

## Process Safety Improvement of an Olefins Plant – from the Hazard Analysis to Implementation and Start-Up

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Shell operates a lower olefins unit at its petrochemical refinery in Wesseling, Germany. The unit was built in the 1970ies and required debottlenecking to increase its capacity. For this it was necessary to check and upgrade the process safety equipment. The key items listed below illustrate the magnitude of the project:

- More than 30 new heat exchangers due to a higher duty requirement and partly due to vibration issues
- More than 400 new sensors
- A two-digit number of new safety instrumented functions (“tripping functions”)
- More than 40 re-designed relief valves
- A new flare line DN600 about 100 m long
- During the execution phase of the project more than 1000 craftsmen and more than 10 cranes were in active in the field

Three topics will be discussed here:

- New relief valves and a new flare line to deal with the flare backpressure issue during a total power failure
- The redesign of a heat exchanger, which was subject to vibration
- The process safety improvement to protect against the runaway in a selective hydrogenation reactor

The selective hydrogenation reactor is adiabatic and the reactions (hydrogenation of Acetylene) are exothermic. Low flow through the reactor leads to temperature increase which in turn starts secondary reactions that generate excessive heat. In confined sections of the reactor bed, this could cause significant temperature excursions and further reactions (polymerization). These localised temperature excursions, so-called “hot-spots,” are a threat, especially if the formation occurs close to the reactor walls. The new safety approach included the installation of 8 temperature sensors per reactor-bed and a new safeguarding concept with emergency depressurization.

However, starting up the newly equipped reactor with fresh catalyst was a challenge.

### 1. Introduction

Insights gained from the investigation of major industrial disasters like

- Flixborough 1974 (UK Department of Employment 1975)
- Seveso 1976 (Fuller 1977)
- Three Mile Island 1978 (Nuclear Safety Analysis Center 1980)
- Bhopal 1984 (Donaldson 2014)
- Texas City 2005 (Hopkins 2012, U. S. Chemical Safety and Hazard Investigation Board, 2007)
- Deep Water Horizon 2010 (Hopkins 2012)

drive regulators and society (EU 2012) to demand continuous process safety improvements.

Documented standards for the design of process safety equipment (e. g. API 2008, API 2014, ISO 2006, ISO 2013) and methods for identifying the process safety hazards (e. g. Bock and Haferkamp 2015, IEC 2016) provide the tools for the operators and designers to fulfill these demands.

This paper will explore the development, implementation, start-up of three improvements in more detail.

