Learnings from a reactor explosion: Towards safer start-ups of catalysts systems

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Catalyst/adsorbent: inert “facilitator” or reactant?

Do you understand exactly what reactions happen during start-up?

Explosion – Root Cause

- Exothermic reaction: Hydrocarbon + copper chromite catalyst → gas

$CuCr_2O_4$ or $CuCrO_3$ → Cr^{III} or Cr^{IV}

$CuCrO_4$ → Cr^{VI}

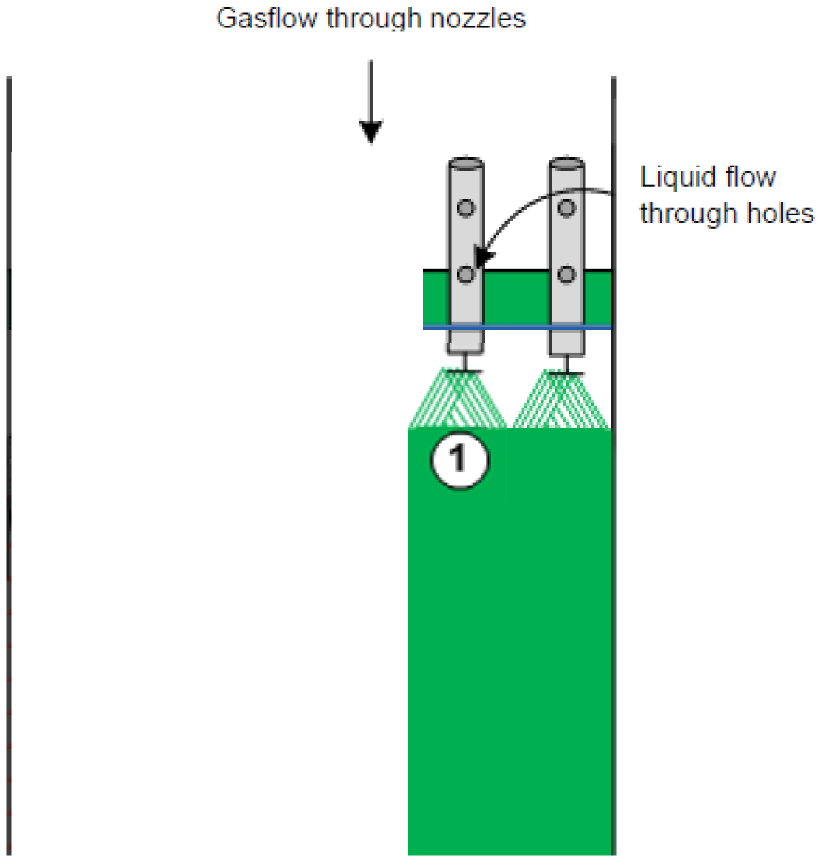
- Investigation showed:
  - Oxidic catalyst contained more Cr^{VI} components
  - At 90°C (194°F): EB reacted with copper chromate
  - From 180°C (356°F): EB reacted with Copper oxide ($Cu^{II}O$)
  - Not enough heat-sink

