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How Reactive Hazard Assessment and New Reactor Internals Improve Safety at the Shell Rhineland Refinery

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Shell operates at its refinery in Cologne three reactors for the selective hydrogenation and desulfurization of a Pyrolysis gasoline stream (Pygas/C5 to C11), using a Ni-based catalyst. The hydrogenation reaction to saturate di-olefins and olefins taking place in these trickle flow reactor-beds is highly exothermic. Part of the hydrogenated liquid stream and unused hydrogen is recycled to the inlet of the reactor, to quench and regulate the temperature in the catalyst bed. A Reactive Hazard Assessment indicated that further improvements could be implemented to mitigate the risk to As Low As Reasonably Practicable (ALARP). Loss of liquid-recycle or hydrogen recycle or maldistribution of the liquid/gas hydrocarbon flow through the reactor lead to temperature increases which in turn can facilitate secondary chemical reactions that generate excessive heat. The heat formation can cause substantial local temperature excursions and subsequent runaway reactions (coking, polymerization). Localized temperature excursions, so-called “hot-spots,” are considered a threat, especially if this formation occurs close to the reactor walls, because it increases the probability of vessel rupture and loss of containment. Several corrective measures were determined that will mitigate these risks. The new and innovative safety approach includes a redesign of reactor internals with new distributor-trays based on extensive research, the installation of over 20 temperature sensors per reactor-bed, a new safeguarding concept with low-rate emergency depressurization and measures to ease safe maintenance and construction. At the same time, the new customized ‘Shell’ reactor internals significantly improve the performance of reactors. The modifications will be installed at the turnaround between June and November 2018. In addition to the above, lessons-learned from the implementation and the start-up of the four reactors will also be included in the presentation.

1. Introduction

Shell Rheinland is the largest refinery in Germany. It is located on two different sites which are connected by a pipeline under the rive Rhine. The refinery includes two hydrocrackers, two visbreakers, various aromatic units, and an olefins unit. It processes approximately 17 million tons of crude oil per year into a range of products such as diesel, petrol, heating oil, naphtha and base chemicals.
The refinery operates several reactors in which undesired side reactions might take place that can potentially lead to hazardous situations. These reactive hazards, defined as any chemical reaction leading to large and rapid increases in temperature and/or pressure, must be assessed to protect people, the environment and Shell’s assets and reputation.
In the past years Rhineland Refinery has via a process safety improvement program assessed the consequence of reactive hazards, with focus on runaway reactions and chemical incompatibilities.
Shell uses a management process to identify, assess and mitigate risks in a structured manner to a level “As Low As Reasonably Practicable” (ALARP). The process consists of hazard identification, assessment and risk determination. Its purpose is to verify that necessary hardware and human interactions are in place to manage risk and that all hardware is operated and maintained correctly.
The hazard analysis process to verify ALARP takes the type of hazard and the associated risk or consequences into account. Several tools are available like Hazard and Operability Studies (HAZOP), Risk

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Oriented Hazard Analysis (ROGA) (Bock F-J, Haferkamp K, 2015) or Process Hazard Analyses (PHA). A RHA is normally used in addition to a HAZOP or ROGA if reactive hazards have been identified.

