Catalytic Processes
Process Safety Requirements

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Introduction

- Research started following the explosion at an SM/PO plant which happened in June 2014.
- Video « Onderzoeksraad voor Veiligheid »
- Review of incident database specific for catalytic processes.

Definitions : Introduction to Reactor Design

The reactor/catalyst is the heart of the process:

- It may be endothermic or exothermic or have little heat effect.
- It determines the separation processes required downstream:
  - Low conversion means large recycles.
  - Low selectivity means additional separation units.
- Take into account deactivation of catalyst during runtime in design:
  - Define Start of Run conditions (SOR)
  - Define End of Run conditions (EOR)

Catalyst Design : Generic features (1/2)

How is a catalyst prepared (generic) :

- Precipitation / impregnation
  - e.g. $Na_2CO_3 + NiCl_2 \rightarrow NiCO_3 + 2\ NaCl$
- Washing and drying
  - Removing solution material + excess of water.
- Calcining: Carbonate or nitrate is reformulated to oxide (e.g. with air)
  - e.g. $Ni(NO_3)_2 + O_2 \rightarrow NiO + (NO + NO_2)$
  - e.g. $NiCO_3 + O_2 \rightarrow NiO + CO_2$

Catalyst Design : Generic features (2/2)

How is a catalyst prepared (generic) :

- Calcining is necessary to obtain a more robust catalyst for the next step in process.
- Rating a “shape” of catalyst: by extrusion and/or tabletting.
- Activation of catalyst.
  - e.g. $NiO + H_2 \rightarrow Ni + H_2O$

Two options : ex situ or in situ activation

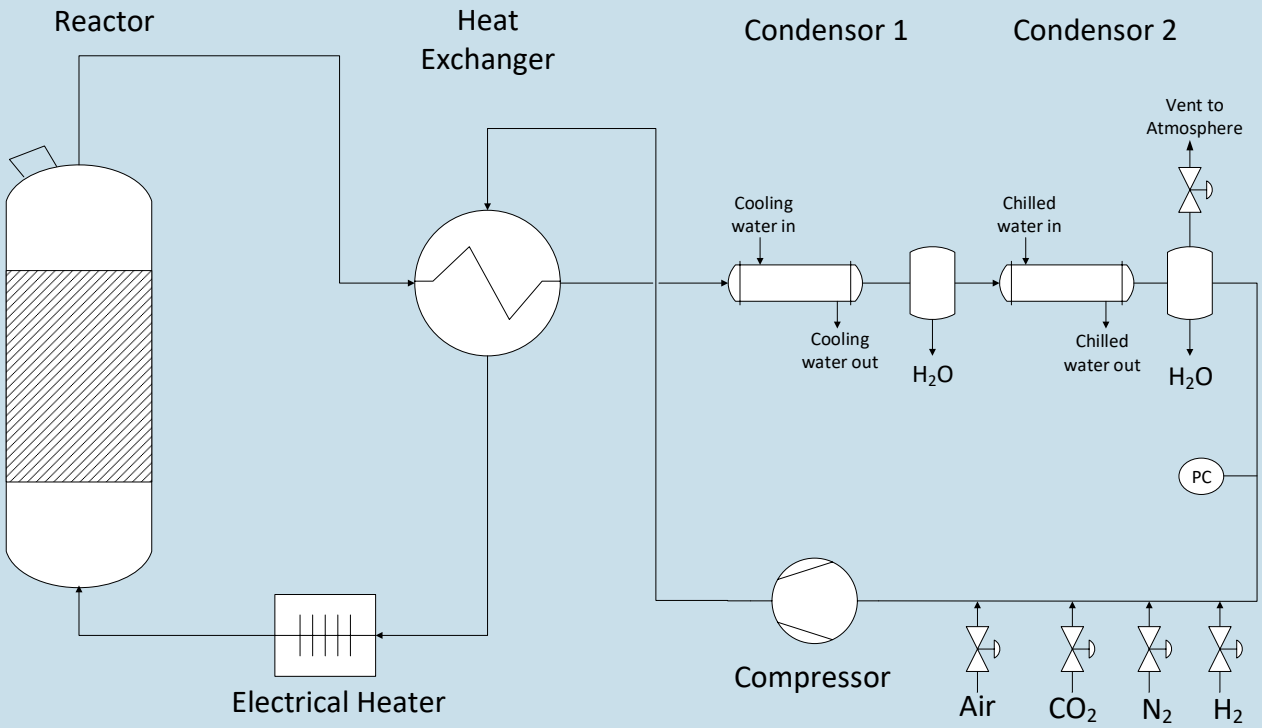
➥ Management to decide based on risk assessment.

