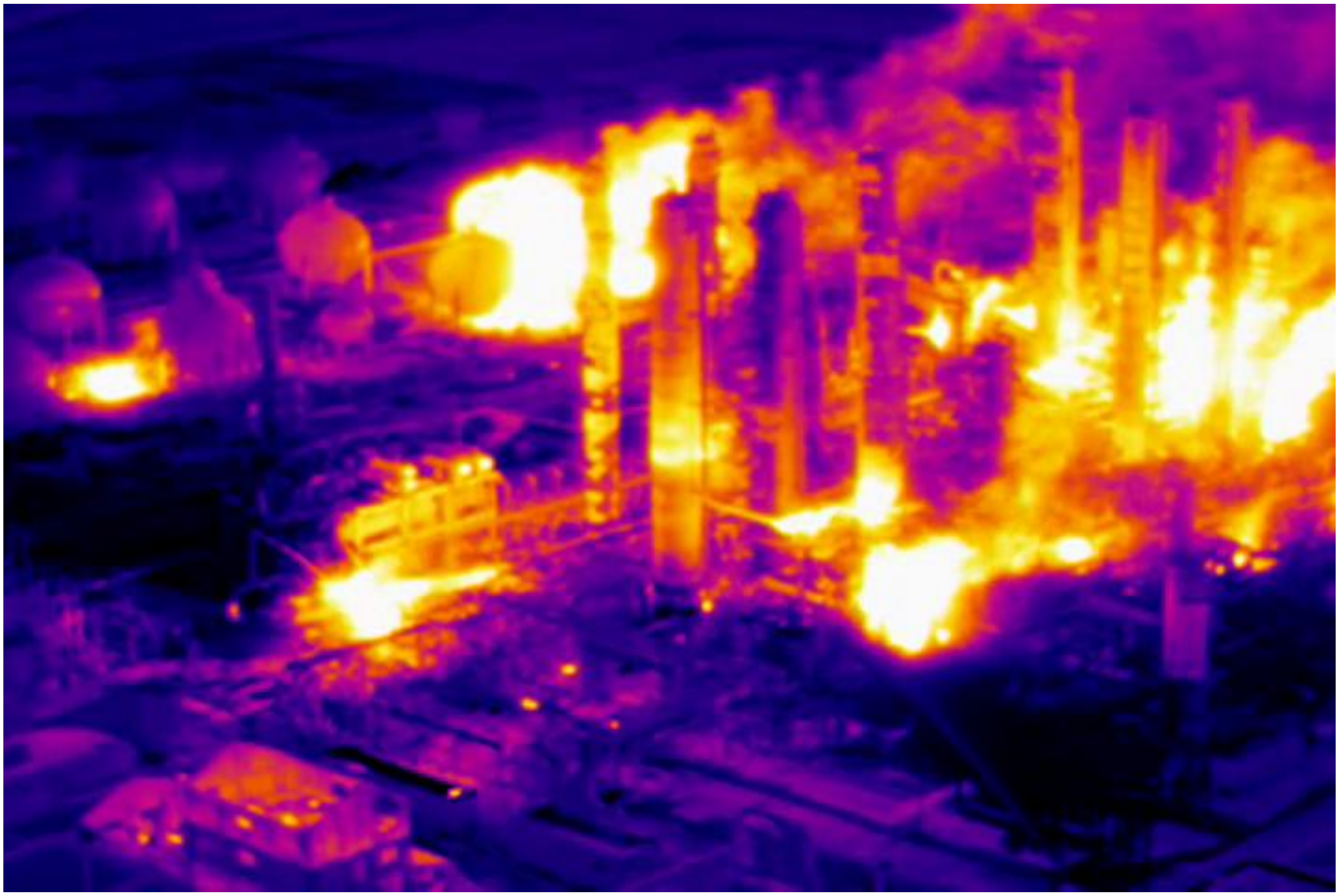

Figure 5. Thermal drone imagery of the TPC PNO facility South Unit taken the morning after the initial explosion. (Credit: TPC)

- At least two additional explosions occurred following the initial blast. At 2:40 a.m., a cell phone recording captured an additional explosion (**Figure 6**). That afternoon at 1:48 p.m., another explosion propelled one of the facility's towers into the air (**Figure 7**). The tower landed within the confines of the TPC PNO facility. In addition to the propelled tower (later identified as an out-of-service debutanizer), four additional towers (**Figure 8**) fell as a result of the blast and/or fires: the final fractionator A, an extractive distillation absorber, an out-of-service water wash tower, and the depentanizer.