## 2. New relief valves and flare line to deal with total power failure

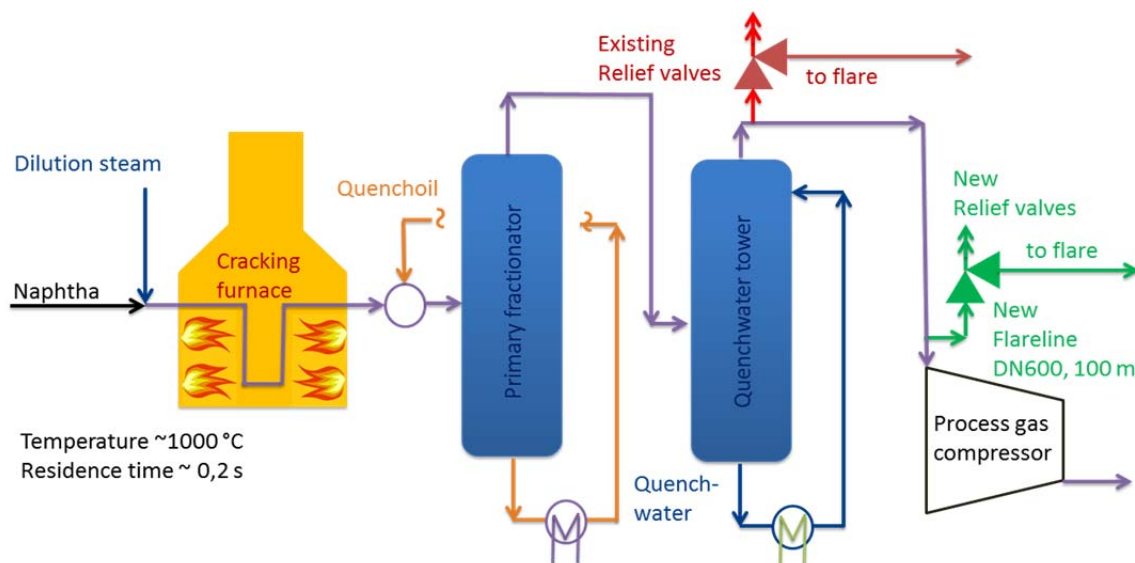


Figure 1: Simplified flow scheme of the cracking furnace and the quench section

Figure 1 shows a simplified scheme of the “hot section” of an olefins plant. The feed (Naphtha) is mixed with dilution steam (hence the word “steamcracking”) and pyrolyzed in a cracking furnace to form mainly Hydrogen, Methane, Ethylene, Propylene, Butadiene, Butenes, and pyrolysis gasoline. The hot furnace effluent is passed through a steam generator, in which high pressure steam is generated. This reduces the temperature and stops the cracking reaction. Then Quenchcoil is injected into the furnace effluent to cool it down further and to condense the heavy fraction. In the primary fractionator the heavy fraction of the furnace effluent is separated by distillation. In the Quenchwater tower the gasoline fraction is separated from the furnace effluent. The overhead vapors from the Quenchwater tower, which are comprised of light gasoline and gases mentioned above, are then compressed by the process gas compressor and sent for further treatment.

The “hot section” shown in Figure 1 is operated at relatively low pressures (slightly above ambient). The safeguard against overpressure is a battery of large relief valves located between the Quenchwater tower and the suction side of the process gas compressor. A major amount of energy (“heat”) is recovered from the furnace effluent in several heat exchangers. The main heat sinks are the Quenchcoil and Quenchwater loops. These loops are maintained using pumps to circulate the liquid through several heat exchangers (steam generators, air coolers, cooling water coolers). These heat exchanges (depicted for simplicity in Figure 1 as a single exchanger) remove the energy from the effluent which was absorbed in the furnace.

Total power failure is a relevant (and quite often governing) scenario for the design of the relief valves (API 2014). In the event of such a failure all rotating equipment stops. This means no energy/material is removed anymore, because

- the Process gas compressor stops sucking the gas from the hot section
- the Quenchcoil stops circulating and condensing heater effluent
- the Quenchwater stops circulating and condensing heater effluent

Some safety functions are activated, which

- trips (closes) the fuel gas to the furnace
- trips (closes) the hydrocarbon feed (Naphtha) to the furnace

However, the refractory of the cracking furnace is still very hot and radiates heat to the tubes in the firebox of the furnace. The tubes need to be cooled. To do this, the dilution steam control valves are fully opened to deliver a large amount of dilution steam to the cracking furnace.

The dilution steam cannot condense as the Quenchwater has stopped circulating. Since the dilution steam pressure is significantly higher than the design pressure of the primary fractionator and the Quenchwater tower the pressure in the hot section increases until the relief valves open and relief to flare.

Further, due to the total power failure, many other relief valves in the same unit open and relief gas to the flare header. Substantially, this results in backpressure (pressure drop) in the flare system, which impedes the flow

of gas from the hot section through the open relief valves. The primary fractionator and the Quenchwater tower would be over pressured.

To avoid this, a battery of new relief valves (green in Figure 1) and a new flare line of considerable diameter (600 mm) and length (about 100 m) were installed.

### 3. Redesign of a heat exchanger due to vibration issues

A lower olefins plant is a gas plant with many heat exchangers. There was “capacity creep” in the past decades, i. e. numerous smaller capacity expansions. As part of the capacity expansion project described in this article several heat exchangers were checked for their thermal and hydraulic capacity. More than 30 shell-and-tube-heat exchangers were replaced – most of them to supply higher duties.

However, some heat exchangers needed to be replaced due to flow induced vibration of the tubes.

Tube vibration mechanisms in order of their increasing severity are turbulent buffeting, vortex shedding and fluid elastic instability. Excessive tube vibrations caused by turbulent buffeting or vortex shedding resonances can result in thinning and eventual failure of tubes at the baffles or leaks at the tube-to-tube sheet joints. Fluid elastic instability tends to have a run-away effect; once cross-flow velocities approach a critical value the tubes may vibrate uncontrollably and can fail very rapidly (API 2015).

