Ebullating Bed Dual Catalyst Systems from ART

Darryl Klein
Global Technology Manager

Balbir Lakhanpal
Segment Director, Ebullating Bed

Joanne Deady
Vice-President, Marketing

Advanced Refining Technologies

Ebullating Bed Resid (EBR) Customer Needs

Refiners today are challenged to convert the bottom of the barrel to meet increasing demands for transportation fuels. Figure 1 shows the rapid growth in gasoline + diesel demand out to 2020, with a significant decline in fuel oil. In addition, there is a strong economic incentive to continue upgrading and converting heavy feeds based on the forecasted crack spreads between diesel and HSFO (Figure 2).

In the EBR hydrocracking process, the principle objective is to maximize conversion of 1000 °F+ (538 °C+) material into lighter and more valuable products like diesel and heavy gas oil. This process also removes sulfur and metals to make products more suitable for further processing and ultimate use in clean fuels. Because of the high temperatures at which the reactions occur (750 °F(399 °C)and higher), thermal cracking is pronounced and the unconverted heavy asphaltenes precipitate out of solution resulting in the formation of sludge - commonly known as organic sediment. The organic sediment causes fouling problems in the downstream circuits, requiring downtime to clean equipment. It also impacts the quality of the low sulfur resid product from the EBR unit.

EBR process profitability could be significantly enhanced with catalyst technology that would allow for maximum conversion while reducing the formation of organic sediment. This would allow for a reduction in downtime and the costs associated with cleaning of the equipment (exchangers, separation vessels, distillation units). Full profitability optimization of an EBR unit also requires consideration of feedstock type and individual unit constraints. To account for all these variables, ART has developed several technology platforms that can be used in dual catalyst systems to help refiners achieve their optimal profitability.

Catalyst Design for Low Sediment

Catalyst design for EBR catalysts leverages the technology strengths of both ART parents. Chevron and Grace each contributed significant residuum upgrading technology, with Chevron's 30+ years of process and catalyst expertise in resid hydrotreating (including ARDS, VRDS, OCR®, and UFR® technology), and Grace's 20 years background with catalysts for the EBR process.

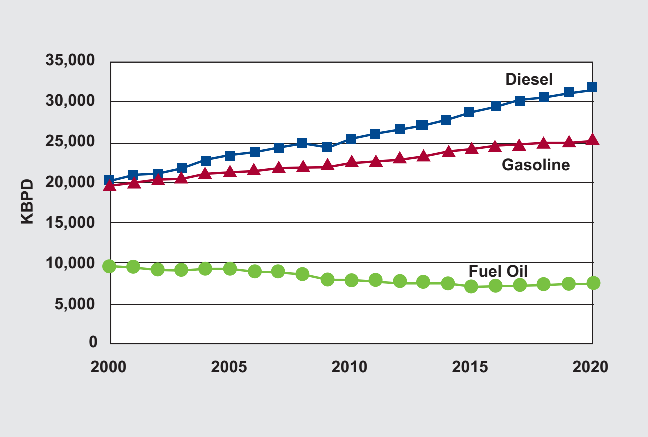

FIGURE 1: Forcasted Global Refined Product Demand

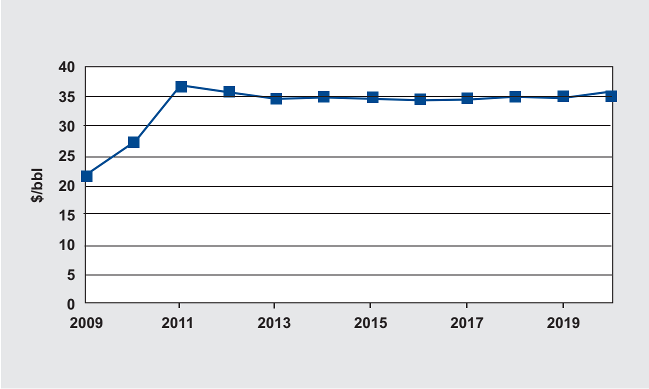

FIGURE 2: Diesel-HSFO Crack Spread (Europe)

The sharing of ideas from each parent provided leads with respect to new catalyst designs, specifically to address high conversion with minimum sediment formation - a problem common to both resid hydrotreating and hydrocracking.

