~~Reactive Hazards in Shell's Hydroformylation Process~~

Reactive Hazards in Refineries: Hydrocracker Runaways

Nick Gonzales

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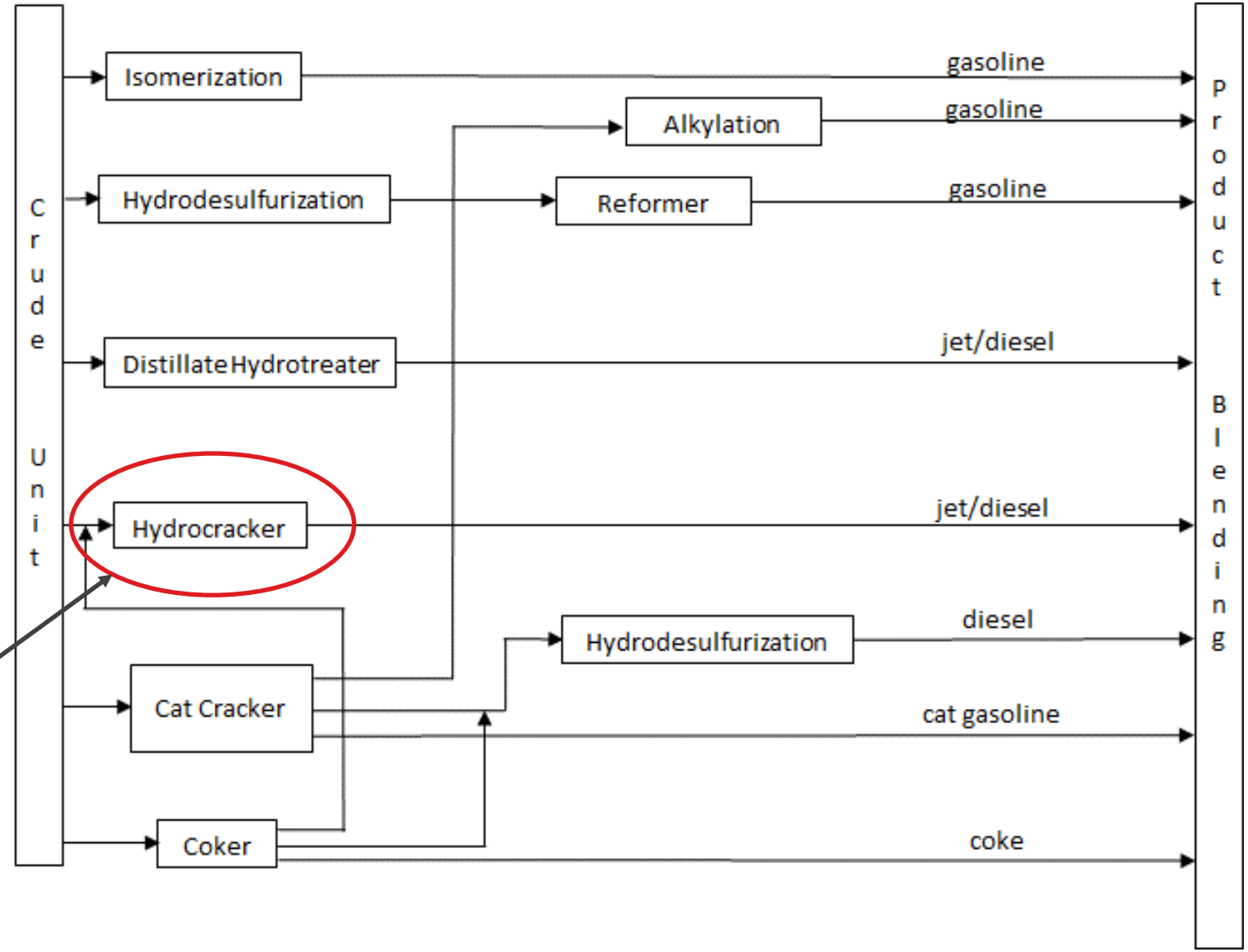
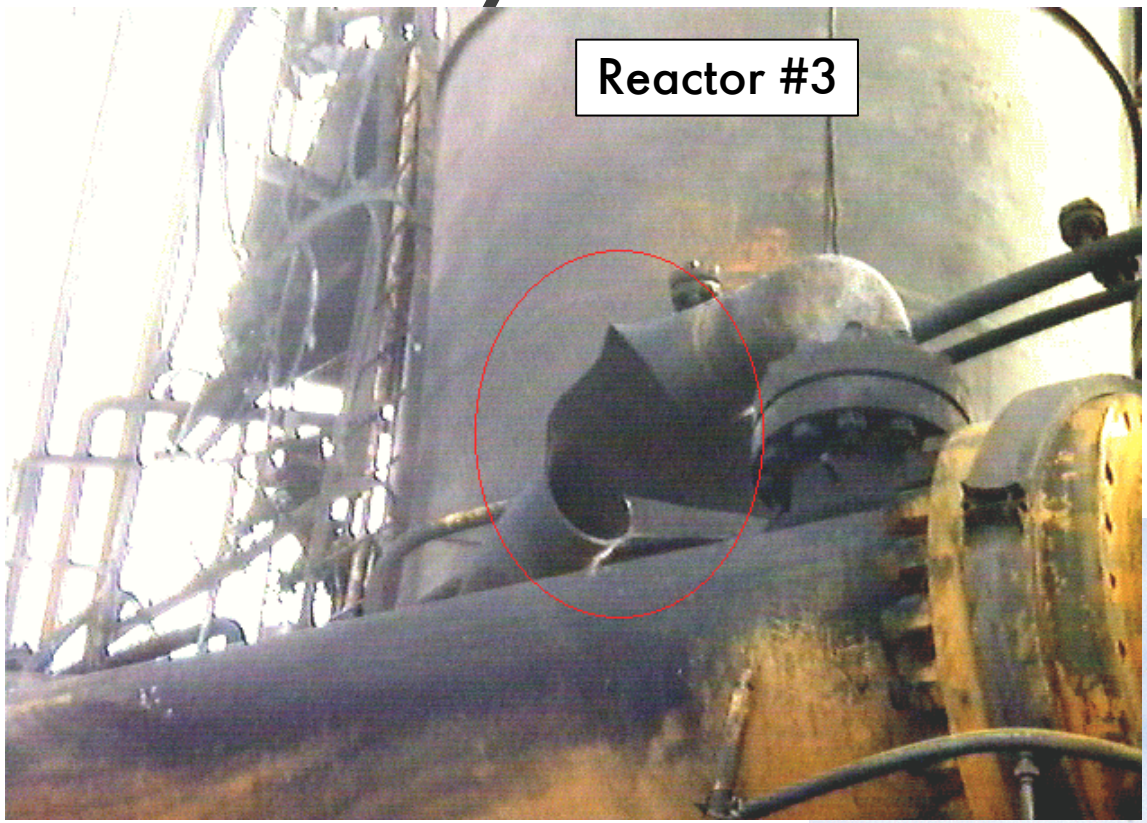
How a Hydrocracker fits in a Refinery

