Refinery catalyst testing

Selecting the best catalyst for a unit demands thorough evaluation of the available options

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Refineries change out catalysts periodically, reloading either with fresh or regenerated used catalysts. Loading schemes include two or more catalysts. For every changeout or loading, the question must be answered: which catalyst or catalyst combination is most appropriate for the next cycle of the unit?

Choosing the best catalyst is of crucial importance. It relates directly to the profitability of the refinery, and therefore represents a tremendous opportunity for increasing refining margins. It has a huge impact on both daily operations and long term planning. For hydrocrackers, such a decision will have a major effect on the economics of the refinery. Also, a catalyst loading represents a significant investment ($10-$20 million), which surely justifies a thorough evaluation of more of the available options.

In recent years, comparative catalyst testing in pilot plants has become the best practice for evaluating catalyst performance and the profit impact of process options. When selecting catalysts, refiners consider several factors: expected performance, price, guarantees, technical service, and previous experience with prospective suppliers.

Important performance parameters include:
- Catalyst activity
- Yields (selectivity)
- Catalyst cycle life
- Deactivation rate
- Hydrogen consumption/production
- Product properties
- Yield flexibility
- Feedstock flexibility (including feed rate changes)
- Pressure drop build-up (dP+).

These terms are explained below in some detail along with some of the questions that commonly arise when considering process changes.

Process parameters for pilot plant studies

Feedstock quality

Refiners frequently change feedstocks before determining the impact of such changes in a pilot plant study. Failure to do so can be exceedingly expensive.

Most refinery planning models assume that all hydrocracker feeds give the same product distribution, regardless of endpoint. They predict that raising feedstock endpoints can be equivalent to converting heavy fuel oil into naphtha and middle distillates. Over small ranges, most vendor kinetic models give similar results. But in fact, especially for FCC heavy cycle oil and heavy coker gasoil, raising endpoints by just a few degrees can be equivalent to pumping liquid coke into the unit. Deactivation accelerates. Conversion drops immediately. To reattain conversion, temperatures must be increased accordingly. The incremental conversion is largely thermal, giving relatively large amounts of gas. In cases where this has happened, a pilot plant test readily would have revealed the impacts in advance.

Catalyst activity

In practice, catalyst activity in fixed bed systems refers to the average temperature required to achieve one or more major primary process objectives, such as sulphur removal or conversion of high boiling fractions into lighter fractions. In lube base stock hydroprocessing, primary objectives may include aromatics saturation, wax removal, or colour stabilisation. Typically, refiners base operations on weighted average bed temperature (WABT) or catalyst average temperature (CAT). Average temperatures are used because hydroprocessing units are adiabatic. Catalytic reforming is endothermic; temperatures go down as feeds pass through the reactors. Hydrotreating and hydrocracking are exothermic; temperatures go up as feeds pass through the reactor(s).

Catalyst deactivation

As catalysts age, they lose activity as coke deposition fouls active sites. Hydrogen inhibits coke formation, so increasing hydrogen partial pressure (H_2PP) decreases coke-induced deactivation. Feed contaminants and process upsets also cause deactivation. To compensate for activity loss, operators increase temperature to maintain performance (for instance, sulphur removal or conversion).

Deactivation rate can be expressed as temperature increase requirement (TIR) expressed as degrees per unit of time. Consider the following sample calculation. A diesel hydrotreater can make ultra low sulphur diesel (ULSD) at a WABT or CAT of 360°C at the start of a cycle. Due to metallurgical constraints, the maximum average temperature is 425°C. If the TIR is 2°C per month, the projected catalyst life (barring upsets or unacceptable pressure drop) is 2.7 years. A tacit assumption here is that deactiva-

Operating conditions to emphasise naphtha or middle distillates

Feed	Straight-run vacuum gasoil		
Naphtha mode	**Naphtha**	**Distillate**	**Total C_{4+}**
Cut point = 216°C	115 vol%	--	126 vol%
WABT = base			
Distillate mode	**Naphtha**	**Distillate**	**Total C_{4+}**
Cut point = 349°C	37 vol%	77 vol%	121 vol%
WABT = base -22°C			

Table 1

tion is linear. In fact, TIR tends to increase, especially at higher temperatures near end of run.

