Hydroprocessing catalysts play an important role in a refinery and their selection is crucial for optimising refinery operations and increasing overall profitability. Catalyst evaluation processes typically involve many steps for selecting the best available catalyst that meets the selection criteria including proposal evaluations, economic evaluations and catalyst testing programs.

The catalyst evaluation process generally starts with the request for technical proposals from different catalyst vendors as well as an initial benchmarking of all technical proposals. In these paper studies, the supplier provides yield projections of the proposed catalyst compared to a base case technology. The most promising catalysts are then evaluated in a catalyst testing program under similar operating conditions to those applied in the commercial process. As a final step, an economic evaluation of the technically acceptable catalyst systems determines the preferred catalyst system.

Catalyst testing is particularly important for mitigating technical risk and supporting basic feasibility studies for commercial applications. As most refiners are reducing their testing capacities in order to save costs, most of the catalyst testing work is either done by catalyst suppliers or by independent R&D service providers such as hte GmbH.

Over the last couple of years hte has developed state-of-the-art high throughput reactor systems and workflows for testing full size commercial catalysts in parallel under a wide range of process conditions in order to significantly reduce catalyst and process development times. The measures required in order to achieve a considerable acceleration of the catalyst evaluation process without compromising data quality will be presented in this joint case study between OMV and hte. This article will discuss the variables that can be tuned to control the hydrodynamics of gas and liquid flow at different scales.
**Testing at different scales**

In order to obtain optimum performance in a trickle bed reactor, catalyst packing, gas and liquid flow distribution and heat management need to be controlled properly. With an optimised reactor configuration, the catalyst is the remaining degree of freedom that can be tuned to further improve the performance. Depending on the scope of the catalyst testing, different types of trickle bed reactor system can be used, from nanoflow type reactors (typically 1 ml catalyst volume scale), right up to pilot scale (typically 1000 ml catalyst volume scale) (Figure 1).

Catalyst development and comparative long term stability testing with basic product analysis, as well as optimisation of stacking configurations or basic reactor operation conditions call for small catalyst amounts (typically 1 ml scale) and a high degree of parallelisation (typically 16 - 48 fold). Basic process studies such as 2 stage processing (e.g. mild hydrocracking) are performed at this scale as well. Pilot tests (typically 1000 ml scale or higher and 1 fold) are used to predict the detailed performance of the preferred catalyst in a commercial unit under realistic process conditions (testing recycles, adiabatic operation and integration of product separation), as well as being able to deliver enough of the product for fleet tests.

Testing at smaller scales only makes sense if the obtained performance data can be transferred to larger and, finally, to industrial scale. An important prerequisite for proper scalability are well defined reaction conditions in bench scale systems by means of well known lab reactor design criteria. Proper temperature control and reactor heating concepts ensure isothermal operation and thus enable well defined temperature performance correlations. Control of reactor length to diameter to catalyst particle size ratio as well as optimised catalyst packing concepts are needed to obtain an even gas and liquid flow distribution over the reactor cross section, and hence efficient catalyst wetting throughout the entire catalyst bed (defined as plug flow conditions).

**Catalyst packing**

A proper packing procedure is an important prerequisite for reproducible catalyst testing. The structure of the packed bed determines the fluid dynamics in the tricklebed reactor, affects the catalyst wetting and hence has a strong impact on the absolute reaction rate measured for a given catalyst.

Packaging configurations with an inner reactor diameter to particle size ratio (aspect ratio) of less than 25, which are typical for full size commercial shapes packed in bench scale reactors, suffer from uneven liquid and gas flow distribution over the reactor cross section. The reactor wall has an ordering effect on the catalyst particles resulting in an increasing void fraction close to the reactor wall. As a consequence, channeling and bypass close to the reactor wall can occur, leading to inefficient catalyst wetting throughout the catalyst bed.

Embedding full size commercial catalysts into a matrix of small diluent particles in bench scale reactors with low aspect ratio can suppress these phenomena. The small diluent particles dominate the fluid dynamics and help meet the reactor design criteria for plug flow behaviour and efficient catalyst wetting. This results in better comparability to pilot and industrial scale reactor packings with a larger aspect ratio. The embedding approach has led to the costly pilot plants used traditionally gradually being replaced by bench scale reactors.

**Reactor scales at hte and OMV**

For case study, hydroprocessing units with different reactor scales at hte (16 fold nanoflow high throughput unit to four fold bench scale) and OMV (two fold pilot plant and finally a commercial plant) (Figure 2) were used. The catalyst volume of these units spans from 1 ml, through 100 ml and 1000 ml, right up to 100 m³ (Table 1). Comparison of the superficial velocities (defined as flow rates over reactor cross section) clearly shows that for a given liquid hourly space velocity (LHSV) and gas to oil ratio (GTO) the industrial scale units typically operate at higher cross sectional load and hence most likely in a different fluid dynamic regime than the test units. The test units do not show a similarly...

