

Advances in catalyst testing

A refining and petrochemical company relied on high throughput experimentation to select a change-out option from competing catalysts for the best ROI

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Independent catalyst testing has become a useful tool for refiners to support their catalyst selection process. Actual testing enables a customised catalyst evaluation under industrially relevant conditions including different industrial operational cases and different representative industrial feedstocks. The comparability of different catalyst systems is based on one and the same foundation, thus significantly lowering the degree of uncertainty as compared to paper studies describing each individual vendor's catalyst systems.

High throughput experimentation has become the state-of-the-art industrial standard in independent catalyst testing and offers the technical means to compare different catalyst systems head to head at the same time under uniform and identical conditions in an efficient and cost-effective way. It has proven to provide industrially significant data in a timely manner with a high degree of accuracy and precision on the basis of relative catalyst ranking as well as absolute data transferability to industrial scale. It is the ideal way to identify properly the optimal catalyst system for a refinery's specific process. Given the high stakes involved in the choice of catalyst for an operation cycle, selecting the appropriate testing technology for conversion units is pivotal, as it has a dramatic and lasting impact on the profitability of a refinery. High throughput experimentation is utilised in the catalyst selection process in a wide array of refinery processes, such as (but not limited to) hydrocracking, hydrotreating, reforming, (de-)alkylation, resid upgrading, lubes pro-

cessing, and also (co-)processing of biofeedstocks.^{1,2,3}

In classic high throughput experimentation set-ups, testing is accelerated by running multiple reactors simultaneously and in parallel for direct comparison of the catalysts under investigation. The gas and liquid distribution technology ensures a uniform feedstock distribution over all reactor positions. The principal methodology in trickle-bed catalyst testing is straightforward: gas and feedstock are fed through a catalyst-loaded reactor under defined conditions. Depending on the nature of the reaction and the product spectrum, the products are analysed by online methods or collected as liquids and later analysed offline. For processes with a consecutive reactor configuration, such as single-stage hydrocracking with mainly a pretreat and a cracking catalyst system, each reactor stage is either investigated separately or the combined reactors are simulated in one test reactor.² In cases where the consecutive reactors are operated at a similar operating temperature level, this approach is viable. However, in many cases, pretreat and cracking reactors are operated at different temperatures. It is beneficial that a laboratory method takes this temperature difference into account to properly simulate the industrial process. In addition, when performing independent catalyst testing for refinery applications, the catalyst systems are typically compared under a constant conversion operation, with the temperature being the tuning parameter to reach the desired conversion level. In order to reach a predefined conversion level in the consecutive reactors as

well as for the different catalyst systems in comparison, an independent temperature control on each reactor is required. Moreover, when evaluating consecutive reactor stages in one and the same test, an inter-stage quantification between the reactors is highly desirable to evaluate the performance of the first reactor. In classic pilot scale testing, the quantification of the upstream reactors is obtained by interstage sampling. Interstage sampling typically has the drawback that only concentration based information is obtained, since only a sample is taken, whereas the flow rate of the gas and liquid phase is left unmeasured. As a second drawback, the required amount of reactant to perform all required analyses is taken away from the downstream reactor. In pilot scale, this reactant loss to the following reactor is typically negligible, likely corresponding to an interruption of feed supply to the order of a few minutes.

In the case of high throughput experimentation with smaller catalyst amounts, removing a few ml of interstage product is equivalent to cutting off the feed supply to the downstream reactor for about 0.5-1 hour and would cause significant disturbances.

These drawbacks in utilising classic high throughput experimentation in simultaneous testing of consecutive reactor stages led hte to develop a new approach for testing consecutive reactor stages in an industrially significant as well as efficient and cost-effective way.⁴ The core principle of the new test approach is illustrated in **Figure 1**. The new concept contains reactors connected in series. The consecutive reactors are equipped with

an independent temperature control. Interstage quantification is not performed by classic interstage sampling, but a third mirror-type reactor reflects the performance of the upstream reactor. The mirror reactor is placed in one and the same heating block as its reference reactor to ensure high comparability. This approach enables a comprehensive mass flow rate based gas and liquid analysis, constituting a clear improvement compared to the traditional concentration based interstage sampling information. With this new concept, interstage dosing of gas and/or liquid becomes a proven reality in high throughput experimentation too.