Figure 6. Explosion at 2:40 a.m. on November 27, 2019 captured by cell phone video (Credit: TPC)

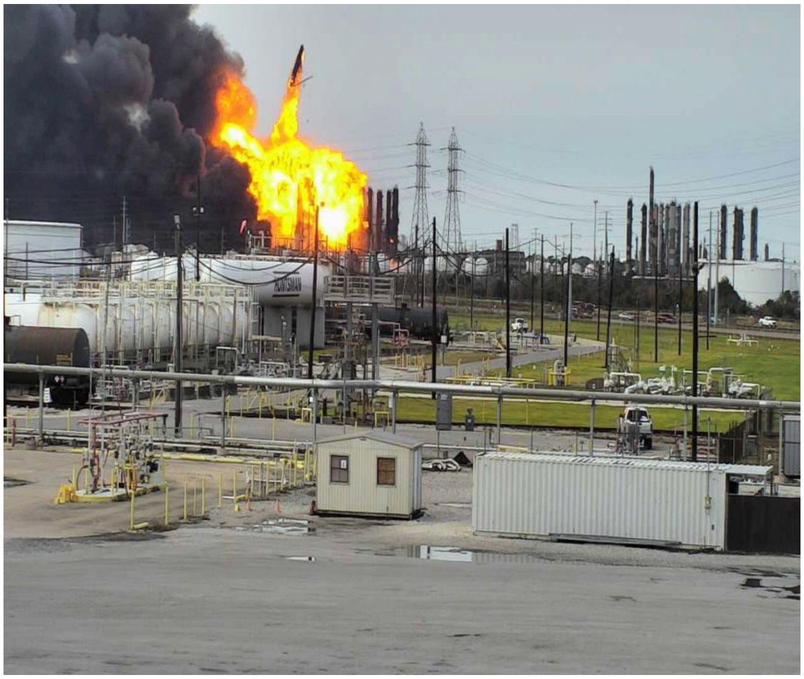

Figure 7. Explosion at 1:48 p.m. on November 27, 2019 which propelled one of the South Unit towers. (Credit: Huntsman Corporation)

- The explosion heavily damaged piping and equipment in the unit. Some of the resulting ruptured portions of piping could not be isolated. For instance, the area of interest indicated in **Figure 3** lies between the final fractionator A and the final fractionator A to B transfer pump, and no remotely actuated isolation valve[a] existed on that piping section upstream of the area of interest as the potential origin of release. Flammable process fluid continued to release from damaged equipment, and the fires burned for over a month. At 10:09 a.m. on January 4, 2020, the TPC Incident Command confirmed that all fires were out.

- At 6:08 p.m. on Wednesday, December 4, 2019, the Port Neches Fire Chief issued a shelter-in-place order for the City of Port Neches "out of an abundance of caution." At 10:00 p.m. that evening, the Jefferson County Judge issued a voluntary evacuation order for the City of Port Neches. At 12:29 p.m. on Thursday, December 5, 2019, the Jefferson County Office of Emergency Management said that the shelter-in-place and voluntary evacuation orders were lifted due to improved conditions.

- Port Neches schools were also impacted. Although Port Neches schools were closed for Thanksgiving break on November 27, 2019, schools did not reopen until December 3, 2019, because school officials needed additional time to clean debris, complete structural inspections, and repair school buildings [10]. After returning to school for two days, the schools were closed again, and they ultimately reopened on December 9, 2019.

[a] A manual isolation valve existed on this piping section downstream of the likely release point.

