Competition in the refining sector demands utilisation of bottom of the barrel (BoB) upgrading technology for a higher yield of high-value products, continuous process optimisation, and efficient troubleshooting. Furthermore, a certain flexibility is required in terms of crude and production in order to meet changing market demands. This challenging environment makes refinery operation a highly complex daily task that needs an expert level of technical proficiency to obtain and maintain a technical utilisation rate above 90% for sustainable economic performance.

In an article by hte GmbH, published in the November 2020 issue of Hydrocarbon Engineering, it was explained how catalyst testing and customised test protocols can support refineries in maintaining operational efficiency in the area of process optimisation and troubleshooting. This article will stress the importance of sustainable catalyst management for catalytic BoB upgrading technologies. The term ‘catalyst management’ covers a variety of topics, including:

- Catalyst selection for a catalyst change-out in an industrial unit.
- Evaluation and re-use of regenerated catalysts.
- Quality control of catalyst batches.
- Predicting the impact of different feedstock qualities on the catalyst performance, including opportunity feedstocks.
- Understanding catalyst deactivation and end-of-run (EOR) performance.

A critical factor for the above topics is that the underlying catalyst evaluation has to be based on the
actual conditions at the refinery. Unfortunately, refineries sometimes have to rely on catalyst predictions or individual catalyst proposals. This increases the risk of not overcoming the actual challenges or of not obtaining a real comparison of the proposed catalyst systems.

In this context, a direct head-to-head catalyst comparison using industrial feedstocks and commercially available catalysts is of the greatest importance. Additionally, high throughput catalytic testing not only allows for proper catalyst comparison, as mentioned; it also generates the necessary data volumes within a very short time while maintaining the same data quality as classical bench scale testing with only one or two reactors.

The following sections will present three industrial case studies that were performed for refineries in order to illustrate how catalyst testing can support catalyst management decisions. The case studies were conducted in different test units that either allowed for maximum flexibility with respect to operating conditions or for lesser flexibility in terms of operating conditions, in order to gain a high degree of statistical significance by running replicates in parallel.

VGO hydrocracking case study 1: classical catalyst selection prior to industrial catalyst change-out

The purpose of this 1st stage hydrocracking test was to obtain a head-to-head catalyst comparison that was close to actual refinery operating conditions, and to investigate the catalyst deactivation behaviour as a function of feed severity.

Catalyst testing for 1st stage hydrocracking is performed by operating two reactors in series. The first reactor is filled with hydrotreating catalysts and the second reactor with hydrocracking and potential post-treatment catalysts. In this particular case study, thet employed a 4x2 bench scale unit with individual feed supply for each set of two reactors connected in series. This way, four complete hydrocracking systems (hydrotreating and hydrocracking) could be tested in parallel. After the initial activation, stabilisation, and de-edging of the catalyst systems, three different VGO blends (VGO 1, VGO 2, and VGO 3) with increasing feed severity were used, in that order. Condition 1 (‘Base Case’ with VGO 1), Condition 2 (‘Severe Case’ with VGO 2), Condition 3 (check back to ‘Base Case’ with VGO 1), and Condition 4 (‘Very Severe Case’ with VGO 3) were run at constant target conversion in accordance with the industrial unit. Contrary to this, the same temperatures for all pretreatment and hydrocracking catalysts were used during Condition 5 (‘Constant Temperature Case’ with VGO 1).

The total liquid products were collected, fractionated, and analysed. As an example, density measurements of all fractions are shown in Figure 1, and it seems that the product qualities are not affected very much by the feed severity. However, the density of diesel and the UCO fraction is lower for catalysts A and B than for catalysts C and D, while the opposite trend is observed for kerosene and naphtha. Thus, for the different catalyst systems, the hydrogenation of aromatic species preferentially occurs either in the heavier or in the lighter fractions.

This type of test gives information on catalyst stability and deactivation by applying properly designed ageing protocols. Furthermore, the catalyst selection is based on facts due to the direct head-to-head comparison, and the correct catalyst choice can save a lot of money for the refinery due to differences in product yield and quality.

VGO hydrocracking case study 2: evaluating the use of a regenerated catalyst

Alongside choosing the optimum catalyst system for certain applications, catalyst management within a refinery also involves the evaluation of regenerated catalysts. While catalyst regeneration is economically very attractive – especially for hydrocracking catalysts – regenerated catalysts have an increased risk of lower performance throughout the cycle length.

