Poly-butadiene formation in Olefins Debutanizer Condenser

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In one of Sabic olefins plant, the condenser of the debutanizer tower was fouling. This was evident through the pressure increase in the tower and the cooling water control valve reaching the maximum opening (69%) limited by the mechanical stopper. The condenser process service is butadiene, which has the tendency of polymerizing and formation of popcorn, which could plug relief piping or accumulate in the condenser until the vessel shell is over stressed causing loss of containment and leading to fire or explosion. The risk assessment team evaluated that the condition could result in multiple fatalities with a likelihood of 10E-2. Dispersion modules were developed for the 2 failure modes identified, flange opening and mouth fish crack for fire and explosion to understand the risk. A new process line that bypasses the debutanizer tower and sends the material to the flare was constructed as interim solution to effectively mitigate the identified. The project execution was remarkable as it was completed in about a week. 15 tons of C4 was being flared per hour. This, however, allowed the olefins unit to mitigate the risk effectively without any interruption of the production. The change was not done before in the local industry, and it reflected how effective measures can be taken to mitigate risk through strong leadership and excellent engineering. Without the effective mitigation, Sabic operation team would have had to shutdown the olefins unit for extended period. This olefins unit feeds two poly ethylene that would shutdown consequently, causing significant losses over the mentioned period. The incident root cause analysis identified several gaps such as improper process hazard analysis, management of change, and inspection strategy/

Background

Butadiene popcorn

Butadiene goes into several undesirable reactions such as: butadiene peroxide formation, popcorn polymer formation, rubber formation, and dimerization (API, 2001). These can impose risk on the manufacturing units if the hazards is not identified or managed properly. Popcorn polymer is the most dangerous form, which propagate at a high rate exerting sufficient force to rupture metal 7. Butadiene popcorn is formed through proliferous polymerization. It is a glassy and brittle varying in colour from white, green or brown (Devins, 1946).

According to the Butadiene product stewardship guidance manual (API, 2001), Popcorn polymer occurs most likely in high diene concentrations (more than 80%), but it is widely reported that there are more incidents in light end unit with low bulk diene concentration. Oxygen, air, water, or can initiate the formation of peroxide radicals, which lead to the formation of active popcorn seeds in the presence of the high diene concentrations. Dead leg or stagnant zones can initiate the formation popcorn as well. Popcorn seeds propagate due to internal stresses generating new free radical sites for the polymer to grow. Popcorn growth is a function of temperature and mass (API, 2001).

EEPC, moreover, developed bench marking on popcorn formation in light end units with remarkable observations. 13 out of 21 observations were reported in services with 1,3 butadiene bulk concentration of 40% or lower (EEPC, 20018).

Accordingly, it is evident that popcorn formation is an issue across the light end units, with more incidents and observations reported. Many units are designed long time ago, with no considerations for popcorn formation, as it was previously perceived that it only occurred in high diene concentrations.

Blast damage

Vapor cloud explosions causes blast over pressure. At 10 psi (690 millibar), people can have irrivarable damage to their health (e.g. ear drum rupture). The threshold of lung haemorrhag is 12 psi (830 millibar), and at 30 psi (2068 millibar), near 100% of people subjected to fatality (HSE, 2006). This data, however, can be misleading. Most likely harm to people in an explosion results from:

- The indirect effects of being inside or close to a building or wall when it collapses or
- The indirect effects of being picked up by the blast wave and turned into missile with subsequent impact on the ground or a structure

Radiation damage

The effects of radiation on people are detailed in table 1 and figure 4.

Radiation intensity kW m^{-2}	Expected / observed effect
0.8 – 1.2	Hot summer day
4.0	Sufficient to cause pain to personnel if unable to reach cover within 20 sec; however blistering of the skin (second degree burns) is likely; 0% lethality
5	Second degree burns after 10 seconds
10	Pain threshold reached after 6-8 sec; second degree burns after 20 sec, potentially lethal after60 seconds
12.5	Minimum energy required for piloted ignition of wood, melting plastic tubing
25.0	Minimum energy required to ignite wood at indefinitely long exposures unpiloted
37.5	Damage to process equipment

Table 1. Radiation damage (Crowl, 2003 & World Bank 1985)

It is essential to understand the effects of radiations and overpressure blasts, as it will be referred to in the risk assessment as part of this paper.