Catalyst Design : In situ vs ex situ

Advantages ex situ :

- Within control of supplier – Quality certificate.
- Final product is “pyrophoric” metal – how to prevent safety issues at client:
  - Mild oxidation before unloading into recipient (drum, big bag).
  - Passivation via a wax layer on top of the catalyst (a coating to prevent possible oxygen ingress).
  - If not possible, unloading in reactor under nitrogen conditions is the only option.
- No provisions to be foreseen for in situ activation.
- See Process Flow Diagram (PFD).

Catalyst Design : PFD ex situ activation

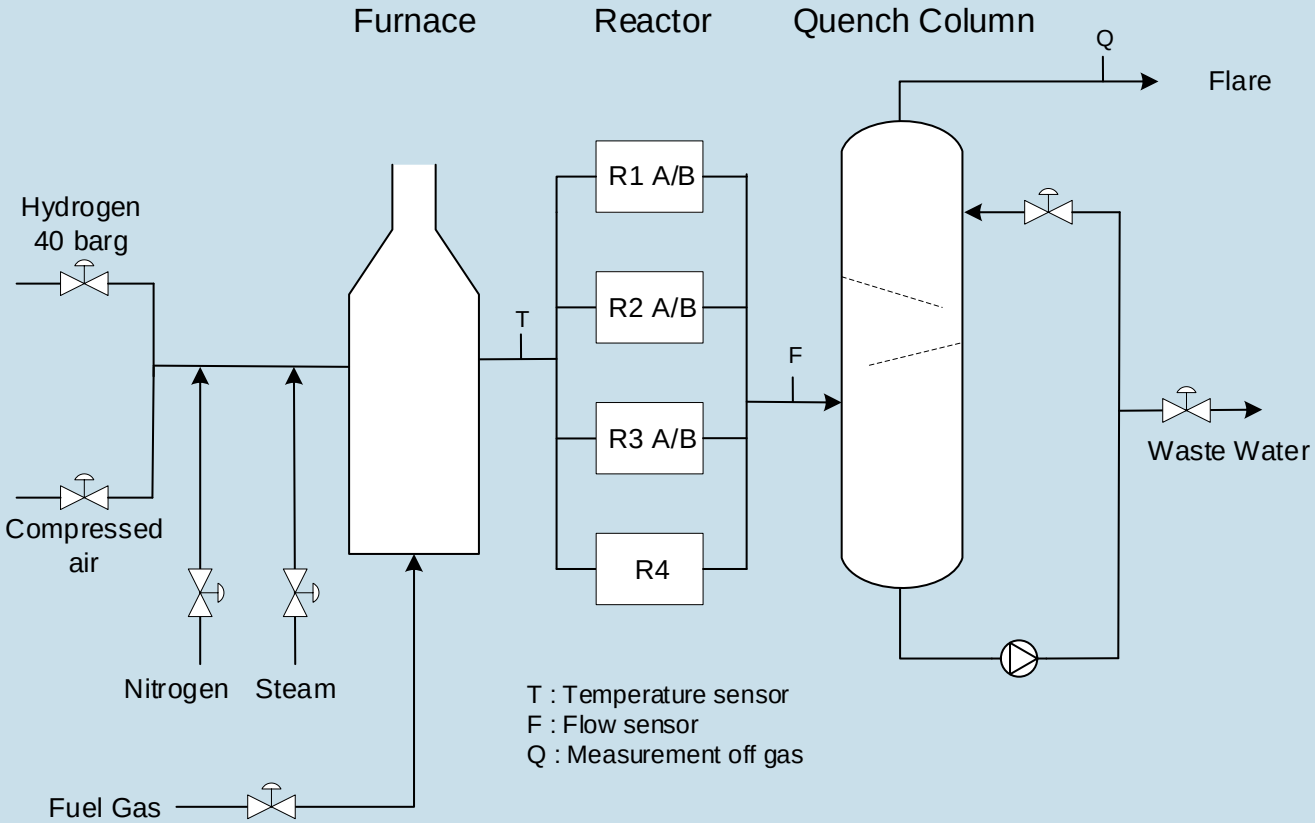


Catalyst Design : In situ vs ex situ activation

Advantages in situ :

- Within control of producer (supplier should be invited to witness).
- Safer to handle in loading and precommissioning phase:
  - Catalyst loading can be done within “normal” circumstances.
  - Complete load of catalyst can be activated in one action (efficiency gain).
- If possible, combine existing infrastructure to execute activation.
- See Process Flow Diagram (PFD).