This new approach is demonstrated in a case study performed for PTT Global Chemical Public Company Limited (GC), a leading Asian integrated petrochemical and refining company, to evaluate commercial hydroprocessing catalysts under commercially relevant conditions for a catalyst change-out in its refinery at Rayong, Thailand. GC selected hte for the evaluation study to benchmark five commercial hydroprocessing catalyst systems using a 24-fold high throughput reactor system optimised for single stage hydrocracking under commercially relevant conditions. The project was completed in 2018 with the overall aim of measuring catalyst performance (activity, selectivity, and stability) and determining key fractional product properties.⁵

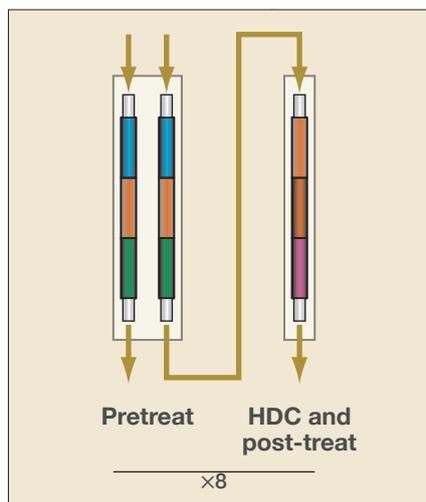


Figure 1 New high throughput approach for processes with serial reactor configuration, inter-stage quantification, and individual operation temperatures

An advantage of the 24-fold testing unit lies in the freedom to adjust the temperatures of all pretreat and cracking reactors individually and actually measure the impact of temperature on each of the catalyst systems connected in series. This freedom minimises the need to extrapolate data when comparing product properties between the different catalyst systems, because each cracking system can be run at an accurately set conversion with the pretreat reactor set to an accurate nitrogen slip.

All reactors share one liquid feed supply and one gas supply, which are respectively equally distributed between the reactors. In a typical test, the catalyst systems are all operated under identical pressure,

liquid hourly space velocity (LHSV), and gas-to-oil ratio to ensure an optimal comparison. If the catalyst systems are to be tested at different LHSVs, this can be accommodated by adjusting the amount of catalyst loaded in order to reach the targeted LHSV at the given flow rate. If a second parallel feed supply is required, this can be realised by adding a second feed module.

Catalyst activation in general involves individual procedures for the different catalyst systems, such as different feed composition and temperature protocols. This requires a certain flexibility of the test units. In a typical approach, the different activation protocols are harmonised to an extent acceptable for all catalyst vendors. The remaining and essential differences in the protocols need to be facilitated by the test unit.

The aim of an independent catalyst test is to find the catalyst system that best meets the requirements of the refinery. This generally implies having a high yield of a target fraction, achieving this yield at a lower temperature, minimising the yield of C₁-C₄ hydrocarbons, and having the properties of the targeted fraction meet various quality standards. As indicated in **Figure 1**, state-of-the-art catalyst systems for single stage hydrocracking comprise a multistack of different catalysts for the pretreat, cracking, and post-treat function. In order to perform an industrially relevant ranking, the catalysts have to be tested in their commercial size and shape. A typical independent catalyst test on a 24-fold unit requires all participating catalyst vendors to provide catalysts and activation protocols, to assist in finding harmonised activation protocols, to provide a target value for the nitrogen slip of the pretreat system and the oil conversion or other parameters of the cracking system, as well as to provide an estimate for the required pretreat and cracking temperatures to reach the targeted values.

In highly optimised refinery operations, the performances of different proposed catalyst systems are very close to each other. Nevertheless, maximising the yield of a target fraction is a key objective (**Figure 2**) and a difference of a few percent in

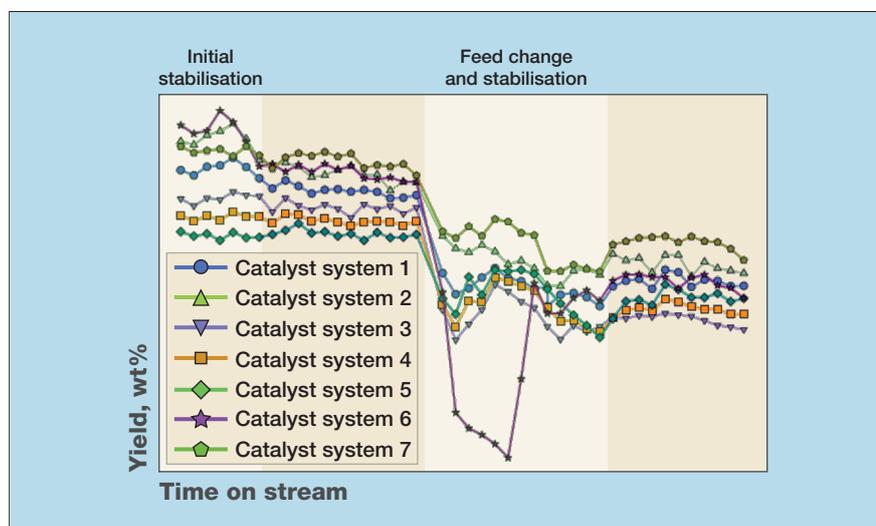


Figure 2 Target product yields vs time on stream for a virtual case

the target fraction yield can make a difference in annual revenue in the order of tens of millions of dollars.

