Refineries without catalyst testing facilities have to rely mainly on proposals from several catalyst vendors when selecting catalysts for their assets. This makes the selection process challenging due to the difficulty involved in getting all the proposals onto a common basis. The availability of high throughput experimentation testing for all refiners has removed this limitation and refiners are now able to perform head-to-head testing of the catalytic systems being considered. The scope of testing can be customised using commercially representative operating conditions and customer-specific feedstocks to evaluate several catalyst systems at the same time, providing greater value to the refiner in the catalyst selection process.

High throughput experimentation tests produce accurate and reproducible data that can be used by the refiner to make reliable comparisons among various catalyst systems. This testing technology has been applied successfully and gained rapid acceptance for industrial catalyst evaluation across all refining applications, including naphtha treating, reforming, diesel and VGO hydroprocessing, hydrocracking for fuels and lubrication production, dewaxing, isomerisation, hydrogenation and heavy oil/residue conversion, as well as bio-feed processing.

High throughput experimentation
The principal methodology in trickle-bed catalyst testing is simple: gas and oil feedstock are fed to multiple reactors filled with whole catalyst pellets in parallel or in series. Online gas chromatography (GC) and offline liquid analytics are deployed to characterise reaction products. The operation of the high throughput units is highly automated. Robust and
smart process control software ensures stable, automated 24/7 operation, utilising online GC and fully automated total liquid product (TLP) sampling. The liquid distribution technology ensures uniform feedstock distribution over all reactors. A proprietary data management software system is deployed to gather, store, and analyse the large quantity of data gathered for all the reactors.

hte’s proprietary test technology in combination with its own process control software, hteControl™, and data warehouse solution, myhte™, allow experiments with industrially relevant test protocols to be performed quickly and cost-effectively. The quality of the data obtained in this way has proven to be suitable for performance differentiation among industrial catalysts.

Figure 1 shows a typical example of one of the company’s state-of-the-art high throughput trickle-bed reactor units optimised for performing commercial benchmarking projects in hydroprocessing applications. It is equipped with 16 parallel reactors that are heated in blocks of four reactors. The liquid products are collected in an automated procedure and stripped in the unit for later offline analysis in hte’s in-house laboratory, while the gas-phase products are fed directly into an integrated online GC. Actual commercial catalyst shapes and sizes can be tested under industrially relevant operation conditions up to 840°F and 2300 psig. A higher pressure and/or temperature can be used on request. The units can process a wide range of industrial feedstocks within the same unit, from naphtha to resid, even bio feedstocks and paraffinic wax. The units are proven to operate in isothermal mode, hence producing a well-defined correlation between operation temperature and catalyst performance. The catalyst is loaded by embedding it with fine diluent particles to generate proper plug flow and complete catalyst wetting throughout the catalyst bed.

The classic first-stage VGO hydrocracking test protocol covers testing of the pretreat catalyst system as well as the combined pretreat and cracking system in separate reactors, but in the same unit as illustrated in Figure 2. The first eight reactors, shown on the left, contain the pretreat systems. They are placed in two block heaters, with each set of four reactors operating at the same temperature. These reactors are used to obtain the N and S removal kinetics after the pretreat reactors. The second eight reactors, shown on the right, contain both the pretreat and the cracking catalyst systems in the same reactor tube. These reactors provide data on the overall oil conversion after the combined pretreat and cracking catalyst system. In the combined system, the pretreat and cracking catalysts are placed in the same reactor tube and are hence operated at the same reaction temperature. For reference, the pretreat-only reactors are operated at the same reaction temperature. In the present study, eight catalyst systems were tested, including the incumbent system. Duplicates were included for the pretreat as well as for the combined system in order to provide a reference check for data reproducibility.

The test campaign is designed with the customer meeting vendors’ start-up recommendations that are most suitable for each catalyst. Overall catalyst performance is characterised by activity, deactivation, product selectivity, \( \text{H}_2 \) consumption, and detailed product properties. The Motiva hydrocracker first-stage study is an excellent case to demonstrate the added value for the refiner resulting from an independent side-by-side study of vendors’ catalyst systems.