Catalyst Design : PFD in situ activation



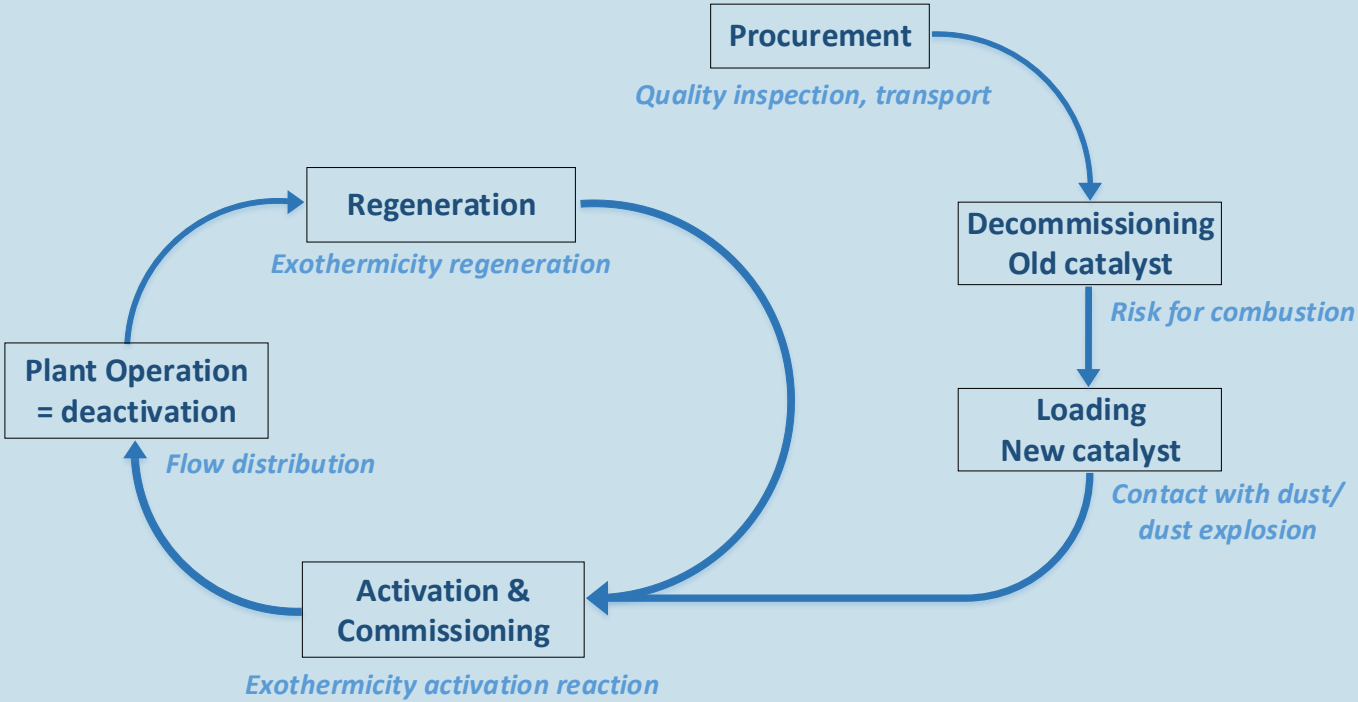
SM/PO Incident : Root cause analysis & conclusion

- A non-activated catalyst was introduced in the reactor.
  In situ reduction design was foreseen.
- New catalyst was introduced – higher Cr-oxide content then previous one.
- During the heating phase (start of commissioning),
  EB reacted with Cr-oxide initiating the reduction of
  Cu-oxide with EB (*).
  - $Cr - O + C_8H_{10} \rightarrow Cr + H_2O + CO_2\,(g)$
  - $Cu - O + C_8H_{10} \rightarrow Cu + H_2O + CO_2\,(g)$
- Uncontrolled reaction resulting in an explosive outburst.

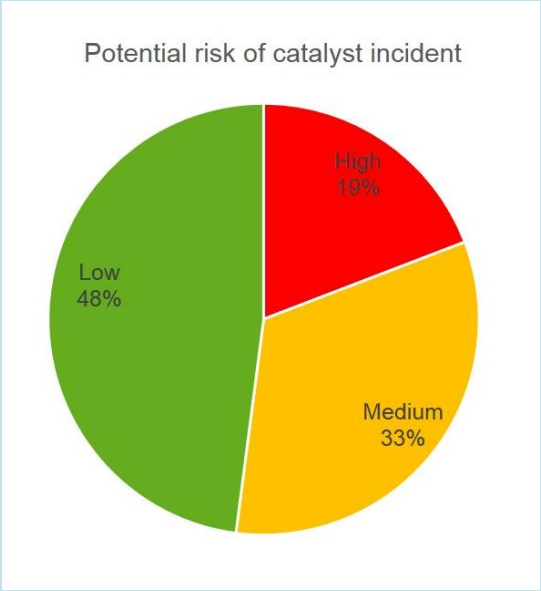

Figure 1 – Hydrogenator structure after the explosion.

