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Hydroprocessing catalyst selection—Part 1: Planning and selecting the catalyst evaluation method

Hydroprocessing catalysts are an essential part of any refinery involved in the treatment/conversion of most petroleum fractions ranging from naphtha to residue (FIG. 1). Hydrotreating catalysts help refiners meet fuel regulations and enhance the performance of downstream catalysts and processes [e.g., naphtha reforming or fluid catalytic cracking (FCC)] by removing sulfur, nitrogen and metals from their feedstocks as well as improving product properties by hydrogen addition. Moreover, hydrocracking catalysts further improve refiners' profits by converting low-value streams [e.g., vacuum gasoil (VGO)] into high-value fuels and chemical feedstocks. Therefore, selecting hydroprocessing catalysts requires great care to ensure maximum asset utilization and profitability.[1]

Part 1 of this article discusses pitfalls in planning and selecting the catalyst evaluation method and provides best practices to guide refiners towards an optimal hydroprocessing catalyst selection.

Planning and invitation to bid (ITB) development. Ideally, refineries should begin the catalyst selection process 18 mos–24 mos before the next catalyst change-out to provide sufficient time for all tasks involved. Typically, catalyst lead time is 6 mos–12 mos, leaving the rest for planning, evaluation and internal processing.[2]

As a general practice, refiners should apply a multi-disciplinary approach to agree on catalyst requirements (e.g., longer run length or more difficult feedstocks). Additionally, the focal point (usually a unit process engineer) should incorporate current operating issues such as high reactor pressure drop or maldistribution into the ITB so the catalyst supplier can properly address the problems in the next cycle. Most importantly, the economic direction should be clear (e.g., naphtha or middle distillates as preferred products).

Be realistic with feed qualities stated in the ITB. While being conservative will minimize the risks of not meeting the intended cycle length, being too conservative can also underutilize the existing unit or even worsen unit performance in some instances.

For example, if metal contents stated in the ITB are too conservative, use the worst-case scenario for every metal species. This usually means the catalyst supplier will propose a larger portion of

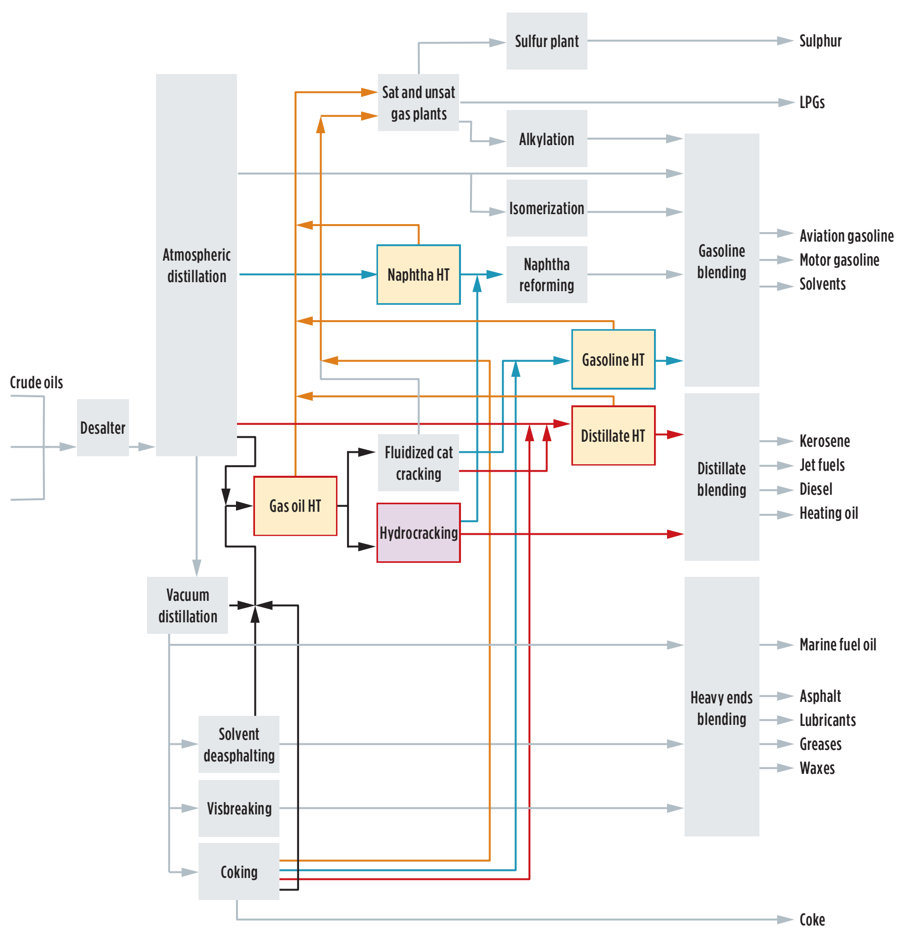

FIG. 1. In modern refineries, hydroprocessing improves the qualities and value of most petroleum fractions (highlighted in yellow and pink blocks).