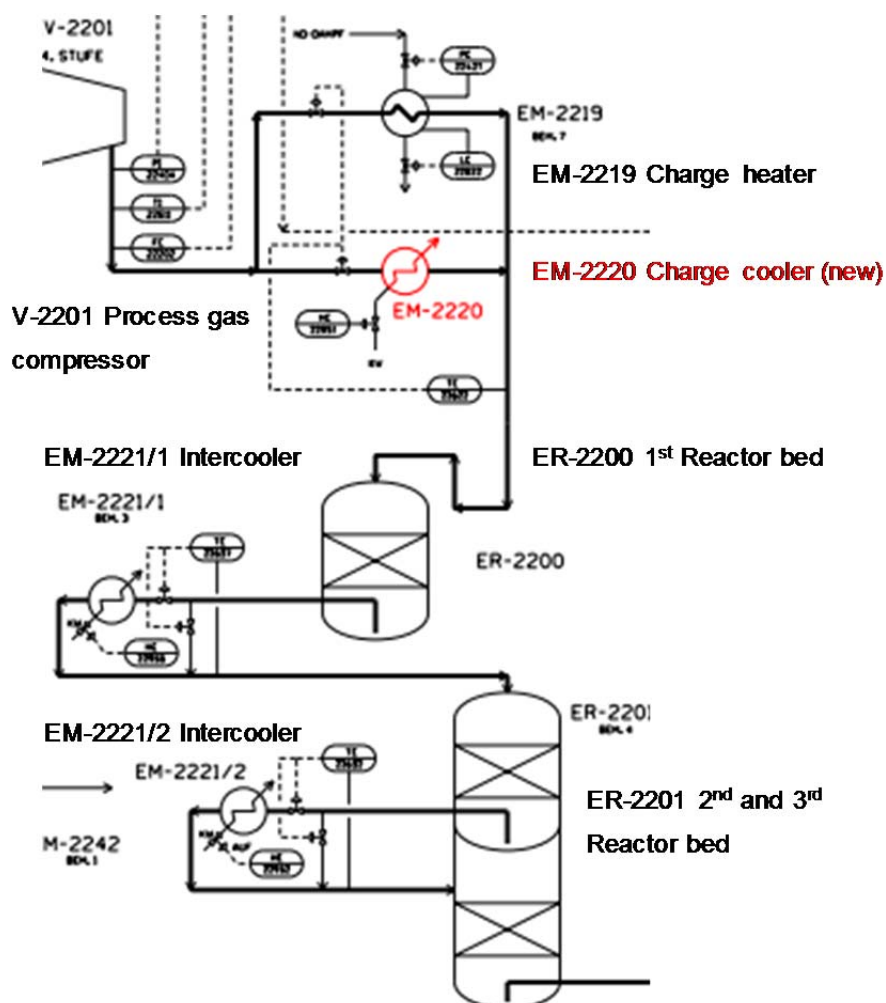


Figure 2: Simplified flow scheme of the acetylene reactor and the charge cooler EM-2220

The heat exchanger under consideration here is the charge cooler to a selective hydrogenation reactor EM-2220 (TEMA Type BJM, fixed tube sheet) shown in red in Figure 2. This cooler is on the discharge side of the process gas compressor. The capacity expansion resulted in a higher gas flow that causes vibration. Therefore, the decision was taken to replace this heat exchanger. The new heat exchanger was designed to handle the duty during normal operation.

However, the determining duty requirement of this heat exchanger was the start-up of the selective hydrogenation reactor (see Figure 2) with a fresh catalyst. Thus, making the new heat exchanger significantly smaller than what was required.

The vibration issue of this heat exchanger was resolved, but a new problem was created – How to start up the reactor with the fresh catalyst, when the feed is too hot?

#### 4. Process safety improvement of a selective hydrogenation reactor

Exothermic runaway reactions haunt the industry ever since (Bundesanzeiger 2012, Dutch Safety Board 2015, Fuller 1977, U. S. Chemical Safety and Hazard Investigation Board 2007) and have triggered legislation – “Seveso directive” (EU 2012).