1.1 Hydrotreating Process

The Pygas Hydrotreater is a three-reactor system that processes pyrolysis gasoline (pygas) with the purpose of hydrogenating olefins and diolefins, removing sulphur and nitrogen containing compounds, as well as producing a C6/C7 hydrocarbon blend to be used as a high-value aromatic feed stream. A general overview is given in figure 1. The first two reactor trains, or first-stage hydrotreaters are operated in parallel to hydrogenate the diolefins and alkenyl-aromatics. Upon entering the first stage hydrotreaters, the liquid feed, liquid recycle, fresh hydrogen and hydrogen recycle are mixed and distributed on top of the catalyst beds using dispersion trays. Due to the low reaction temperatures the reactors operate in the trickle flow regime. The reaction runs with excess hydrogen and the reactor temperature is maintained with the exothermic reaction heat. The stream existing the reactor is routed to a set of separation drums, where excess hydrogen and light components flash off the top, and liquid exits the bottom. The hydrogen rich vapour stream is recycled back to the reactor inlet and lighter C4s are removed from the reactor train. A portion of the liquid is cooled and pumped back to the reactor, while rest of the liquid is routed to the third reactor train, or second stage hydrotreater (SSHT). The gas and liquid recycle are critical to ensure the exothermic reaction heat/reactor temperature are controlled. Between the first- and the second-stage hydrotreater, a series of distillation columns is used to separate the lighter (C5) and heavier (C7+) hydrocarbons. The C6-C7 heart cut is sent to the SSHT where the sulphur and olefin content is reduced, while minimizing aromatic saturation. The reactor contains three catalyst beds with a quench between each bed. There are two reactors, A and B, operated alternately. One of the particularities of the SSHT reactor train is the presence of a fired heater downstream of the reactor. The heated stream is cooled by the reactor feed stream, in the reactor feed/effluent exchangers, before it is flashed in the separator system. Part of the liquid recovered is then recycled back to the first inter bed of the reactor. The hydrogen rich steam from the separators is recycled back to the second interbed of the reactor. This is used to maintain hydrogen partial pressure as well as to keep the exothermic reactions under control. The emergency depressurisation valve is located on the hydrogen recycle line. The remaining hydrogen rich vapour is taken from the separator overhead and returned to the refinery fuel gas system while regulating the pressure in the system. The liquid phase leaves the system as a product via the stabilizer column.

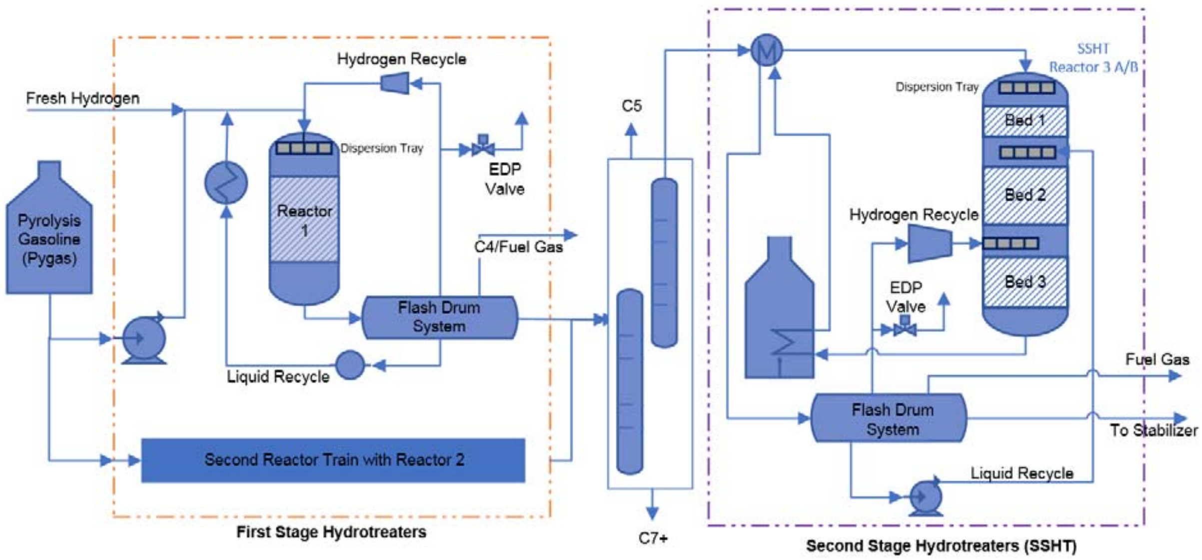

Figure 1: Process overview of Pygas Hydrotreater system

1.2 Reactive Hazard Assessment (RHA)

Many chemical reactions produce heat and have risks associated with reactive hazards. Reactive hazards have contributed to some major industrial incidents, e.g. the Texas City SS Grandcamp ammonium nitrate explosion in the USA in 1947, the toxic gas leak in Bhopal, India, in 1984 which resulted in more than 1,000

fatalities, and more recently the explosion in Shells Moerdijk SMPO Hydrogenator in 2014 (Dutch Safety Board, 2015) resulting in extensive damage and two contractors injured with burns.
Reactive hazards are chemical reactions that can lead to large and rapid changes in temperature and/or pressure. The definition of a reactive hazard does not include flammability or combustibility.
There are two general types of reactive hazards (Urben, 1999):

1. Runaway reactions: A runaway reaction occurs when an increase in temperature leads to an increase in the reaction rate, which leads to a further increase in temperature and, therefore, a further rapid increase in the reaction rate. Consequently, a runaway reaction will lead to a thermal explosion or a release of the vessel contents. Examples are styrene polymerisation, hydrocracking runaways, ethylene oxide decomposition, isocyanate reacting with water (Bhopal) or ethyl benzene reacting with unreduced copper chromite catalyst (Moerdijk SMPO Hydrogenator explosion).
2. Chemical incompatibilities: Here two incompatible components react exothermically. The reaction that takes place between an acid and a base is an example of a chemical incompatibility.