Data quality and reactor-to-reactor reproducibility of the test results is of crucial importance for the validity of the data. An excellent mass balance and high degree of accuracy and precision can be obtained with high throughput test systems. Figure 3 shows that the mass balance obtained in the presented case study is within \( \pm 2\% \) of 100%.

Figure 4 shows the pretreat nitrogen slip plotted against the reaction temperature for some selected pretreat
catalyst systems covering the whole activity range. A low nitrogen slip of basic organic nitrogen compounds is important to avoid titration of the acidic sites and hence deactivation of the subsequent cracking catalyst. Nitrogen slips down to below 5 ppm were measured accurately and with good repeatability. The horizontal red arrow indicates the overall spread in nitrogen slip for the pretreat systems shown. A significant difference in the start of run weighted average bed temperature (SOR WABT) was found between the different systems, allowing for either longer cycle life or more severe operation for the most active system, assuming a similar deactivation rate.

Figure 5 shows the overall oil conversion for selected combined pretreat and cracking catalyst systems. The graph covers a wide activity range of oil conversion vs operation temperature. The horizontal red arrow indicates the activity spread of the combined pretreat and cracking systems shown. A significant difference in SOR WABT was found between the different systems, allowing for either longer cycle life or more severe operation for the most active system, assuming a similar deactivation rate.

One of Motiva’s test objectives was to identify first-stage cracking catalyst systems with higher diesel selectivity. Figure 6 shows diesel selectivity for some of the tested catalyst systems. The vertical red arrow identifies a first-stage catalyst system with significantly higher diesel selectivity.

In addition to activity, catalyst stability, and product yield selectivity, Motiva was interested in evaluating overall volume swell across the first-stage hydrocracking system. Hte was able to calculate each catalyst system volume swell based on product yields in the gas and liquid samples and densities. Hydrogen consumption, another important economic parameter for Motiva, was calculated from online GC analysis for the gases and offline elemental analysis for the liquid. The data showed the increasing H₂ consumption with higher oil conversion. Good tube-to-tube repeatability was achieved for both pretreat and cracking catalysts.

Hte carried out total liquid product (TLP) fractionation using a micro-distillation column with a high separation efficiency comparable to ASTM distillation. All liquid products were selected from the cracking catalyst system at target conversion level. Key fractional properties were measured as requested by Motiva. Analytics included density, S, N, C, H, SimDist for all fractions. The following additional analyses were measured: PIONA for the naphtha fraction; aromatics, cloud and pour points, cetane index for diesel; aromatics, VI for the unconverted oil. Hte typically customises key fractional characterisation according to each customer’s needs.

Conclusion
In summary, this first-stage hydrocracking test was successfully completed within six weeks, including two different feedstocks. Hte was able to accommodate the different start-up procedures required by catalyst vendors. Excellent data accuracy was attained for mass balance, activity, selectivity, and H₂ consumption. As a result of this test, Motiva was able to identify and select pretreat and cracking catalysts showing higher activity and/or diesel selectivity, resulting in greater added value for Motiva through either a longer cycle life or more severe operation.

Motiva has successfully been able to use hte’s state-of-the-art high throughput technology to test and differentiate among multiple catalysts for its first-stage hydrocracking unit. Motiva was pleased with the test and has commissioned and completed additional tests for naphtha reforming and VGO hydrotreating.
Are you still selecting your catalyst the old-fashioned way?

Catalyst performance has a significant impact on refinery profits. With independent catalyst testing you can base your decision for a catalyst change-out on reliable data.

hte uses high throughput experimentation to test catalysts from different vendors head to head under realistic process conditions.

- Naphtha reforming and hydrotreating
- Aromatics processes
- Diesel, VGO, and Resid hydrotreating
- Hydrocracking (first and second stage)
- Lubes upgrading (dewaxing, hydrofinishing)
- Biofuels and Biochemicals

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