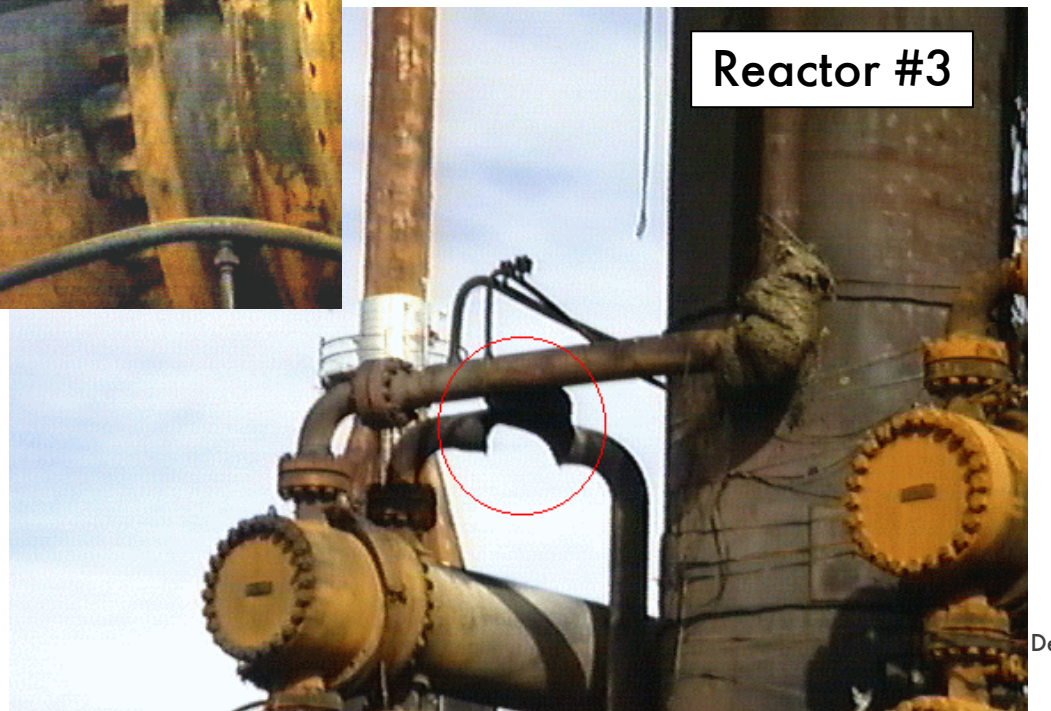
Crude Oil



Converts low value hydrocarbons to high value products (i.e., Heavy Gas Oil to gasoline/jet/diesel)

1997 Tosco Avon Hydrocracker Incident – Overview





Source: EPA Investigation Report

1997 Tosco Avon Hydrocracker Incident – Overview

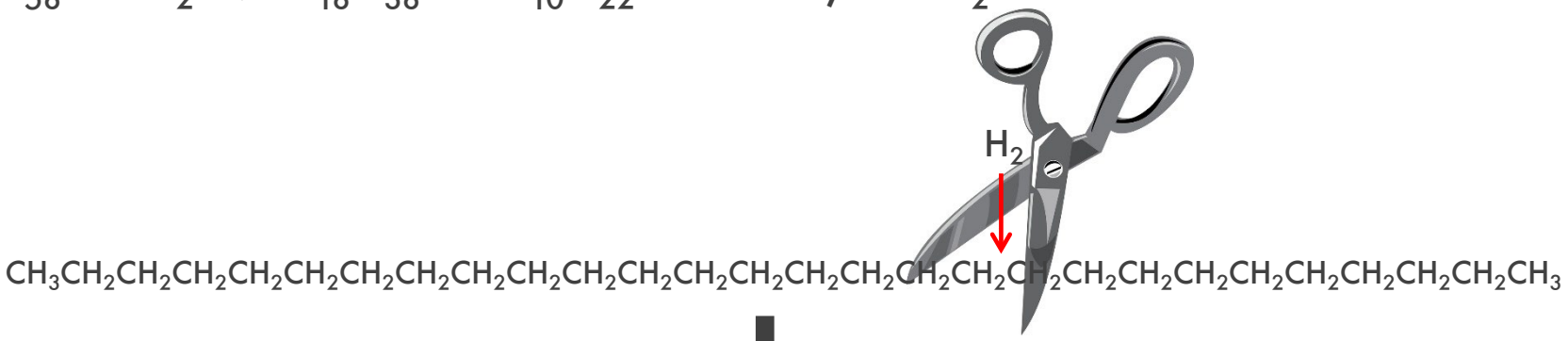
- Process upset led to increasing the reactor temperature.
- Process upset resolved but the reactor temperature not returned to normal.
- The increased reactor temperature eventually led to a runaway exotherm.
- Operations thought they could "save" the situation and did not activate safeguards.
- Time from high temp alarm to Loss of Containment (LOC) was 7 minutes.
- The LOC was followed by an explosion and a fire.
- There were 46 injuries and 1 fatality.