Yields (selectivity)

Yields and selectivity are closely related. A typical refinery yield report includes the following:

- Methane (C_1)
- Ethane (C_2)
- Propane (C_3)
- Butanes (i-C_4 and n-C_4)
- Light olefins (propylene and butylenes)
- Light naphtha (primarily pentanes) defined with a boiling range
- Heavy naphtha
- Light gasoil (may also be called kerosene)
- Heavy gasoil
- Unconverted oil
- Hydrogen

Yield tables show results in both wt% of feed and vol% of liquid feed. The sum is 100 wt% plus H_2 consumption or production (wt%).

Selectivity is the relative yield of a product or group of products. Selectivity calculations might exclude unconverted oil. So-called 'gas make' is C_1+C_2+C_3. Naphtha selectivity is the sum of light and heavy naphthas. Middle distillate selectivity is the sum of light and heavy gas oils.

With respect to selectivity, hydrocracking can be quite flexible. For a given catalyst, operating conditions can be adjusted to emphasise either naphtha or middle distillates. **Table 1** gives an example for a recycle hydrocracker with a high activity zeolite based catalyst:

Hydrocracking catalysts have inherent differences in product selectivity. Catalysts based on amorphous silica/alumina (ASA) are the least active, but they have the highest middle distillate selectivity. Certain ASA based catalysts give more than 90 vol% middle distillates. Catalysts based on high activity zeolite supports are designed to produce mainly naphtha. As shown in **Table 1**, they also can give significant yields of middle distillates.

So-called flexible catalysts are less active than naphtha-selective catalysts, but for a given once-through conversion at a given conversion cut point, flexible catalysts give higher middle distillate yield. But for refiners that switch seasonally between naphtha mode and distillate mode, there is a price to pay: with lower activity flexible catalysts, it may not be possible to maximise naphtha, not without sacrificing catalyst cycle life and product quality.

Catalyst cycle life

Catalyst cycle life affects profitability significantly. Obviously, when a unit is down for a changeout, it is not making products. Downtime is expensive: depending on local and temporal prices for feeds and products, the profit for a typical 50 000 b/d hydrocracker can be $1 million per day.

The following parameters affect catalyst life: feed quality, conversion, start-of-run catalyst activity, deactivation rate, dP+, and hydrogen quality. It is difficult to measure dP+ in a pilot plant, especially if it is due to feed contamination. But a pilot plant can evaluate the impact of remedial measures, such as replacing some active catalyst with grading material.

Planned vs unplanned shutdowns

Ideally, a cycle ends as planned in advance, just as the catalyst TIR reaches the specified limit. A turnaround affects every unit that supplies feed and utilities to the downed unit and also affects every downstream unit, including product blenders. While planning a unit shutdown, refiners adjust the operation of other units, build inventories in storage tanks, and make alternative arrangements to supply products to customers. Catalysts and chemicals are purchased, received, and stored on site. Contractors are brought on site to perform maintenance work, including catalyst unloading, loading, and activation. For an unplanned shutdown, perhaps due to rapid catalyst deactivation, costs are considerably higher.

Pressure drop build-up

To mitigate dP+, refiners consider increasing amounts of size grading and switching from dense loading to sock loading. Either option decreases the amount of the main catalyst. With a pilot plant study, one can determine the impact of extra grading material on the activity and selectivity of different catalyst systems.

Hydrogen purity and partial pressure

In catalytic reforming, isomerisation, and other processes that employ noble metal catalysts, the H_2 must be pure, with minimal CO and H_2S. In hydrotreating and hydrocracking, purity is less critical; non-noble metal catalysts can tolerate a few percent H_2S. More important than purity is H_2PP which is (H_2 purity)*(system pressure at the HP separator). H_2 purity is affected not just by CO and H_2S, but also by relatively inert gases such as CH_4 and N_2.

Product properties

These have a tremendous impact on profitability. For heavy naphtha, the paraffin, naphthene, and aromatic (PNA) of reformer feed determines the N+A of reformate. Certain hydrocracking catalysts saturate aromatics less than others; for reformer feed, less saturation is desired. The n-paraffin content of an isomerisation feed determines the iso/normal ratio of the product. It may not be possible to sell a gasoil as diesel if the pour point and cloud point are too high. Pour point and cloud point can be reduced with hydrodewaxing, but how much dewaxing is needed?

Estimating performance

Estimating expected performance is quite complex, because changing any single parameter affects all of the others to some extent or another. Mistakes due to lack of testing are not uncommon, and some are very expensive. Here are three examples:

- In one US hydrocracker, switching from the usual feed to deasphalted oil increased the catalyst deactivation rate by six-fold
- In several US refineries, switching from conventional crudes to synthetic crudes from Canada dramatically reduced catalyst cycle life in diesel hydrotreaters. The cause: unexpected traces of arsenic
- In a European hydrotreater, re-routing hydrogen purge gas to the make-up compressor led to a rapid build-up of methane in the recycle gas, reducing hydrogen purity and decreasing cycle life.

