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## **Question 19: In a hydrocracking unit, what methods do you use to determine the pretreat reactor operating temperature for optimum nitrogen slip to cracking catalyst?**

### **AMIT KELKAR (Shell Catalysts & Technologies)**

Nitrogen slip is a key variable in balancing the performance of the pretreat and cracking catalysts for cycle optimization. The optimum nitrogen slip depends on the specific unit objectives and constraints. In general, the pretreat temperature is adjusted to maintain sufficiently low slip to the cracking catalyst to achieve the target conversion while also balancing the activity to fully utilize both catalyst systems. Lower nitrogen slip results in improved product quality and more volume swell but can lead to faster utilization of the pretreat system which may reach EOR before the cracking catalyst.

Hydrocrackers with separate pretreat and cracking reactors are often equipped with an inter-reactor sample to track N-slip. In units without adequate sampling, top cracking bed dT is used as a real time indicator of nitrogen poisoning. Decreasing top bed dT suggests increasing N slip which in turn requires higher cracking severity to maintain conversion. If the slip is high enough, N inhibition can progress down the lower beds as evident in loss of dT. Nitrogen inhibition is reversible and cracking activity recovers once pretreat WABT is raised. Cracking bed temperatures should be monitored carefully as N-slip is lowered to avoid excessive cracking as activity recovers. It is important to note that N-slip is one of many variables that impacts bed dT and should only be used as a qualitative indicator. Kinetic modeling and pilot plant testing are useful tools to understand impact of N slip on cracking activity and selectivity.

Customized catalyst system design is critical in optimizing pretreat and cracking activity for maximum performance. Pretreat limited units are designed with a robust cracking catalyst system that can withstand higher N slip in the later part of the cycle without loss of conversion. A H<sub>2</sub> constrained unit might need to be designed with a higher N slip and the appropriate cracking system to meet performance objectives. In some instances, the HCPT WABT is rapidly raised at start of the cycle to the optimum temperature for maximum aromatic saturation and maintained there. This is often the case with highly aromatic feeds like LCO to maximize volume swell.

In addition to WABT, temperature profile is an important handle in balancing pretreat and cracking severity. For pretreat, optimum catalyst utilization is achieved by operating in an equal bed outlet mode so that each bed deactivates at a similar rate. At times, pretreat must be operated in an ascending profile to generate enough heat input for the cracking reactor or to optimize metals uptake. On the other hand, cracking beds should be operated at equal bed dT to ensure similar deactivation. The top bed is exposed to the highest nitrogen inhibition and maintaining equal bed dT means operating in a descending profile. This can lead to higher temperature in the lower beds and possible runaway in case of loss of quench. Hence the recommendation is to target lower dT in the top bed and equal dT's for the lower beds.

Understanding the nature of the molecules being converted and specific unit constraints is key to selecting the appropriate catalyst system and managing the temperature profile for overall unit optimization.

The pretreat temperature is ideally set to hit a desired nitrogen slip to the cracking catalyst. However, in some circumstances the nitrogen slip cannot be measured. This could be because there are pretreat and cracking beds in the same reactor with no way to sample between beds. Or, even when there is a separate pretreat reactor there may not be facilities to obtain a sample of the effluent before it is mixed with recycle oil to the cracking reactor or effluent from the cracking reactor. In such circumstances the pretreat temperature needs to be set based on cracking catalyst performance.

A typical nitrogen slip from the pretreat reactor would be in the range of 20-60 ppmw but can sometimes be higher or lower. The target depends on how active the cracking catalyst is and the need to balance pretreat and cracking catalyst life. More nitrogen slip allows a reduction in pretreat temperature and extends pretreat catalyst life. Less nitrogen slip increases the activity of the cracking catalyst – this can be used to operate at a lower temperature and extend cracking catalyst life or increase conversion.

The simplest way to operate the pretreat and cracking beds is to monitor their respective weighted average bed temperatures (WABT) and exotherms. If the exotherm in the lead cracking bed decreases at the same inlet temperature, nitrogen slip may have increased and the pretreat WABT should be increased. This principal applies to a single stage unit where there is simply pretreat followed by cracking catalyst and also to a two stage recycle unit – in both cases a higher pretreat WABT will reduce nitrogen slip to the cracking catalyst and increase conversion at the same cracking bed temperature.