- Limited focus on transient conditions

Explosion – main catalyst learning

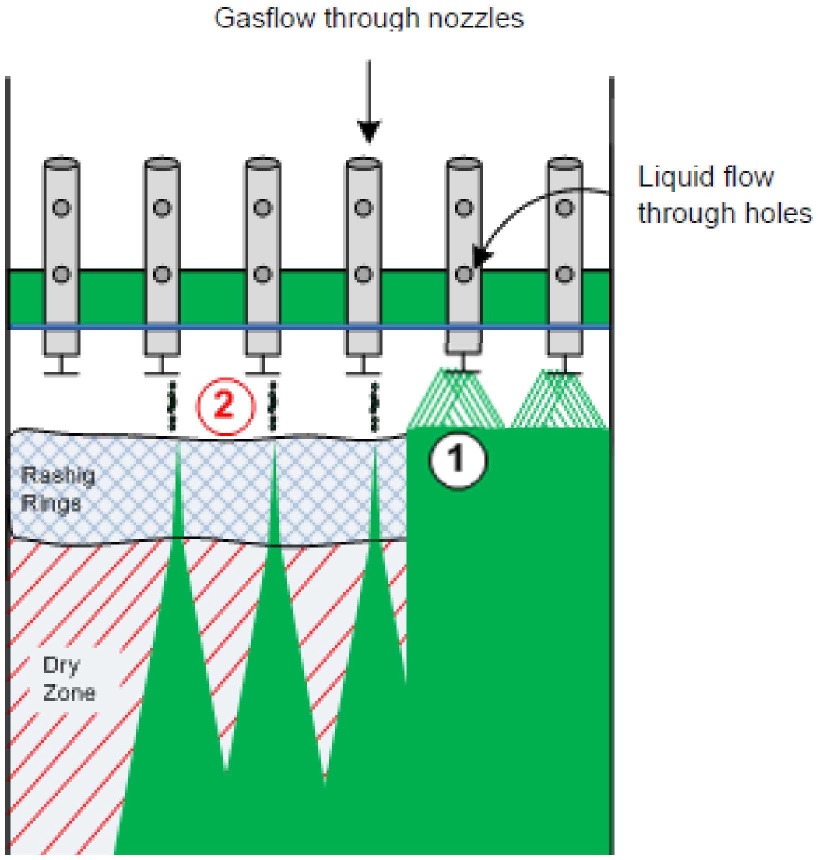
- Tons of latent oxygen present in reactor
- Latent (reactive) oxygen from catalysts can react exothermally with a hydrocarbon
- Crucial to review the reactive hazards in both transient and steady state operations

