Testing times

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Refineries have always aimed to maximise the value gained from a barrel of oil. In the current challenging global context – marked by an excess capacity in refining – and with oil demand expected to peak around 2030, refineries are now, more than ever, being forced to squeeze all the value they can out of their operations. A high degree of process integration, technical optimisation, and maximised uptime, as well as a high-value product portfolio, are key elements for a refinery’s future strategy. However, even the best economic strategy only succeeds if it is backed up by a constant pursuit of operational excellence. Technical know-how and an understanding of feedstock, catalyst, and processes, and how they interact are therefore required. The necessary competence level can only be maintained and further improved through constant awareness of the operation, identifying problems and future challenges, and responding rapidly and in a sustainable manner.

The use of models and simulations to aid with problem-solving might be feasible when operating under relatively known and predictable conditions. In recent years, however, certain opportunity feeds have posed an attractive alternative in order to reduce costs. Nevertheless, their use can lead to unforeseeable operational issues. The quickest and most reliable way to determine the reaction outcome with these opportunity feeds is laboratory testing, because the confidence level that mathematical models alone can offer decreases as the feed complexity increases. Technical service providers, such as hte GmbH, support refiners with relevant experimental data for solving technical challenges and problems that arise from daily operations or future challenges.

Depending on the degree of freedom required for the experimental parameters to be investigated, different unit configurations may be chosen. For process optimisation studies, the operational flexibility of the test unit is a key aspect of the test. With this aim in mind, hte operates bench scale units with reactor volumes of up to 100 mL and reduced parallelisation. On the other hand, in a head-to-head comparison of multiple catalysts for a benchmarking study, the operating conditions can be similar for all reactors. The advantage of high throughput test units with reactor volumes of up to 10 mL is evident here. Parallelisation provides a cost-effective solution to comparing a multitude of catalysts at various process parameters, such as conversion, sulfur or nitrogen content, and others. Regardless of the scale, hte’s units possess the operational flexibility required to allow individually tuned catalyst activation protocols in parallel testing that accommodate each catalyst vendor’s requirements, within reasonable margins.2

This article will examine two technical support studies performed for refineries in recent years. These made use of high
throughput catalyst testing equipment operating at the two different scales and degrees of parallelisation. The studies highlight the benefits of customised laboratory test protocols that match industrially relevant test conditions, using real and representative feedstock samples and true commercial catalysts in extrudate form.

The first study will show how a laboratory testing protocol can assist a refinery in evaluating the feasibility of employing an amine scrubber to remove hydrogen sulfide (H₂S) from the recycle gas used in a diesel hydrotreating application. The other study will indicate how hydrocracker troubleshooting in the case of abnormal yield patterns can be achieved with well-defined laboratory testing.

The crucial prerequisite for both studies is an in-depth knowledge of downscaling industrial operation conditions to laboratory scale. In this context, hte has experience in verifying laboratory results at different reactor scales against each other, as well as against results obtained in industrial units.³

Case study: diesel hydrotreating

Catalyst lifetime and catalyst resilience to conditions of varying severity, due to different feed grades in response to market changes, are a main concern in diesel hydrotreating. The margin for error in desulphurisation processes is very low, with acceptable sulfur concentrations in the diesel product of 15 ppm or below. The catalyst also needs to perform above 99% sulfur conversion during the entire lifecycle. The high severity of the reaction conditions, as well as the tendency to co-process highly aromatic cycle oils from fluid catalytic cracking (FCC) units, provides a fundamental basis for catalyst deactivation. With this underlying problem of diesel hydrotreatment applications, refiners are generally wary of choosing a catalyst where the benefits of a lower start-of-run (SOR) temperature are overshadowed by a lower catalyst stability. The principle of accelerated catalyst ageing is an important testing approach in order not only to assess SOR catalysts but also to get an idea about the catalyst’s performance at a later stage of its lifetime. The benefits of such a testing methodology have been previously elaborated upon.⁴

The diesel hydrotreating that is the focus of this case study was performed in a 4-fold bench scale unit that is designed for maximum flexibility. Each reactor had an individual gas and liquid feed supply as well as individual active pressure control and regulation. To avoid merely testing the initial high SOR catalyst activity, the catalysts were at first aged under severe operational conditions (increased liquid hourly space velocity [LHSV] at the same temperature) for a defined period of time. This makes it possible to obtain a stabilised catalyst in which the least stable active sites have been deactivated for further testing.

The objective of the main test protocol was to mimic the industrial gas feed composition. During industrial operation, the gas feed was recirculated in such a manner whereby a certain amount of H₂S was always present in the gas feed. This was simulated by adding dimethyl disulfide (DMDS) to the feedstock during the laboratory test. DMDS decomposes at temperatures above 230°C. This creates a H₂S-rich atmosphere corresponding to the concentration in the industrial hydrotreater. In order to benchmark the catalysts, the temperature of each reactor was adjusted to maintain a sulfur level of 10 ppm in the total liquid product (TLP) (Figure 1). Samples were analysed to determine key properties such as volume gain, cetane index, and cloud point. Catalyst performance data and diesel product properties obtained under the main test conditions provide the refiner...
with experimental facts to enable an informed decision to be made (Figure 2). This in turn leads to an optimal operational margin after the upcoming change-out.

The second part of the study simulated the impact of H₂S removal from the recycle gas on catalyst performance. In the laboratory, this was achieved by stopping the dosing of DMDS to the feedstock. With this seemingly simple experimental detail, it became possible to evaluate the technical and financial feasibility of employing an amine scrubber to remove H₂S from the recycle gas in the industrial unit.

