WHITEPAPER

Refinery Catalyst Testing

A Practical Approach and how it can help Refineries Select the Best Catalysts

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Introduction

Refineries change out catalysts periodically, reloading either with fresh or regenerated used catalysts. Loading schemes include two or more catalysts. For every every change out 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-$20MM), 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 partial pressure (Hydrogen consumption/production)
- Product properties
- Yield flexibility
- Feedstock flexibility (including feed rate changes)
- Pressure-drop buildup (dP+)

These terms are explaind 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. Of the following examples, the first two are mentioned in the introduction:

- In one U.S. hydrocracker, switching from the usual feed to deasphalted oil increased the catalyst deactivation rate by 6x.
- In several U.S. refineries, switching from conventional crudes to synthetic crudes from Canada dramatically reduced catalyst cycle life in diesel hydrotreaters. The cause: unexpected traces of arsenic.

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 gas oil, 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 sulfur removal or conversion of high-boiling fractions into lighter fractions. In lube base stock hydroprocessing, primary objectives may include aromatics saturation, wax removal, or color stabilization. Typically, refiners base operations on weighted average 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 is 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 (H2PP) decreases coke-induced deactivation. Feed contaminants and process upsets also cause deactivation. To compensate for activity loss, operators increase temperature to maintain performance (e.g., sulfur 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 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 deactivation 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 (C1)
- Ethane (C2)
- Propane (C3)
- Butanes (i-C4 and n-C4)
- Light olefins (propylene and butylenes)
- Light naphtha (primarily pentanes) defined with a boiling range
- Heavy naphtha
- Light gas oil (may also be called kerosene)
- Heavy gas oil
- Unconverted oil
- Hydrogen

Yield tables show results in both wt.% of feed and vol.% of liquid feed. The sum is 100 wt.% plus H2 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 C1+C2+C3. 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 emphasize either naphtha or middle distillates. Table 1 gives an example for a recycle hydrocracker with a high-activity zeolite-based catalyst:

Feed	Straight-run vacuum gas oil		
Naphtha mode	*Naphtha*	*Distillate*	*Total C4+*
Cut point = 216°C	115 vol.%	--	126 vol.%
WABT = base			
Distillate mode	*Naphtha*	*Distillate*	*Total C4+*
Cut point = 349°C	37 vol.%	77 vol.%	121 vol.%
WABT = base -22°C			

Hydrocracking catalysts have inherent differences in product selectivity. Catalysts based on amorphous silica/alumina (ASA) are the least active, but they have 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 the table, 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 cutpoint, 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 maximize 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 change out, it isn't making products. Down time is expensive: depending on local and temporal prices for feeds and products, the profit for a typical 50,000 b/d hydrocracker can be US$1 million per day.

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The following parameters affect catalyst life: feed quality, conversion, start-of-run catalyst activity, deactivation rate, pressure-drop buildup (dP+), and hydrogen quality. It is difficult to measure pressure drop buildup in a pilot plant, especially if the dP+ 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 Versus 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 onsite. Contractors are brought onsite 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 Buildup. 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, isomerization, and other processes that employ noble metal catalysts, the H2 must be pure, with minimal CO and H2S. In hydrotreating and hydrocracking, purity is less critical; non-noble metal catalysts can tolerate a few percent H2S. More important than purity is H2 partial pressure (H2PP) which is (H2 purity)*(system pressure at the HP) separator). H2 purity is affected not just by CO and H2S, but also by relatively inert gases such as CH4 and N2.
- Product Properties. These have a tremendous impact on profitability. For heavy naphtha, the 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 isomerization feed determines the i/n ratio of the product. It may not be possible to sell a gas oil 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 expected performance is quite complex, because changing any single parameter affects all of the others, to one extent or another. Mistakes due to lack of testing are not uncommon, and some are very expensive. Here are three examples:

- In one U.S. hydrocracker, switching from the usual feed to deasphalted oil increased the catalyst deactivation rate by 6x.
- In several U.S. 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 makeup compressor led to a rapid buildup 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%[1]. 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 C3-minus yield can be worth several million dollars per 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.

Refiners are motivated to select of the best catalyst system and increase refinery margins.

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. Our industry proven Flowrence® high-throughput technology with outstanding 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 govern catalyst selection, in order to maximize the value obtained from comparative catalyst testing. Independent testing requires some planning and 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 best practical and should serve as reference relative to the planned catalyst change out. Catalyst lead-time is typically between 6 and 12 months. The selection process, including testing, must start several months before that.