Link to Investigation Report:

https://www.hsdl.org/?abstract&did=234304

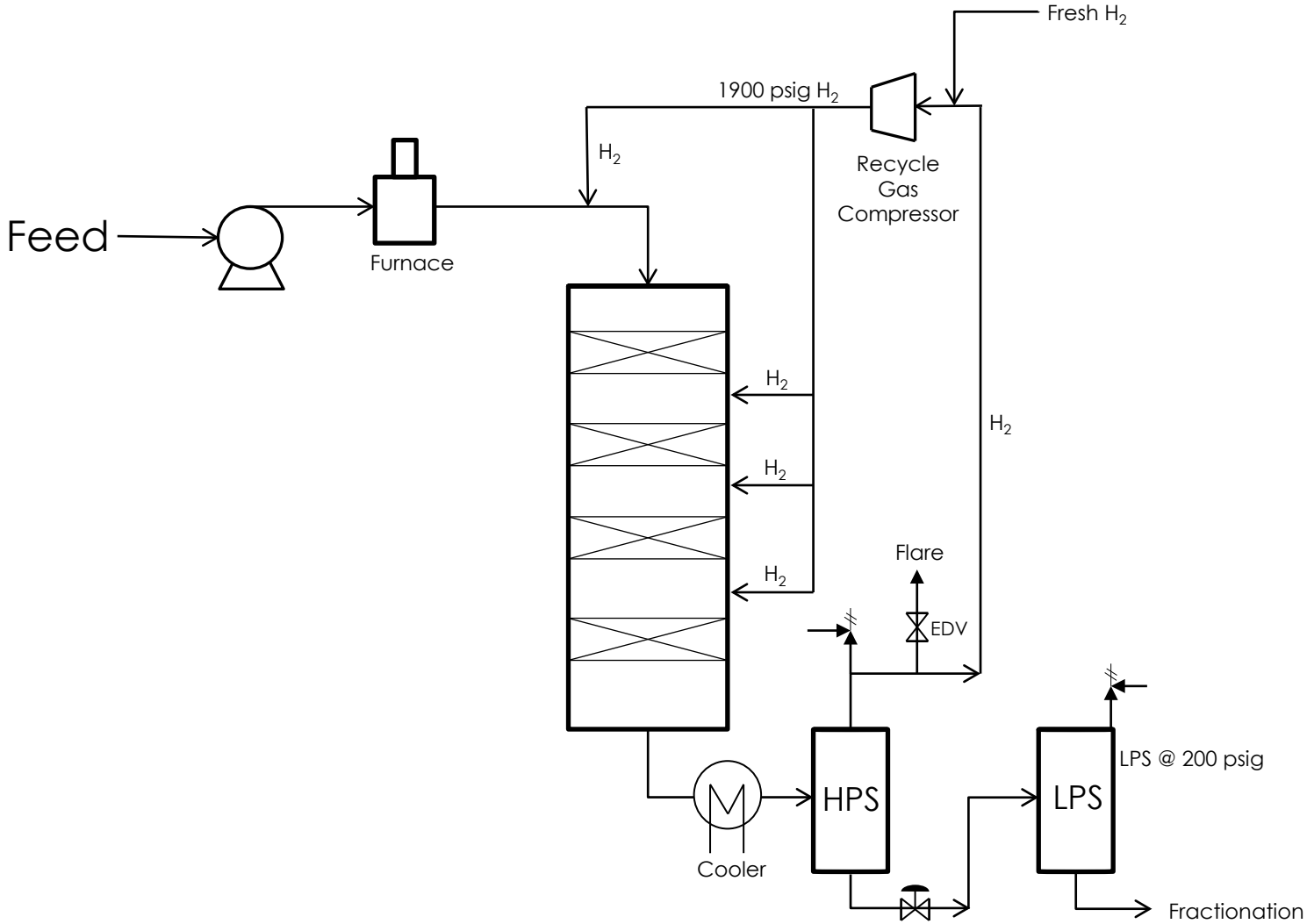
Example Hydrocracker Operating Conditions & Chemistry

- Operating conditions: 650°F at 1900 psig (340°C at 130 barg)
- Reaction: $C_{28}H_{58} + H_2 \rightarrow C_{18}H_{38} + C_{10}H_{22} + 50$ kJ/mol H_2