The heat of reaction in manufacturing processes is normally controlled through adequate cooling and/or through limiting the flowrate of reactive material (e.g. using flow control) or adjusting the concentration of the reactive material (e.g. by dilution). If the heat of reaction is not controlled, it leads to a pressure rise by either increasing vapour pressure and/or gas generation.
To understand and mitigate the reactive hazards of a system, Shell uses the Reactive Hazards Assessment (RHA). The tool helps to describe reactive hazards in chemical processes, identify potential events, characterize risks, and propose modifications to reduce the risk of hazardous events to tolerable levels.
The RHA work process has five steps (Donkers-Dijken et al., 2004):

1. Process Description: Understand in detail the process and conditions and all chemical components and their quantities that might be present in the process as part of feed streams, products, impurities, utilities or in-situ due to construction materials, catalyst or other conditions. Incompatibility and flammability data of all material present in the process will be listed.
2. Reactive Chemistry: Execute a detailed expert review and list all reactions and reactive conditions that could lead to runaway reactions. Understand any chemical incompatibilities that might be present. This includes understanding the process chemistry of runaway reactions.
3. Scenario Identification: Determine unit upsets and credible pathways that could develop into runaway hydrocracking reaction. Existing safeguarding and mitigation are not taken into consideration at this stage to ensure thorough scenario identification.
4. Scenario Assessment: Determine which of the identified scenarios need prevention or mitigation. All scenarios are evaluated to determine the consequences, especially pressure and temperature. These results are then compared to relevant design specifications of the equipment (i.e. design pressure and design temperature).
5. Development of Safeguards: Assess the likelihood of the scenarios by using a Layers Of Protection Analysis (LOPA) to determine if ALARP criteria are met. Existing safeguarding and mitigations are considered at this stage and for the scenarios that did not meet the ALARP criteria, mitigating measures are recommended to close gap and demonstrate ALARP.

2. RHA findings for Pygas Unit and Risk Mitigation

The RHA conducted on the four reactors in the Aromatic Unit identified opportunities for further risk reduction which did not meet ALARP criteria. Process upsets such as loss of hydrogen recycle, loss of liquid-recycle, hotter than normal feed to reactor and abnormal feed compositions or temperatures were taken into account for the assessment. Other situations considered in the scenario identification included anomalies during catalyst loading, wetting and activation and hotspot formation close to the reactor walls. The study concluded that the reactors were currently insufficiently equipped to detect temperature excursions and to timely prevent escalation and runaway.
Investigation of the existing reactor internals and set-up as well as past unit experience showed the potential for high pressure drop, bed fouling, thermal-maldistribution and reliability issues.
It should be noted that, in addition to the reactive hazard evaluation other process safety analysis tools such as HAZOP were also used to systematically assess the process threats such as blocked outlets, unintended valve opening, loss of cooling, high heat or pressure generators which could lead to over pressure and over temperature.
The following measures were implemented to mitigate the deficiencies:

- Upgrade of the reactor bed thermocouple arrays to provide radial temperature monitoring

- Installation of new instrumented automatic low-rate depressurization functions to remove reactive substances from the system
- Installation of high dispersion (HD) trays and Ultra Flat Quench (UFQ) for optimal, even flow distribution and mixing, thereby reducing the likelihood of hot spots

2.1 Reactor Internals

The site installed the latest generation SHELL reactor internals such as HD trays, Ultra-Flat Quench (UFQ), Scale Catching trays, catalyst support grids and bottom baskets.
Previously the reactors had been using conventional distribution trays leading to low uniformity of vapour-liquid distribution and undesirable radial temperature maldistribution. The customised nozzles of the HD trays, use the gas flow momentum to disperse the liquid as a mist. Unlike all existing distributor trays in the industry, the nozzles uniformly wet the entire catalyst surface and make efficient use of the upper layers of the catalyst bed. High-dispersion, which achieves near-perfect wetting of the catalyst right at the top of the bed enables an ultra-uniform utilisation of the catalyst and minimises radial temperature differences. After installation, the radial temperature difference at top of the bed was less than 1K. Above the HD tray is an anti-fouling abatement with highly efficient scale catching and filter elements which reduce the pressure drop over time.

