
Question 12: Is there any harm adding cracked stocks too quickly after break-in following catalyst activation? What is a typical introduction rate?

Tim Lewer (Shell)

On freshly activated catalysts, the surface is relatively clean (free of coke) and therefore is unusually active. This is sometimes referred to as hyperactivity. In order to maximize catalyst stability for good cycle length, it is important that the rate of coke lay down on freshly sulfided catalyst is gradually controlled. Upon completion of metals sulfiding, catalyst hyperactivity exists, but is short lived as feed processing lays initial coke on catalyst. Processing cracked stocks that contain more reactive molecules and coke precursors too early over the hyperactive catalyst can result in operability issues through cracking while accelerating the initial coke lay down on catalyst.

Cracked stocks contain large amounts of aromatics and olefins, which release large amounts of heat when saturated. Aromatics and olefins undergo saturation, but they can also condense or polymerize to form larger molecules, gums, and coke. When cracked stocks are introduced too soon, passing such highly reactive molecules over hyperactive catalysts leads to excessively high reaction rates. The resulting high exotherms aggravate the situation, because reactions like polymerization are faster at higher temperatures. By processing only straight run feeds for the first 72 hours after catalyst activation, the initial coke lay down is gradual for improved long-term stability.

The cracked stock introduction rate varies by unit, but should allow for exotherm stabilization, reestablishment of unit pressure as H₂ consumption increases, and coordinated with smaller temperature additions to treat the more reactive feed molecules.

Minh Dimas (CITGO)

I understand “break-in” to be the same as “catalyst conditioning period” – i.e., three days of straight run material only (no cracked stock). It is imperative to adhere to the three full days of break-in (or catalyst conditioning) period following the catalyst activation/sulfiding (which is not included in the three days). After the catalyst is successfully conditioned, the cracked feed can be introduced as quickly as desired by Engineering and Operations (comfort factor) and as manageable by the unit equipment and utilities (i.e., charge heater, hydrogen makeup rate vs. consumption, reactor quench ability, etc.). Since the catalyst conditioning period “quenched” the hyper-active sites of the catalyst, the introduction rate of cracked material after the catalyst break-in / conditioning is negligible.

Kaspar Vogt (Albemarle)

Cracked and heavy feedstocks contain significant quantities of hydrogen deficient molecules known as “coke precursors”. These coke precursors (olefins, poly-nuclear aromatics, asphaltenes, concarbon) tend to polymerize, condense or form coke, given the right set of reaction conditions. Freshly sulfided catalyst, with little or no carbon deposits, is in an ultra-active state. Coke precursors in the feed readily react on the catalyst to produce a molecule with an extremely reactive free radical site. Ideally, this site would react with hydrogen but, because there are so many reactions taking place on the catalyst in its ultra-active state, there can be localized hydrogen deficiency. Without hydrogen readily available to react with the free radical site, the molecule may polymerize or condense with another active molecule, or it may simply deposit on the catalyst surface as coke. All of these outcomes result in blocked pores and/or active sites. Fresh catalyst has hyperactivity due to the absence of coke. Once coke has laid down, the catalyst reaches its design activity, and the coke prevents the agglomeration of metals.

Testing shows the loss of activity between immediate and a three-day waiting period before cracked feed introduction to be 10-15%. We recommend to stepwise increase the amount of cracked stock, which will have a higher exotherm, so that the unit does not incur large temperature swings. It varies per unit depending on the feeds and operating conditions but typically addition of 10% of cracked stocks per two-hour period is good operating practice.

There are commercial offerings available to ex-situ sulfide the catalyst with a special cracked feed protection (CFP) treatment for direct introduction of the cracked feed.

Ben Sim (ART)

Introducing cracked stocks too early after sulfiding will cause noticeable loss in activity. Coke precursor molecules in cracked feeds will have a tendency to form coke over the fresh and highly active sites on the catalyst. By delaying the introduction of cracked stocks for at least 3 days after sulfiding will allow the catalyst activity to be passivated which helps to minimize these effects.

After running for three days on straight run the cracked material should be added to the feed stream gradually. ART typically recommends adding the cracked feed in small increments every shift making sure the reactor exotherm remains under control and within acceptable limits before increasing the cracked feed amount any further.

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