Because of these considerations, the advantage of running one independent test where catalyst systems from multiple vendors are compared in one test unit under relevant conditions with the actual test feed from the refinery becomes obvious. The simplest argument in favour of an independent test comparing all proposed systems in parallel is that any measurements that one performs will have a certain variance. Thus, when comparing measurements performed by several parties in different test units, one ends up comparing very heterogeneous sets of data when considering how they were obtained and what the possible errors are for each individual data set. However, when all systems are compared in one test unit, one can be confident that all systems have been treated equally and variances stemming from the comparison of different testing units in different laboratories are minimised. Moreover, the relative order of target fraction yields for a set of

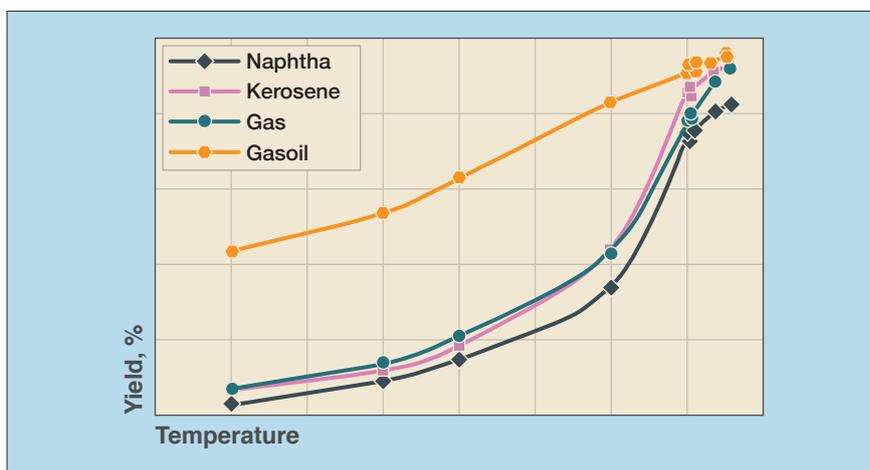


Figure 3 Yield vs temperature correlations

catalyst systems can change if different feeds are being tested. In the virtual example shown in **Figure 2**, the same catalyst system gives the highest yields for both feeds, but the relative order of all catalyst systems is different. When performance margins to the order of 1% make such a considerable impact, the best confidence one can have in the choice of catalyst system is gained by performing an independent test.

The first measure of the validity of the results produced by a 24-fold

unit is the comparison between the required temperatures estimated by each vendor to reach the targeted N-slip and conversion, and the actual temperatures determined in the test unit. With a rigorous calibration of the reactor temperatures within $\pm 1^\circ\text{C}$, the requirement that the mass balance is at $100 \pm 2\%$, with our meticulous and exact reactor loading protocols we generally observe that there is less than 3°C difference between the temperatures predicted by the catalyst vendors

Typical analysis package for key fractional properties of different product cuts

Gas phase hydrocarbons Pseudo-PIONA analysis	Naphtha	Kerosene	Gas oil	UCO
	Density (D4052)	Density (D4052)	Density (D4052)	Density (D4052)
	Sulphur content (D5453)	Sulphur (D5453)	Sulphur (D5453)	Sulphur (D5453)
	PIONA analysis	Flash point (D3828)	Calculated Cetane Index. (D4737, from SimDist)	Viscosity (D7042)
	RON/MON (calculated)	Smoke point (D1322)	Cloud point (D2500)	Aromatics
		Freezing point (D2386)	Pour point (D97)	Ni/V (D2622)
		Mercaptan sulphur (D3227)	Viscosity (D7042)	Carbon residue (D4530)
			Aromatics (DIN EN 12916)	

Table 1

and the temperatures measured in our test units.

From such a test, one can also derive the dependence of key properties on reactor temperature for both the pretreat and the cracking reactor, since each of these are individually controlled. For example, **Figure 3** shows schematically how the yields of several product fractions are influenced by temperature. Overlaying the correlation plots of each catalyst system being tested gives probably the quickest overview of the strengths and weaknesses of the systems being tested.

