Close co-operation between customer, licensor and Criterion results in improved solutions for residue conversion

Summary

Criterion believes that, in the current challenging refining environment, significant improvements in performance are still possible provided a good co-operation between customer, licensor and supplier can be achieved. In support of this belief, the following article describes the improvements made in the Shell designed residue hydro-treater of the Yokkaichi refinery in Japan (SYS). Through careful study of customer feedback and a team approach with the licensor, Shell Global Solutions, Criterion has been able to deliver catalyst systems that showed significant improvements in HDM performance while maintaining sufficient HDS activity performance.

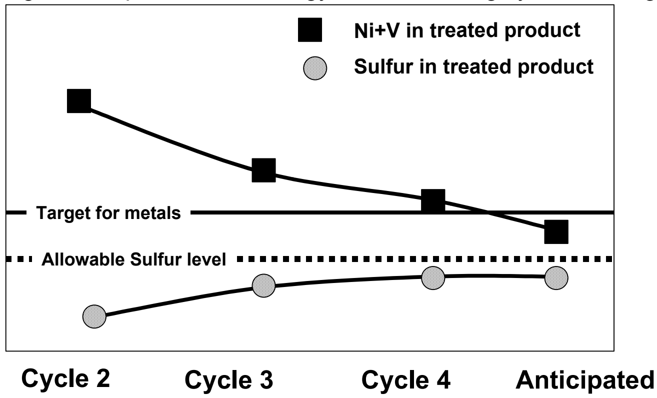
Introduction

Many papers have been written on how to design an appropriate catalyst to treat residual feeds. The theories all revolve around how a catalyst system is able to overcome the diffusion constraints and still maximize activity and/or stability. In order to keep its catalyst portfolio relevant, Criterion focuses on end-product characteristics. These properties include metals (amount, type and dispersion), pore structure (pore size, pore distribution and pore volume), alumina-technology, catalyst size & shape and manufacturing technology. Criterion's knowledge base has grown through the years where it is now possible to tune catalysts for specific levels of Hydro-demetalization (HDM), Hydro-desulphurization (HDS), Hydro-denitrogenation (HDN), microcarbon reduction (HDMCR) and conversion (540 C^o +) based on customer needs and operation limits.

In residue hydro-treatment reality, a one-catalyst-solution does not exist. Today, a refiner's needs have to be met through appropriate stacking of individual products to achieve the overall objectives (see appendix 1). The life of a catalyst supplier is made even more challenging as economic forces often drive refiners away from their original design feed to pursue more profitable crude-slates based on LP models or emerging opportunities. As most refiners will be aware, different feeds show different characteristics in terms of reactivity and yields (see appendix 2). Such situations require a versatile catalyst solution that is optimized over time through intimate contact between supplier and user. Keeping this in mind, the design of an appropriate catalyst system for a residue conversion unit is still one of the bigger challenges facing a fixed-bed catalyst supplier and is best done through a team-like effort involving representatives from the customer, licensor and catalyst supplier. Only in the case that knowledge about the building blocks -the individual catalysts-, the operational environment and unit design meet can the refiner achieve the best solution.

This approach was used effectively at the Yokkaichi (SYS) refinery in Japan. The paper will now describe how the interface process has developed and what improvements have been achieved so far. As shown in figure 1, the driving force behind all efforts to date have been to reduce metals in treated products with each cycle while keeping the HDS activity sufficient to meet the allowable sulphur target.

Figure 1 Improvement strategy followed during systems design



1 Description of the unit and catalyst systems

Yokkaichi's Shell-designed residue hydro-conversion unit was started up in 1996 and is currently in its 5th cycle. The unit pre-treats feeds to a Shell-designed resid Fluid Catalytic Cracking Unit (RFCCU). HD-MCR, HDN, HDM and HDS are especially important reactions in the feed to the RFCCU due to the potential product and operational improvements. The special design features in the SYS design are listed below:

- It is a one-train-four reactor system
- Inside the reactors are Ultra Flat Quench™ * inter-bed internals which ensure a flat thermal profile across reactor diameter within minimum reactor volume, thus maximizing catalyst inventory / utilization, and maximizing operational control.
- Shell Global Solutions designed state-of-the art heat integration to reduce operational costs as much as possible.
- It also makes use of High Dispersion distribution trays*, HD trays™, which ensure that the unit is able to maintain uniform distribution of gas/liquid, witnessed by very small radial delta T's.

