Start-up guidelines for a unit loaded with Sulficat® presulfided catalyst

Principle of hydrogen activation

When a hydroprocessing catalyst is preconditioned according to the SULFICAT process, sulfur necessary for the activation is already chemisorbed on the catalyst surface. The sulfidation reaction (Metal oxide + S chemisorbed + Hydrogen $\Rightarrow$ Metal sulfide + Water) occurs at around 100°C - 150°C (210-300°F). This activation is followed by a high temperature finishing step in which the final active sulfide phase is formed by the migration of the Cobalt (or Nickel) towards the edges of MoS_2 (or WS_2) slabs.

Start-up guidelines

Prior to catalyst activation, complete all routines normally applied before starting up (leak testing, safety, mechanical ...). Avoid any prolonged period under air or hydrogen without gas circulation. Do not pressurize the reactor under air.
A separate drying step is not required, as SULFICAT® treated catalysts do not absorb moisture.

1. Purge reactor with nitrogen to remove air. Ensure that oxygen content is less than 0.5 % vol.

2. Switch to hydrogen and increase the pressure at normal rate according to the vessel manufacturer's cold temperature pressure limits (temperature embrittlement curve) at minimum 5 bars (70 psig), preferably around 30 bars (430 psig).

3. Recycle gas at maximum gas flow rates. MEA scrubber preferably by-passed or not in operation (except if feed sulfur content exceeds 0.5wt%)

4. Raise reactor inlet temperature at 10-20°C/h from ambient towards a 180°C target. To avoid H_2O condensation in the catalyst at bottom of the reactor, control the heating rate so that the reactor inlet temperature does not exceed the reactor outlet temperature by more than 30°C.

5. At 80°C inlet temperature, start the liquid flow at normal start-up rate or at least 50% of the design feed rate.
   Hold the heating rate, resume heating when some liquid appears in the high pressure separator.
   At this point, the feed temperature should not be higher than 150°C. Hot feed (>150°C) introduction is not recommended. Feed temperature must be high enough (typically >80°C) to prevent pressure drop problems because of high liquid viscosity.

EURECAT SA
Quai Jean-Jaurès - B.P. 45
F07800 LA VOULTE-SUR-RHÔNE – France
Tel : 33.4.75.62.04.02 - Fax : 33.4.75.85 32.69
eurecat@eurecat.fr www.eurecat.fr

EURECAT US Inc
13100 Bay Park Road
Pasadena TX77507-1194, USA
Tel : (281)-474-2600 Fax: (281)-474-7776
eurecat@eurecat.com www.eurecat.com

Put oil on recycle, if possible. Due to a slight sulfur leaching from the catalyst, the liquid effluent can contain higher amount of sulfur than the feedstock. Liquid should be a straight-run light gas oil with a final boiling point (FBP) not higher than 380°C. Do not use any blend with cracked feedstock.

6. At 100°C-150°C, the catalyst activation will occur.

- A slight exotherm can be observed. If this is the case, hold reactor inlet temperature until the exotherm has stabilized, i.e. [T_{out} - T_{in}] decreases during at least 15 minutes.
  The magnitude of the exotherm will be affected by unit conditions such as: heating rate, gas and liquid flow rate (if liquid has been introduced) and catalyst metal content.

- Ensure hydrogen make-up is available to control the unit pressure as H_2 is consumed in the activation reactions and water condenses in the separator.
  Typical H_2 consumption is around 1 %wt of the catalyst load, i.e. roughly 85 Nm^3 Hydrogen/m^3 (85 SCF/ft^3) oxide catalyst during the time of the activation, typically ~2 hours.
  Monitor H_2S content in the recycle gas at the reactor outlet (decomposition of sulfur containing compounds in the presence of H_2. H_2S will increase at the beginning of the activation, then decrease as it is consumed. Typical values are in the range of 0.5 to 4 % vol. H_2S in the recycle gas. Minimize purge of the recycle gas (prevent H_2S loss).

- Water formed must be drained off from the High Pressure separator. Typical H_2O production is roughly 10 % wt of the catalyst load, i.e. 70 kg water/m^3 (0.5 gal/ft^3) oxide catalyst.

7. When the temperatures of the beds are equilibrated at roughly 180°C, raise the inlet reactor temperature to 315 - 320°C (may be 20-30°C higher for tungsten containing catalysts) at a rate of 20-30°C/h. Hold this temperature for at least 2 hours to fully activate the catalyst.
If sulfur content of the recycling feed drops below 0.09 wt% or if H_2S concentration in the treat gas entering the reactor goes below 200 ppmv, stop liquid recycling and go to once through liquid operation. The injection of a sulfur containing fresh feedstock will result in H_2S build up due to the start of HDS reactions when bed temperatures reach 240-260°C.

The liquid recycle can be stopped as soon as HDS reactions are effective, which can be witnessed by an increase of the H_2S in the recycle gas.

8. Switch from LGO to normal straight-run feedstock (if different) and go to normal conditions, according to the normal start-up procedure (start-of-run temperature, feedstock, make-up, pressure, treat gas).

Do not add any cracked feedstock during the following 3 days in order to prevent the catalyst from premature coking.

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