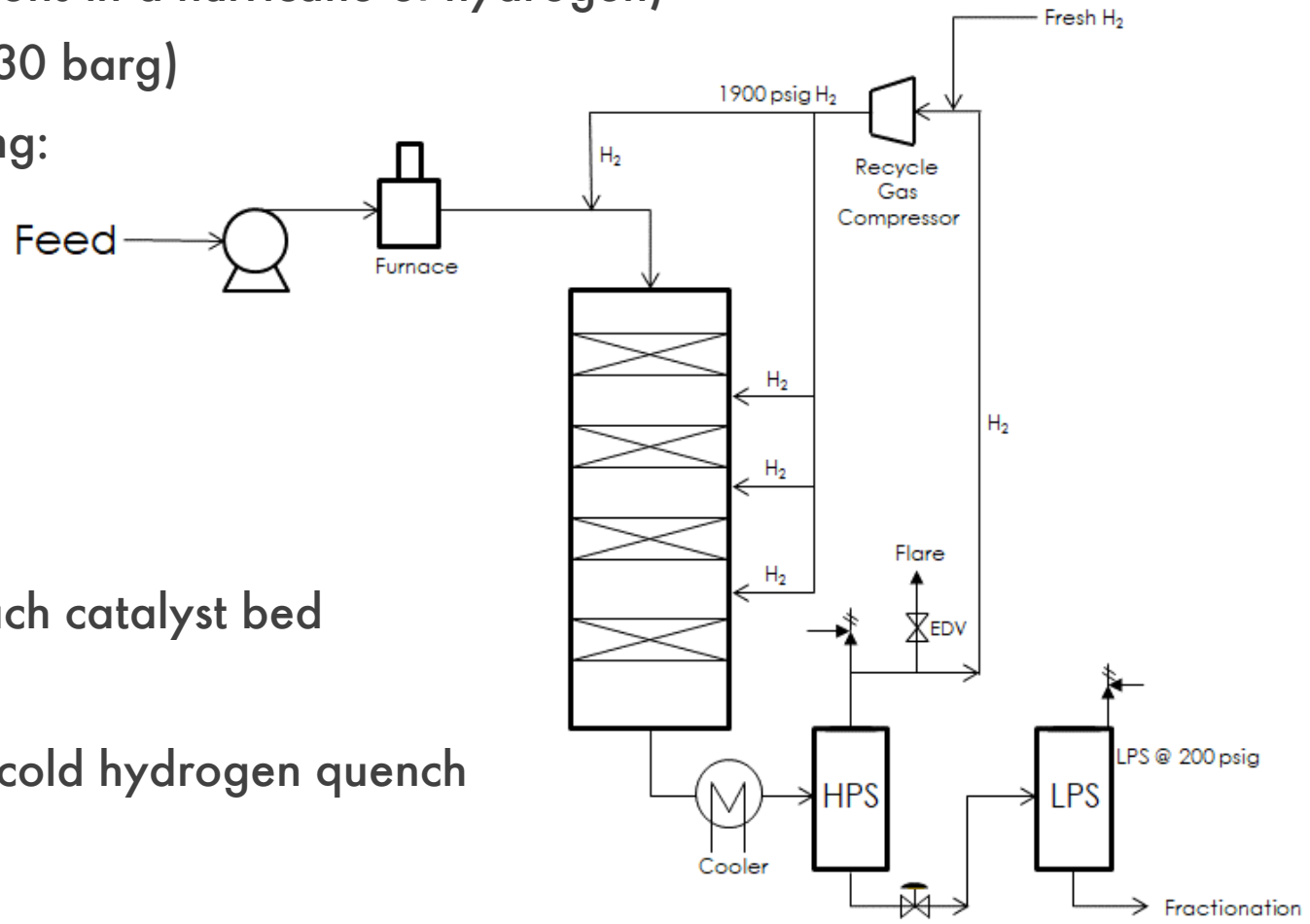
- We want hydrocarbons to be "snipped" only once in a hydrocracker.

Example Hydrocracker Process Layout



Example Hydrocracker Operation

- Trickle Flow Reactor (i.e., it rains hydrocarbons in a hurricane of hydrogen)
- Conditions: 650°F at 1900 psig (340°C at 130 barg)
- Need all 4 of the following for hydrocracking:
  - Hydrocarbon
  - Hydrogen
  - Catalyst
  - High temperatures
- Reaction heat → temperature rise across each catalyst bed
- Temperature rise controlled via injection of cold hydrogen quench



How Hydrocracking Develops into a Global (full diameter) Runaway

How a Hydrocracker Temperature Runaway Develops

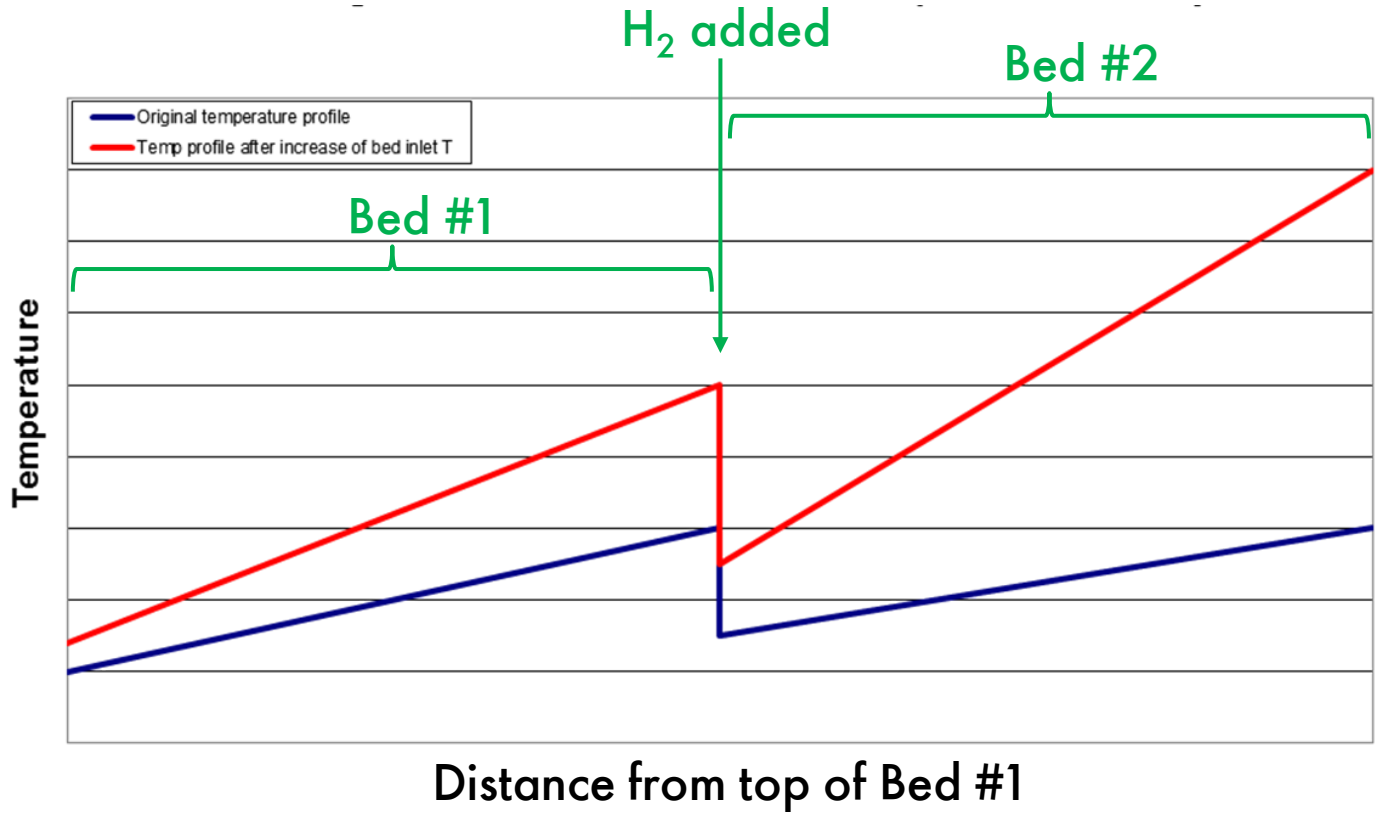
If temperature control is not sharp (e.g., temp overshoot allowed) or temp control is lost, desired reactions become undesired & dangerous