Results and discussion

Site Description

The incident occurred in one of Sabic olefins plant. The plant produces mainly Ethylene and Propylene using ethane and propane. Ethane and Propane are supplied from outside refinery to the site. They are fed to 7 furnaces out of 8 available. 4 furnaces are fed with ethane and 3 with propane. The temperature of feed material is raised to around 850 using, integrated circuit and the furnace. At this temperature the cracking occur. The cracker effluent is cooled and then fed to a compressor to raise the pressure to 37 bar. Then supplied to a series of 5 main towers to recover the unreacted ethane and propane, and split the final products and by-products. The debutanizer column seperates C4s from C5s and heavier fractions. Where mixed C4's product is sent the the C4 hydrogenation unit. It is usually operated at 3-4 barg and equipped with shell and tube total condenser that uses cooling water as cooling media and reboiler with desuperheated low pressure steam.

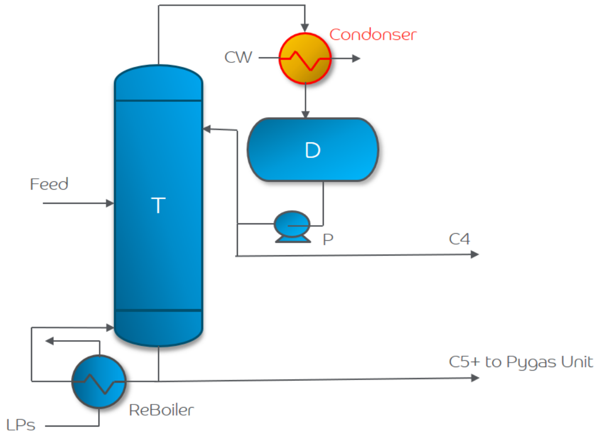

Figure 5. Simplified process description.

Incident Description

Exchanger channel cover leaked (water) due to shell deformation. Then operations observed that over a period of several weeks, the tower pressure is slowly increasing. Cooling water control valve reached the maximum opening (69%) limited by mechanical stopper. Survey was conducted and high delta pressure was found in the condenser which confirms the fouling. Risk assessment was conducted accordingly. The condenser shell side was bulged as shown in figure 6. Material obtained from pump strainer was tested and confirmed that the fouling is due to popcorn.

[redacted]

Figure 6. Evidence of bulged exchanger.

Figure 7. Popcorn found in the strainer

Factors considered

- Condenser shell is 1.3 meter inside diameter
- Tube attachment to tube sheet is rolled not welded (suggesting that tube failure and process upset is likely to occur before shell failure)
- Shell side process pressure is 4.9 barg, tube side water pressure is slightly higher (6.5 barg at water pump discharge). Water entry into the process is more likely if tube failure occurs resulting in a process upset
- Process fluid is a C4 mixture, approximately 65% 1- 3 butadiene
- Process temperature at condenser inlet is approximately 53 C, which is high enough for popcorn polymer formation
- Popcorn polymer has been found in pump screen downstream of the condenser

Consequence analysis

Risk assessment was conducted, and two potential incident scenarios were identified. Safe site was used to develop consequence analysis. The details as follow:

Scenario 1: Accumulation of popcorn material in PRV inlet nozzle plugs nozzle or PRV rendering the device inoperable, over pressure event occurs, PRV unable to function resulting in a loss of containment and possibly leading to fire or vapor cloud explosion.

- Failure Mode: flange opening of the biggest piping causing an opening equivalent to 20% of its area. The biggest piping is the process inlet with diameter of 10 inches. The bore size suspected is 2 inches
- Release rate: 32.6 kg/s
- Energy released due to blast: 2.8E9 J
- Event probability: 10E-2
- Risk evaluated: An explosion can cause multiple fatalities with a likelihood of with a probability of 10E-2, which is not acceptable according to Sabic risk tolerance criteria
- Figures below are illustration of the consequence analysis.