When measuring nitrogen slip, it is best to look at the nitrogen content of the unconverted oil (UCO) after naphtha and diesel have been removed. Catalyst vendors will recommend a target nitrogen slip that should work well for their catalysts in a particular unit but this may need to be adjusted as operating conditions change and the catalyst ages.

#### **ROBERT STEINBERG (Motiva Enterprises)**

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### **SYED SHAH (Honeywell UOP)**

In a hydrocracking unit, the most effective way to optimize the nitrogen slip to the cracking catalyst is by taking a pretreat effluent sample and testing it for nitrogen using ASTM D4629 or ASTM D5762. Knowing the nitrogen slip from the pretreating catalyst allows determining the relative performance and stability between the pretreat and cracking catalyst systems to make optimum use of each. UOP Unicracking design includes a sample point on pretreat reactor effluent that is specifically designed to take a sample of this hot stream. Based on nitrogen slip result, pretreat temperatures are adjusted to maintain the nitrogen slip close to the target required for optimum performance of the cracking catalyst. It is important to balance the deactivation rates of treating and cracking catalyst. Over-converting of nitrogen can result in accelerated deactivation of the pretreat catalyst. Under-converting of nitrogen can result in higher temperatures for the hydrocracking catalyst along with reduced yield selectivity and product quality. Depending on specific unit objectives such as product quality or maximum hydrogenation, optimum target nitrogen slip may be anywhere from <1 ppmw to >100 ppmw.

Hydrocracking units without an intermediate sample point between the pretreating and hydrocracking catalysts are becoming more common due to units with both catalyst types in a single reactor or due to reluctance based on safety concerns with taking the inter-reactor sample. Without the intermediate sample, judgment must be made based on the information available, although this is difficult to do accurately. First priority is that both catalysts must be operated within the safe operating limits of the unit including heater duty, quench availability, and bed temperature rise limits. If these conditions are satisfied, then estimating techniques for monitoring catalyst performance can be considered.

The total temperature rise of the pretreating catalyst is the primary indication of hydrotreating severity. With a given feed composition, the relative temperature rise between pretreating and hydrocracking can be evaluated. A decreasing pretreat temperature rise along with increasing hydrocracking temperature rise may imply a shift of the hydrotreating reactions to the hydrocracking catalyst. In this case, a higher pretreating temperature may return balance to the catalyst severities. In the past, a decreased temperature rise in the first hydrocracking bed was interpreted as an increased nitrogen slip, particularly with noble metal catalysts. However, today's base metal hydrocracking catalysts are more tolerant of increased nitrogen slip and can often have a significant temperature rise from hydrotreating reactions alone. Therefore the hydrocracking temperature rise may not always be reliable for this purpose. The catalyst supplier can assist by providing operating targets and operating response curves.

### **RAHUL SINGH (Haldor Topsoe, Inc)**

A hydrocracker unit consists of a hydrocracker pretreat section and a hydrocracking section. This can be

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housed in one reactor or two or more separate reactors depending on the unit configuration. Hydrocrackers process a variety of feeds (gas oils, cycle oils, coker gas oils, deasphalted oils, coker naphthas, etc.) with a wide range of properties (S, N, SG, Aromatics, SIMDIST) under variety of process conditions (T, P, LHSV, H<sub>2</sub>/oil). Feed is introduced in the pretreat (P/T) section, where predominately saturation reactions (hydrodenitrogenation [HDN], hydrodesulfurization [HDS] and hydrodearomatization [HDA]) occur on the catalyst surface. The effluent of the pretreater is then processed over the cracking catalyst where cracking and saturations reactions occur to produce the desired products, i.e., naphtha, jet, diesel, with desired yields and specifications.

A hydrocracking catalyst is comprised of metals (Ni, W, Pt, Pd) supported on zeolites. Cracking reactions occur on the zeolite while saturation reactions occur on the metal sites. Nitrogen in the pretreat effluent, i.e., nitrogen slip, has an important role in optimizing the operation of a hydrocracker. Various ways to determine the optimum nitrogen slip to the cracking reactor are discussed below.