For best performance with respect to sediment formation, it is critical to have the right balance of porosity in the meso- and macropore regions. The intrinsic reaction rate, which is inherently related to the mesopores (i.e., the catalyst surface area), controls the HDS, HDMCR, and resid conversion characteristics of the catalysts. The diffusivity, which is more related to the macropores (greater than 200 Å), controls the demetallation and the sedimentation functions of the catalyst. The optimization of both pore volume and pore size distribution (PSD) is critical to catalyst development as illustrated in Figure 3.[1]

- Pores in the < 200 Å range are most useful for HDS and HDMCR activity
- Pores in the 200 -1000 Å range are effective in allowing diffusion of the majority of the asphaltene molecules into the catalyst
- A select amount of pores >2000 Å is essential to allow the largest asphaltene molecules to readily enter the catalyst to achieve maximum HDM, while cracking the molecules with minimum sediment

The above characteristics are established via the proper combination of chemical composition and preparation technique.

The active metals, both molybdenum and the Group VIII promoters, are also extremely important to get proper catalyst performance. The correct amounts of the two (or more) elements throughout the pellet are necessary for full metal utilization. This requires exact control of the metals distribution and dispersion. Catalytic metals loading must often be tailored for different operating conditions and/or feedstock. Verification of the proper formulation must be done with pilot plant tests under the conditions of the application, and the catalyst cannot necessarily be extrapolated from other applications. The full life cycle of the catalyst must be considered, as the metals pick-up and pore volume reduction changes the performance with time.

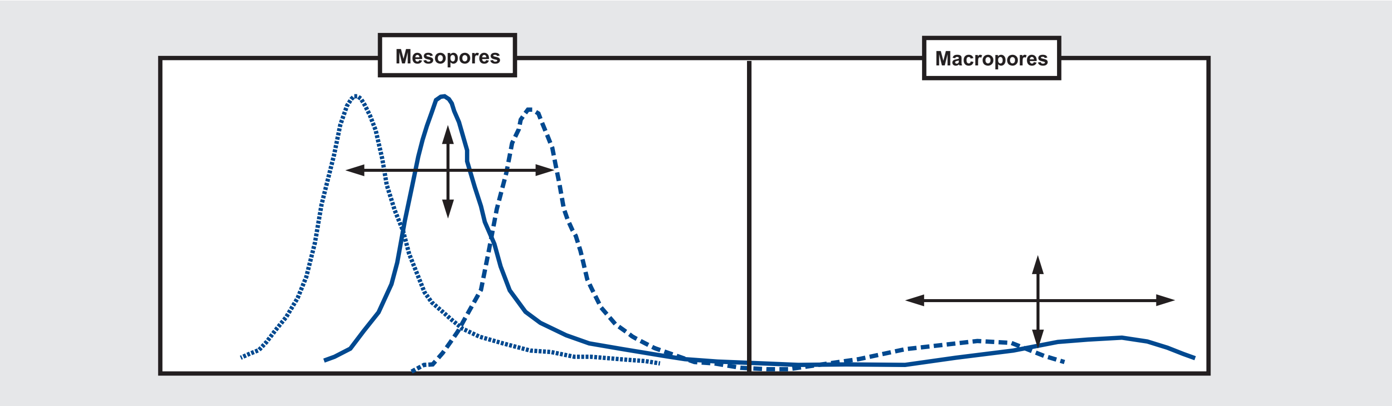

FIGURE 3: Pore Size Optimization in EBR Catalyst Development

EBR Technology Platform	Application
HCRC™	High Catalytic Activity for Resid Conversion and Contaminant Removal
HSLS™	Low Sediment With Improved Stability and Demetallation Function
LS™	Low Sediment Performance on a Variety of Feedstocks

TABLE I: ART's EBR Technology Platforms

The optimum catalyst is designed to allow maximum resid conversion, with emphasis on asphaltenes conversion, and acceptable HDS activity, for the lowest organic sediment formation. The feedstock plays an important role in delivering the key objectives.