This second case study illustrates a typical test for evaluating catalysts in a stacked-bed configuration while at the same time checking the performance of a regenerated hydrocracking catalyst. It should be noted that the same type of test unit was used as in the first case study.

Four catalyst systems were tested in parallel with two reactors in series containing hydrotreatment, hydrocracking, and post-treatment as well as regenerated catalysts, as can be seen in Figure 2. The incumbent catalyst system was used as an industrial benchmark as well. Due to the short overall runtime and low metal content of the feed, de-metallisation catalysts typically have no influence on the overall catalyst stability during such tests and no such catalysts were used.

![Figure 1. Product properties: density for naphtha, kerosene, diesel, and UCO fractions for conditions 1 – 5.](image-url)
All four catalyst systems were tested in parallel at several reaction temperatures over a period of more than one month under operating conditions as applied in the refinery. To compare the hydrocracking activity of all systems, the rate constant $k$ was calculated assuming first-order kinetics.

The comparison of the catalyst systems with respect to overall hydrocracking activity is shown in Figure 3. The Base Case and System 1 show comparable hydrocracking activity. Here it seems that the loading order of the hydrocracking catalysts C and D appears to have only a minor influence on the overall hydrocracking activity. Catalyst System 3, using a more active catalyst G to replace some of catalyst C, performs better, especially at higher temperatures. For Catalyst System 2, which uses a significant amount of regenerated catalyst C, the refiner must reckon with higher reactor temperatures to reach the same conversion level as compared to the Base Case and the pure fresh catalyst (System 1). Savings from such catalyst purchase therefore might be consumed by higher operational costs and inferior product quality.

The results show that laboratory catalyst testing can assist in evaluating the profitability of loading regenerated catalyst batches at different positions in the industrial reactor. As per these findings, the performance of the regenerated catalyst was not as good as that of the fresh catalyst, but it may still be of use as a protective layer in the top of other catalyst beds instead.

**VGO pretreatment case study 3: quality control**

As a complement to the bench scale units presented in the previous case studies, high throughput test units add another level of efficiency. Highly parallelised test units with up to 24 reactors enable cost-effective and time-effective testing. At the same time, large amounts of data are generated within that short timeframe while maintaining the same data quality as bench scale testing.

In the following case study, four hydrotreating catalysts were tested in a 16-fold high throughput test unit using a VGO feedstock. Each catalyst was loaded into four reactors in order to speed up catalyst testing by running more conditions in parallel for one catalyst. In order to investigate the batch homogeneity, two batches of catalyst C (Batch 1 and Batch 2) were each loaded into four reactors. Having four reactors for each material also helped to evaluate the statistical significance of the results by repeating conditions in parallel. A total of eight conditions were screened over a period of three weeks, two in parallel for each catalyst. To obtain the same data volume and statistical significance with a classical single-fold unit would have required 40 weeks.

Figure 4 shows a box-and-whisker plot for all 16 reactors under identical operating conditions to evaluate the statistical significance of the catalyst ranking and the performance of the two batches. The variance of the N-slip observed for all catalysts is quite small, indicating a small experimental error. Catalysts A, B, and C can be clearly distinguished beyond experimental variance. The similar hydrodenitrogenation (HDN) performance of the two batches of catalyst C demonstrates the constant quality of catalyst production across these batches.

**Conclusion**

Refineries all over the world are facing challenging times and proper catalyst management is of the utmost
importance. The case studies presented in this article show how catalyst management decisions benefit from test data generated under actual industrial conditions with relevant feedstocks and commercial catalysts. Catalyst performance predictions or individual catalyst tests performed in separate laboratories are often used by refineries to predict the future performance of the unit. However, an independent pilot test using parallelised test units is the only way to ensure an equal comparison of the different catalyst systems on the market. This is especially the case when leaving the well-known operation window by considering new catalyst generations or processing opportunity feedstocks. A direct head-to-head comparison of catalysts in laboratory testing, and especially high throughput testing, is the perfect tool for refineries to address challenges in the field of catalyst selection, evaluation of regenerated catalysts, quality control, feed, or ageing studies.

References