Reactor Internals: sprays



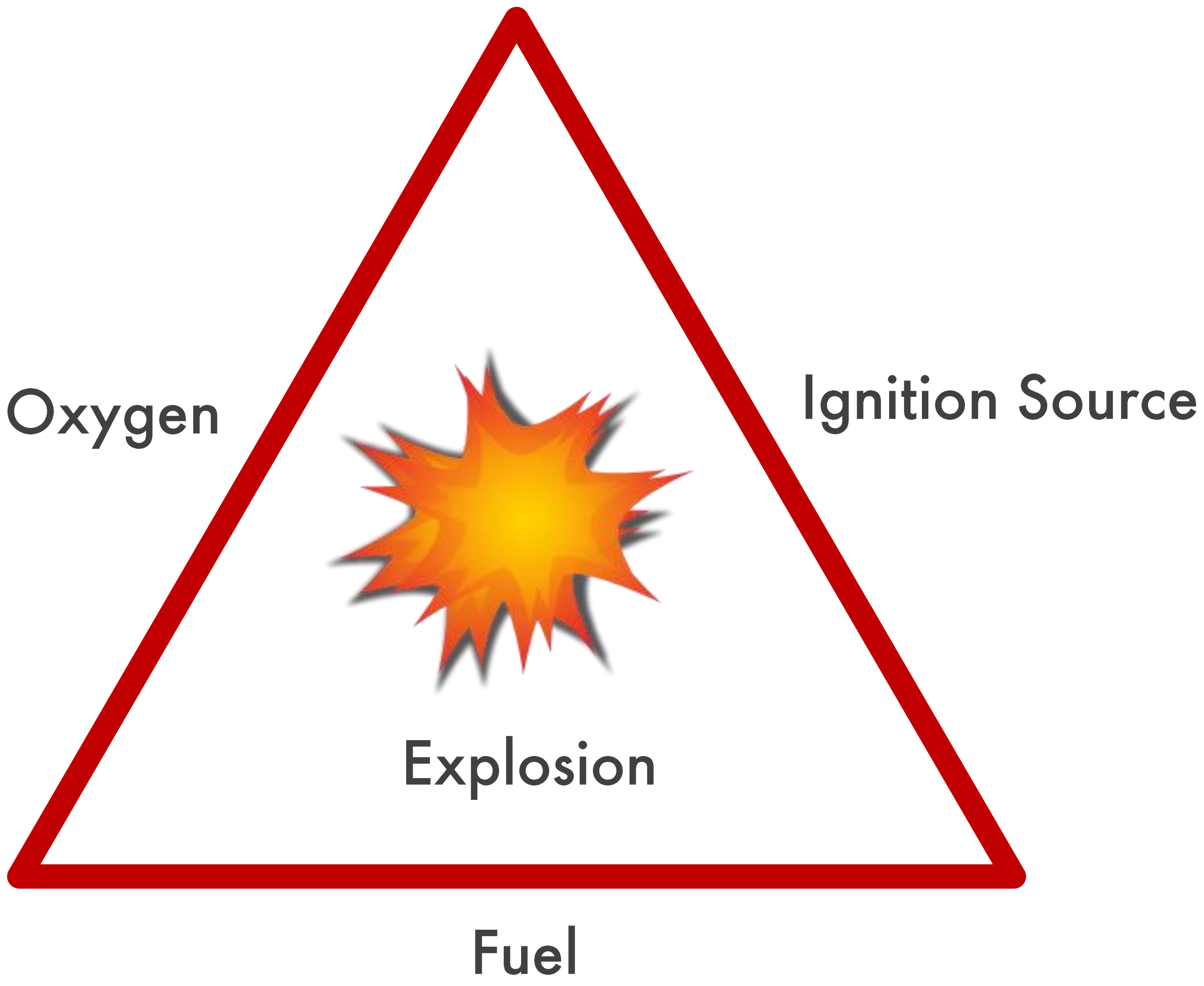
(1) Properly working nozzle

Reactor Internals: sprays