ART's Technology Platform Development

ART has developed several technology platforms to achieve different benefits within specific EBR unit constraints. The LS platform, developed in 2002, was the first commercially available EBR catalyst to provide low sediment on paraffinic type of feeds like Ural. Further development work in the area of low sediment technology led to the commercialization of the HSLS platform in 2007. The HSLS platform allows refiners to reach the next step in sediment control with improved stability and demetallation.

The HSLS technology incorporates a novel base structure, along with a unique process technology for efficient metals impregnation. This combination of proprietary alumina, leading to a very specific pore size distribution, and unique metals impregnation process technology allows efficient use of the active metals.[2]

Key performance features of the HSLS technology platform are:

- Lower sediment formation (7-20%), allowing reduced frequency of clean out of downstream equipment, gives higher on-stream factor and lower maintenance costs. In some cases, this has allowed higher resid conversion and/or flexibility of more opportunity crude processing.
- Higher MCR removal – better coker feed quality.
- Improved HDS of the distillate and unconverted resid.
- Significant reduction (5-15%) in fresh catalyst usage with higher HDM, which also means more value for metals recovery on spent catalyst.

In 2012, ART developed the step-out HCRC technology platform. This technology is based on a next generation alumina and base, and brings the flexibility to move to a lower reaction severity (less thermal conversion). This provides the opportunity to significantly

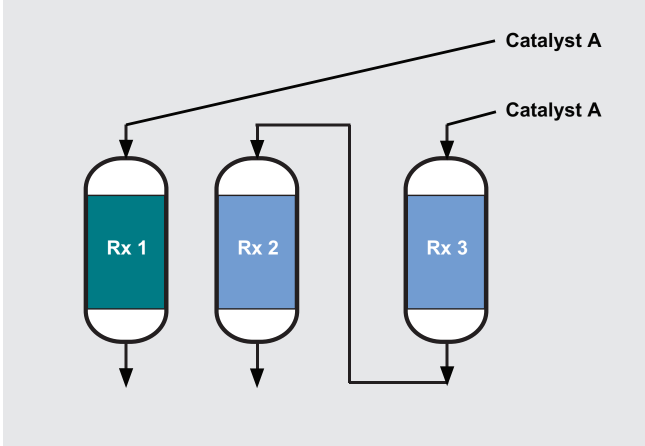

FIGURE 4: Dual Catalyst Systems in EBR Units

reduce sediment/coke formation, and allow higher catalytic conversion in the EBR process.[3]

At constant reaction severity, the HCRC platform yields:

- 4% Higher Resid Conversion
- Preferentially to Distillate and VGO
- 4% Higher HDS
- Lower sulfur in the bottoms and converted products
- 6% higher MCR removal
- 3% Higher HDN
- Lower Nitrogen in distillate and VGO

ART's latest catalyst technology portfolio is summarized in Table I, with the description of its newest technologies.

Dual Catalyst Systems

ART has tested both in their pilot plants and commercially the use of the dual catalyst systems in the EBR units. The use of a dual catalyst system as shown in Figure 4 allows optimizing the catalyst technology in Stage 1 and Stage 2/3 to achieve maximum resid conversion, HDS, HDCCR and HDM with good sediment control and to minimize catalyst costs. Various combinations of the dual catalyst systems shown in Table II, using the above listed catalyst technology platforms, are described in this paper.[4]

HCRC/HSLS Dual Catalyst System

The HCRC/HSLS dual catalyst system was designed to provide high resid conversion activity at identical operating conditions while maintaining good sediment control. This objective can be achieved in a single HCRC catalyst system, but the combination of the HCRC technology platform and the HSLS technology platform gives increased flexibility with respect to choice of feedstock and optimization of catalyst cost. The increased resid conversion, combined with