![Figure 1. Trickle bed reactor scaling with typical catalyst volume and degree of parallelisation.](image-url)
dramatic difference among each other with respect to superficial velocities. They lie within a range of factor four. Alignment is possible by adjusting the reactor length to diameter ratio.

Testing units typically work with smaller diluent particles to improve isothermal operation and fill up the void space for better gas and liquid distribution. A decrease in void space results in an increase in the actual interstitial velocities. Nonetheless, this further increase by smaller diluent particles cannot compensate reaching the much higher cross sectional load of industrial scale. Consequently, the strategy for test units is not necessarily to reproduce the exact same fluid dynamic profile as in the commercial unit. Instead, techniques such as catalyst embedding are applied to assure an even flow distribution throughout the entire reactor cross section. This plug flow profile in the trickle bed reactor and the resulting efficient catalyst wetting ensure optimum catalyst utilisation and avoid masking artefacts from poor fluid dynamics.

Hydroprocessing case studies

The case studies presented here comprise an independent catalyst ranking of two full size commercial catalyst systems A and B for two stage mild hydrocracking (MHC) of vacuum gas oil (VGO) with 1 wt% sulfur and 1000 ppm nitrogen. In the first case study, the HDS/HDN catalysts A and B in the first MHC reactor stage were ranked against each other (reactor pressure 60 bar(g), LHSV 1.5 l/hr, GTO 300 NL/ltr). The ranking was performed in a hte 16 fold high throughput system (nanoflow), as well as in an hte four fold bench scale unit. The setup comparison was done to prove the possibility of reasonable downscaling of full size commercial catalyst ranking from typical bench scale to 1 ml scale. In the second case study, the base case MHC catalyst system A was utilised to compare the hte bench scale unit with the OMV pilot plant for the combined two stage MHC of VGO (reactor pressure 60 bar(g), LHSV 0.72 l/hr, GTO 300 NL/ltr). In all cases, the apparent rate constants were obtained with irreversible, ideal plug flow kinetics with reaction order n = 1.6.7

Downscaling from hte bench scale to hte nanoflow scale

Two full size commercial quadrilobe extrudate catalysts A and B were ranked in the nanoflow system and in the bench scale unit according to defined test protocols for combined hydrodesulphurisation (HDS) and hydrogenitriﬁcation (HDN) of VGO. Some difference exists between both tests due to somewhat different run modes. The bench scale unit was operated in a constant MHC conversion mode, i.e. the temperature was adjusted to maintain a certain conversion. The high throughput unit was operated in a temperature scan mode, i.e. the temperature was increased stepwise over defined time intervals in order to produce a temperature history and run time close to the one in the bench scale unit. Thus, the test protocols for the two units were not identical but close enough to ensure a reasonable level of comparability. The catalyst activation protocol was identical.

The high throughpout unit was additionally used to measure the HDS/HDN kinetics over a broader temperature range than that offered by the catalyst ranking protocol. Figure 3 shows HDS conversion and the corresponding apparent rate constant for full size extrudate catalysts A and B as well as catalyst A crushed to a powder fraction as a function of temperature.

Commercial catalyst ranking is typically performed under industrially relevant conditions, i.e. often at high conversion levels far in excess of 90% conversion for HDS/HDN. As can be seen in Figure 3, the measured conversion differences are very small in this domain, while the calculated apparent rate constants expand the difference. As a consequence, the conversions in this domain must be determined with absolute precision in order to accurately distinguish even slight conversion differences and avoid experimental artefacts that are blown up when converted to rate constants. An imperative prerequisite for this is a reproducible catalyst packing protocol ensuring plug flow since artefacts from uneven flow distribution and incomplete catalyst utilisation may significantly corrupt the catalyst ranking.

The result of the comparative catalyst ranking in the nanoflow and bench scale unit (Figure 4) shows that catalyst B is approximately 2.5 times more active than catalyst A. Although there is a slight deviation between both setups due to different run modes, the catalyst ranking on both scales lead to the same
remarkably, the high throughput unit produces the same result as the bench scale system while using up to 100 times less catalyst and feed per reactor tube. The degree of parallelisation is therefore increased fourfold while the catalyst and feed amount is up to 25 times lower. Thus the same catalyst ranking conclusions can be obtained while saving infrastructure costs and at the same time enabling more catalysts to be tested simultaneously.