(1) Properly working nozzle
(2) Too low gasflow

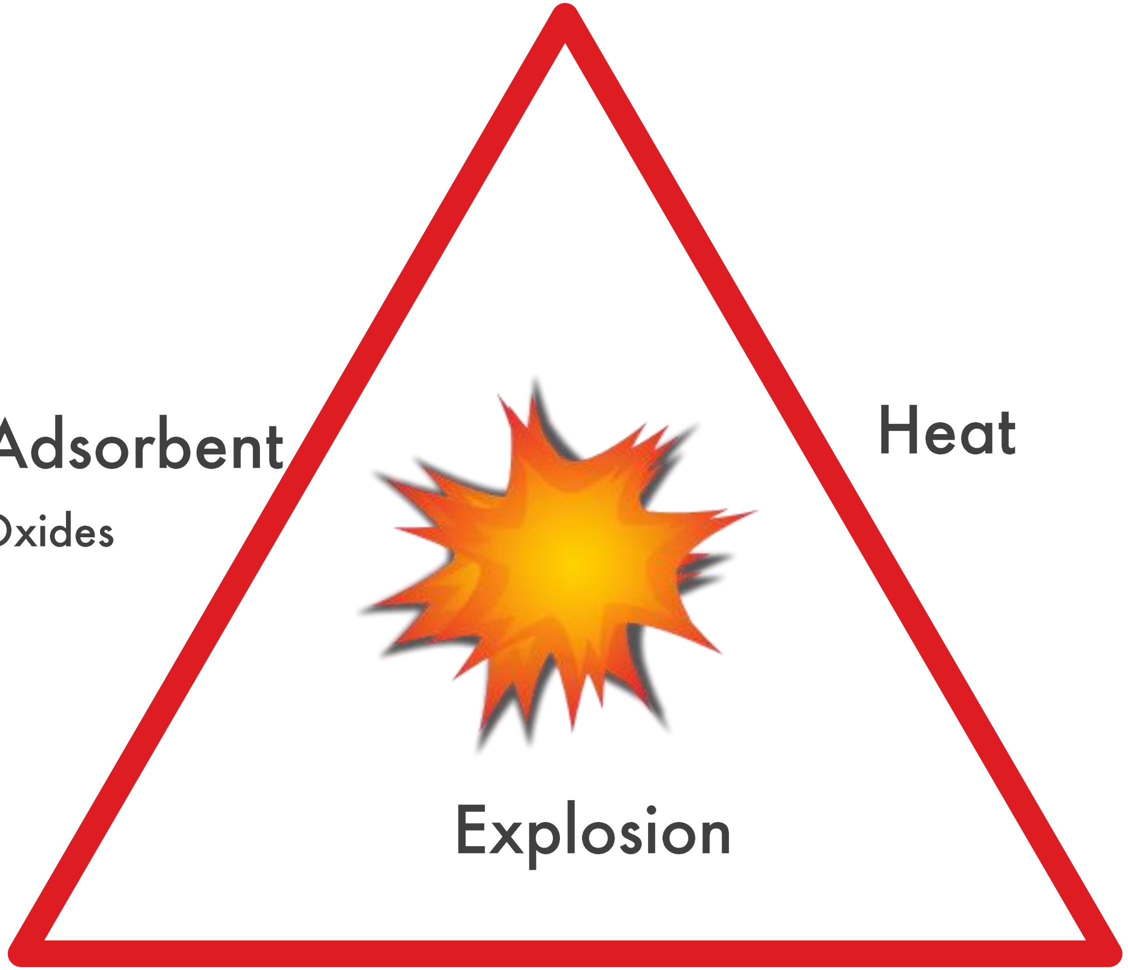
Could other systems have similar phenomena?