Technology Platform	Stage 1	Stage 2/3	Status
	HSLS	LS	
Catalyst Function	Good HDM/Good HDS & HDMCR/Excellent Sediment Control	High HDS & HDMCR and Very Good Sediment Control	In Use

Technology Platform	Stage 1	Stage 2/3	Status
	HSLS	HCRC	
Catalyst Function	Good HDM/Good HDS & HDMCR/Excellent Sediment Control	Very High HDS, HDMCR and HDN and Good Sediment Control	In Use

TABLE II: ART's Dual Catalyst Systems in EBR Units

higher contaminant removal, gives higher yields of better quality products, and allows for options to maximize conversion at constant temperature. Refiners may also choose to improve selectivity by maintaining conversion and reducing temperature. Catalyst systems utilizing HCRC also display superior HDS, HDCCR and HDN activity, allowing refiners even more flexibility in operation.

The HCRC/HSLS dual catalyst system was pilot plant tested against the HCRC technology platform, using a Ural feedstock, in ART's mini ebullating bed unit (MEBU) using a standard protocol operating at 0.26 LHSV, 815 °F (435 °C), and 2400 psig. The Ural feedstock properties are shown in Table III.

The HCRC/HSLS dual catalyst system also shows improved HDM activity over the full HCRC catalyst technology with small reductions in HDMCR, HDN and product API, as shown in Table IV.

	Ural VR Feed
Nitrogen, wppm	5888
Sulfur, wt.%	3.1
MCR, wt.%	17.5
Density, API	7.4
Hot C7 Asph., wt.%	5.1
C5 Asph., wt.%	12.4
Fe, wppm	15
Na, wppm	8
Ni, wppm	66
V, wppm	206
Carbon, wt.%	85.3
Hydrogen, wt.%	10.6
H/C Ratio, w/w	0.124
1000 °F, wt.%	89.2

TABLE III: Ural Feedstock Properties

Based on pilot plant work, the HCRC/HSLS dual catalyst system offers the following key opportunities at constant reaction severity:

- Excellent Resid Conversion/Sediment ratio is shown in Figure 5 with flexibility to enhance conversion by controlling reaction severity.
- Offers great flexibility of controlling the HDS, HDN and HDM (Cat Usage) with dual catalysts depending on feedstock and unit objectives
- Yields and product selectivities can be adjusted by individual catalyst optimization, catalyst mix ratio and reaction severity

The HCRC/HSLS dual catalyst system also brings a greater degree of flexibility to the EB refiner to allow a higher or lower reaction severity depending on the feedstock being processed, and also provides higher catalytic conversion and less thermal conversion in the EBR process.

HSLS/LS Dual Catalyst System

The HSLS/LS dual catalyst system was designed to provide excellent resid conversion activity for those units that run paraffinic feeds that are prone to sediment, thereby giving the ability to run at higher severity. This system offers a combination of a relatively high metals tolerance catalyst in the first stage with the relatively higher conver-

	HCRC Catalyst Platform	HCRC/HSLS Catalyst Platform
Resid Conv., wt.%	Base	Base - 1.4
Sediment, wppm	Base	Base - 380
HDS, wt.%	Base	Base - 1.0
HDMCR, wt.%	Base	Base - 1.4
HDN, wt.%	Base	Base - 1.2
HDM, wt.%	Base	Base + 1.7
TLP Density, API	Base	Base - 0.1