- Thus, SMALL increases in reactor temperature STRONGLY advised (~1.0°F)

- How to lose temperature control:
  - Feed too hot
  - Loss of quench cooling
  - Catalyst too active
    - Fresh catalyst
    - Tosco scenario

← Poor operation

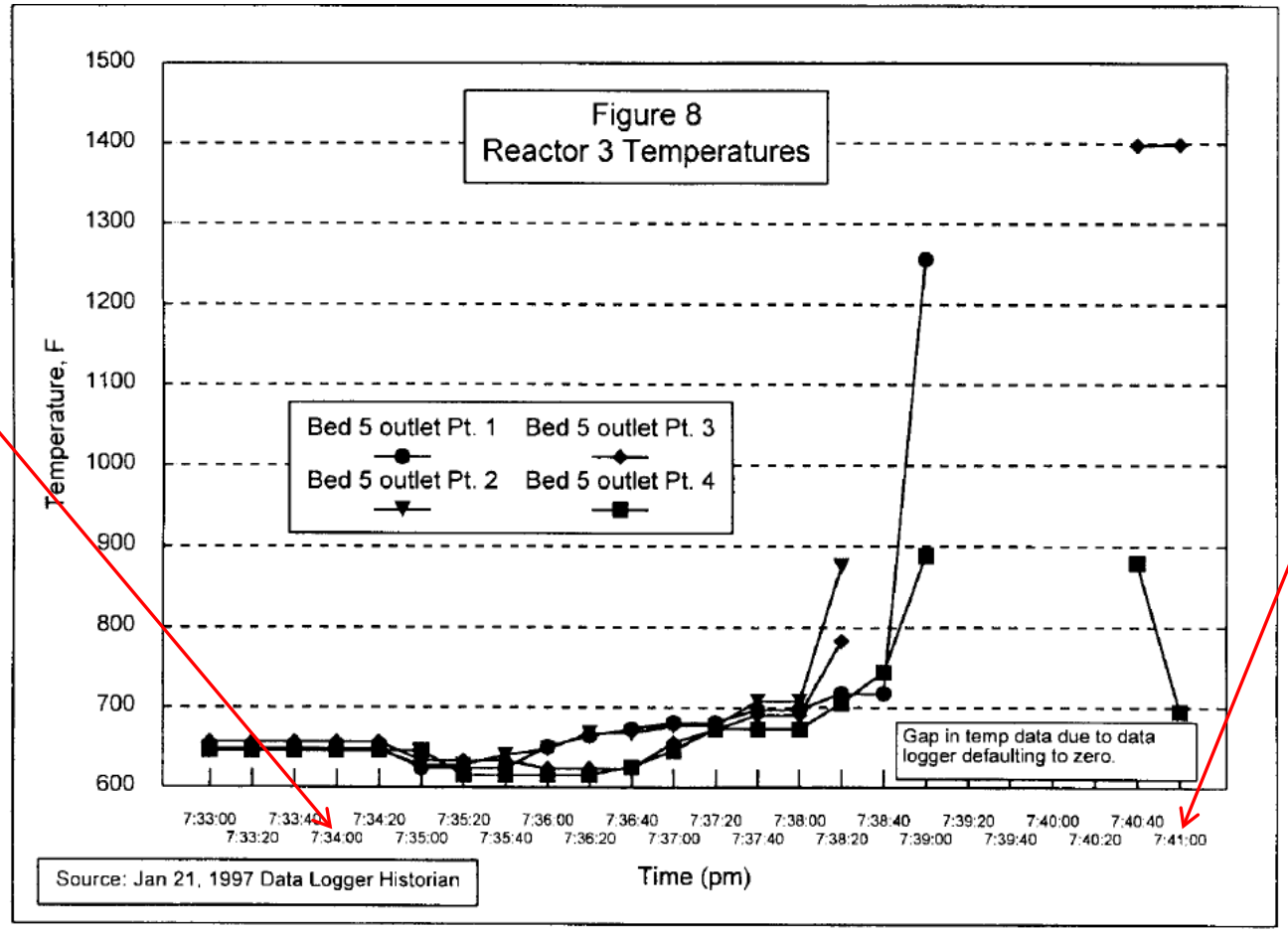
What a Hydrocracker Temperature Runaway Looks Like