Downscaling from OMV pilot scale to hte bench scale

Two stage mild hydrocracking of VGO with a base case catalyst system A (a combination of full size commercial quadrilobe and cylindrical extrudate catalysts) was used to establish a scaling correlation between the OMV pilot and the hte bench scale unit. The MHC catalyst test was carried out such that the reaction temperature was adjusted once a day to maintain the conversion of the 623K+ fraction as close as possible to the target of 35%M, based on SimDist data. The comparison was done without any preparatory alignment of the experimental procedures in both labs. The main difference between the lab procedures lay in the packing procedure. The hte packing was a compacted intimate mixture of catalyst and diluent. The OMV pilot consists of a fixed reactor tube, meaning that compacting is not possible to the same extent as with a detachable reactor tube. OMV therefore generates defined sandwich type loadings of catalyst and diluent material.

Figure 4. Catalyst ranking on both nanoflow and bench scale for full size commercial extrudate catalysts. Ratio of apparent HDS rate constants for catalyst A and B.

Figure 5. Comparison of hte bench scale and OMV pilot for two stage MHC with base case extrudate catalyst A.

| Table 2. Comparison of product distribution and mass balance for 2 stage MHC with base case extrudate catalyst A in hte bench scale and OMV pilot at steady state (Day 19 - 21) |
|---|---|---|---|
|   | Bench | Pilot |   |
|   | Yield | Selectivity | Yield | Selectivity |
| C1 | %M | 0.4 | 1.0 | 0.5 | 1.1 |
| C2 | %M | 0.3 | 0.8 | 0.4 | 1.1 |
| C3 | %M | 0.6 | 1.6 | 0.8 | 1.8 |
| C4 | %M | 1.0 | 2.5 | 1.0 | 2.3 |
| C5-448 K | %M | 8.9 | 22.8 | 10.3 | 24.5 |
| 448-498 K | %M | 5.6 | 14.3 | 5.6 | 13.2 |
| 498-623 K | %M | 21.0 | 54.0 | 22.5 | 53.2 |
| 623 K+ | %M | 61.8 | 58.6 |   |
| H2S | %M | 1.1 | 2.9 | 1.1 | 2.7 |
| Mass balance | %M | 100.7 | 100.8 |
| 623% conversion | %M | 33.0 | 36.4 |

This case study illustrates that well adjusted test systems produce reasonable results with direct relevance to industrial operation. Consequently, comparative or relative ranking of catalysts within a test system can immediately rate and distinguish different catalyst candidates for industrial operation. In general, relative ranking, i.e. ranking of relative or normalised rates, is typically straightforward and requires only modest fine tuning for the transfer between different scales. However, when directly comparing absolute rates between different scales, there are usually some differences. This issue can be handled using a number of different methods. A typical fast approach is the use of scaling factors to transfer results from one scale to another. These correlations are determined by means of a base case or benchmark catalyst that is tested in both units under the same operation conditions, or in!
the fine tuning of setups to align operational details and hence the absolute rates as closely as possible. Some challenges need to be tackled, especially when comparing different scales, and these challenges are different for each scale. The embedding technique for ensuring a proper plug flow for small reactor inner diameters has already been mentioned above. Another classical challenge is taking the right temperature for comparison, especially when comparing an isothermal small scale reactor and an adiabatic large scale reactor. One approach here is to use a well defined weighted average bed temperature (WABT) for large scale adiabatic systems. Another approach would be a comparison not via a WABT but by mapping the large scale adiabatic temperature profile with the small scale isothermal reactor. In the present case study, a next step towards further alignment between the two scales would be the harmonisation of the loading patterns.

Conclusion
In this article, it has been demonstrated that full size commercial hydroprocessing catalysts can be ranked at different test reactor scales, from nanoflow scale (approximately 1 ml catalyst volume) to bench scale (typically up to 100 ml catalyst volume) to pilot scale (catalyst volume in the range of 1000 ml). The importance of correct catalyst packing for well defined and reproducible catalyst testing was described, pointing out that reasonable gas and liquid flow distribution and hence efficient catalyst wetting can be obtained by means of the embedding technique.

The evaluation process for catalyst selection and catalyst management (optimisation, deactivation, regeneration) for refinery applications can clearly be accelerated by combining different test scales and degrees of parallelisation. In general, small scale testing units have low cost and infrastructure demands per catalyst test and enable very fast testing due to their high degree of parallelisation. In contrast, large scale testing units deliver more detailed information and larger quantities of product samples per catalyst test. A proper combination of the different test scales can result in a significant acceleration of commercial catalyst testing.

References