TABLE IV: Performance of HCRC/HSLS Dual Catalyst System

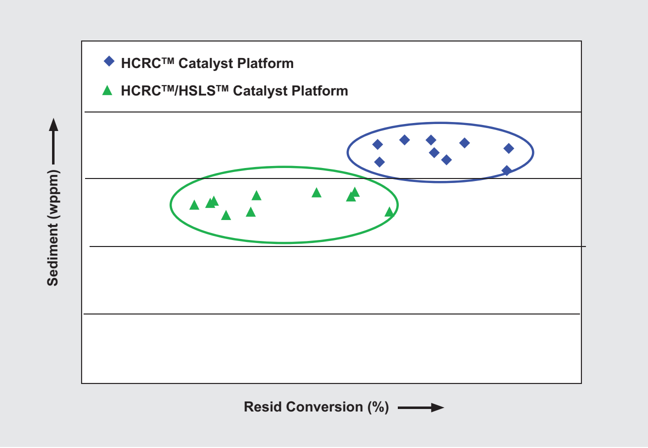

FIGURE 5: Resid Conversion/Sediment Ratio for HCRC/HSLS Dual Catalyst System

sion/low sediment system in the second stage. By allowing maximum metals removal in the first stage, the second stage can be operated at higher severity. By virtue of low metals on the second stage catalyst, this will result in maximizing the reactivity toward the difficult and unconverted feed components coming from the first stage. The catalyst addition rate split to the first and the second/third stages can be optimized, depending upon the feed contaminants levels, and the degree of the conversion reactions required in Stage 2/3. This system has been in commercial use very successfully for several years.

The HSLS/LS dual catalyst system was pilot plant tested in ART's mini ebullating bed unit (MEBU) against the LS technology platform, using the same Ural feedstock as in Table 2, using a standard protocol operating at 0.26 LHSV, 815 °F (435 °C), and 2400 psig.

Figure 6 shows the excellent conversion that the HSLS/LS dual catalyst system has over the base LS system, with a significantly lower sediment.

The HSLS/LS dual catalyst system offers excellent resid conversion improvement, with exceptional sediment control compared to a full LS catalyst platform, with similar activity in HDS, HDCCR, HDN and product API, as shown in Table V.

Summary

All pilot plant data with various feeds shows that ART's Dual Catalyst Systems offer increased 'synergy' in order to exploit the merits of each catalyst. The results of the two catalyst platforms, when used in the Dual System and in the optimum order, are better than the standalone catalysts in most cases. Each of these dual catalyst systems have been used commercially. In all trials, the results have been very positive, and confirm the pilot plant data presented here.

	LS Catalyst Platform	HSLS/LS Catalyst System
Resid Conv., wt.%	Base	Base - 0.7
Sediment, wppm	Base	Base - 1400
HDS, wt.%	Base	Base + 0.5
HDMCR, wt.%	Base	Base + 0.9
HDN, wt.%	Base	Base - 0.4
HDM, wt.%	Base	Base + 0.9
TLP Density, API	Base	Base + 0.2

TABLE V: Performance of HSLS/LS Dual Catalyst System

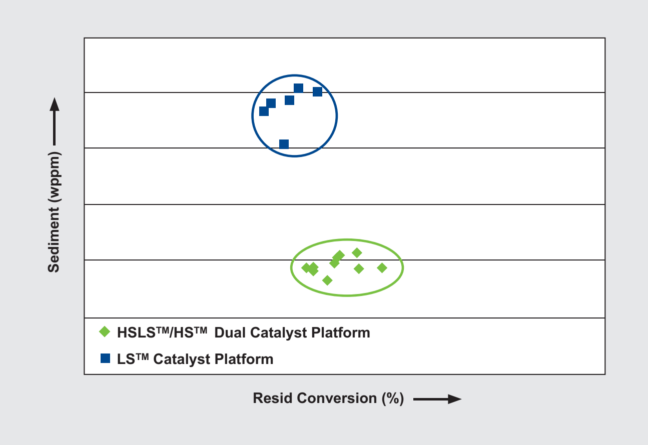

FIGURE 6: Resid Conversion/Sediment Ratio for HSLS/LS Dual Catalyst System

The use of ART's dual system technology offers higher flexibility to the EBR refiner to make changes efficiently to cater to the varying feedstocks being processed or unit objectives, over and above the flexibility of optimizing fresh catalyst usage/costs. Catalyst cost savings of 5% with ART's dual catalyst systems are not uncommon.

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3. Lakhanpal, Klein; ART's newest "High Catalytic Resid Conversion" (HCRC™) Catalyst Technology Platform for EB Resid HC;BBTC, Rome May 2012.
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