  * NOTE - HD trays™ and Ultra-Flat-Quench™ internals will have a significant impact on catalyst performance.

Criterion has been supplying catalysts for the SYS residue hydro-conversion system since start-up, with partial fills in Cycle 1 and 2 and full fills from then on. Over time, Criterion has had the opportunity to develop a close relationship with the operator, SYS, and the licensor, Shell Global Solutions . This close working relationship resulted in improved catalyst solutions for each subsequent cycle.

Looking back over the last three cycles, Criterion offered various combinations of catalysts in order to meet the needs of the customer based on the team effort employed to learn from previous cycles. These combinations included RM-430, RN-410, RN-450, RN-650 and RN-412 (see appendix 1 for more details). Based on the work with Shell Global Solutions to improve the catalyst performance in response to different operating requirements, Criterion developed RN-412 that is also used in other resid units globally.

Criterion and its technology partners also studied operational data to target a dedicated effort in R&D. Based on this study and frequent interactions with SYS and Shell Global Solutions, Criterion adjusted product-types and ratios as well as new product development over time to improve unit performance. During the entire process, the governing constraint has always been to make measurable improvements that would not jeopardize product qualities at any point during the cycle.

2 Improvements made over the past three cycles

Looking back over the last three cycles, the combined effort of all parties involved has resulted in a clear improvement in metals removal. This improvement had a positive impact on the operational savings of the RFCCU without creating a debit on the hydrogenation requirements in the resid unit.

As one example of the benefits earned by SYS through this process, the table below shows how reduction of 1 ppmwt V in treated residue would result in a saving of 10% of make up (M/U) RFCCU catalyst when running to a constant V loading on E-Cat.

Table 1 Impact of product vanadium on FCC cat make up rate.

Fresh M/U RFCCU catalyst	10 t/d
V on E-cat	5000 ppmw
Vanadium disposed off with E-cat	50 kg/d
Residue Feed to RFCCU	5000 t/d
Vanadium rate prorated for 1 ppmwt in residue feed to RFCCU	5 kg/d
Saving in Fresh RFCCU-cat	10%

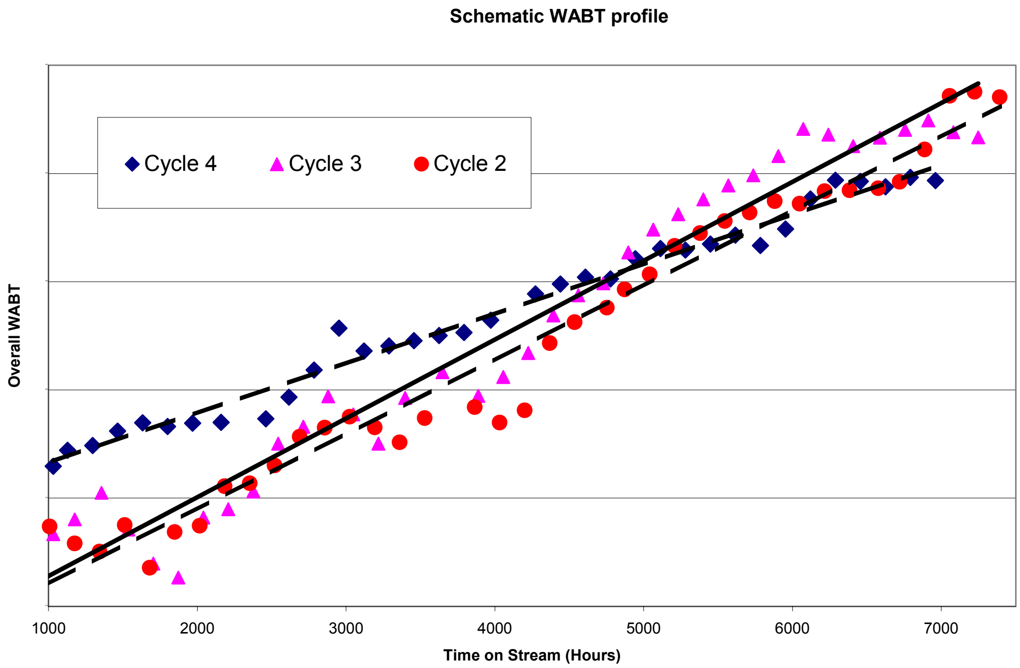
Knowing the benefits of increased HDM, the improvement strategy for the design of subsequent catalyst systems has always focused on maintaining sufficient HDS activity while still increasing HDM activity. The guiding principle has been to avoid any risk of not meeting the HDS target for the unit. As Table 2 shows, a complicating factor throughout the 5 cycles has been that the operational severity has constantly increased in terms of both feed throughput and feedstock heaviness.