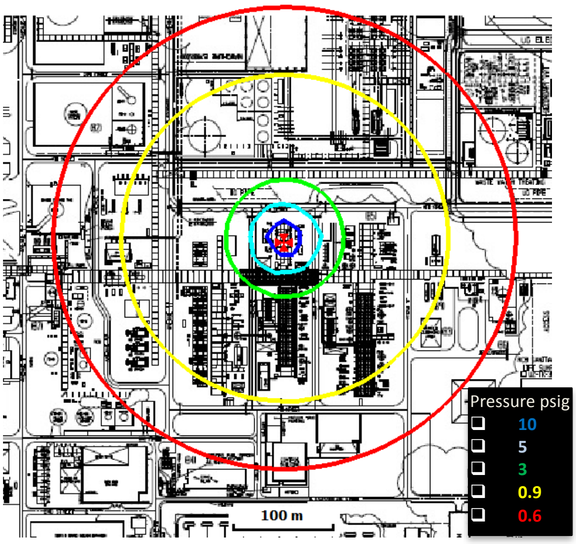

Figure 8: Blast contour for scenario 1

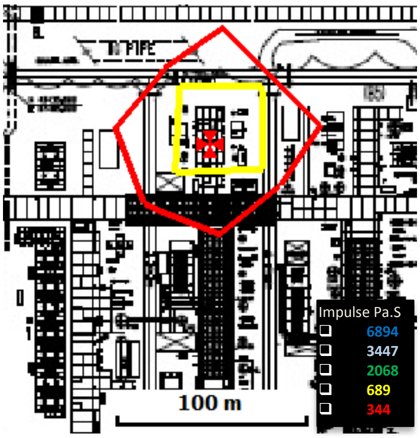

Figure 9: impulse contours for scenario 1

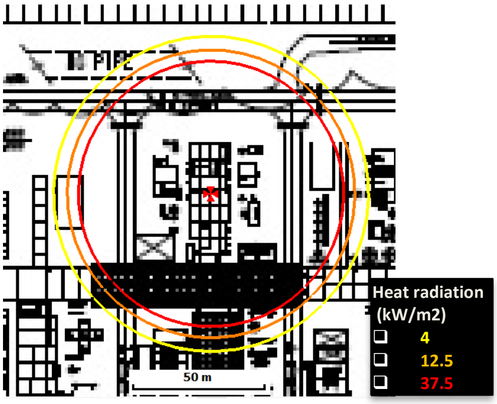

Figure 10: Jet fire radiation contour for scenario 1

Scenario 2: Presence of popcorn polymer propagating in condenser developing local fouling at a weak point of the tube sheet or shell wall, rupture occurs resulting in loss of containment and possibly leading to fire or vapour cloud explosion.

- Failure Mode: mouth fish crack due to popcorn propagation exerting stress on the shell side. The crack would be more than 10” long
- Release rate: 408 kg/s
- Energy released due to blast: 4.2E9 J
- Event probability: 10E-3
- Risk evaluated: An explosion can cause multiple fatalities with a likelihood of with a probability of 10E-3
- Figures below are illustration of the consequence analysis.

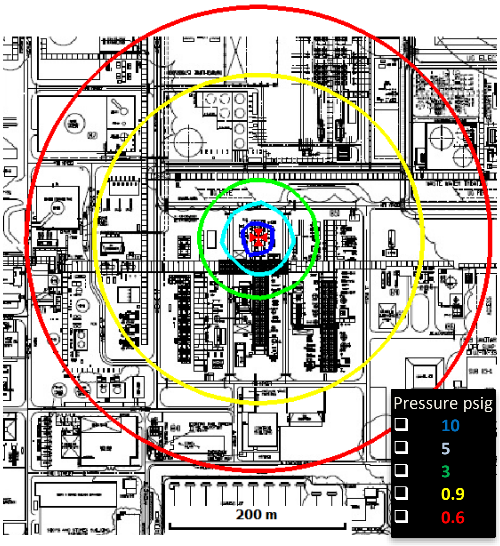

Figure 11: Blast contour for scenario 2

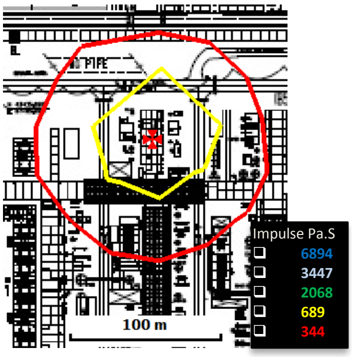

Figure 12: impulse contours for scenario 2

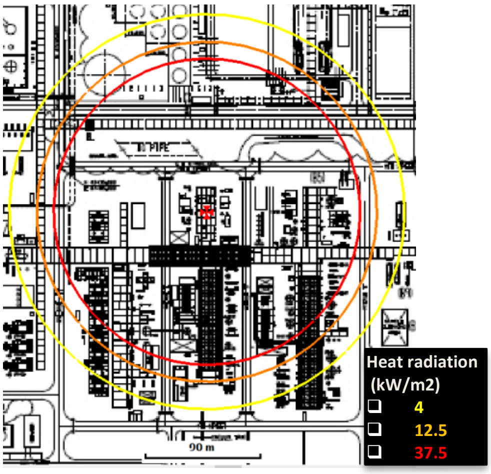

Figure 13: Jet fire radiation zone for scenario 2

The heat radiation emitted from fire or overpressure blast created by vapor cloud explosion can be fatal as detailed in section 1.2 and 1.3.