Oxygen
Ignition Source
Explosion
Fuel

Catalyst/Adsorbent

- Metal Oxides

Example:
Hydroprocessing reactor
often contains
> 10 tons of oxygen



Heat

Examples:

- Liquid adsorption
- H_2 chemisorption
- Sulfiding/Reduction
- Poor heat removal
  (e.g. Flow maldistribution)

Hydrocarbon feed
Organic package on catalyst

Catalyst/adsorbent: inert “facilitator” or reactant?

Catalyst Trends

Debottlenecking existing assets

Quick response to market

Energy Transition

More activity

↓

Higher chance of more activity in all phases of start-up

→

Understand exactly where catalyst risks are during transient start-up phases

Shell’s approach for improved focus on risks during transient phases of start-ups with catalysts and adsorbents:

Catalyst Safety Assessment (CSA)

CSA focus

- Behaviour of catalyst/adsorbent <u>in transient modes of operation</u>
- Main focus: reactivity of metal oxide with hydrocarbons
- Other important aspects
  - Adsorption of gases on catalyst
  - Liquid heat of adsorption
  - Release of gases from freshly loaded catalyst
  - Enough heat sink
- Risk assessment based on Thermodynamics and/or calorimetric experiments

CSA screening tool

- Gibbs energy and Enthalpy:

  $M_xO_y + HC \rightarrow M + CO_2 + H_2O$

- Flow regime:

  liquid full/trickle phase/gas phase

- Metal oxide loading

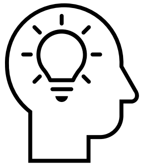
- Calculation of maximum P and T
  if all metal oxides are converted

Medium/High risk systems

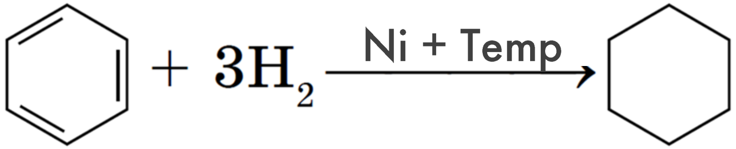
- Negative ΔG & ΔH_r
- Liquid full
- Trickle phase > 5% Metal oxides

When to do a CSA?