Pleasant surprises also occur. Replacement of a previous catalyst increased middle distillate yields in a diesel-oriented hydrocracker by 5.6 wt%. The difference was so dramatic that it debottlenecked the entire refinery. Prior testing might have revealed the full extent of the benefit, giving the refiner more time to plan for the improvement.

Refineries determine performance parameters in different ways. Companies with in-house pilot plants may evaluate different catalysts and loading schemes themselves. But typically, refiners do not have in-house pilot plants. Refiners without pilot plants may send feeds to catalyst suppliers for testing in vendor-operated facilities. Most refiners rely on projections (forecasts) from licensors or catalyst suppliers, projections which are based on kinetic models.

All three approaches have problems. In-house testing in large conventional pilot plants is expensive and time-consuming. Usually, it requires so much feed and catalyst that relatively few options are tested.

Tests conducted by vendors in vendor-owned units lack uniformity. For example, different units have reactors with different dimensions, leading to differences in reactor dynamics. The differences can be economically significant. A few percent change in C_3^- yield can be worth several million dollars in a year. A delta of 2°C in activity can be equivalent to 2-4 months of cycle life.

Comparing all available options from paper estimates/forecasts based solely on kinetic models is the riskiest approach. To be accurate, they require sound starting points – data from pilot plants or commercial units.

Today, refineries still underestimate the impact of catalyst selection. Choices often are based on incorrect assumptions, few catalyst options are considered, and decisions are made without appropriate, supporting test results. We estimate that more that 50% of catalyst selections are based on vendor forecasts only.

Independent testing has been available to the refining industry for over 30 years and, although a known concept in the industry, has only be adopted by a limited number of refiners. More and more refineries regularly conduct independent catalyst testing (side-by-side comparative testing) for all major catalysts procurement.

For pilot plant testing, a paradigm shift is needed. With high throughput pilot plant technology, it is possible to test up to 16 options simultaneously at no extra cost and with no increase in testing time. Independent catalyst testing addresses most of the pilot plant problems mentioned above. It enables refiners to obtain test results for several sets of process variables, including catalysts from various vendors under the same conditions in the same facility. Avantium's Flowrence high-throughput technology with high reactor-to-reactor repeatability allows the parallel testing of 16 catalysts options under the exact same conditions. Side-by-side tests in an independent lab allow for a direct comparison of unit performance under identical operating conditions using the refinery provided feedstock.

Milestones for successful catalyst testing

Successful catalyst testing requires early planning to allow sufficient time to establish necessary agreements and timely obtain test results.

It is important to understand the stakeholder interplay that governs catalyst selection, in order to maximise the value obtained from comparative catalyst testing. Independent testing requires some planning and it is important to assign a testing coordinator (focal point) to coordinate the various activities, interface with vendors, and effectively drive the process.

The proposed milestones and indicative timeline are are the best practical approach and should serve as reference relative to the planned catalyst changeout. Catalyst lead time is typically 6-12 months. The selection process, including testing, must start several months before that.

The catalyst evaluation for most refinery processes – reforming, isomerisation, hydrotreating, and hydrocracking, for instance – will take 1-3 months (common test programmes). In case the test programme needs to be longer (for instance, to test multiple feedstocks and/or process conditions), the testing milestone needs to be adjusted.

We recommend performing the catalyst test with sufficient time to obtain the test results and carry out the necessary techno-economic evaluation and effectively compare the catalyst options. The timing for the other milestones will be mostly dependent on the refinery internal processes and procedures.

Define the milestones plan

The process starts with the decision to perform independent testing to assess the performance of multiple catalysts under the required process options, feedstock(s), and operating conditions.

At this point, it is not yet relevant how many catalysts will be tested; the number and vendors can be defined later.

It is important to consider at this stage:

- Identifying and contacting independent testing labs

• Defining the catalyst suppliers to be contacted
• Overall required time schedule.

The testing coordinator should prepare a milestones plan accordingly and seek internal buy-in to secure necessary resources (see **Figure 1**).

Initiate vendor agreements (call for bids)

Refineries typically approach catalyst suppliers, issuing an invitation to bid and requesting catalyst offers for their unit's technical specifications and operating conditions. At this point, catalyst suppliers are informed of the intent to conduct independent testing to support the catalyst selection. Refineries may choose to collect all catalyst samples and send them to Avantium or request that vendors send the sample directly to us – common practice with Avantium.

