
Question 22: In your experience, how are ULSD units maximizing catalyst life/ cycle length? Do you use feedstock or catalyst analysis to locate sources of contaminants, especially arsenic?

Brian Moyse (Haldor Topsoe)

Many factors impact the cycle length in a ULSD unit, and in order to ensure the longest possible cycle length in such units it is important to:

Have an optimal flow distribution and gas mixing using latest generation reactor internals designed for the actual operating conditions. This is very important in order to ensure maximum catalyst utilization with no channeling in the catalyst bed.

Ensure hydrogen availability all through the reactor using optimum flow rates and quenches. Hydrogen is not only used for the hydrotreating processes, but also to minimize coke formation and thus lower catalyst deactivation rate.

Optimize the quench injection and rate to ensure the lowest possible WABT throughout the run as higher temperature will accelerate coking rates.

Have a complete feedstock analysis and composition, in particular the organic feed nitrogen. Organic feed nitrogen plays a key role for catalyst performance. It is not only important to know the feed nitrogen, but also the catalyst's ability to lower the organic nitrogen. The level of nitrogen in the product dictates the optimal catalyst for the given service, be this CoMo, NiMo, or a high activity HDN catalyst.

CoMo catalysts perform best if organic feed nitrogen is high, and product cannot be reduced to 1-2 ppm level. A NiMo, high activity HDN catalyst is the optimal catalyst if product nitrogen can be reduced to < 1-2 ppm N.

Select the appropriate catalyst for the given operating conditions. If the right catalyst choice is made, it can operate at the lowest temperature and thus ensure a long cycle. Failure to achieve this will result in a catalyst load which will suffer a rather fast deactivation rate. Also, catalysts containing any elements that improve the HDN activity will have a tendency to deactivate faster if they are not able to lower the feed nitrogen to very low levels under the actual process conditions. This is often the case where the feed blend contains cracked stocks like cycle oil, coker gas oil, etc.

Feed impurities that contaminate and deactivate catalysts must also be addressed and removed. Typical elements are V, Ni, Fe, P, Si and As; and these will deactivate the high activity catalysts in different ways. They can however be trapped in a well-designed grading or in specific traps which are optimized for contaminant pickup to protect the high activity downstream catalysts.

Typically, Haldor Topsøe uses feedstock analysis to identify and quantify feed contaminants such as described above, (feed nitrogen, V, Ni, Fe, P, Si and As). Arsenic (As) is known as a very strong catalyst

poison, even in ppb levels. To quantify Arsenic content new techniques, have to be applied to quantify the ppb levels in order to be able to properly design the optimal grading/trap solution. We also use spent catalyst analyses when these are available from previous cycles, as this will help support the feed analysis.

Vern Mallett (UOP)

This is a two-part question the first part being maximizing catalyst life/cycle length, and the second being feed contaminants.

Part 1: Regarding maximizing catalyst life/cycle length. This will greatly depend on several factors mainly economic on how a ULSD complex or individual unit is optimized. Economic decisions within the organization dictate the operating conditions necessary to achieve product yields and properties, what feed components are processed in the unit, balanced with getting the optimum performance from the catalyst. This balance is challenging from an economic and operational aspect. The need to maximize margins by processing higher than design raw feed rates and heavier feed components, is resulting in a more exact monitoring of the catalyst performance. Refiners are operating units with higher than design reactor catalyst bed axial rises, and radial temperature spreads, as units process a wider range of feed components.

Expected catalyst life is also closely linked to refinery turnaround schedules for other processing units, which presents challenges on how best to optimize catalyst performance and still achieve the desired cycle length to coincide with refinery wide turnaround schedules.

Part 2: Regarding using feedstock or catalyst analysis to locate sources of contaminants especially arsenic. In order to identify the source of contaminants a monitoring program must be established designed to separate components that may be contributing to the contaminant issue(s). These components are usually but not always the individual feeds that a unit is processing. The first phase of a program is generally centered on the feeds that are being processed in the unit. Other sources of contaminants such as scale or FeS may enter into the unit from upstream processing equipment and fractionation within the hydroprocessing unit itself, which will contribute to catalyst bed pressure drop or increase maldistribution and depending on type and accumulated amount of the scale can contribute to loss of catalyst activity. It is important to understand what contaminant or accumulation of contaminants is causing the issue. Catalyst activity loss can be attributed to many factors. Metals such as Nickel and Vanadium are common in nearly all raw feed stocks that are processed in a hydroprocessing unit, whereas Arsenic at one time not as common is now found in most crude and feed stocks and is contributing to the deactivation of catalyst. Silicon, Sodium, and other exotic contaminants are now more commonplace. One of the successes of an analysis program is the correct laboratory testing methods be used. Second is having a broad approach to identifying contaminants, there may be one or a combination of several contaminants that will contribute to either catalyst performance or catalyst bed pressure drop increases. It is also important that the analysis program take into consideration the full feed processing range in order to ensure that all the feeds being processed are being analyzed.