- New catalyst/adsorbent

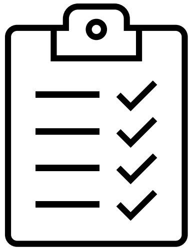


- New application



- Change in catalyst composition/production

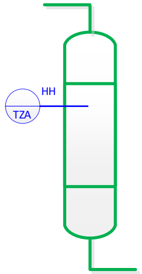
CSA outcome



Changes to start-up procedure

or

Unwanted reactivity of catalyst
as part of catalyst selection

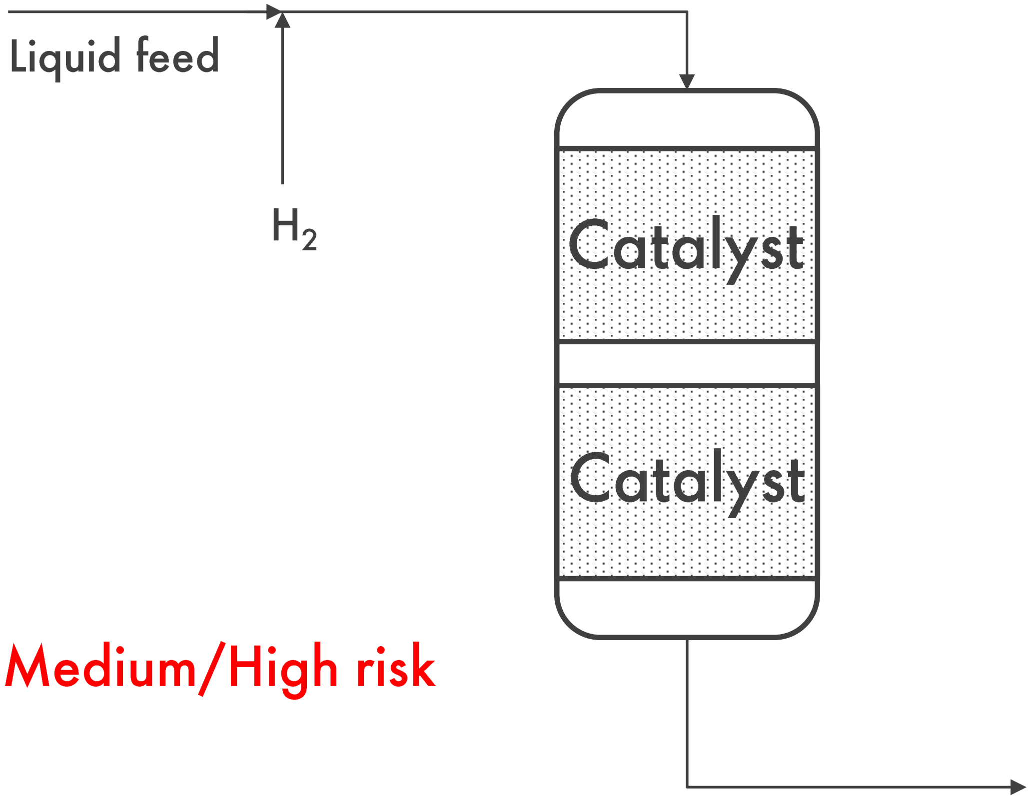


Changes to reactor safeguarding
or reactor design