TABLE 1. Qualitative comparisons between two experimental approaches, conventional pilot-scale vs. high-throughput system

Aspect	Conventional pilot-scale system	High-throughput system
Feed and catalyst shipment costs	Higher costs from more feed and catalyst requirements, 150 l (liters) of feed per one loading scheme (one test scenario)	Much lower, 20 l of feed per one loading scheme (one test scenario)
Number of catalyst loading schemes and time requirement	Limited catalyst loading schemes, usually require more time from limited reactors in parallel	Up to 16 parallel reactors: an attractive option when catalyst loading schemes exceed four; usually require less time as there are more available reactors in parallel
Catalyst homogeneity	Statistically less affected by non-homogeneity due to a larger reactor volume	Practically no issue with good catalyst screening
Feed storage and control	Has a dedicated feeding section for each reactor, possible to process different feedstocks in parallel	Common feeding section, therefore the same feedstock for all reactors in parallel (distributed via the flow distribution device); distribution quality affects mass balance errors
Product analysis	Takes less time for the same sample amount: an ideal choice when frequently varying process conditions or analyzing detailed product properties	Takes more time for the same sample amount; requires close monitoring and control to ensure sample's uniformity
Nitrogen slip control*	Directly measured from interstage sampling	Indirectly measured via a mirror parallel pretreating reactor[1]
Recycle operation*	Possible but may not be accessible by the majority of refiners; primarily available in licensing/catalyst companies	Impractical, mainly from difficulties in flow control, e.g., smaller recycle flowrate
Testing fee	Not necessarily more expensive	Not necessarily cheaper

*Specifically for hydrocracking applications

FIG. 2. A simple loading scheme of a six-bed hydrocracking reactor (not to scale), where grading materials and demetalization catalysts—highlighted in light blue and green, respectively—protect the hydrocracking reactor against high pressure drop and rapid metal deactivation.

demetalization catalysts (lower activity), which will, in turn, limit the volume of the main hydrotreating catalysts (higher activity) for a fixed reactor volume (see an example of a typical loading scheme in **FIG. 2**). As such, the refiner might miss out on opportunities to process more difficult feeds or increase the unit throughput from unrealistic metal uptake requirements. Incorporating past spent catalyst analyses (for both metal and particle size distribution) along with actual feed qualities will help refiners develop realistic grading and demetalization volume requirements. Nevertheless, refiners should be careful when balancing risks and opportunities.

Clearly communicate with catalyst vendors about unit configurations and constraints. The authors have seen a diesel hydrotreating catalyst vendor that once designed the catalyst loading scheme without realizing there was no amine scrubber in the recycle gas loop until the catalysts were later put under operation.

Catalyst evaluation methods. While some refiners still rely on vendor estimations/predictions, independent catalyst testing has become more popular as a tool to reveal the actual catalyst performance. This evaluation approach is particularly crucial to a critical unit like a hydrocracker, where a slight difference in product yield can result in multi-million dollars of profit/loss per year.

In contrast with a general notion, comparing paper estimates/predictions from different catalyst vendors is not an apples-to-apples comparison; nonetheless, this is prevalent among refiners due to its simplicity. In fact, catalyst vendors employ different design assumptions, feed characterization techniques, kinetic models and product property estimators, such as basic to non-basic nitrogen ratio or aromatics distribution. Consequently, it is fundamentally incorrect to compare estimates/predictions between catalyst vendors. Sadly, many refiners are unaware of this fact.

To make matters worse, some catalyst vendors are more aggressive than others. It is not uncommon to see catalyst vendors distort results from their kinetic model to make their proposal more attractive. The authors worked with a diesel hydrotreating catalyst supplier that proposed a close-to-nil offgas yield without any logical explanation. When this was challenged as impossible, the supplier nonetheless confirmed that it was a result of their kinetics model. This is a perfect example of how refiners should always be skeptical of data presented in vendors' proposals and how paper-based evaluation can be subjective.

Despite these shortfalls, it is still acceptable to use paper-based evaluation for less critical applications, such as a naphtha hydrotreater, although the best practice is to have your catalysts tested before the actual reloading.

For refiners without an in-house catalyst testing facility, several companies can provide an independent catalyst testing service. Two available primary approaches are presently in use: a conventional pilot-scale system and a high-throughput system (**FIGS. 3A** and **3B,** respectively).

Each method has its advantages/disadvantages, as summarized in **TABLE 1.** Refiners must select the best independent catalyst testing laboratory to suit their requirements and constraints. While the authors' experience confirmed that both approaches provided essential information for hydrocracking catalyst benchmarking,[1,3] many refiners favor some laboratories more than others. It is recommended to proactively contact these independent laboratories as soon as the new cycle starts. One laboratory requires at least 24 mos of pre-booking before the actual test date. Generally, a typical catalyst testing campaign could last between 1 mos and 3 mos, but this may vary upon the number of test scenarios.