Table 2 Severity increase with cycles.

	Feedrate	WABT	Sulfur	Metals (Ni+V)
Cycle 2	Base	Base	Base	base
Cycle 3	base + 1.1%	Base	base + 3.6%	base + 5%
Cycle 4	base + 8.3%	Base + 2°C	base + 6%	base + 3%

Despite these challenges, the combined efforts of all parties involved have resulted in a significant unit performance improvement. Figure 2 (below) shows an overall unit WABT normalized over the past cycles. It clearly indicates that the design of the catalyst system for the most recent cycle has resulted in greater catalyst system stability, despite the higher operational severity. As a result, the reduction in initial HDS activity has been compensated towards end-of-run by a better stability of the total catalyst system.

Figure 2 Overall unit WABT versus runlength



Figures 3 through 6 illustrate the improvements achieved over the past three cycles. For simplicity and clarity, the Figures only display the fits of the actual operational data that have been represented. As shown, metals removal in cycle 3 and 4 has progressively been improved upon versus the base case, Cycle 2. At the same time HDS performance has been consistently better than what was required by SYS.

In addition to the improvements that have been achieved through adjustments in catalyst stacking, SYS adopted operational recommendations by Shell Global Solutions and new catalyst technology from Criterion resulting from the extension of the product portfolio. RN-412 was developed through this process which helped to enhance the portfolio as highlighted during a review of earlier operational feedback received from SYS.

Figure 3 Sulfur levels in treated product, normalized for constant feed rate, versus time on stream