After the H₂S concentration in the feed gas was reduced, the reaction temperature also needed to be lowered in order to maintain 10 ppm of sulfur (S) in the TLP. The results reveal different H₂S sensitivities in the commercial catalysts. Depending on the individual contribution of the desulphurisation routes during the reaction (direct desulphurisation or hydrodesulphurisation), one can observe the distinct temperature differences which are required by each catalyst in order to maintain 10 ppm S at different H₂S concentrations in the feed gas. The direct desulphurisation route is inhibited by H₂S and might benefit from a recycle-gas treatment. Based on these test results, by assessing the temperature difference, and, hence, the potential for lifecycle improvements by lowering the H₂S level in the feed gas, the refiner can estimate whether an amine scrubber is economically attractive.

In general, by using a defined test protocol that is tailor-made for the customer, different sections within a refinery can be simulated and optimised. In other applications, such as hydrocracking, it could be important to assess the effect of the ammonia (NH₃) level in the gas feed. It may also be worthwhile to investigate the impact of hydrogen purity on the catalyst performance. Increasing the hydrogen purity may reduce the overall operation temperature to reach a certain conversion level (e.g. product sulfur), which in turn may result in a longer lifetime or overall energy savings. In general, process optimisation studies supported by laboratory testing can offer valuable insights into the feasibility of future revamping projects.

Case study: VGO hydrocracking troubleshooting

In the event that a refinery operation is disturbed, or the performance of a reactor is irregular with regards to the yield pattern, fast and conclusive troubleshooting is crucial. In the first instance, this troubleshooting is carried out within the refinery and simple issues can be fixed without third-party assistance. For more complex or severe matters, external support from equipment suppliers, catalyst vendors, or service providers is necessary. However, in the case of catalyst performance issues, the support of an independent laboratory test is a valuable tool for verifying certain hypotheses. Laboratory testing has the advantage that the corresponding catalyst investigations can be performed under well-defined and controlled operational conditions in a small-scale isothermal reactor. This removes uncontrolled technical artefacts from the industrial operation. Thus, the cause and effect correlation on the catalyst performance can be investigated in a direct way with clear conclusions. Having understood the problem, a more comprehensive approach can be defined to remedy the situation, which consequently saves the customer resources, time, and money.

In this case study, a correlation was found between unexpected yield patterns in the industrial unit – particularly defined by an increase in the light naphtha fraction – and non-ideal reactor performance.

As part of troubleshooting, a kinetic study (screening of several temperatures and LHSV) was performed to verify how the abnormal yield pattern is linked to local exotherms inside the reactor. In the industrial reactor, the product spectrum was an overlap of all the various channels formed by the feed maldistribution. In the laboratory test, individual reaction channels could be simulated by individual trickle bed reactors in a high throughput unit. Parallel to this, the refinery performed further investigations, such as local temperature mapping, evaluation of liquid distributor plates, and arrangement of the catalyst beds, to better understand the performance of the industrial reactor.

Figure 3 shows the yield pattern as a function of oil conversion. In order to comprehend the causes of the abnormal yield pattern, the kinetic study focused on the area beyond the ideal and typical industrial operation window. The yield plot clearly shows the consecutive nature of hydrocracking heavy compounds to diesel, followed by kerosene, then naphtha, and finally light ends. The increased light naphtha production was an indicator of overcracking in hot-spot zones. Combining all the findings from the industrial investigation and the kinetic study performed by hte, it was possible to draw a comprehensive picture of the issue. It was shown that non-ideal liquid distribution can lead to local hotspots in the industrial reactor, depending on the catalyst bed length. The local hotspots resulted in overcracking, favouring a yield pattern with an increased amount of light naphtha. It was also

![Figure 3. Yield pattern vs oil conversion beyond the ideal commercial operation window.](image)
concluded that the latest generations of highly optimised catalysts require an industrial reactor configuration in optimal working condition. With previous catalyst generations, non-ideal industrial reactor performance, such as liquid maldistribution, was not as critical within a similar range of operating conditions. As catalyst performance was further optimised with every new change-out, reactor performance ran into limitations that did not allow the high-performance catalyst system to utilise its full potential.

The overall timing of this test was critical due to the urgent nature of a critically elevated local reactor temperature. This test employed a 24-fold high throughput testing unit from the company. Thus, it was possible to screen 36 operation conditions in the kinetic study of the refinery’s incumbent hydrotreatment and hydrocracking catalyst systems within a runtime of five weeks. Compared to a single-channel bench scale test unit, the high throughput unit delivered the required results in a seventh of the time, or 28 weeks earlier. When put in perspective like this, it is easy to see how a six- or even seven-figure cost advantage can be gained by using highly parallelised yet flexible testing technology.

Furthermore, the 24-fold high throughput unit also offers the option to use two feeds in parallel for different sets of reactors. This allows for easy accommodation of incompatible catalyst activation procedures. Product collection and fractionation were also of key importance for this test. The smaller catalyst volumes used in a high throughput unit still warrant the collection of sufficient product volumes for fractionations. With the use of microfractionation units, sample volumes between 20 and 1000 mL can be fractionated into naphtha, kerosene, diesel, unconverted oil (UCO), and other fractions as required to replicate the same products obtained in the refinery. Generally, a high throughput unit can produce the required sample amount for a detailed analysis of the individual fractions in less than one week. Depending on the analyses to be performed for each of the individual product fractions and on their individual yields, shorter collection times are possible.

Conclusion

The core expertise for operating a refinery is typically well-developed and maintained among a refinery’s staff, since this is critical to achieving operational excellence. Nevertheless, in particular cases, it makes sense to call in specialised competencies to support decision-making processes. Laboratory testing minimises risks in an environment with decreasing feedstock qualities and increasing use of opportunity feedstocks.

References