
Question 96: How do you manage sulfur in the feed to a catalytic reformer? What is the minimum allowable sulfur for CCR, semi-regen, and cyclic reformer feeds? What are your sampling frequencies and allowable ranges? What is your experience with carburization and/or metal-catalyzed coking?

Joe Zmich (UOP LLC)

UOP has extensively researched the tendency of metal surfaces to promote coke formation. UOP will provide specific recommendations on operating guidelines based on unit design and operating conditions. We are aware of two fixed bed units that have each operated with feed sulfur below 0.05 wppm and experienced coke growth in the reactors. Subsequent operation with a target of 0.15 wppm S successfully prevented repeat coke growth. Most fixed bed reforming catalyst systems must be properly sulfided following regeneration to attenuate the catalyst metal function. UOP has no direct experience with cyclic reforming unit operation as it relates to sulfur management. UOP's philosophy is to regulate feed sulfur concentration and perform regular feed analysis as well as sampling recycle gas and stabilizer off gas once per shift. In addition to reactor section metal surface passivation and prevention of metal catalyzed coke, sulfur also contributes to inhibiting heater tube carburization.

In general, reactor section coke is metal catalyzed that can be prevented by ensuring adequate sulfur in the feed to the unit. UOP would need to evaluate the specifics of the unit operating conditions and the history of the coke growth to determine the course of action that UOP would recommend to prevent future coke growth in a cost-effective manner.

Rick Grubb (Chevron USA)

We have experience with both carburization and metal-catalyzed coke. In the past, we have had a furnace develop a tube leak and we have collected stringy coke on occasion in other units. We currently manage sulfur in the reformer feeds by either adding DMDS or by removing the sulfur sorbers on the effluent of the NHT's. The spec is 0.3 to 0.5 ppmw in the feed. This spec is more critical in the lower pressure units and those units inject DMDS into the feed. Some of the older existing semi-regen units don't have sulfur control other than what is in the product from the NHT. We test the feed for sulfur daily and test the recycle gas for H₂S each shift (every 12 hours). For the older higher pressure semi-regen units that depend on the NHT's, there are occasions where the feed sulfur is non-detectable. In those cases, we feel safe if we have some H₂S in the recycle gas. If we don't detect anything in the recycle gas then we backdown the severity in the NHT's.

Javier Quintana (Valero Energy)

Sulfur management in reforming feed is essential to ensuring adequate protection from metal-catalyzed coking. However, this is not to suggest that it is acceptable to reduce hydrotreating severity in an attempt to control sulfur slip, as such a practice would generally be associated with slip of other impurities such

as nitrogen and possibly metals. Rather, Valero's best practice is to ensure maximum hydrotreating to remove all feed impurities, sufficient reflux in the hydrotreater stripper to ensure complete stripping of all moisture and hydrogen sulfide, followed by a controlled injection of a sulfiding agent into the liquid feed to the unit.

Our minimum recommended injection rate is 0.3 wt ppm on feed, although higher levels may be necessary depending on unit-specific history. If a unit has evidence of metal-catalyzed coking, including trace levels of carbon build-up on reactor walls between scallops or in other low flow areas of the reactors, then that unit should increase the minimum target level of sulfur injection. Negative yield effects of sulfur are not expected until injection rates are in excess of 1.0 wt ppm, at which level most units (even those at extremely high severity) should be adequately protected. Injection rate should be confirmed with draw down of the level in the sightglass of the vessel or skid containing the sulfiding agent. All reforming units are at risk of metal catalyzed coking, with some units having higher risk than others – we have experienced such coking in relatively high pressure fixed bed units, as well as in moderate pressure CCR units.

If any maintenance work is done in the hot portions of the unit, such as retubing a furnace or even taking a tube sample for metallurgical testing, then the new furnace tubes will lack the necessary passivating layer of sulfur, and may be at higher risk of forming metal catalyzed coke. In such a case, an elevated level of sulfur injection is recommended on restart.

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