Question 20A: What are the recommended guidelines for operating temperature and temperature rise in reactor beds during the initial month of operation? What determines these limits?

BRANDON MILLER (Shell Catalysts & Technologies)

Operating temperature and bed temperature rise during the first month of operation can be critical with regards to safety and stable unit performance. In general, the limits of temperature and temperature rise are meant to keep the unit within the mechanical & metallurgical design of the equipment, to maximize the catalyst performance, to minimize the catalyst deactivation for the entirety of the cycle, and to meet the desired product quality. In addition, several factors influence the current and potential temperature and temperature rise of any given unit including feed rate/type, treat gas availability, and catalyst type.

One of the main risks early in the cycle with high temperature or high temperature rise is localized hydrogen deficiency leading to increased deactivation and reduced performance. Freshly-sulfided catalyst has not yet accumulated a significant amount of carbon deposits on its surface, and is therefore in a highly active state, sometimes called hyperactive or ultra-active. With the catalyst in this state, coke precursors in the feed speedily react to produce a molecule with an extremely reactive free radical site. Ideally, this site would react with hydrogen; but because of the accelerated reaction rate at the surface of the catalyst in this highly active state, there can be localized hydrogen deficiency. Without hydrogen readily available to react with the free radical site, the molecule will polymerize or condense with another molecule or it may just deposit on the catalyst surface as coke. When coke deposits in this hurried, sloppy way, it often blocks the entrance of the catalyst pores or active sites, resulting in premature permanent deactivation.

To help reduce this risk, it is generally advised that cracked stocks be avoided during the first 3 days of operation on fresh catalyst, and then slowly introduced following the 3-day period. Cracked and heavy feedstocks are rich with coke precursors (PNAs, asphaltenes, etc.), so controlling these feeds early on minimizes the quantity of coke precursors and allows the initial layer of coke to deposit on the catalyst surface in a more controlled manner. Once the initial layer of coke has laid down, it helps stabilize the active sites and prevent agglomeration of metals. This maximizes long term catalyst activity.

Treat gas balance is also critical in ensuring there are no pockets of hydrogen deficiency in the reactor, thereby minimizing coke formation in reactor beds. Since temperature rise is a result of hydrogen consumption reactions, the bottom of high heat release beds often experiences increased coking tendency due to the reduced hydrogen partial pressure. This can be especially true in top beds where the feed is in its least saturated state. During the initial month of operation many units are especially vulnerable because the heat release profile has just changed from near-spent catalyst operating at end of run conditions, to fresh catalyst at start of run conditions. For instance, the top beds, which had been poisoned and deactivated over the course of the previous cycle, may now generate significantly more heat release. So, the treat/quench gas strategy will need to be adjusted, sometimes drastically, to ensure desirable hydrogen to oil ratios throughout the bed.

Another thing to keep in mind is that coming out of a prolonged downtime the feed mix may be different than usual. Sometimes during an outage, inventories of high value feeds buildup in tankage and upon starting the unit there is an urgency to run-off the excess feeds (cracked stocks, heavy cuts, etc.) at higher-than-normal rates/ratios. In some cases, the combined effect of running more cracked stocks during the most active month of the catalyst's life can be limiting. For example, a unit that is not usually limited by hydrogen consumption may need to reduce operating temperature during the initial weeks of operation to keep the hydrogen consumption within the availability limits.

Often when we talk about temperature, or temperature rise, we refer to an average number. However, it is important to realize that many of the limitations faced will be determined by the peak temperature of a reactor/bed, not the average. Most hydroprocessing beds have some amount of radial flow maldistribution. The amount of maldistribution varies wildly and can be caused by imperfections in the reactor internals or installation thereof, catalyst loading, reactor configuration, etc. This maldistribution leads to differences in the radial temperature profile that must be considered when setting unit limits. For example, peak temperature can be critical when considering metallurgical, product aromatic, or mercaptan recombination limitations. So, depending on the amount of maldistribution experienced/expected, the strictness of the limits may need to be adjusted.

Some of the limits we encounter are dynamic and can depend on the current operating conditions of the unit. Here are two examples in addition to a feed change discussed previously:

- Due to maldistribution, more temperature rise in a bed leads to larger variation in peak temperatures, leading to a changing limit. This may lead to slightly more generous temperature rise limits at start of run compared to the previous limit at end of run.
- Thermal cracking increases with the absolute temperature. Early in the cycle, temperatures may be low and there is minimal thermal cracking taking place, but at the higher end-of-run temperatures there will be much more thermal cracking. So, the maximum acceptable temperature rise limit may vary with the current absolute temperature. For example, in some units, a high temperature rise could be acceptable at the low start of run temperatures and unacceptable at the higher end of run temperatures when thermal cracking is more prevalent.

Operating temperature and bed temperature rise limits are often set by the maximum allowable temperature of the equipment, under the unit's operating conditions. These limits are impacted by the feed coming into the unit, the unit operating conditions, the catalyst type, and the operator's ability to keep the unit within the limits under abnormal or excursion events (e.g. quench availability, quench valve operation, etc.). The overall temperature or temperature rise in any given bed may be limited, especially at start of run, by a combination of these factors; the intent being to safeguard the unit against a temperature excursion, or runaway that cannot be easily controlled. These safeguarding limits and guidelines should be reviewed on a case-by-case basis with the appropriate safety experts, unit designer, and catalyst vendor.

Once all the safety & design limits are accounted for, temperature and temperature profile can be set based on meeting the target outcomes of the unit; whether that be equal bed outlet temperatures at maximum aromatic saturation, or an ascending profile tailored to give fixed product quality. During the first month of operation we typically advise units to slowly and incrementally move towards their ideal operating conditions to avoid inadvertently causing a localized disruption that could lead to premature deactivation, and to avoid overreacting to the changing conditions without giving the unit time to equilibrate and respond.

Print as PDF:

Tags

Tankage

Year

2019

Submitter

Consultant

Operator