The catalyst evaluation for most refinery processes e.g. reforming, isomerization, hydrotreating and hydrocracking will take between 1 and 3 months (common test programs). In case the test program needs to be longer (e.g. test multiple feedstocks and/or process conditions) the testing milestone (MS04) needs to be adjusted.

We recommend *performing the catalyst test* (MS04) with sufficient time to obtain the test results and perform the necessary techno-economic evaluation and effectively compare the catalyst options. The timing for the other milestones (MS01 and MS02) will be mostly depended on the refinery internal processes and procedures.

01: Define 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 condition(s).

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

Important to consider at this stage:

- Identify and contact independent testing labs
- Define 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.

02: Initiate vendor agreements (Call for bids)

Refineries typically approach catalyst suppliers issuing an Invitation to Bid requesting catalyst offers for their unit 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 to Avantium or request that vendors timely send the sample directly to us; common practice with Avantium.

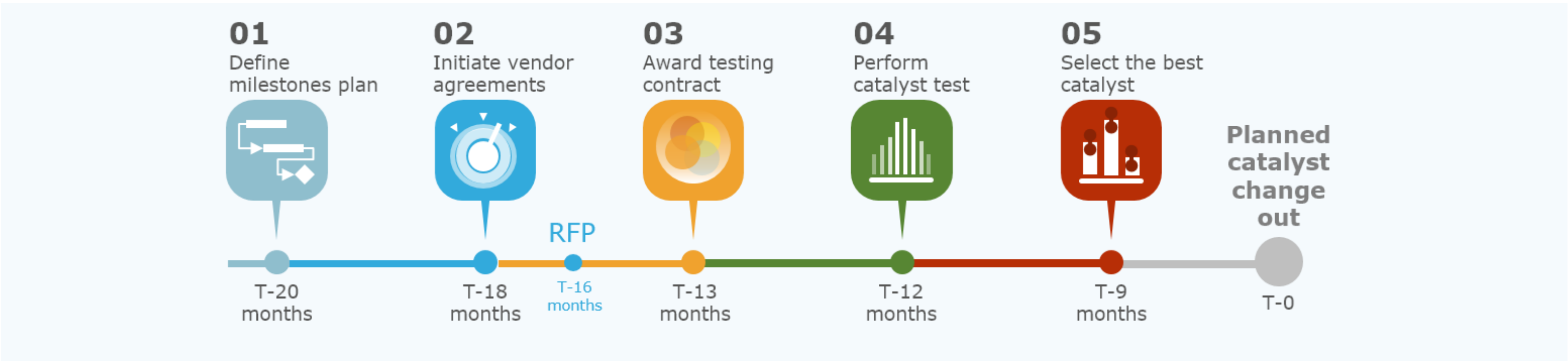
If requested, the vendors can recommend an independent lab, and share the catalyst(s) activation protocol and recommended procedures; if permitted by the refinery, the catalyst suppliers will have the opportunity to review and agree on the test protocol with the company that performs the test work.

We recommend to include in the Invitation to Bid the key milestones for testing (e.g. shipping of catalyst samples and timing of the test) to ensure required agreements are timely in place/established.

Three practices are common: (1) refineries pay the total cost of the test; (2) refineries ask the participating catalyst suppliers to share the costs; and (3) the selected catalyst vendor, or "test winner" pays for the test.

Request For Proposal (RFP)

In order to maximize 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 a proper selection of the catalyst options and to obtain the test results in time for ordering the catalyst(s).



Note that the refineries only need to identify available catalyst suppliers and is not yet required to choose a particular type or types of catalyst to be tested. The Invitation to Bid can already include the pre-requisite for third party independent testing and potentially the select testing facilities (or pre-selected list). Is important to include due dates for sending catalyst samples as per testing schedule.

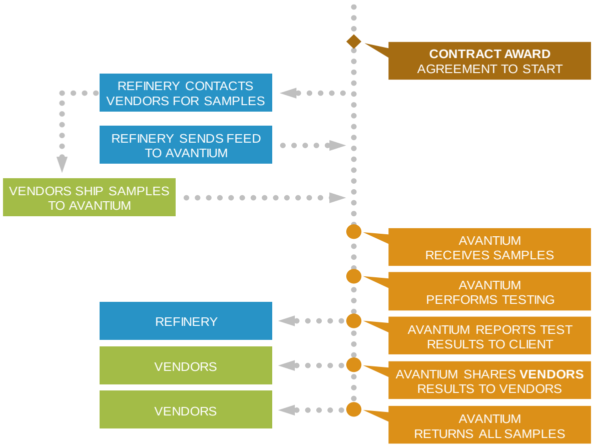
At this stage, refineries do not need to decide on exact number of catalysts (e.g. a range of 4 – 12) nor the number of vendors to be tested.