If requested, the vendors can recommend an independent lab and share the catalysts' activation protocol and recommended procedures. If permitted by the refinery, the catalyst suppliers will have the opportunity to review and agree on the test protocol with the company that performs the test work.

We recommend including in the invitation to bid the key milestones for testing to ensure required agreements are in place/established in timely fashion.

Three practices are common: refineries pay the total cost of the test, refineries ask the participating catalyst suppliers to share the costs, or the selected catalyst vendor, or 'test winner', pays for the test.

Request for proposal

In order to maximise the value obtained from (independent) comparative catalyst testing, it is important to understand the dynamics and stakeholder interplay that govern catalyst selection. These tests require significant planning; refineries should start early to allow for proper selection of the catalyst options and to obtain the test results in time for ordering the catalyst(s).

Note that refineries only need to identify available catalyst suppliers. It is not yet necessary to choose

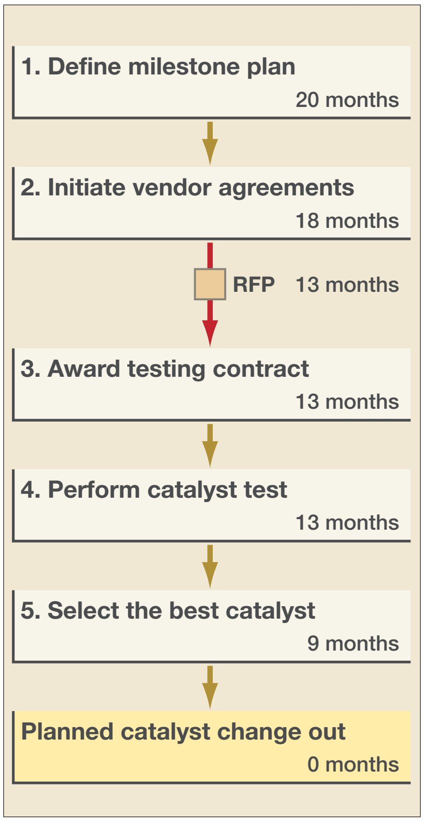

Figure 1 Milestones plan for catalyst testing and selection

a particular type or types of catalyst to be tested. The invitation to bid can already include the prerequisite for third party independent testing and potentially the select testing facilities (or pre-selected list). It is important to include due dates for sending catalyst samples as per the testing schedule.

At this stage, refineries do not need to decide on the exact number of catalysts or the number of vendors to be tested.

Award independent testing contract

The selection of the independent testing party is obviously important. Equally important is the assurance that the testing will be representative and accepted by the catalyst suppliers. For this, the vendors should be involved in the test design to obtain their buy-in and necessary input. Avantium recommends the involvement of the participating catalyst suppliers and a regularly interface in the alignment with all stakeholders.

After contract award, Avantium interfaces with the catalyst suppliers to ensure buy-in on the test protocol, catalyst loading, and activation procedures, in consultation with the refinery.

Figure 2 shows a general workflow for third party catalyst testing with Avantium.

Perform catalyst test

Avantium's test programmes are based on industry best practice and designed to compare the performance of commercial catalysts with real feedstocks and industrially relevant process conditions. The duration will vary depending on the refining application and number of test conditions and feeds.

We can in one test load up to 16 different catalysts, or load catalysts multiple times to increase statistical accuracy. The tests can include multiple feed changes and multiple pressure sweeps. Typical amount of feed required is 5 litres for reforming and 20 litres for hydrotreating/hydrocracking.

Potential use of parallel catalyst testing programmes include:

• Evaluate catalyst vendor claims on activity, selectivity, start-of-run WABT, aromatics saturation, and hydrogen consumption – independent evaluation of commercial catalysts
• Evaluate particular catalyst vendor options and compare against the incumbent catalyst
• Opportunity (crude) feed studies – catalyst flexibility
• Evaluate regenerated/rejuvenated catalyst usage, evaluating various percentages of total reactor load filled with regenerated catalyst in stacked/sandwiched configurations with fresh catalyst to increase confidence in the regenerated material
• Spot sample activity testing after delivery of catalyst by vendor: presulphided catalysts, regenerated/rejuvenated catalysts
• Process studies, like treat gas purity impact, liquid hourly space velocity (LHSV) impact, end-of-run estimation, and hydrogen consumption studies
• Step out technology options (for instance, dewaxing in ULSD)
• Kinetic measurements, feedstock and contaminant effects
• Obtain relevant data to support

refinery revamps and consideration of alternative feeds.