The flow scheme of the selective hydrogenation reactor, which will be examined in the following, is shown in Figure 2.

The process gas contains Hydrogen, Methane, Acetylene, Ethylene, Ethane, Propyne (Methylacetylene), Propadiene, Propylene, and Propane.

The unwanted alkynes (mainly Acetylene) are selectively hydrogenated in the three adiabatic beds of the reactor ER-2200 (1<sup>st</sup> bed) and ER-2201 (2<sup>nd</sup> and 3<sup>rd</sup> bed).

The temperature and thereby the selectivity of the reactor beds is controlled using split range controllers for each bed. Charge heater EM-2219 and the charge cooler EM-2220 are located upstream of the first bed ER-2200. The EM-2220 caused impediment to the process through the significantly reduced area resulting from the erroneously sizing this heat exchanger for normal operating conditions (see 3. Redesign of a heat exchanger due to vibration issues). The intercoolers EM-2221/1 and EM-2221/2 downstream of the first and second bed were both equipped with a bypass to control the temperature of the feed to the next bed. The heat of reaction of the main selective hydrogenation reactions are summarized in Table 1.

The heat of reaction of the side non-selective hydrogenation reactions are summarized in Table 2.

All these reactions are strongly exothermic. Hydrogen is the limiting reactant, but according to the reactions shown in Table 1 and Table 2, the reaction of all the hydrogen leads to such a high temperature, that oligomerization or polymerization reactions (see Table 3) start and lead to a temperature, that would be above the design temperature of the reactors ER-2200 and ER-2201. This is called reactive runaway.

Table 1: Main reactions in the Acetylene reactor

Main reactions = selective hydrogenation	Heat of Reaction
$C_2H_2 + H_2 \rightarrow C_2H_4$	-164 kJ/mol
$C_3H_4$ (Propyne, “Methylacetylene”) + $H_2 \rightarrow C_3H_6$	-165 kJ/mol
$C_3H_4$ (Propadiene) + $H_2 \rightarrow C_3H_6$	-171 kJ/mol

Table 2: Side reactions in the Acetylene reactor

Side reactions = non-selective hydrogenation	Heat of Reaction
$C_2H_4 + H_2 \rightarrow C_2H_6$	-137 kJ/mol
$C_3H_6 + H_2 \rightarrow C_3H_8$	-124 kJ/mol

Table 3: Polymerization in the Acetylene reactor

Polymerization at high temperatures	Heat of Reaction
$n * C_2H_4 \rightarrow \text{Polymer } (C_{20}H_{40})$	-107 kJ/mol

Since the reactor is adiabatic, a disruption of the process gas flow interrupts the heat removal from the system and leads to a temperature rise and ultimately a reactive runaway.

The original instrumentation consisted only of temperature sensors at the inlet and outlet of the reactor beds.

Therefore, the onset of a reactive runaway inside one of the beds could only be detected if there is flow.

Moreover, the formation of local hot spots (local runaway) in the reactor bed could not be detected.

To control these reactive hazards, the following new safety instrumented functions were installed:

- 2 new flow measurements between compressor discharge and inlet 1<sup>st</sup> bed to detect the stop of the flow
- 8 new temperature measurements per reactor bed distributed inside each bed to detect hot spots
- Automatic isolation and depressurization of each bed, if low flow or high temperatures are detected.

Figure 3 shows the support grid inside each reactor. The support grid for the temperature sensors rests on the support grid for the mesh in the bottom part of the reactor. The temperature sensors (orange lines right picture Figure 3) are introduced into the reactor through a special flange and fixed to the support grid. These support grids were used, because otherwise supports would have to be welded to the inside of the reactor. This was to be avoided, because welding on a pressure vessel entails extensive inspection.