03: 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.

Below a general workflow for third party catalyst testing with Avantium.



04: Perform catalyst test

Our test programs are industry best practice and purposely designed to compare the effectiveness 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 different 16 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 liters for reforming and 20 liters for Hydrotreating/Hydrocracking.

Potential use of parallel catalyst testing programs include:

- Evaluate catalyst vendor claims on activity, selectivity, deactivation, 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 stacked catalyst bed options, e.g. regenerated/rejuvenated catalyst usage; evaluating various percentages of total reactor load filled with regen cat in stacked/sandwiched configurations with fresh cat.
- Evaluate regenerated catalysts; refiners are the owners of the spent catalysts that can be regenerated and included in comparative testing to increase confidence in the regenerated material. Regenerated catalysts are about an order of magnitude cheaper than fresh catalysts.
- Spot sample activity testing after delivery of catalyst by vendor: presulfided catalysts, regen/rejuvenated catalysts.
- Screening of different types of feeds, i.e. impact of feed properties process parameters and catalyst life; Perform new crude oil feasibility and selection for refinery feedstock on sets of catalysts
- Perform biomass feedstock feasibility testing for refinery feedstock on sets of catalysts
- Validate/Verify claims for new vendors in the market
- Stability testing / deactivation studies on sets of catalysts.
- Process studies, like treat gas purity impact, LHSV impact, End of Run estimation, hydrogen consumption studies.
- Step out technology options (e.g. dewaxing in ULSD).
- Kinetic measurements, feedstock and contaminant effects.
- Build a model to support unit performance optimization/troubleshooting reforming (CCR, SR and CR), Isomerization, hydrotreating and hydrocracking.
- 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; *cost-effective comparison*.
- Testing replicates that allow for *reliable results* that are *statistically significant*.

At the end of the pilot plant test, Avantium will provide the full data set together with a complete report, within 2 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 will 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.
- C5+ yield, total aromatics and H2-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 will provide catalyst performance data on:

- Activity; measurement of at least 5 temperatures required for the Arrhenius relation.
- Selectivity (yield pattern and hydrogen consumption).
- Stability (commercial deactivation rates are in the order of 1-5°C/1000 h). These tests are normally done by varying the temperature and repeating temperatures to check for changes in activity (using SimDist to check differences in performance).

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

05: Select the best catalyst

We realize that the efficiency of different catalysts has a huge impact on refinery economics, operations and long-term planning. Avantium provides enhanced testing with the highest data quality (repeatability, reproducibility and scalability).

The test results enables the refinery to independently validate catalyst performance and better determine the most efficient catalyst that most likely will provide the maximum economic benefit.

Avantium micro-pilot plant allows for the highly efficient testing of catalysts for fixed bed processes, producing the highest data quality (repeatability, reproducibility and scalability) with low amounts of feed (less waste generated). Avantium' proven high throughput parallel testing technology[2] (See peer-reviewed paper for a detailed description of the micro-pilot plant) offers the possibility to test up to 16 different catalysts systems and/or process options side-by-side. Refineries can now cost-effectively explore more options or catalyst systems.

Our Refinery Catalyst Testing (RCT) team is able to translate specific test requirements and refinery objectives into best practical test programs to collect reliable performance data. With high-throughput technology, refiners can run replicate reactors and significantly increase precision on the anticipated activity, and selectivity of catalyst systems under a variety of predefined conditions, providing relevant results to evaluate the economic impact of the catalysts performance (e.g. using the refinery economical/optimization models).

For hydrocracking catalysts testing, our technology allows to discriminate 1 °C difference in catalyst activity, and 0.5 wt.% in middle distillates yields. This is important because a lower gas make of e.g. 1 wt.% could result in savings up to $3MM; one month increase on cycle length could result in savings up to $0.5MM.

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1 Krenzke D., Vislocky J., 2007, Cracking Catalysts Systems, *Hydrocarbon Engineering*, November 2007, http://www.chevrontechnologymarketing.com/Documents/HE_Nov2007.pdf

2 https://www.catalysis.avantium.com/knowledge-base/performance-testing-of-hydrodesulfurization-catalysts-using-a-single-pellet-string-reactor/