Analyzing spent catalyst once the catalyst has been removed from the unit, does not necessarily determine where a contaminate source comes from. The catalyst analysis does identify the various contaminant components that contribute to either the loss of activity or to the increase of catalyst bed pressure drop. Catalyst sampling is very important when identifying contaminants. The information

gained will benefit the design of graded bed catalyst systems for possibly the next cycle to help mitigate the impact of contaminants. The spent catalyst analysis combined with the analysis of the various streams coming into the unit will provide a broad outline of the source of contaminants and also specify accumulated amounts of contaminants that are being deposited on the catalyst.

Sal Torrisi (Criterion Catalysts & Technologies)

After the first one or two ULSD cycles, some refiners have learned a few additional ways to squeeze a little more performance out of each run relative to the original plans.

- Using multiple catalysts in the same reactor system to maximize performance – custom catalyst design to balance contaminant protection, HDS, HDN and aromatic saturation (H₂ consumption). Many of the ULSD units have migrated from a single CoMo or NiMo catalyst in the first cycle to a two or three catalyst system in the subsequent cycles, creating opportunities to maximize cycle life and processing capability
- Altering operating temperature strategy – multi-bed ULSD units can operate with much different temperature profiles depending on quench and furnace capabilities. In order to keep some of the catalyst in a favorable hydrogenation regime not only to minimize coking/catalyst deactivation but also to maximize HDS, particularly at EOR conditions.
- Taking full advantage of maximum EOR temperatures – Typical EOR is defined by one of three limits: ability to make product sulfur target (kinetic or thermodynamic limitations), to achieve product color or to fire furnace harder. Many refiners have done test runs toward the end of run to probe which limitation they will hit first, finding that they can go 5-15 °F higher in operating temperature than previously anticipated. This can give an additional 1-6 months of cycle length depending on the individual unit feeds and conditions.
- If a refinery produces ULSD from multiple hydrotreaters or hydrocrackers, there may be an opportunity to adjust product specification on an individual unit to optimize combined cycle lengths for each unit. If these units change catalysts at different intervals, there may be an opportunity to relax sulfur specification for a ULSD unit as it approaches EOR conditions, particularly if another ULSD unit or hydrocracker is near SOR conditions during the same period. In addition, advanced control systems have been implemented in some locations to utilize unit on-line sulfur analyzers to minimize overtreating, product giveaway and maximize cycle length.
- Optimizing cut points of individual feed components, because the desulfurization reactivity and deactivation behavior for incremental diesel from different streams/crude sources can vary significantly. The 650-750°F boiling range from SR, Coker, LCO and other diesel streams usually contain not only varying amounts of refractory sulfur, but also nitrogen and polyaromatics that largely determine operating temperature and catalyst deactivation rates. Catalyst cycle length and diesel volume can be maximized for a given refinery operation by investing time to evaluate in detail the incremental heavy diesel barrels from each component and their subsequent impact on the ULSD operation.

David Krenzke (ART) ULSD units are maximizing cycle by controlling several critical operating parameters including:

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- Hydrogen partial pressure: Hydrogen purity and recycle gas rate need to be maintained at target levels to minimize coke formation. For ULSD operations, ratios of hydrogen consumption to hydrogen to oil in excess of 5 to 6 provide greater stability and optimum performance of the catalyst.
 - Feed distillation: The feed end point has a significant impact on the required temperature to meet a product sulfur target. Increases in feed boiling point quickly increase the concentration of hard sulfur as well as increasing nitrogen and PNA levels. A high-end point tail on the feed distillation will reduce the temperature span between SOR and EOR by requiring a higher WABT to produce the same product specifications, which in turn increases the deactivation rate as well as increasing hydrogen consumption.
 - Sulfur conversion: Over-conversion even by 1 or 2 ppm can significantly increase the catalyst deactivation rate. Higher temperatures to produce a lower product sulfur than needed increase coke deposition causing a higher rate of deactivation. Some refiners are using closed loop control with an on-line product sulfur analyzer to maintain on-spec product to prevent over-conversion.
 - Feed composition: Higher concentrations of cracked stocks (coker & LCO) increase the concentration of hard sulfur which requires higher temperatures to remove. Cracked stocks also increase the olefin and PNA concentrations in the feed resulting in an increase in hydrogen consumption, higher exotherms and lower outlet hydrogen partial pressure. The net effect is a shorter cycle length due to higher operating temperatures and an increase in deactivation rate.
 - Consistent feedstock analysis is important to determine the presence of contaminants which can significantly impact catalyst life. Some of the more common ULSD catalyst poisons are Silicon and Arsenic. These can be difficult to detect in the feed at low concentrations and may also occur intermittently depending on the feed source.
 - Spent catalyst analysis: a post mortem on spent catalyst is a useful way to detect the presence of unexpected contaminants and helps to optimize subsequent catalyst loadings in the unit. A good way to determine the average concentration of poisons like arsenic and silicon is from an analysis of spent catalyst from various locations in the reactor. Once the concentration is estimated an appropriate catalyst loading with guard materials can be utilized.

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