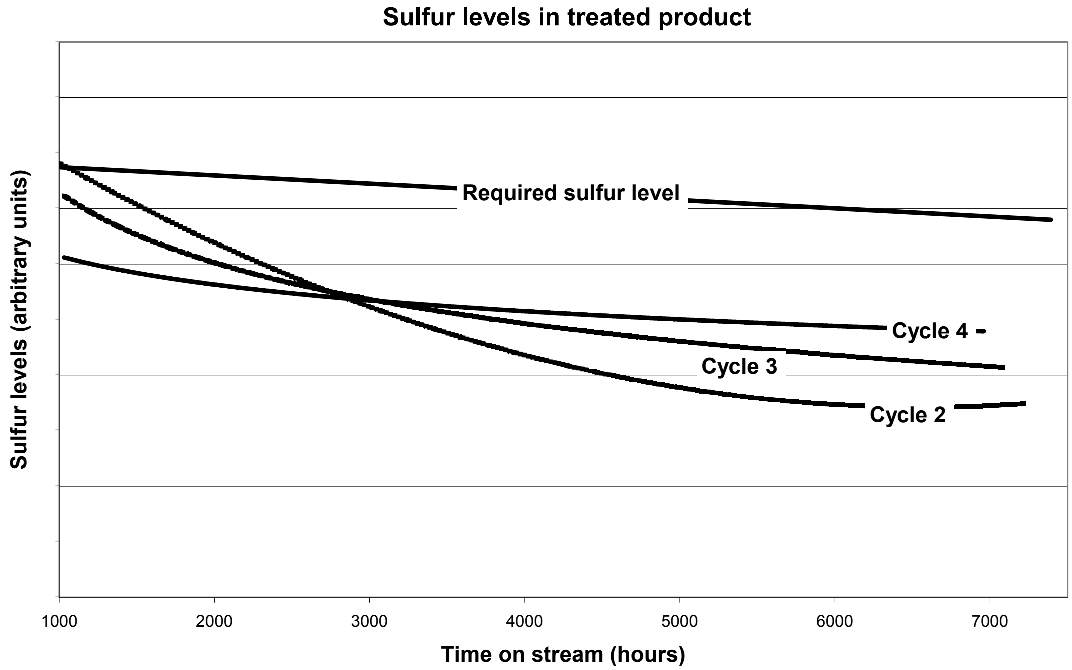
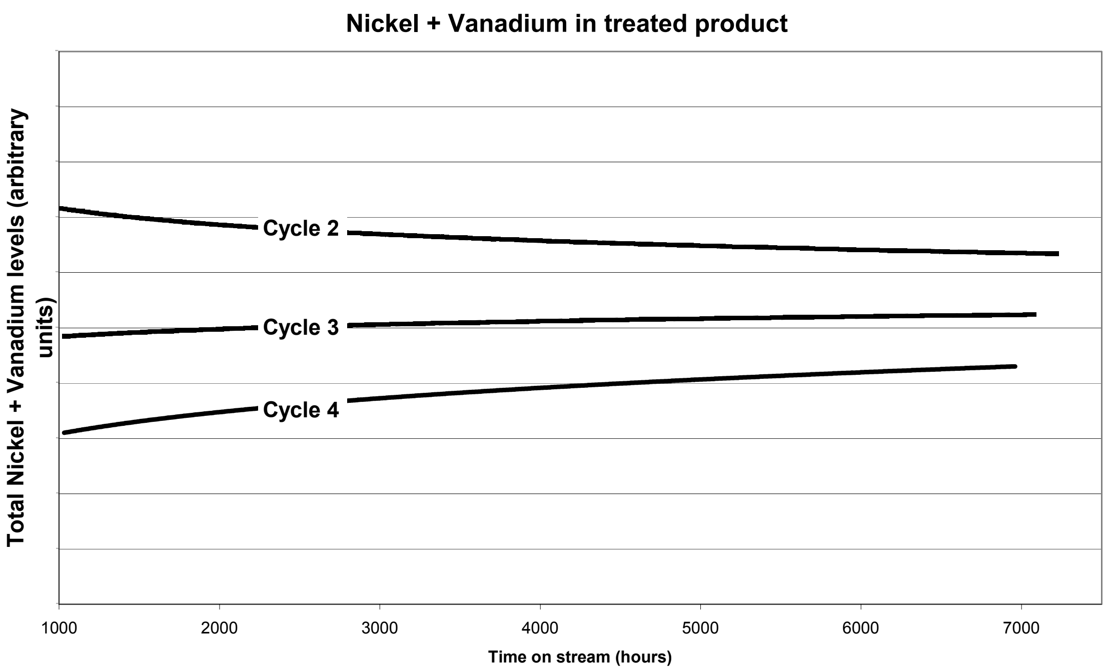
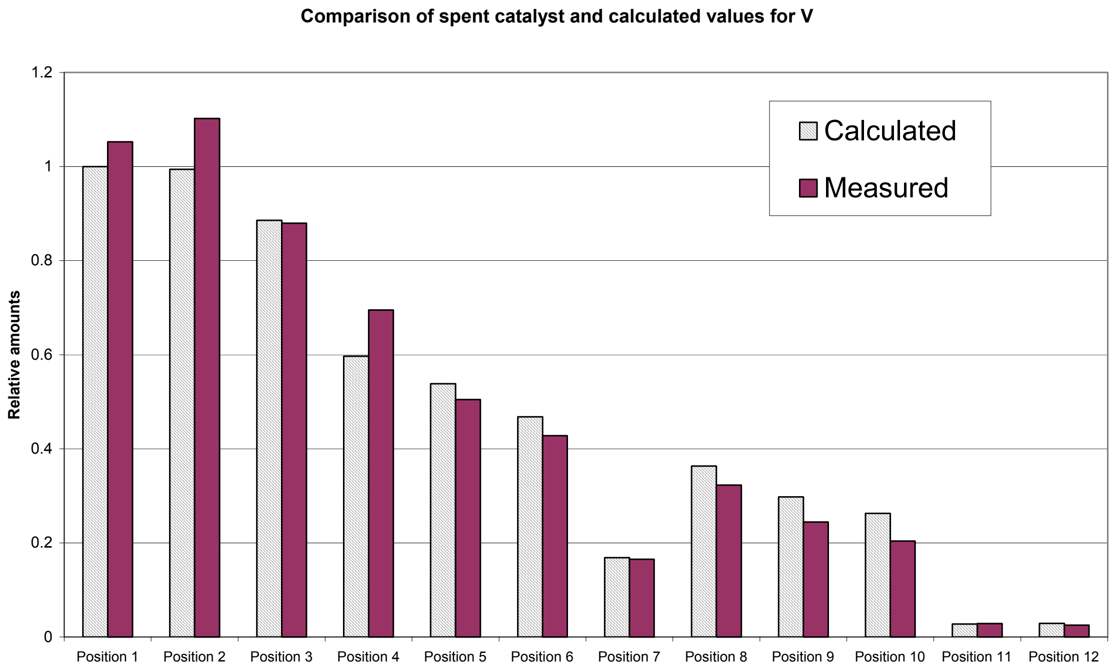