Comparative catalyst testing with 16 parallel reactors offers significant advantages:

- Testing up to 16 different process and catalyst options simultaneously gives a cost-effective comparison
- Testing replicates allow for reliable results that are statistically significant.

At the end of the pilot plant test, Avantium provides the full data set together with a complete report, within two weeks of test completion. The test results include a set of plots (agreed during kick-off), the most important data on conversion, mass balances, H_2 consumption, and all test conditions, together with a relevant comparison between catalysts.

Reforming tests provide catalyst performance data at fixed times on stream (from the iso-RON data):

- Temperature required to achieve the desired severity (RON) from interpolation of the iso-RON data at specific times on stream, for each catalyst
- C_{5+} yield, total aromatics and H_2 produced from interpolated results
- The interpolation of data will be obtained from non-linear regression (polynomial) for all catalysts tested
- The statistical error resulting from the fitting of the data (error bands around the interpolated values).

Hydroprocessing tests provide catalyst performance data on:

- Activity: measurement of at least three temperatures required for the Arrhenius relation
- Selectivity (yield pattern and hydrogen consumption)

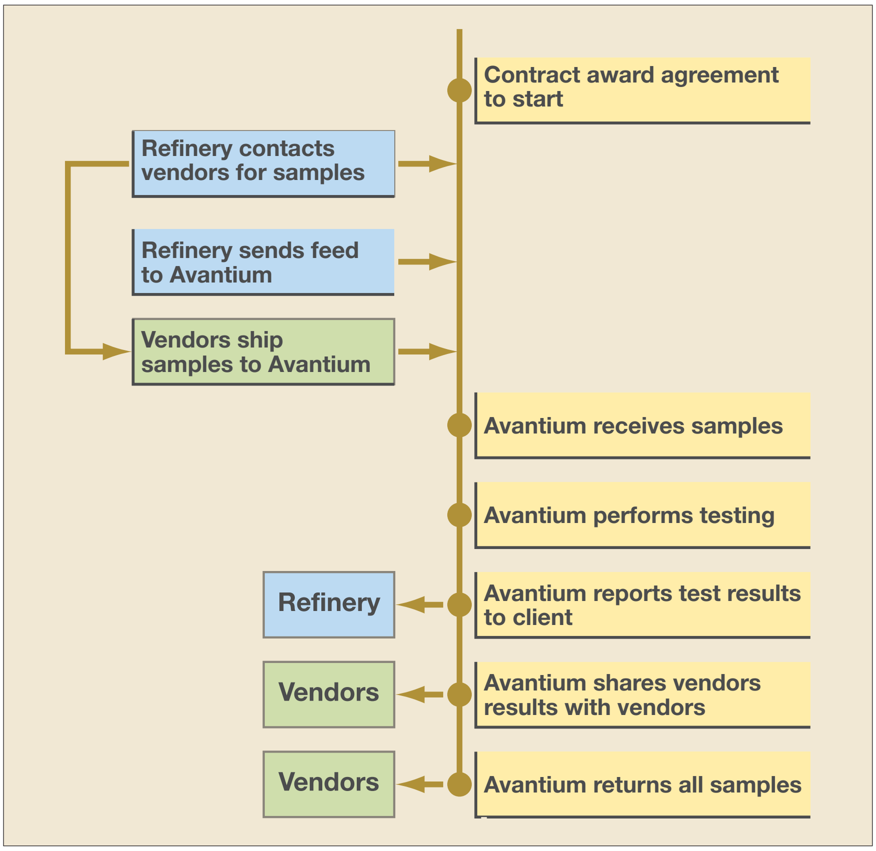

Figure 2 Workflow for third party catalyst testing

- Stability: these tests are normally done by varying the temperature and repeating temperatures to check for changes in activity (analysing the products to check differences in performance).

Conclusion

The efficiency of different catalysts has a huge impact on refinery economics, operations and long term planning. Avantium Flowrence high-throughput 16 parallel reactors system provides enhanced testing with high data quality (repeatability, reproducibility and scalability). The test results enable a refinery to independently validate catalyst performance and better determine the most efficient catalyst that most likely will provide the maximum economic benefit.

Flowrence is a trademark of Avantium.

Tiago Vilela is Director of Business Development for Refinery Catalyst Testing with Avantium. He is responsible for development, improvement and growth of global services intended for refineries, catalyst suppliers, and technology licensors in the oil refining industry.