- A small increase in feed temperature is magnified as it passes through each catalyst bed
  - As Temp ↑, reaction rate ↑ because all reactants are available
  - Reactor temperature builds after each bed, so the outlet temperature climbs quickly

Time Available to Respond During a Hydrocracker Runaway

Temperature Excursion Detected in Bed #4



LOC

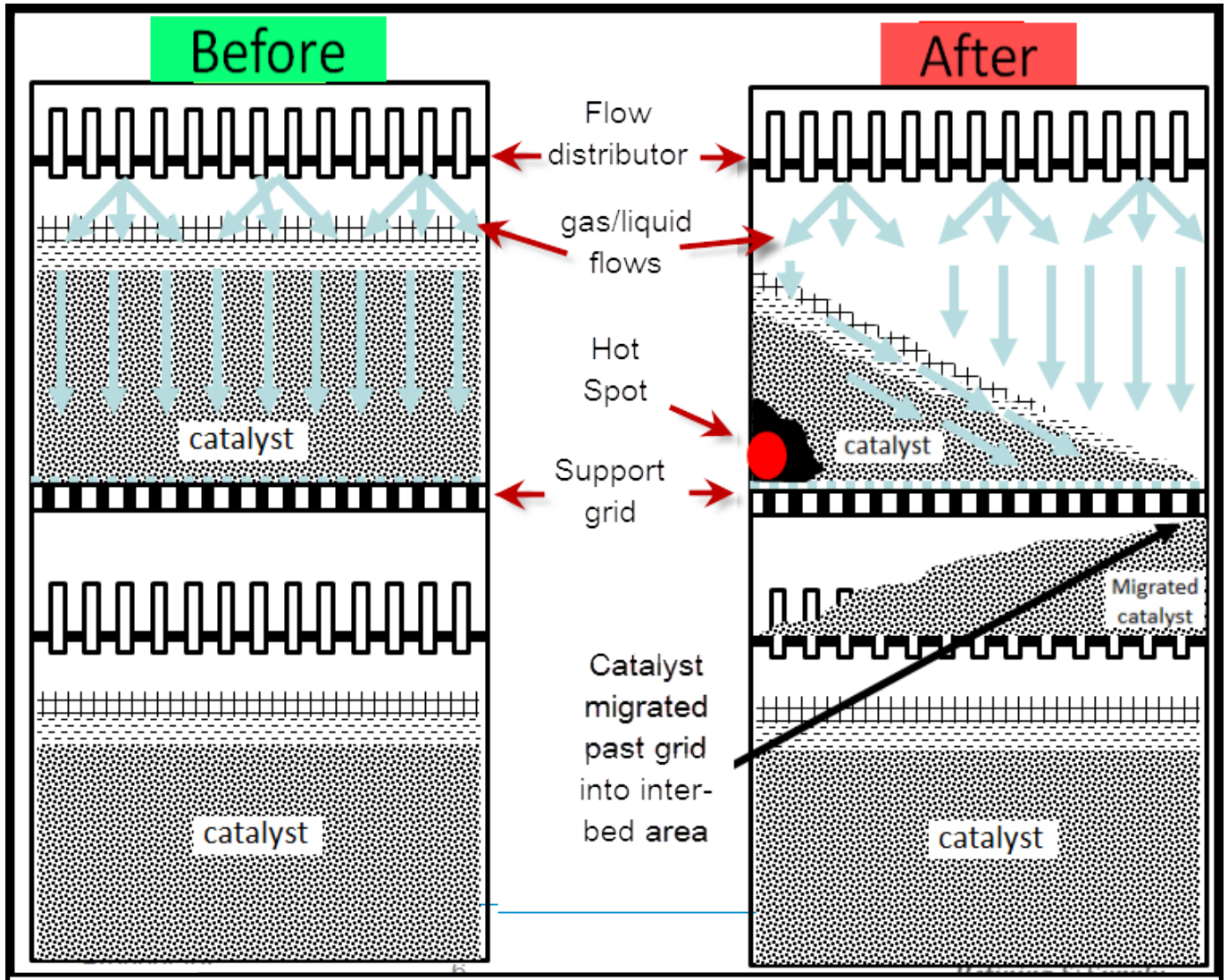
Tosco incident: 7 minutes from start of temperature excursion to LOC

How Hydrocracking Develops into a Hot Spot Runaway

Hydrocracker Temperature Runaway Due to Hot Spots

Hot spot led to LOC of the Exxon Baytown hydrotreater (2012)

2012 Exxon Baytown Hydrotreater Incident



Reactor Before and After Catalyst Migration

Consequences of a Hydrocracking Runaway

Hydrocracker Runaway: Overtemperature or Overpressure?