Figure 4 Total metals levels (Ni+V) in product, normalized for feed rate, versus time on stream



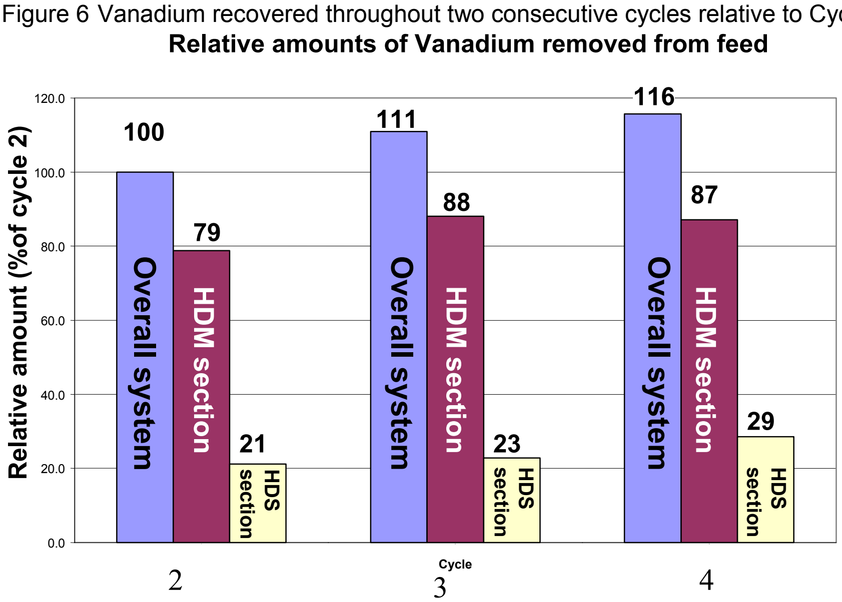
To further quantify the benefits of improved HDM, the team investigated the effect of increased metal deposits on catalysts in subsequent cycles. As figure 5 illustrates, the calculated Vanadium deposited (from feed and product analysis) versus Vanadium actually measured in the spent catalyst samples (from spent catalyst analysis) agree very well. The difference between measured and calculated total Vanadium deposition was less than 1% relative.

Figure 5 Relative comparison of measured and calculated Vanadium deposition versus catalyst position



Knowing this accuracy, the cycles have been further compared based on calculated Vanadium depositions. As clearly shown in figure 6, improvements in Vanadium removal have been significant with a measurable increase of more than 15% relative to cycle 2 over the last two cycles. These improvements have been made in two stages; firstly an improvement in the HDM system and subsequently in the HDS system. Assuming that the FCC E-cat contains about 5000 ppm Vanadium, each 1000 kg of Vanadium recovered could save up to 200 t of FCC make-up catalyst per annum, an obvious benefit.

Figure 6 Vanadium recovered throughout two consecutive cycles relative to Cycle 2. Shown on an overall