Once the targeted N-slips and conversions have been reached and the catalysts have all reached line-out conditions – a process that can take 2-3 weeks after activation – it is also important to collect product for fractionations to allow for a detailed investigation of the properties of each product fraction. The yield of each fraction can be estimated from the simulated distillation analysis of the daily TLP sample and, depending on the requested analysis package, we can estimate how much product we need to collect. For example, when one of the fractions is

produced at a yield of 10% and the requested analyses require 100 ml of sample from that particular fraction, we know we have to collect at least one litre of TLP under the targeted unit operation conditions to perform all the required analyses. An example of an analysis package that has been requested and performed for the characterisation of the individual fractions is shown in **Table 1**.

The essential requirement in order to measure individual properties of the product fractions, like those described in **Table 1**, is to perform an accurate fractionation of the collected product. Using automated micro-fractionation units, hte is capable of performing fractionations on sample sizes in the range of the product volumes that our high throughput units produce in a period of 1-10 days. This is the relevant duration of the product collection period depending on the product analyses that are requested and the flow rates used in the test. The parameters of the micro-fractionation are optimised in order to reduce the overlap of the separated fractions to less than 2 wt% (see **Figure 4**).

As discussed above, the mass balance is expected to lie within 100 +/-2%. In order to account for this margin of error and to compare the different catalyst systems at the same mass balance level, a final data reconciliation is typically performed. The yields obtained are corrected to add up to 100%. The standard method for reaching this goal is to multiply the yields by a reconciliation factor which ensures that the elemental balances close at 100%. The hydrogen content of the feed and of the liquid product is determined by H-NMR analysis, and the carbon content is calculated from this. By performing the data reconciliation step, we calculate the product yields and the hydrogen consumption accurately.

The entire duration of a competitive catalyst test – starting from the time when the catalysts and test feed are received by hte, activation and testing parameters have been agreed upon by all the vendors, and continuing until hte is able to deliver a complete data report – is around three months. This estimate is valid for tests where only one feed is tested and two sets of fractionation samples are taken for each catalyst system. If more feeds or different reaction conditions are to be investigated, or if more samples are to be fractionated, the duration of the test increases. Over the entire duration of the test, hte provides regular updates to the contracting parties. This can be the refinery and/or the individual catalyst vendors participating in the test. Regardless of who is paying for the work, hte always encourages discussing the results with both the refinery and the vendors to ensure in real time that the results being

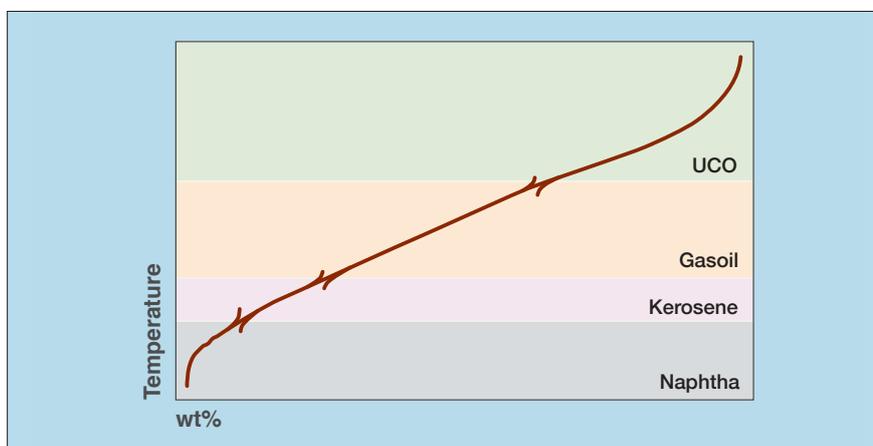


Figure 4 Distillation resolution

obtained are in line with the vendors' expectations and to verify that the test is being conducted in a manner that is agreeable to all parties.

The competitive catalyst testing programme performed in 2018 by hte on a 24-fold unit has provided GC with the relevant data to make the best decisions for the upcoming hydroprocessing catalyst change-out in 2019. GC has estimated that the yearly differential in earning between the best and worst performing catalyst would amount to several million dollars due to differences in selectivity and product volume gain. When considering the possible impact of a less than optimal choice in catalyst selection, it is obvious that such a test practically pays for itself many times over.

In the end, GC was able to make the optimal catalyst choice based on the data produced by hte throughout the benchmarking test. In view of hte's capability to measure industrially relevant data as well as to assist with discussions with vendors regarding both the experimental and contractual aspects of the test, GC will consider the services of hte again for competitive catalyst testing in future catalyst change-outs.

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