From the authors' recent experience, the testing fee for each catalyst loading scheme (hydrocracking, one-test scenario) can range between \$40,000 and \$95,000. In general, the service fee for a hydrotreating catalyst testing campaign is less expensive than a hydrocracking one, as it is less complicated. A more important question is who will pay for the test. The refiner may pay for the total cost or ask the catalyst suppliers to share. In general, the willingness of the catalyst supplier to share the cost increases with the value of the catalyst package.

Takeaway. On the surface, independent catalyst testing seems costly. However, the service fee is often trivial compared to the opportunity to distinguish the best catalyst supplier from an average one. In the authors' recent experience, a performance gap for a 54,000-bpd hydrocracker could be up to \$20 MM/yr.

In the June issue of *Hydrocarbon Processing*, Part 2 will discuss critical aspects of a hydroprocessing catalyst testing program and present best practices/suggestions to ensure a successful catalyst benchmarking campaign. HP

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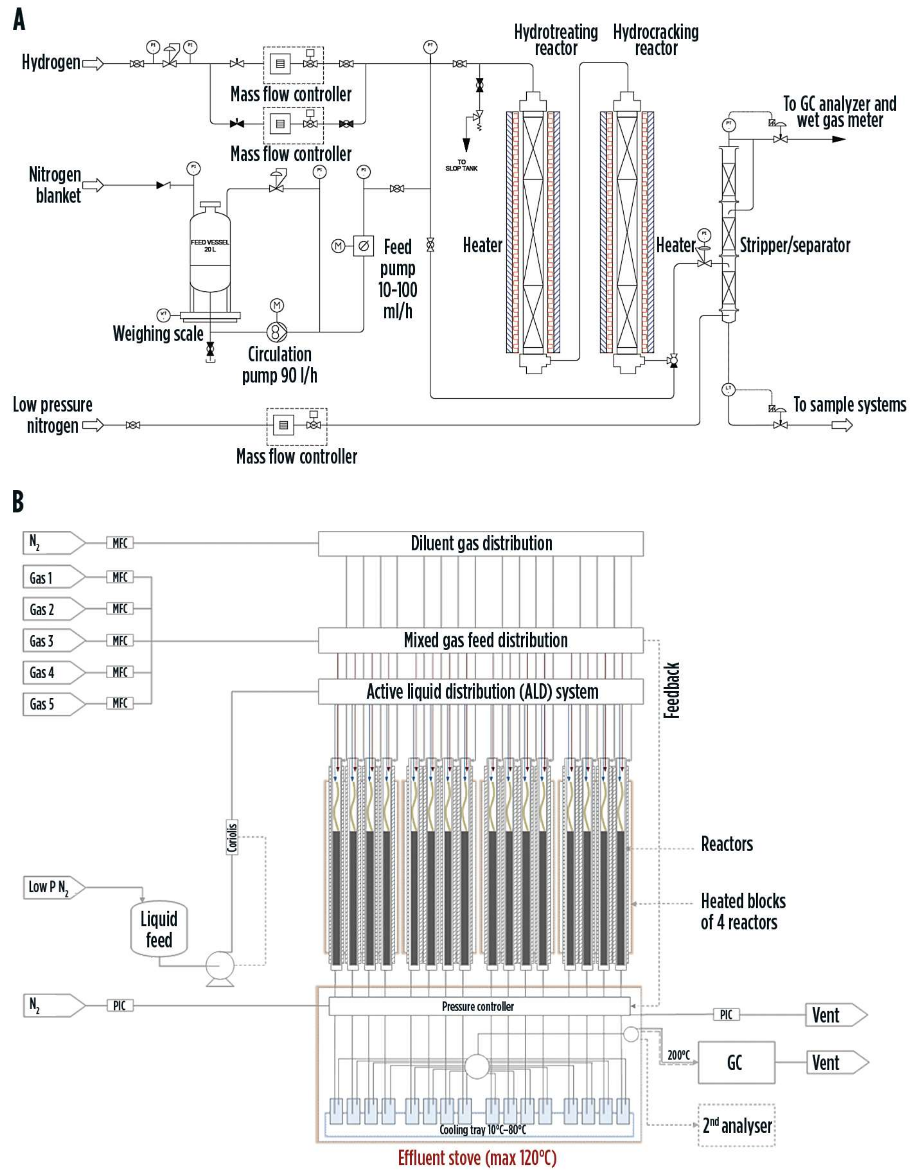

FIGS. 3A AND 3B. A conventional pilot-scale (A) vs. high-throughput bench scale system (B). Courtesy of Avantium.

LITERATURE CITED

Complete literature cited available online at www.HydrocarbonProcessing.com

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