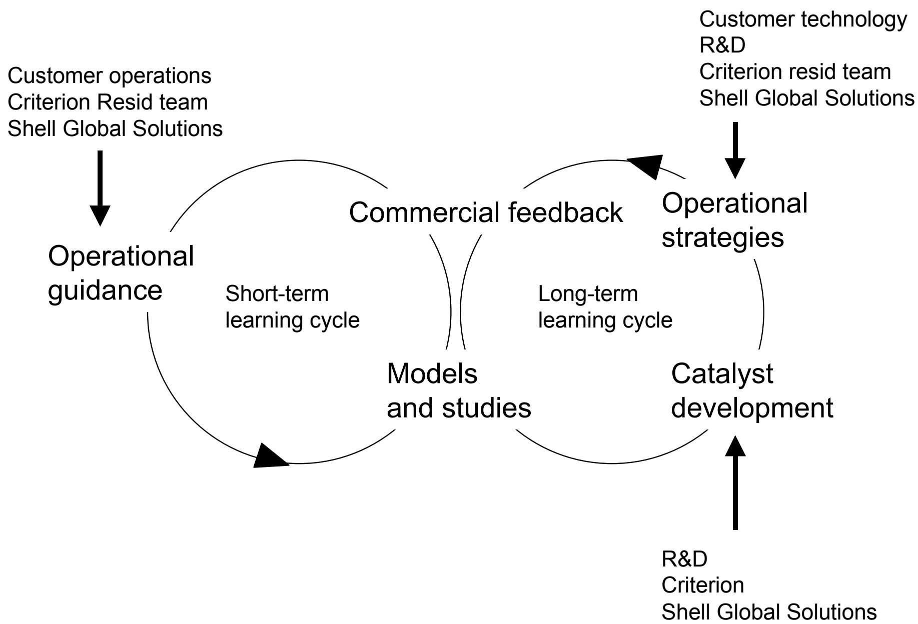


basis and as removal from each section.

3 The improvement process and methodology

Criterion strives to increase value it delivers to its customer and to that extent has created a residue conversion team. This team has played a key role in achieving the observed improvements at SYS. Included in the team are product-application experts from the USA, Europe and the Far East as well as R&D members and representatives from manufacturing. However, as clearly stated in figure 7, progress would have been impossible without involvement of and close co-operation between all parties involved: SYS operations, Shell Global Solutions and Criterion's residue conversion team.

Figure 7 The improvement process



A key factor in the improvement process involves frequent interaction between all parties. Members from the residue team interface with the licensor, evaluate the the performance of the catalyst system in the commercial unit and give operational guidelines designed to optimize the operation as much as possible ("short term improvement loop").

This work is strongly facilitated by a dedicated, proprietary residue hydro-conversion model, developed by Shell Global Solutions. Throughout the improvement process, this model is tuned for the customer's unit on the basis of the validated commercial data that Criterion obtains throughout and after the cycle. Further input is provided when, after the cycle, spent catalysts are analyzed for metals deposition.

Once the commercial data is validated and used to tune the residue conversion model, the guidelines for improvement in the catalyst system and operation can be developed ("long term loop"). This part of the process requires in-depth discussions with SYS and Shell Global Solutions to define the requirements and operational constraints. Subsequently Criterions residue conversion team finds out how to fulfill the targets. In this phase new insights and leads are compared to the customer's situation so that possible improvements could be identified and assessed.

Given the importance of a well-functioning resid unit for a refinery there is no room for negative surprises. This is why improvements, even where breakthrough technologies indicate large potential for improvement, are preferably made in a controlled manner. When a consensus is reached on how to improve on a system, it will be thoroughly tested in a long-term pilot plant test under appropriate conditions and representative feedstock, to demonstrate performance over time. To this extent, Criterion avails of specialized testing facilities to perform this kind of demonstration cost-effectively and reliably.

4 Further improvements

Having observed the improvements over the last few cycles does not imply that the team can rest on its laurels. Further reductions in product metals whilst maintaining all constraints have to be found. This implies a design of new products as well as testing stacking concepts and related operational advice from Shell Global Solutions.

By performing pilot plant tests and studying commercial feedback, the relationships between pore structure and catalyst stack composition on one hand and HDM-, HDS-, HDN-, HDCCR- activity and -stability on the other have been well-established within Criterion. Future product development builds on the knowledge and insights gained. On top of this, the current Criterion development philosophy attempts to relate characteristics of individual products to both new stacking schemes and commercial operations. In this concept, it is important to know that a powerful tool to achieve deeper conversion, be it HDS or HDM, is simply a higher WABT. As an illustration, if a catalyst system is stable enough to allow a10°C higher WABT throughout the entire cycle, this would be equivalent to 40-50% higher catalyst activity. It will also lead to more conversion to diesel and naphtha, which are often very welcome economical spin-offs.

The main challenge, however, is to develop systems that can operate at those higher temperatures without the usual deactivation. Criterion has recently managed to create products that perform remarkably well under higher WABT conditions, thus taking full advantage of kinetic rules.