- Temperature: Reactor temperature can exceed design temperature
  - oil + H_2 → diesel + jet + heat

- Pressure Possibilities:
  - oil + H_2 → diesel + jet + heat (reaction consumes moles of gas)
  - oil + H_2 → hydrocarbon + methane + heat (moles of gas unchanged)
  - PV = nRT (when temperature ↑, pressure ↑)

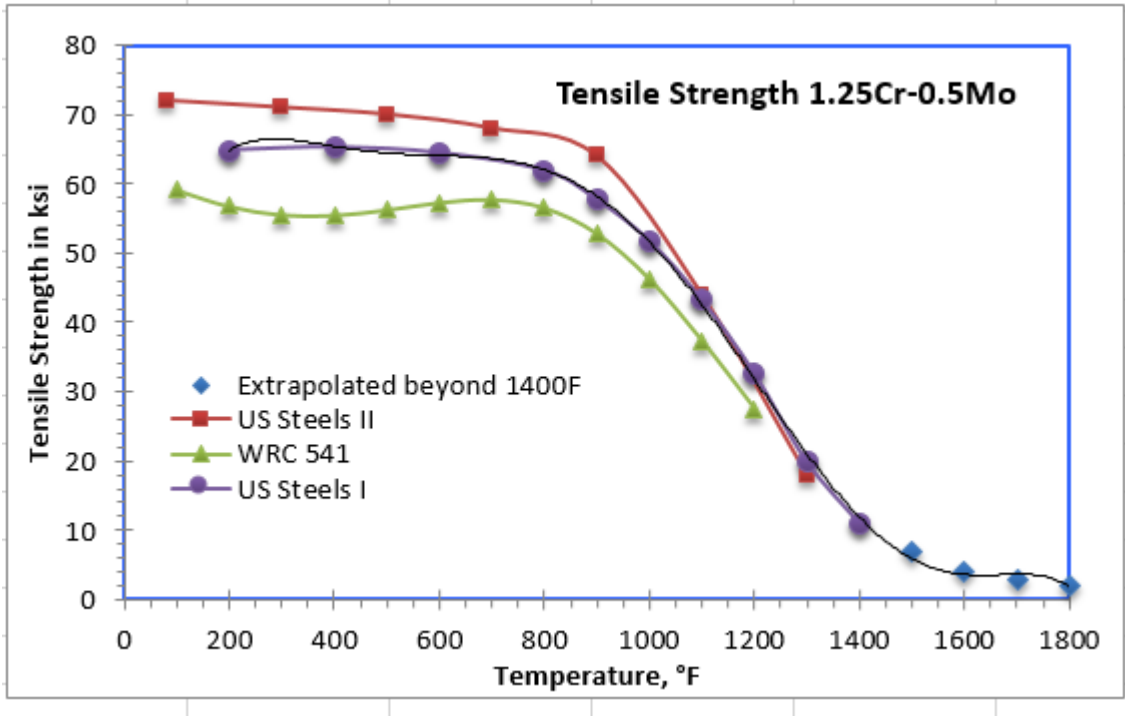
- Reality: Reactor pressure does not increase substantially
  - No relief valves have lifted during previous temperature runaways.

This is an over temperature scenario.

No protection from the relief device!

Consequence of a Hydrocracker Temperature Runaway

Tensile Strength Estimations for 1¼Cr-½Mo



Consequence of a Hydrocracker Temperature Runaway

- Equipment wall thickness
  - Reactor: 10 – 12 inches (25 – 30 cm)
  - Outlet piping: 1 inch (2 – 3 cm)

- Location of high temperatures
  - Global Temperature Runaway: The outlet pipe is the mostly likely point of failure
  - Hot Spot Temperature Runaway: The reactor wall is the most likely point of failure