Resolution strategy

To ensure effective risk mitigation, a major plant modification was executed by constructing a new process line that bypasses the debutanizer tower and sends the material to the flare. The project execution was remarkable as it was completed in about a week. 15 tons of C4 was flared per hour. This, however, allowed the olefins unit to mitigate the risk effectively without any interruption of the production. The change was not done before in the local industry, and it reflected how effective measures can be taken to mitigate risk through strong leadership and excellent engineering. Interim mitigations, moreover, were in place until the modification was completed: for example, inhibitor injection in the exchanger to inhibit the popcorn formation as soon as possible, and an emergency procedure in case loss of containment. Without the effective mitigation, Sabic operation team would have had to shutdown the olefins unit for over 2 months. This olefins unit feeds two poly ethylene that would shutdown consequently, causing significant losses over the mentioned period. New exchanger was manufactured and installed subsequently.

Time Line

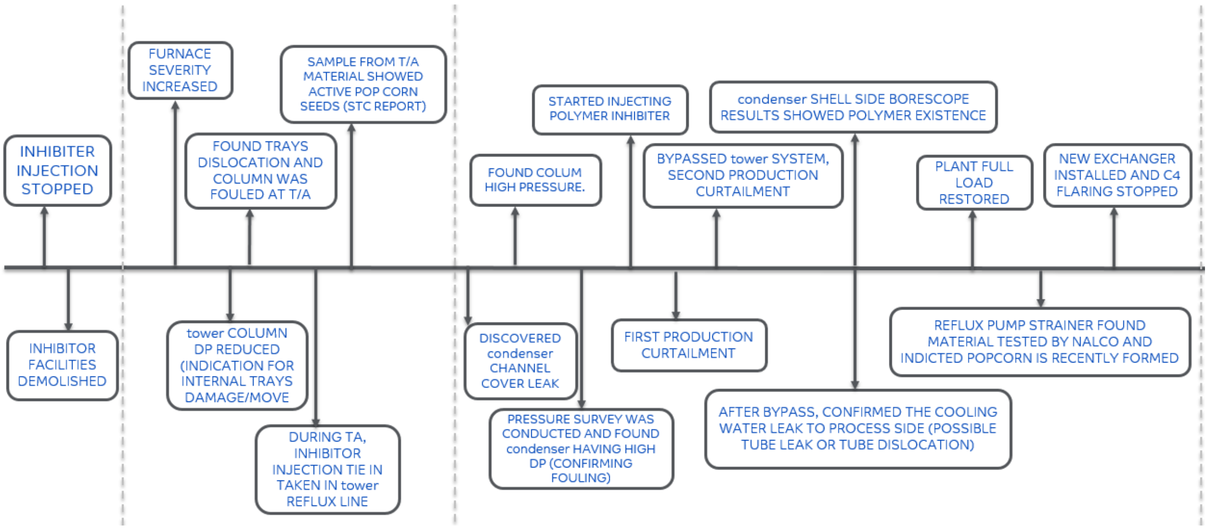

Figure 14. Incident timeline.

Incident investigation

The following were key findings in the investigation:

- Popcorn inhibitor injection was stopped at 2005 and facilities demolished at 2012. No safety assessment performed either during stoppage or through Management of change. In addition, at least two re-do hazop conducted that did not address inhibitor requirements
- 2006 condenser borescope inspection found the shell clean with yellow deposits on outside tube surface
- Since 2015, higher butadiene concentration exist due to higher propane furnaces conversion to cope with the additional feed allocated. Inhibitor tie in’s re-constructed at 2017 turn around but actual inhibitor injection started at July 2018 after the realization of popcorn formation.
- Found debutanizer column delta pressure reduced (indication for internal trays damage/movement)
- Inspection found trays dislocation and column was fouled at 2017 turnaround
- Sample from 2017 turnaround material showed active popcorn seeds
- After condenser bypass, cooling water leak from tube to process side was found
- Shell side borescope results showed polymer existence

Conclusion

Proper management for light end systems are essential to prevent butadiene popcorn formation. Changes around critical systems have to be accurately reviewed to avoid introducing risk to the process. For old plants, best practices issued, for example by EPCC, need to reviewed and evaluated for their feasibility. Process hazard analysis/HAZOP studies shall consider the popcorn scenarios for proactive approach to avoid high risk operation. Services which are prone to having popcorn formations should have adequate inspection strategy and not be overlooked. Management has an important role to lead by example, and intervene when necessary to mitigate risks found. Creative solutions, moreover, shall be encouraged as they are available and effective but often dismissed. Qualitative risk assessments sometimes undermine risks found; therefore, semi quantitative approach and dispersion models are recommended for potential flammable releases as they provide distinct insight of the evaluated condition. Consequence analysis conducted for butadiene release shows that such potential incident can result in severe consequence to the people, environment, and asset. All of this require high competency and knowledge of popcorn formation phenomena and management across organizations, as without it, none will be achievable.

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Credit

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