Keeping the above in mind, Criterion achieves further improvements for SYS and other customers along two separate routes:

(i) Maintain current operation and improve individual catalysts to obtain further incremental improvements in HDM

(ii) Tune catalyst systems and operations to achieve the combined effect of a higher WABT with more active and stable catalysts

Area (i) is taken care of by introduction of a number of new products that are currently being commercialized. These new systems are detailed in separate Criterion literature. Specifically, Criterion's portfolio is currently being enhanced by the introduction of RM-5030 (HDM), RN-5210 (intermediate) and RN-5650 (HDS).The combined effect of these new catalysts and operational changes is expected to generate the highest improvements for SYS and Criterion's resid partners. In line with Criterions' improvement methodology, pilot plant work has recently been conducted to demonstrate the longer-term stability of the improved system. As in previous cycles, the overruling requirement would be HDM-related, but with a clear constraint for HDS. Therefore, long-term Pilot plant tests have been conducted to demonstrate sufficient HDS activity and stability. As shown in figures 8 and 9, keeping HDS activity within the available margins, the improvement in HDM will be clear enough, another 30% less in treated long residue, to show under commercial conditions.

Figure 8 Long-term pilot plant results showing HDS activity retention

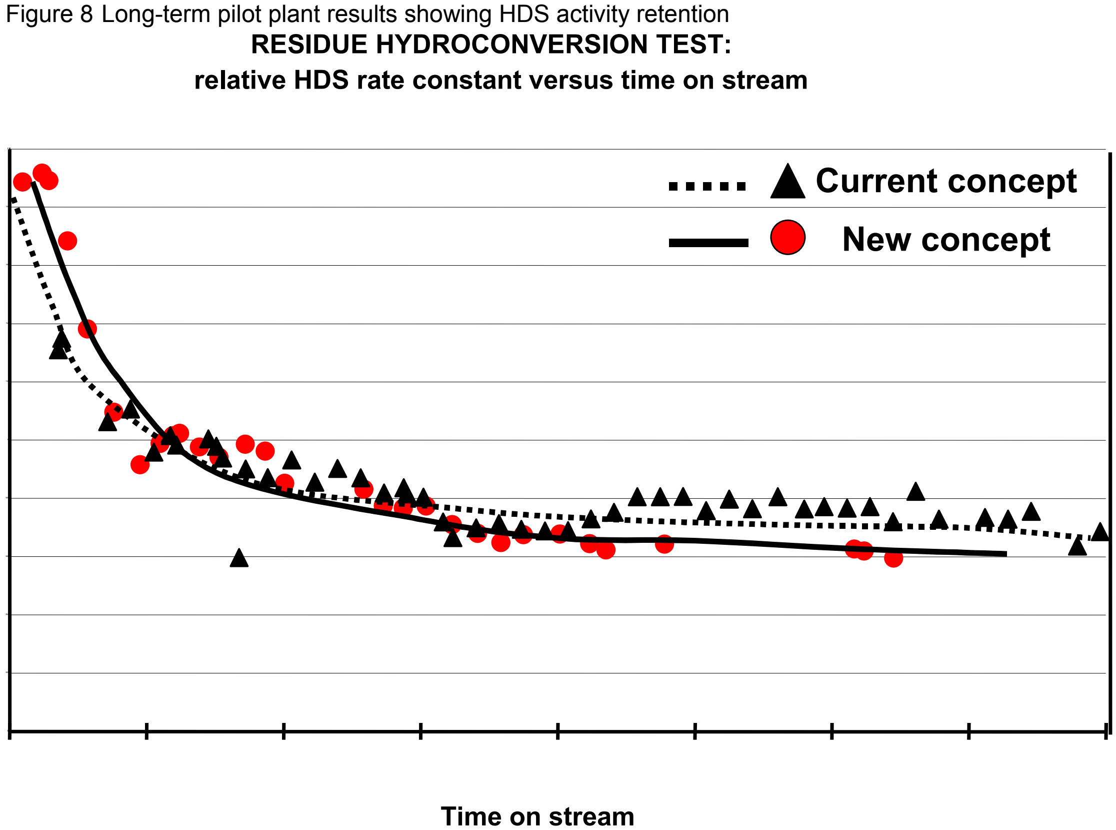
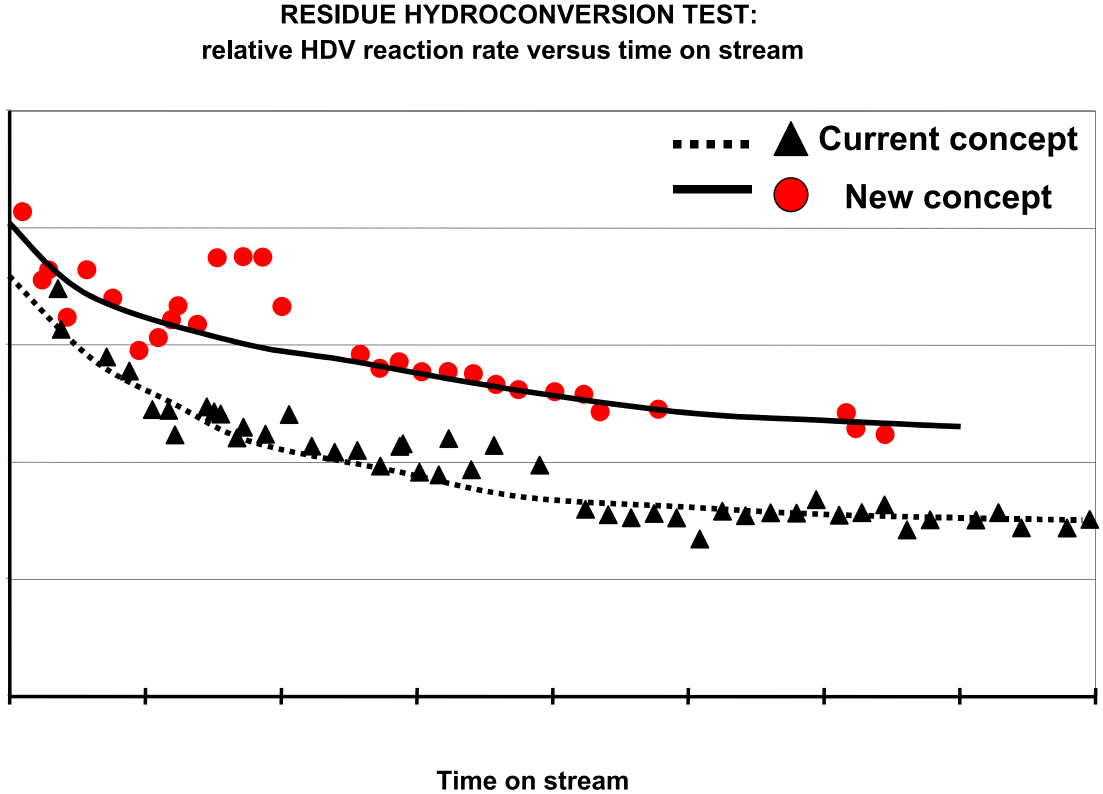