Consequence of a Hydrocracker Temperature Runaway after LOC

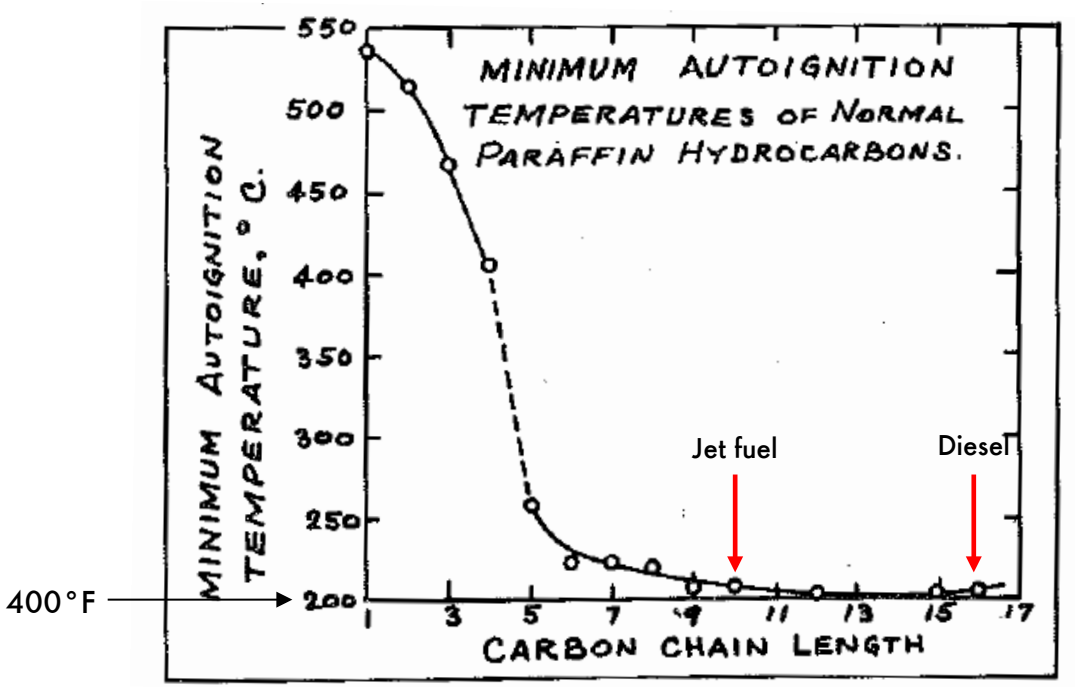


Figure from
"*Fundamentals of Fire and Explosion*"
By Daniel Stull

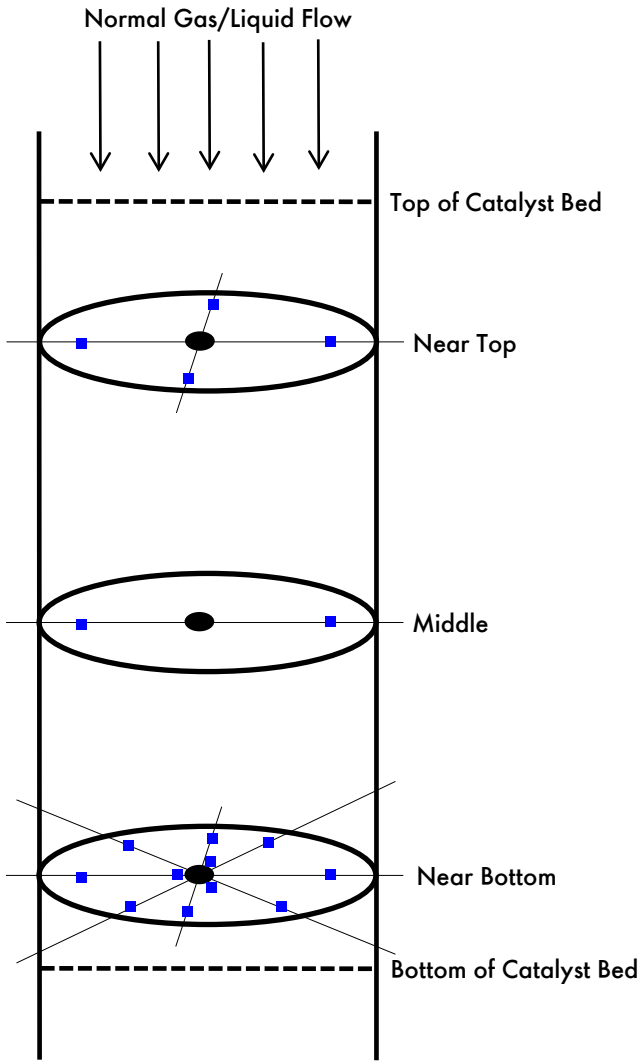
- Tosco maximum recorded temperature was 1950°F (1060°C)

Hydrocarbons 800C above AIT will ignite upon contact with air → instant jet fire!

Safeguarding Hydrocracking Runaways

Hydrocracker Safeguards for Temperature Runaway

Example radial thermocouple arrays to monitor catalyst bed temperatures



4 thermocouples

2 thermocouples

11 thermocouples

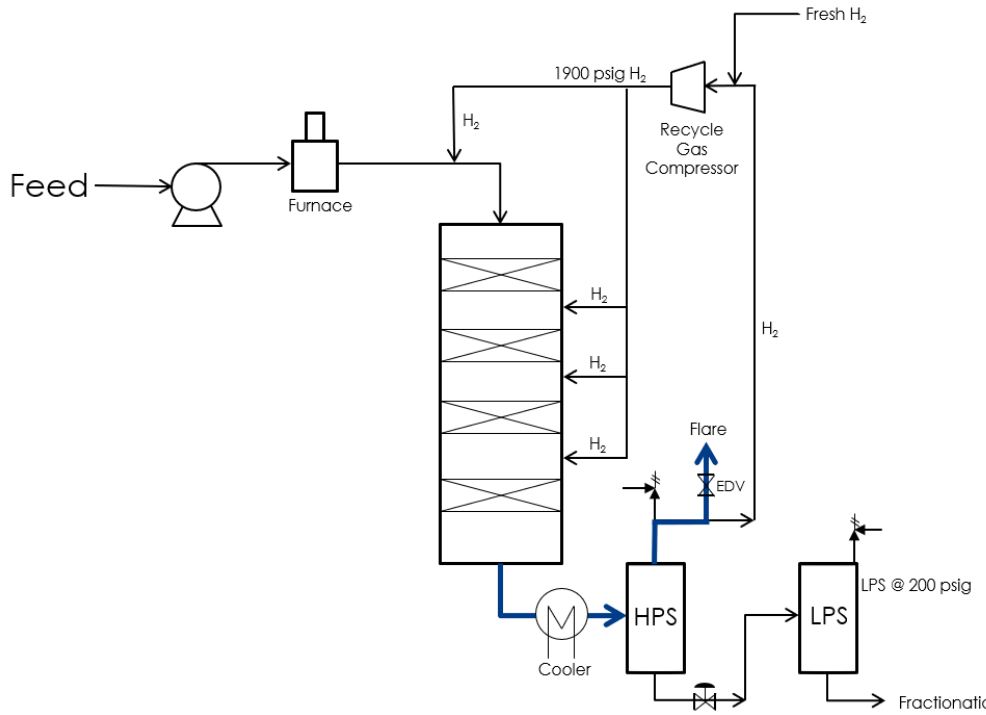
17 thermocouples per bed

Hydrocracker Safeguards for Temperature Runaway

Recycle hydrogen flow too low or thermocouples detect high temp:

- Depressure reactor system on low recycle hydrogen flow ← **Runaway imminent**
  - Loss of hydrogen recycle cannot be mitigated by increasing fresh H_2 flow

- Depressure reactor system on high reactor temperature ← **Runaway underway**
  - Depressuring will outpace reduction in tensile strength as the wall temperature increases
  - Depressuring removes hydrogen (the limiting reactant)



Hydrocracker Runaways: Final Thoughts

- Small changes in operating conditions can lead to a runaway
  - 8–10°F (4–5°C)
- Not an overpressure scenario. Thus, a relief device is not an effective mitigation.
- The runaway can happen in minutes. Do we have time for an operator response?
- Final temperatures can be very large
  - Up to 2000°F (1000°C)
- Effective safeguarding against runaways is critical
  - Contact the experts when modifying the process and/or safeguards (thermocouple design, alarm settings, trip points)