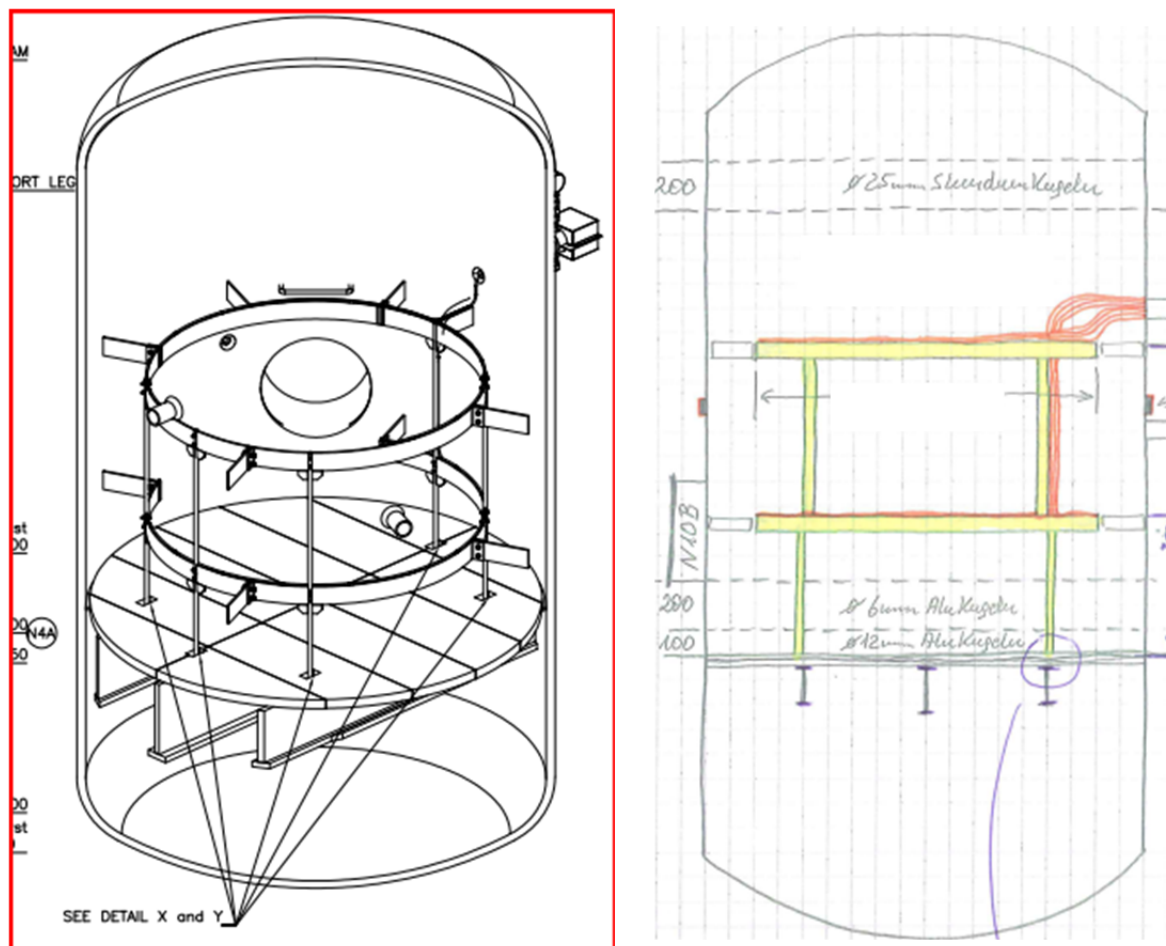


Figure 3: Grid to support the new temperature measurements inside the reactor bed

## 5. Start-up

The combination of a charge cooler EM-2220 (see 3. Redesign of a heat exchanger due to vibration issues) with an insufficient area/duty, a fresh catalyst in the Acetylene reactor, and the newly introduced temperature measurements inside the reactor beds made the start-up of the Acetylene reactor a challenging undertaking. In the same year in the same company a major accident happened during start-up of a reactor (Dutch Safety Board 2015).

High expectation from customers to deliver products to them, put additional pressure on the start-up team. Ultimately, the Acetylene reactor was started up successfully.

## 6. Conclusions

Regulators and society (EU 2012) demand continuous process safety improvements. The designers and operators have a plethora of knowledge, standards and tools at their disposal to improve the process safety of their facilities.

Three practical examples for real world process safety improvements were discussed in this article. If the tools and methods for designing new process safety equipment are used properly and the pitfalls - like sizing the charge gas cooler for normal operation - are avoided, process safety improvements can be implemented and commissioned successfully.

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