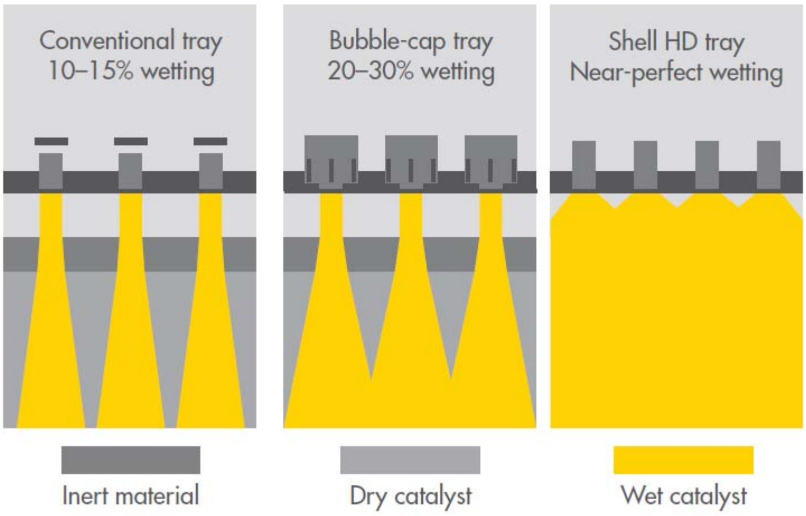

Figure 2: Comparison of conventional and HD trays

The wire mesh catalyst support grids panels were also obsolete. They required significant maintenance and confined space residence time during turnarounds and increased the risk of catalyst migration. The solution was to replace the wire mesh panels with latest-generation SHELL catalyst support grids. These feature a wedge-wire screen construction to help prevent catalyst fall-through and resists fouling. Wedge wire offers key advantages compared with wire mesh. There is almost no fouling as the V-shape of the wire means that it is self-cleaning. Moreover, as there are no loose layers of wire mesh, no overlay for the wire-mesh pads and no knitting is required. Wedge wire also lasts up to five times longer than wire mesh.
In addition, the installation of ultra-flat bottom baskets and reactor internal skirts minimised the required inter-bed spacing and hence maximised the catalyst bed utilisation and volume.
The installation of HD trays allowed to convert one of the reactors from a three bed to a one bed design. This had economic advantages as it reduced the number of installed parts and at the same time made the installation easier (McFarland et al., 2018) Through the use of wedge pins and split keys for the assembly, the new reactor internals can be mounted and removed using just a hammer. This eliminate the need for cutting and welding during construction and makes catalyst loading and unloading faster as well as servicing later-on much easier. There are now fewer inter-bed manway panels to open and close. It is expected to cut the time required for shutdowns in the unit by about four days (Shell Global Solutions, 2016). In addition, there are safety advantages because the SHELL reactor internals reduce the time required for confined space entry by 50% as they are quicker to open, clean, inspect and close. The internals' manways are also larger and allow for the quick egress of people, therefore increasing personnel safety.

2.2 Temperature Sensors and low-pressure depressurization

The previous thermometry system was unreliable. Each reactor had been fitted with two old-fashioned vertical thermobars enabling temperature measurements only at locations near the reactor wall of each catalyst bed. Moreover, due to the low number of temperature measurement points in each bed, the existing sensors could not be used to detect undesirable flow patterns. To resolve this and to ensure the detection of potential hotspots, the revamp team implemented a major upgrade.

The reactors only had a few free nozzles for the insertion of 20-50 thermocouples. Welding additional nozzles was no option, because it could cause cracks in the reactors' interior lining. The issue was solved by replacing the existing thermobars with multiple state-of-the-art flexible thermocouples. These thermocouples enable both radial and axial coverage that is in line with the latest design guidelines on tight, hydrocracking bed temperature control and extensive temperature monitoring. In addition, the plant's distributed control system and safety-instrumented system were upgraded to collect and process the information from the sensors. This provides now both site operations and technologists with more robust automatic temperature control and with software tools to identify early indications of temperature instability or maldistribution. On detection of too high temperature the thermocouples will automatically initiate a reactor shut-down by opening the emergency depressurization (EDP) valve to flare to disposal of the reactor inventory, and thus ensuring remedial actions in a timely manner. Also, all feed sources and heat inputs to the reactor will be shut-off, while maximizing any available cooling.