CSA example:
Nickel catalyst in hydrogenation function

CSA example: nickel catalyst in hydrogenation function

- Catalyst in reactor
  - >10% NiO on carrier
  - Trickle phase reduction

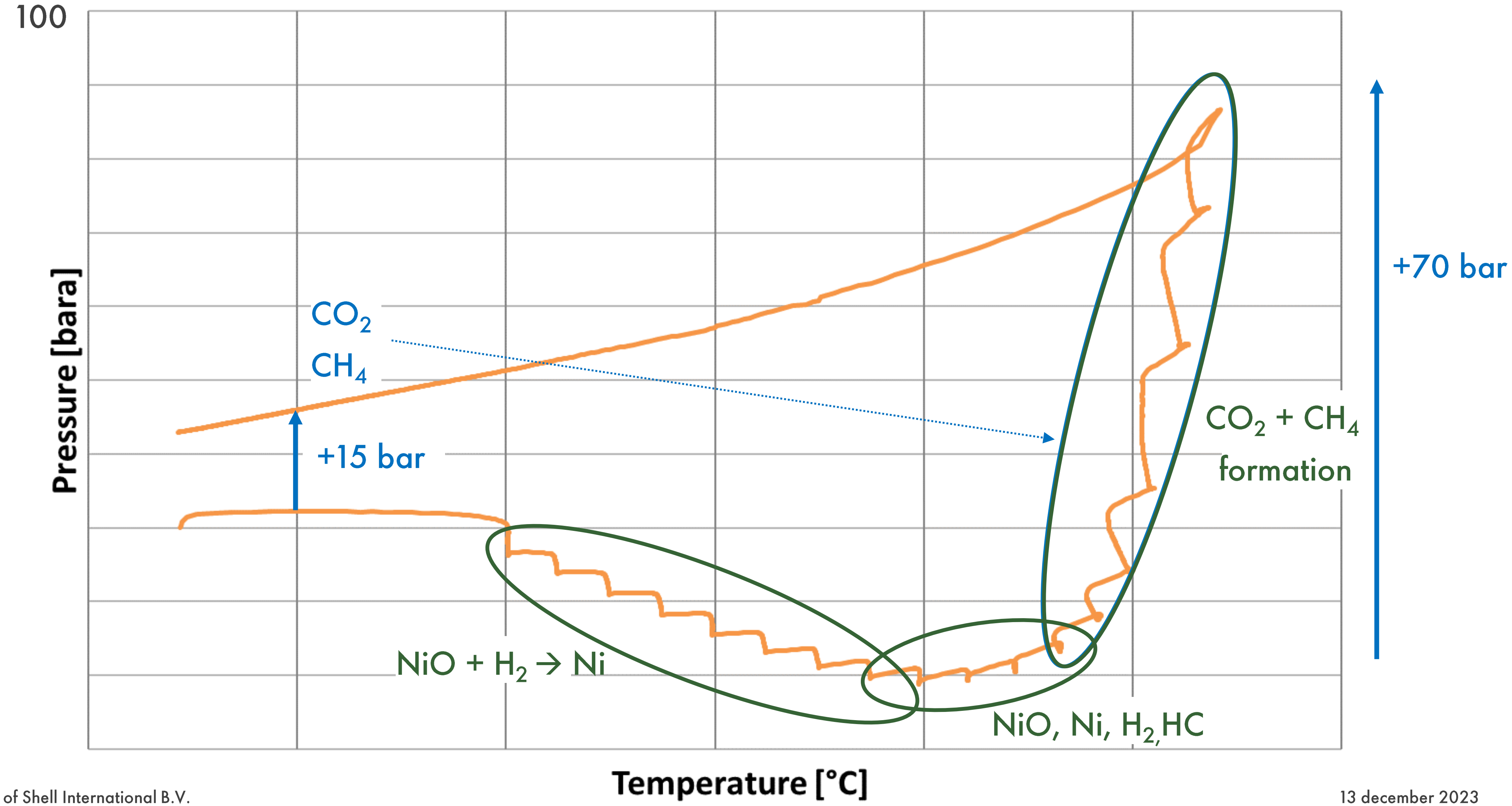


<u>CSA assessment</u>

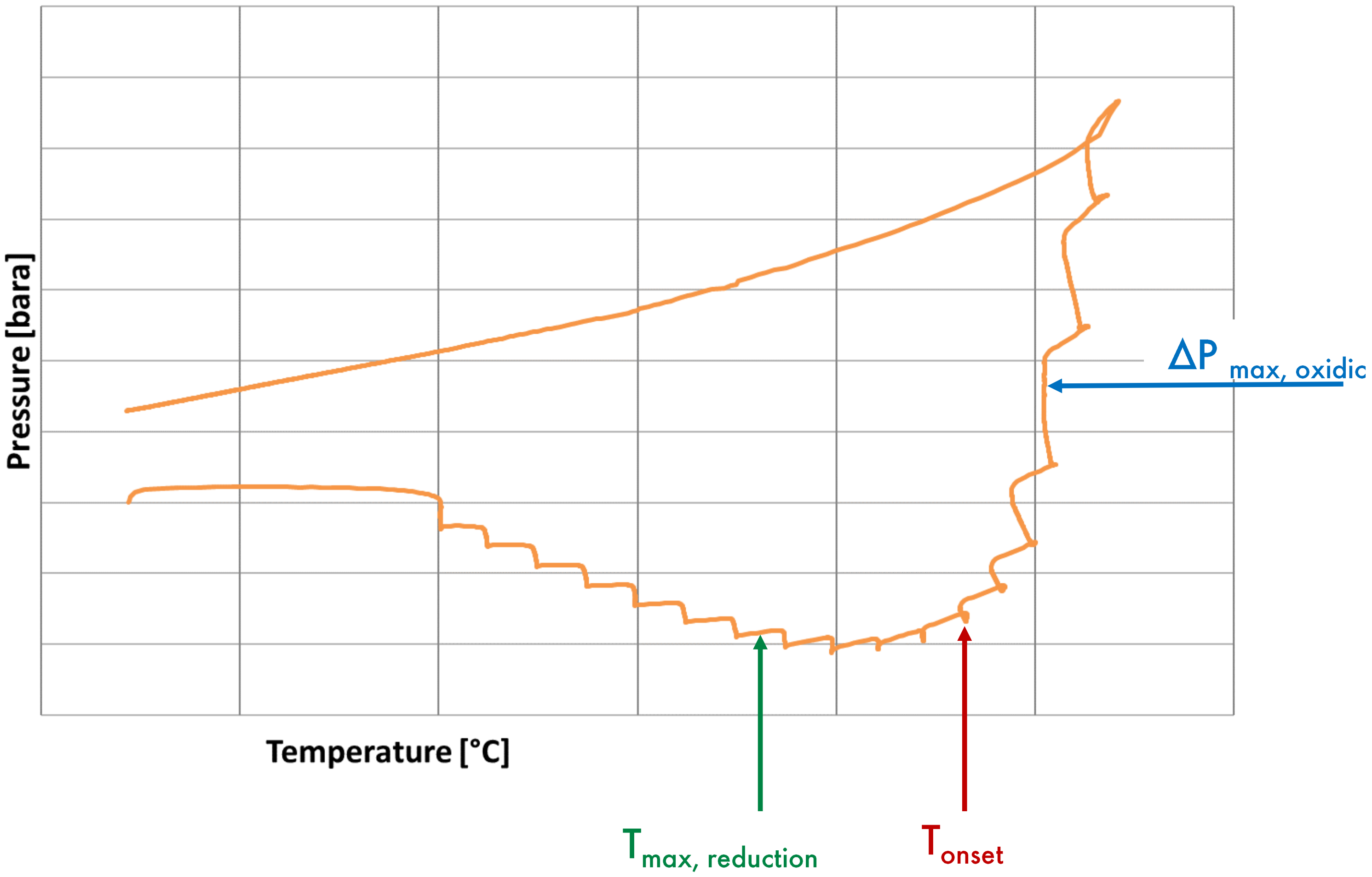
- Thermodynamic results NiO + HC → **Medium/High risk**
  - Potential for design pressure exceedance