(a) Cycle Length - Refiners have a target of cycle length of the hydrocracker. A majority of hydrocrackers are pretreat activity limited. This means that the EOR WABT is reached earlier for the pretreat catalyst compared to the hydrocracking catalyst. EOR WABTs are known and depend on design specifications or process limitations. To meet the cycle length, SOR WABT of the P/T can be determined from the expected deactivation rates and EOR WABT. The SOR WABT of the P/T determines the nitrogen slip based on the reaction conditions. For example, a higher nitrogen slip will allow the HDC P/T to be operated at a lower temperature and hence, a longer cycle length can be expected. A high zeolitic catalyst can be placed in the hydrocracker to counter the effect of high nitrogen slip on the activity of the HDC catalyst.

(b) Volume Swell - Nitrogen slip is determined by the HDN activity of the pretreat catalyst. For the same wt % conversion in a hydrocracker, a high HDN, HDA, HDS activity of a certain P/T catalyst would generate a P/T effluent with a high API, which will be further processed in a hydrocracker producing a higher volume swell. If there is hydrogen available on the site, it is always good to use the hydrogen to upgrade the feed to valuable products, and increased swell. The desired volume swell can be translated into API upgrade, which can be interpreted into HDN activity and ultimately a function of WABT for a given feed. A disadvantage of operating in a higher nitrogen slip mode is putting the burden of this work on the cracking catalyst, which causes it to lose its selectivity to desired products. This selectivity deteriorates from SOR to EOR when operating in high nitrogen slip mode.

(c) Hydrogen consumption - Saturation reactions, i.e., HDS, HDN and HDA occur on the pretreat catalyst which require hydrogen. The available hydrogen for chemical consumption to the unit is determined from make-up gas rates and hydrogen purity. Nitrogen slip depends on the mono, di and tri+ aromatic saturation activity of the P/T catalyst, which combine with HDS and HDN activity to control hydrogen consumption. Hence, available hydrogen consumption from M/U can be correlated to nitrogen slip from the P/T.

(d) Conversion - Every hydrocracker unit has a specific conversion target. Nitrogen slip is a factor in determining the required WABT for the hydrocracker to achieve a specific conversion. Cycle length requirement, together with conversion, in Hydrocracker can be used to determine the optimum nitrogen slip. At higher nitrogen slip, the hydrocracking catalyst must run hotter and thus will shift the selectivity from liquid towards gas make. It is therefore necessary to use P/T catalysts which produces lower nitrogen slip and still meet cycle length requirement.

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(e) Product quality - Hydrocrackers add hydrogen, to lower quality oils, which produces quality products (Naphtha, Jet and Diesel). Most of the product specifications (Sulfur, Nitrogen, API, Cetane Index, Smoke point) are a function of saturation which is strongly affected by nitrogen slip from the P/T. A low nitrogen slip from the P/T would produce inter-stage effluent with high API upgrade. This automatically translates into a better product quality, after it gets further upgraded on a hydrocracking catalyst. Therefore, the product property objectives would set the HDN activity of the P/T. Nitrogen in the P/T effluent has a strong affinity to adsorb on the HDC catalyst and hinder the cracking and saturation activity, which cannot be compensated by increasing the temperature as the product selectivity would change towards higher gas makes.

(f) Process constraints - Last, the M/U availability, quench limitations and treat gas play a role in determining the nitrogen slip from the P/T. Hydrogen availability has to be above a minimum number for a good deactivation rate of the P/T catalyst. We know from earlier discussions that nitrogen slip is related to hydrogen consumption in the P/T. Therefore, hydrogen consumption and availability can be used to determine the required nitrogen slip. Saturation reactions occur in the pre-treater, which is exothermic. A low nitrogen slip would result from a high degree of saturation activity which would result in large exotherms. Operations can dictate the accepted temperature profile, i.e., equal bed outlet or ascending temperature profile, or what is the difference in temperature between HDC P/T last bed outlet temperature and HDC inlet temperature. The available quenches and reactor heater limitations would be a factor in determining the target N slip.

(g) Operating conditions - The hydroprocessing reactions are all a function of hydrogen-to-oil, temperature, pressure and feed properties (S, N, SG, SIMDIST). These factors, together with all of the above, are used to determine the nitrogen slip from the P/T. The goal is to have a high HDN activity to produce low nitrogen slip which leads to a scenario of superior profits to the refinery by producing high volume swell, excellent product properties, heavy feed processing ability, extended cycle length, operational stability and improved selectivity of the products from SOR to EOR. Haldor Topsoe offers industry leading superior HyBRIM™ and Hyswell™ hydrocracker P/T catalyst providing refiners with the choice of optimizing their hydrocracker performance, ease of operation and excellent profits over the cycle.

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