The temperature sensors in each reactor bed were designed to form a 1ooX trip function sending the reactor into depressurization if activated. With 20-50 sensors in each reactor, it is necessary to ensure no spurious trips are activated. This is achieved by distinguishing the source of peak readings/inputs for all thermocouples. In case of loop failure, an internal fault in the transmitter or a fault caused by an open/short circuit in the transmission wires, the signal moves outside a specified mA range. Faulty signals can be recognised, and spurious trips avoided by overriding these transmitter/loop failure or transmitter faults. This functionality in combination with selecting reliable thermocouples has brought the rate of spurious trips in line with latest standards.

3. Project Execution and Learnings

The reactors are the key component of the aromatics unit. The refinery which led the preparation and execution phases, was closely supported by Shell Global Solutions. During the turnaround many contractors worked on-site engaged in numerous activities in a highly congested area.

The execution strategy included the following key elements:

- Adopting successful practices from other sites: Because Rhineland's experience with projects of this type was limited, it actively sought out best practices and key lessons from other refineries. It visited other sites and learned from their projects.
- Highly skilled team: Rhineland refinery and Shell Global Solutions formed a highly qualified and experienced, multidisciplinary team and acknowledge Daily Thermetrics, and Mourik did the same.
- Highly experienced contractor: Shell Global Solutions proposed construction contractors that had experience of similar projects. Rheinland refinery evaluated track records and technical capabilities and paid special attention to the contractors' leadership teams knowing that this would drive the success of the project. A mixed team of people with experience working in Rheinland refinery and others who had experience in this type of rector revamp, was selected for the job.
- Building reactor mock-ups: During the turnaround window, the reactor internals had to be assembled inside the four reactors. By building reactor mock-ups beforehand, the contractors had the opportunity to practice the assembly offline. The contractors repeated this assembly until they were confident that they could install the new hardware safely and efficiently during the turnaround window.
- Detailed execution plan: The execution plan addressed all the activities that had to be carried out in the reactors during the turnaround window and helped to ensure alignment with other activities planned in the same area.
- Scope optimisation workshop: Through this activity Shell Global Solutions, Rheinland refinery and the execution contractor challenged the scope and optimised the duration for many tasks and the execution plan. The workshop also helped to ensure that nothing had been missed.
- Clear interfaces: Establishing clear interfaces with the contractors who were working in the same area for other projects, ensured that all activities were aligned; supporting each other versus creating bottlenecks.

- Readiness assessment review: A different Shell team took a fresh look at the preparation work to confirm that the project was ready to be implemented. This help to verify that all critical work had been prepared well and if existing would have flagged outages.
- Performing risk assessments for every critical activity: To ensure that all critical activities would be executed safely without creating undue risks to people or the environment, risk assessment were performed. Though the primary objective is to protect people and the environment, it also helped to warrant incidents would not jeopardize the tight installation schedule.

Because of the extensive preparation, the team gained on its schedule during the shutdown and was able to hand over the unit for start-up in-time with an excellent safety record. Great teamwork was a key factor in the success of this project. There was high-quality interaction between the all parties that enabled the project to benefit from the refinery's site-specific knowledge and the licensor and catalyst supplier's global operational and technical expertise.

4. Conclusions

An RHA is a proven approach to go beyond the standard process safety tools like HAZOP which in many cases will not deeply enough look at the risk of chemical reactions of process components among each other or with construction materials. Reactive hazards due to runaway reaction and chemical incompatibilities can pose a significant and often underestimated or insufficiently investigated risk. An RHA delivers additional perspective and addresses reactive hazards which might be otherwise overlooked.
An example of risks only revealed through an RHA, are runaway reactions in hydrogenation reactors at the Shell Rheinland refinery. Once identified through the RHA, the risks could be mitigated by new reactor internals in combination with thermocouples and an appropriate control system. In addition, the measures improve the safety of personnel and minimise the required downtime for future turnarounds.

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