Question 35: How far can the hydrogen to hydrocarbon ratios be decrease in gasoline hydrotreating units before experiencing high reactor pressure drops? Please provide some details of your experience with reference to the run length limitations and operating performance.

Ujjal Roy (Indian Oil Corporation)

We have number of naphtha hydrotreatment units in our refineries, some operating with straight-run naphtha as feed and others in mix mode with significant cracked feedstock varying from 10% to 40%, to produce feedstock for catalytic reformers. I suppose, the question here is for hydrotreating units processing cracked components.

Straight-run naphtha hydrotreatment units, in our case, are designed for low pressure (i.e. 20-25 kg/cm2.g) and with 40-75 Nm3/M3 of gas to oil ratio depending on feedstock characteristics and desired product quality. In case of hydrotreaters designed to process FCC gasoline, designed gas to oil ratio is about 400 – 500 Nm3/M3 of feed operating at about 50 kg/cm2. The designers recommend the partial pressure of hydrogen through gas oil ratio and system pressure based on the given feed characteristics and target product w.r.t. olefin, sulphur and nitrogen content. Difficult feedstocks with higher nitrogen content require higher hydrogen partial pressure. Reduced gas to oil ratio can only be compensated partially through higher RIT for equivalent nitrogen removal. But running at higher RIT compensating for lower gas to oil ratio with cracked component in feed will accelerate the coking rate on catalyst leading to high pressure drop. Coke formed on the top of catalyst bed can lead to excessive pressure drop and channeling within reactor which will reflect in radial temperature spread. Delta T across the first bed of the reactor will increase due to less availability of hydrogen as heat sink. Also, lower gas to oil ratio aggravates coke formation in the preheat exchangers resulting in high pressure drop. All these would finally lead to slippage of sulphur and nitrogen in product apart from reduced cycle length. This phenomena has been experienced in one of our hydrotreaters with cracked component in feed due to problem in RGC resulting in low flow over days. We normally do not practice lower gas to oil ratio below recommended value as the penalty is large over the time period as compared to pushing extra capacity or reduced energy consumption.

However, in one of our units, we have optimized gas to oil ratio to nearly 90% of recommended value with the advice of licensor, by shifting some reaction from Bed-1 to Bed-2 through reduced reactor inlet temperature in Bed-1 and reduced quench rate in Bed-2. This in turn has led to ascending temperature profile i.e. drop in Bed-1 peak temperature as compared to that of Bed-2 peak temperature. By doing so, we could maintain uniform radial temperature and no appreciable increase in reactor Delta P since about two years of operation inferring no appreciable reduction in run length due to these adjustments.

In case of coking or fouling, pressure drop across reactor will increase steadily over operation and spikes are not expected. Despite maintaining design gas to oil ratio in many of the hydrotreaters, we have experienced high pressure drop leading to frequent skimming of catalyst bed. The reasons for these incidents have been identified to be caustic carry over from upstream caustic wash units, dissolved oxygen in tank wagon while being transported from one refinery to another and carryover of foulant from feed tanks.

The decrease in run length on account of lower gas to oil ratio operation on continuous basis is a factor of type of feedstock i.e., olefin, sulphur and nitrogen contents and target product specifications. In case of margin available in the feedstock quality, gas to oil ratio can be optimized based on adjustment in reactor severity and conversions.

Praveen Gunaseelan (Vantage Point Consulting)

It is assumed that the question pertains to FCC gasoline hydrotreating. Due to the variability in unit designs, process configurations, feed compositions, contaminant levels, product quality targets, etc., a specific answer to the question cannot be provided. For site-specific guidance, refiners are advised to consult with the gasoline hydrotreating process licensor or a qualified engineering contractor.

Maintaining adequate partial pressure of hydrogen is a critical element of hydrotreater operation, as it minimizes coke formation on the catalyst. An adequate feed gas to oil ratio is also essential as the gas plays a critical role in heat removal from the reactor. For these reasons, hydrotreating process licensors often require a minimum gas to oil ratio during operation to prevent premature catalyst deactivation and reactor overheating. While a common rule of thumb is that the minimum gas to oil ratio should be at least 4 times the hydrogen consumption per barrel of feed, it is critical to recognize that this ratio is inherently unit-specific, and the licensor or designer’s operating recommendations should be strictly followed.

Other potential complications of operating at low hydrogen to hydrocarbon ratios include reactor fouling due to incomplete saturation of diolefins, accelerated catalyst deactivation due to higher temperature operation, and unsatisfactory product quality.

The chapter on Hydrotreating by A. Gruia in the Handbook of Petroleum Processing (D.S.J. Jones, P.R. Pujadó, eds., Springer, 2008) has useful information pertaining to this question.

Olivier Le-Coz (Axens)

As a general guideline, in viewpoint of catalytic performances and cycle length it always recommended to operate naphtha HDS reactors at maximum recycle gas rate. Because those reactors operate in gas phase Hydrogen partial pressure is significantly affected when the recycle gas rate varies. Maximized recycle has rate and thus Hydrogen partial pressure, allows minimizing catalyst temperature and maximizing cycle length. In the case selectivity towards HDS versus olefins saturation is targeted, maximizing recycle gas rate to maximize hydrogen partial pressure and minimize catalyst temperature is crucial.

Brad Palmer (ConocoPhillips)

COP sets the lower limit on gas/oil ratio at 300 scf/b (with a minimum of 70% hydrogen in the treat gas). Remember that the hydrogen is diluted by vaporized hydrocarbon, especially in a naphtha unit. Hydrogen partial pressures are actually very low. We also set a minimum of 3:1 treat gas hydrogen to chemical hydrogen consumption, i.e., the treat gas hydrogen rate per barrel must be at least 3 times the per-barrel hydrogen consumption. Both of these criteria are supposed to be met. In practice, some units do not meet the minimum rates.

Once the minimum is met, there are many other factors that are more critical than the hydrogen/oil ratio. These factors include the operating pressure, LHSV, feed composition, feed contaminants and percent cracked stock.

With respect to hydrogen gas/oil ratios, we can offer direct comparisons where two units feed essentially the same feedstock and operate at primarily the same conditions, except for the gas/oil ratio. The best comparison basis is barrels of oil processed per lb catalyst because in this case the units do not have exactly the same catalyst volumes.

•Case 1: Straight-run naphtha feed at about 360 psig. One unit has more catalyst in it, but the cycle lengths are the same at 18 months. One unit has 140 scf/bbl hydrogen and the other has 270 scf/bbl. The oil amounts processed in 18 months in these units are 195 and 241 Bbls/Lb catalyst, respectively. The unit with the higher gas rate processes about 24% more oil per pound with a gas/oil ratio about 93% higher.

•Case 2: Straight-run naphtha feed at about 450 psig. Again, the amounts of catalyst in the units differ, with the cycle lengths the same at 48 months. Gas/oil ratios are 570 scf/bbl and 710 scf/bbl. The barrels per pound catalyst processed are 571 and 740, respectively. The unit with the 25% higher gas rate can process about 25-30% more oil.

Tags

[Catalysts]

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