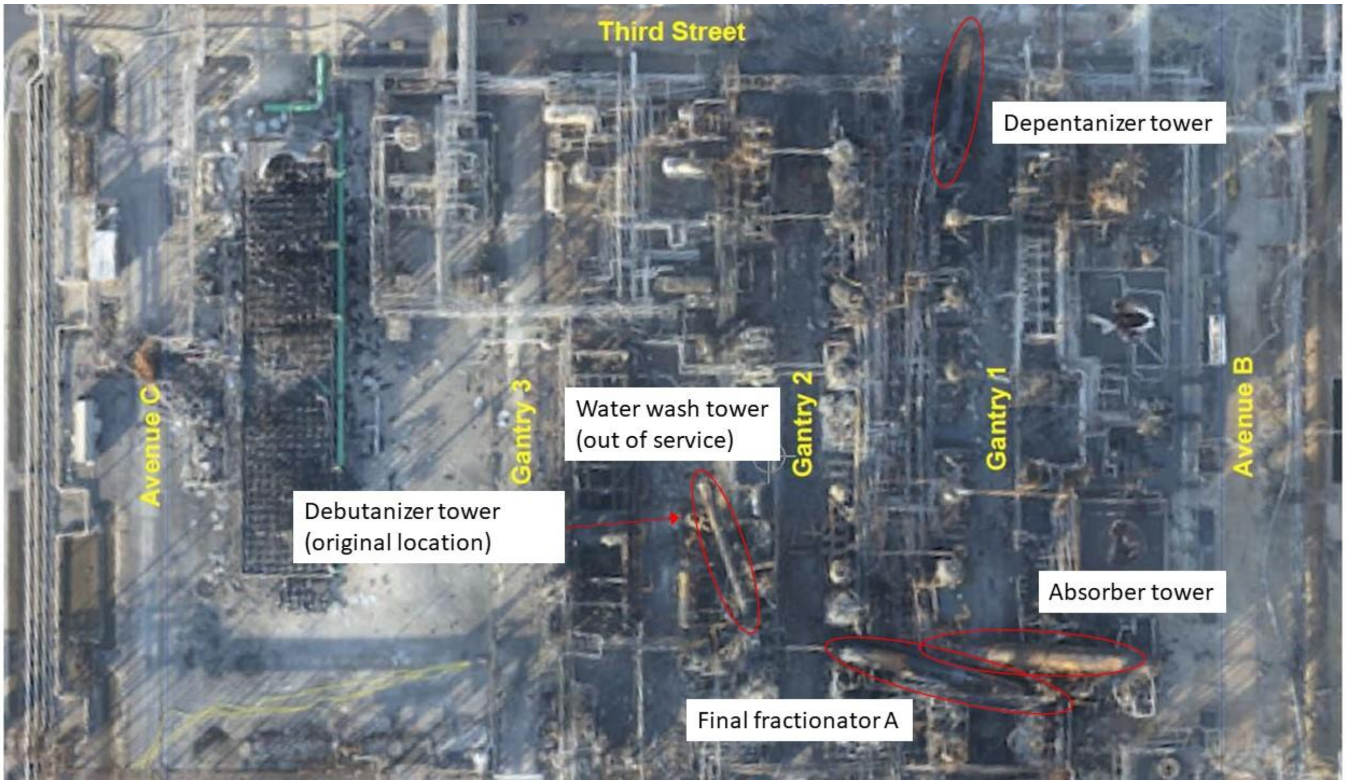

Figure 8. Overhead depiction of TPC PNO South Unit showing the locations of the fallen towers. (Credit: TPC)

Popcorn Polymer

- A solid substance called "popcorn" polymer[a] (**Figure 9**) can form in process vessels containing a high concentration of butadiene. Popcorn polymer is a hard, porous, opaque material created when oxygen reacts with butadiene in various areas of a butadiene production plant [11, p. 830]. Popcorn polymer formation involves two phases: initiation (seed formation) and propagation to polymer chains (seed growth) [11, p. 830]. Oxygen reacts with butadiene to form peroxides; butadiene peroxides react with butadiene to form popcorn polymer [8, pp. 8-9].