(*) Simplified reaction scheme

Catalyst phases



Potential risk of catalyst incident : Cfr Incident database (1/3)



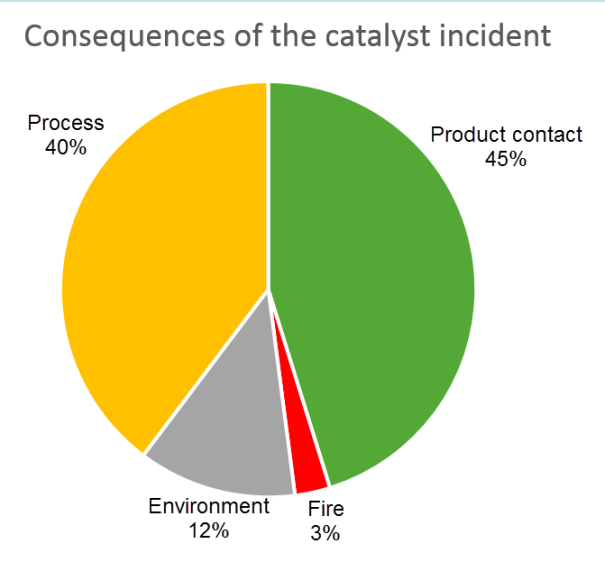
Examples:

- During commissioning, catalyst dust in eyes (not expected at this stage of commissioning).
- Underestimation of the exothermicity of a new catalyst, start-up procedure is written by trial and error.
- Heating of the catalyst during decommissioning caused by insufficient reduction/deactivation.

Case study with 73 catalyst incidents found in the incident database.

The potential risk levels weren't always indicated in the incidents. Some of the potential risks are thus a personal judgement call.

Potential risk of catalyst incident : Cfr Incident database (2/3)



Case study with 73 catalyst incidents found in the incident database.

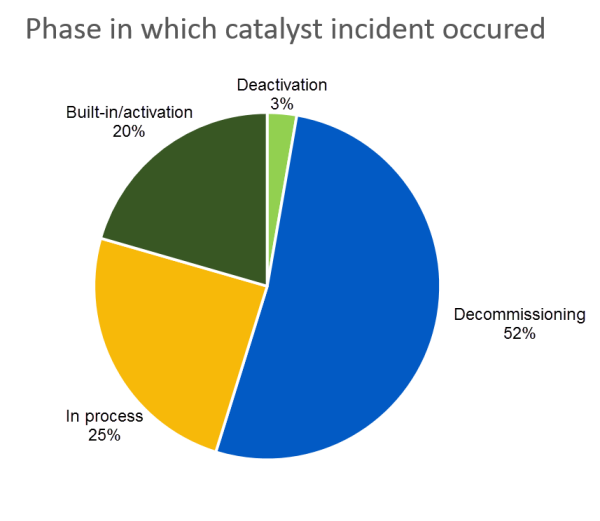
Examples :

Environment : Leakage in sieve container where decommissioned catalyst was deposed.

Fire : Hole in suction hose for decommissioning of pyrophoric catalyst. Through this hole, air was sucked inside the hose, leading to a fire.

Process : A change in catalyst causing production of too many by products.

Potential risk of catalyst incident : Cfr Incident database (3/3)



Examples :

Decommissioning : Dust explosion during suction of catalyst.

In process : Local hotspot around temperature measurement.

Deactivation : Unknown pressure increase during deactivation (new procedure).

Case study with 73 catalyst incidents found in the incident database.

Process Safety Competency of Management

- Increase awareness for process safety risks connected to catalysts.
- Checklist for occupational safety regarding the handling of a catalyst.
- Always contact vendor prior to start-up!
- SHE-review of (de-)commissioning catalyst.

  Guidewords: dust, pyrophoric, adsorption energy, SOR-conditions

Conclusion

- No similar procedure where a flammable liquid is used as cooling medium during the activation phase has been found.
- Nevertheless, review of the incident database learns criticality of handling with catalysts.
- Checklist(s) and a good vendor contact should give enough guidance to prevent catastrophic incidents.

Thank you … for your attention !