Figure 9 Long-term pilot plant results showing HDM improvements



Appendix 1 Criterions current product portfolio

To accommodate the reality of increasing demands on versatility of the systems, Criterion has been working on a portfolio of residue-conversion products over the last few years. Each member of the product family has its dedicated characteristics with respect to metals tolerance, coke-stability and catalytic hydro-processing activity for HDS, HDM, HD-MCR (-CCR), HDN and conversion. , The result of this is that Criterion has FIX with ERD developed additional product improvement to its product-portfolio. These have been achieved through the introduction of RM-5030, RN-5210 and RN-5650.

Criterion Fixed Bed Resid Catalyst Properties

	HDM	**Transition**		**Tail-end**			**Conv.**
	RM-430	RN-410	RN-412	RN-450	RN-650	RN-5610	RN440
Ni/Mo	Low	Medium	Medium	High	Medium	High	Medium
CBD	Low	Medium	Medium	High	Low-Med	High	Low-Med
Surface Area	Low	Low-Med	Low	Medium	High	High	Very High
Pore Volume	Very High	High	High	Low	High	Medium	Medium
Pore Diameter	V. Wide	Wide	V. Wide	Medium	Medium	Small	Medium
Max Metal Deposition -%wt	Very High	High	High	Medium	Medium	Medium	Medium

Criterion believes that this "tool-box" of catalyst products enables today's modern refiner to meet its requirements for their residue-conversion operations. The challenge lies in the proper stacking of the individual products to balance metals tolerance, coke deactivation and catalytic activity for the various reactions. Criterion has the know-how to design the stacked systems correctly.

Appendix 2 Catalyst system versatility

Criterion is aware of changing needs of refiners. This is why new catalyst systems are normally subjected to a wide range of feeds to reduce the risk of negative surprises in commercial operation. The figure below, based on a recent pilot plant test, illustrates the mentioned variation in residue activity, using HDS as example. Differences reflect variation in crude origin as well as boiling point distribution.