- Conclusion: calorimetric tests are needed

Experimental result: NiO catalyst + hydrocarbon + H_2



Experimental result: NiO Catalyst + Hydrocarbon + H_2

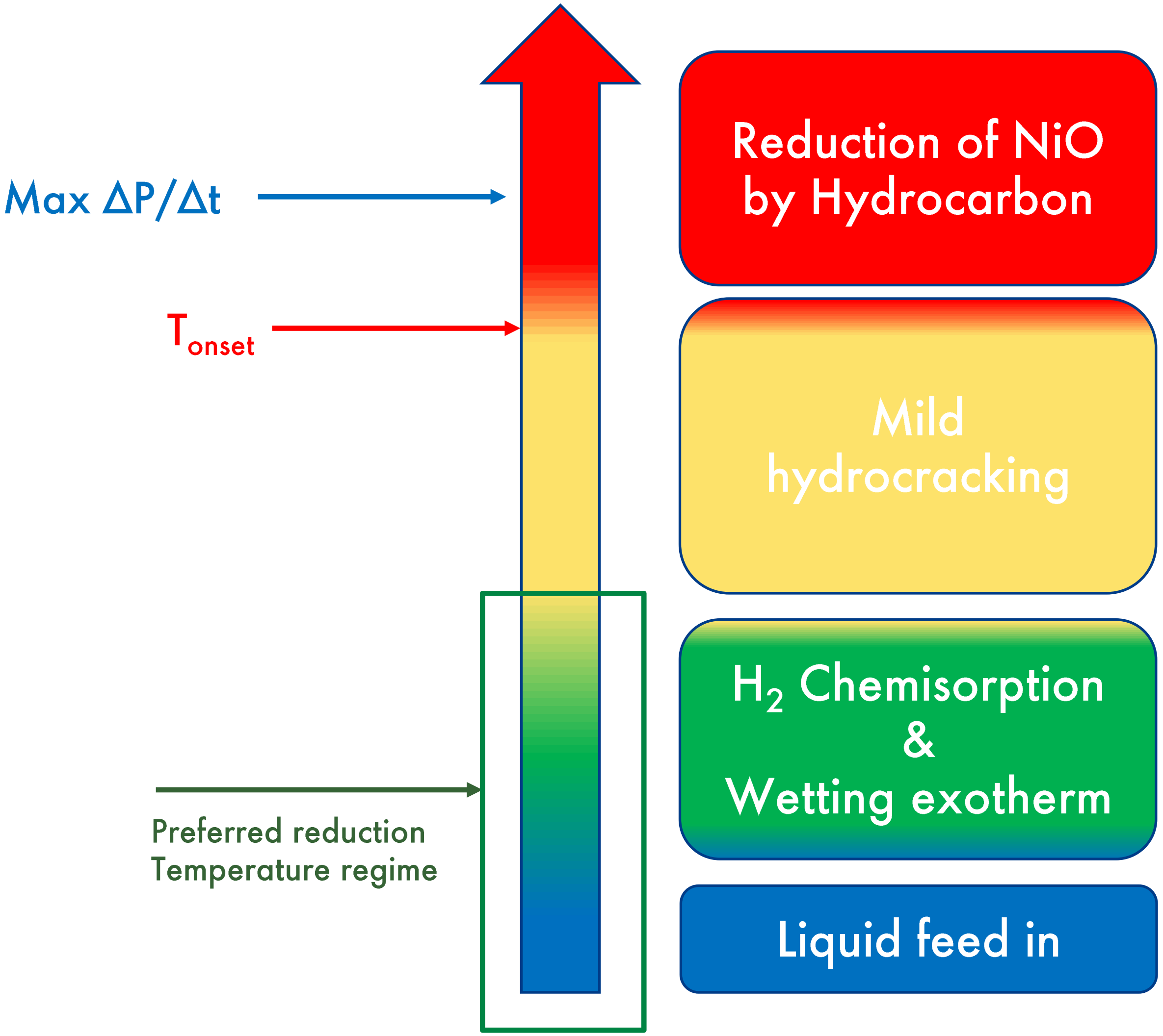


If trickle phase reduction, what is safe reduction temperature?

Shell decided

$T_{max,\ reduction} = T_{onset} - 50^{o}C$

Overview start-up Temperature diagram Nickel oxide catalyst



Processing biofeeds to make fuels

Stability certain bio-oils

	Without catalyst
Exotherms	320-390°C
Start exobar	320-350°C

Data given are indicative for certain triglycerides

Avoid hot spots in stagnant parts of the feed pre-heat train!

Effect catalysts on reactivity bio-oils

	Without catalyst	With catalyst
Exotherms	320-390°C	220-300°C
Start exobar	320-350°C	220-360°C

Data given are indicative for certain triglycerides

- Catalysts lower the reactivity temperature
- Consider a non-reactive start-up feed

Summary

Summary

Catalyst/adsorbent can be a reactant!

- Focus on transient conditions for catalysts/adsorbents
  - Start-up is crucial:
    Catalyst in reactive state + transient operating conditions → increased risk
  - Metal oxides can be oxidizing agents for hydrocarbons

- Which reactions happen at which temperature during start-up?

- Take proper mitigation against exothermicity of bio-oils

- Shell's Catalyst Safety Assessment is a process that helps make catalyst/adsorbent start-ups safer.

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