[a] Popcorn polymer is so called because it is pyrophoric and makes a popping sound when exposed to air [14, p. 29]; it also has a physical appearance resembling popcorn [5, p. 32]

Figure 9. Popcorn polymer in a manhole from another undisclosed butadiene unit, published in the Butadiene Popcorn Polymer Resource Book. (Credit: International Institute of Synthetic Rubber Producers Inc. [12, p. 261])

- High internal strain inside the popcorn polymer chains causes them to rupture and form new polymer seeds, thereby increasing the total volume of popcorn polymer as the process repeats [8, pp. 8-9]. This large increase in volume can produce enough pressure to swell or crack steel equipment. Throughout the industry, the buildup of popcorn polymer historically has caused equipment ruptures leading to loss of containment. **Figure 10** shows a pipe rupture caused by the buildup of popcorn polymer in another butadiene unit at the Lavera petrochemical complex located in Martigues, France in 2000 [12, pp. 154-159]. **Figure 11** shows another pipe rupture, which occurred at the PNO facility in 1999.[a]

[a] In 1999, the PNO facility was owned by Huntsman Corporation.

Figure 10. Pipe rupture caused by popcorn polymer in a butadiene unit in the Lavera petrochemical complex. (Credit: French Ministry of the Environment [12, p. 157])

Figure 11. On July 29, 1999, a section of pump suction piping ruptured at the Huntsman PNO facility. Huntsman Corporation owned the facility until TPC acquired it in 2006. (Credit: TPC)

- A piping segment that is open to the process but that does not have flow through it, for example due to a closed valve in the segment preventing flow, is known as a "dead leg" [13, p. 1]. Dead legs are known by the industry to promote popcorn polymer formation [12].[a]

- From September 6, 2019 through the date of the incident (at least 82 days), the final fractionator A to B transfer pump was out of service. The suction piping into this pump was open to the process during this period but with no flow through it, and was therefore a "dead leg." As discussed above, this is the piping segment that workers in the unit observed to have ruptured.

- Popcorn polymer was known to form in the South Unit before the incident. **Figure 12** shows a heat exchanger bundle pulled from one of the methyl acetylene removal tower reboilers on or around September 10, 2019. A TPC employee also noted that the emergency pressure-relief valve on this bundle "was plugged solid with popcorn and polymer." **Figure 13** shows multiple locations where the TPC PNO facility has experienced polymer fouling problems since July 2019.

Figure 12. Polymer found on methyl acetylene removal tower reboiler bundle pulled on or around September 10, 2019. (Credit: TPC)

[a] The Butadiene Popcorn Polymer Resource Book contains numerous examples of popcorn polymer incidents attributed to the existence of dead legs.

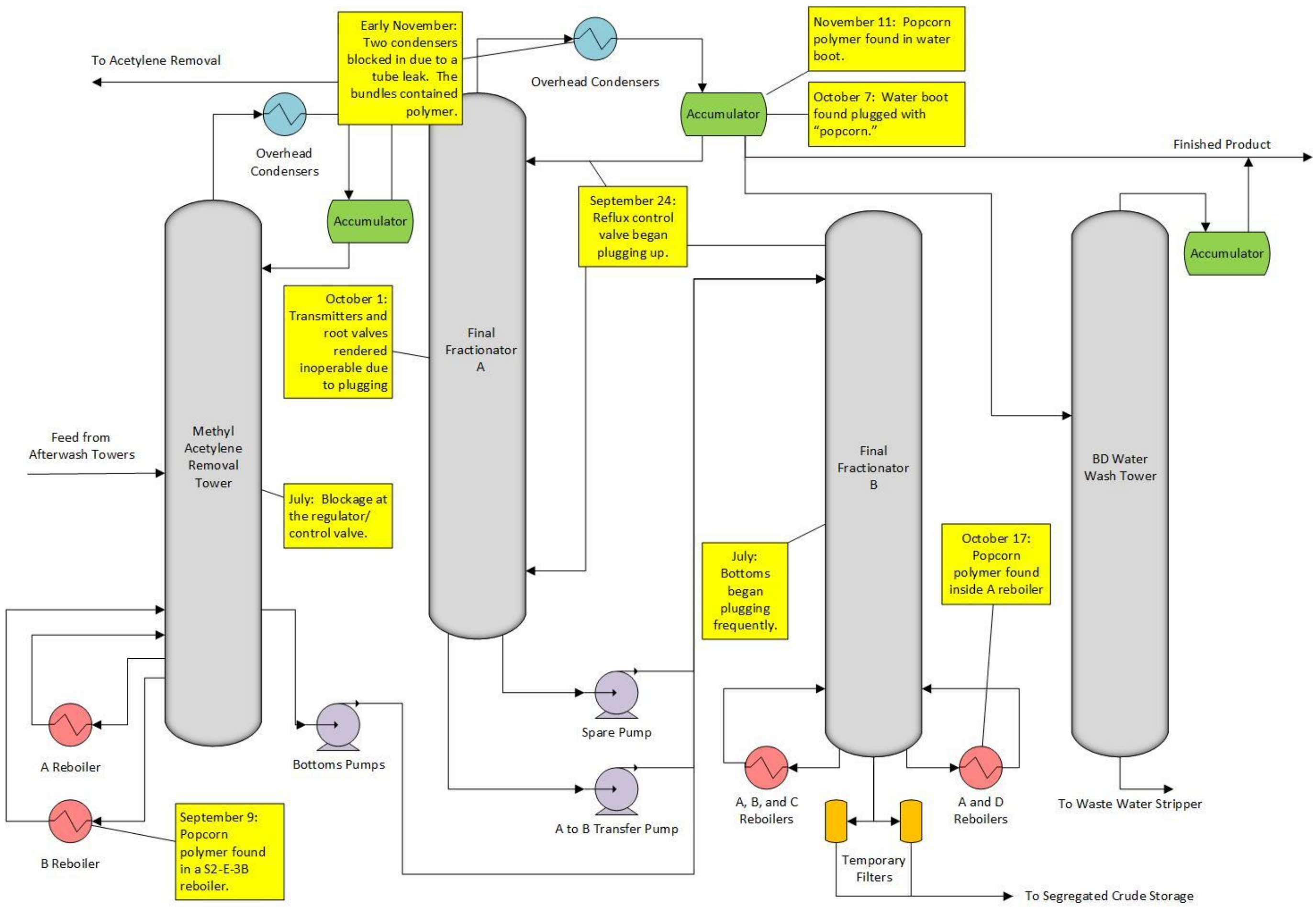

Figure 13. Simplified process diagram showing locations of recent polymer fouling (all dates shown are from 2019). (Credit: CSB)

- On November 19, 2019, TPC installed temporary filters on the liquid outlet of the final fractionator B to "catch any popcorn polymer chunks before they reach the downstream piece of equipment." On November 25, 2019, TPC collected a sample of polymer obtained from these temporary filters for analysis. The CSB and OSHA requested that TPC perform an analysis to determine the characteristics and activity level of this butadiene polymer sample. The test characterization results indicated that the polymer collected was butadiene-based popcorn polymer. Also, those portions of the sample that were tested for activity level all experienced limited growth (between 5 and 19 percent weight increase) over a six-day period.

Investigation Path Forward

- The CSB is continuing to conduct its investigation of this incident. CSB investigators analyze a wide range of aspects relating to incidents, including:
    - Equipment and system design;
    - Regulations, industry standards, and guidance;

- Training, operations, and procedures;
- Human and organizational factors;
- Safety management systems; and
- Historical and event data.

At the conclusion of the investigation, the CSB will publish a final investigation report discussing the facts, conditions, and circumstances of the event; the cause(s) or probable cause(s); and may issue safety recommendations to prevent the recurrence of similar incidents.

References

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