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Consider using integrated hydroprocessing methods for processing clean fuels

New catalyst systems fine-tune cracking heavy refractory feeds for FCC and hydrocracking units

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Refining heavy crude oils involves applying new and innovative processing methods and catalyst systems. Demand for heavy products such as fuel oil is diminishing; thus, refiners are challenged to retool their operations to upgrade residue streams into high-value products such as diesel and middle distillates. New processing options are now available which involve application of advanced hydroprocessing catalysts and processes as well as innovative hydrotreating catalysts for distillates, residuum and other heavy, difficult feeds.

The following presents several examples of applying new catalysts and technologies for upgrading very refractory, heavy feeds into high-value products.

Hydrotreating FCC feed. New high-performance catalysts and technologies are aimed at assisting refiners to meet new refining challenges of processing more difficult feedstocks cost-effectively. Several new technologies have been developed for pretreating heavy feeds for the fluid catalytic cracking (FCC) unit.

One new technology is designed to provide significant improvements in hydrodesulfurization (HDS) activity and significantly upgrade FCC feeds. The performance of this technology is driven by using a staged dual-catalyst system consisting of a high-activity nickel-molybdenum (NiMo) catalyst over a high-activity cobalt-molybdenum (CoMo) catalyst. Both catalysts have been specifically designed for hydroprocessing heavy feeds.

There are several important objectives when pretreating FCC feed. Primarily, most feed sulfur (S) is removed, along with metal contaminants such as Ni and vanadium (V) which contaminate cracking catalyst and increase gas-make and coke yield. Additionally, hydrotreating FCC feed removes nitrogen (N) which improves FCC catalyst activity and reduces NO_x emissions in full-burn catalyst regeneration. An additional

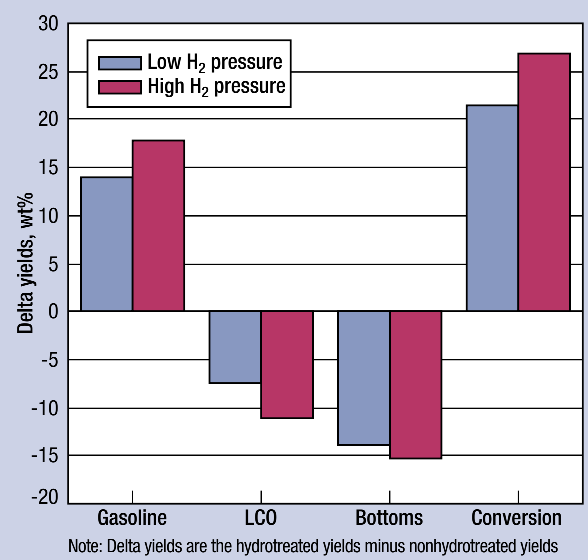

FIG. 1 Benefits of FCC pretreating—hydrotreated feed vs. nonhydrotreated feed.

TABLE 1. FCC feed and product properties

	Base case	LP case	HP case
FCC feed S, wt%	2.28	0.13	0.07
FCC feed N, ppm	1,890	860	320
FCC feed PNA, %	19.6	10.9	5.4
FCC products			
Gasoline octane	83.8	84.1	84.2

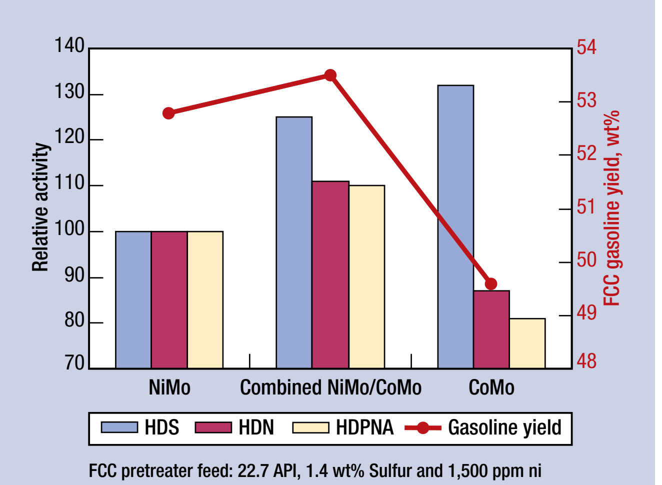

FIG. 2 Activity and gasoline yield using the combined NiMo/CoMo catalyst system to hydrotreat coker gasoil for FCC pretreatment.

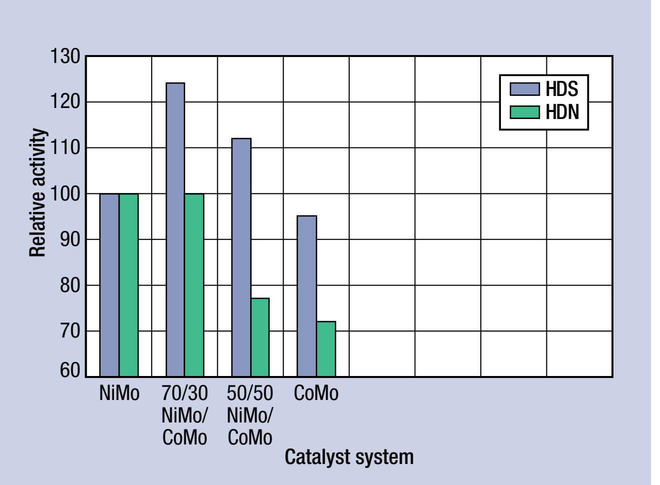

FIG. 3 Activity of using combined NiMo/CoMo catalyst systems to hydrotreat HCGO/VGO blends at high pressure conditions.

benefit is reducing aromatics, especially polyaromatics, and providing higher FCC conversion and gasoline yield.

Fig. 1 summarizes pilot-plant work demonstrating the benefits of FCC pretreating. This figure shows the difference in FCC yields between hydrotreated FCC feeds and nonhydrotreated feeds. The base case is a nonhydrotreated heavy-coker gasoil (HCGO) blend. The work investigated low-pressure (800–900 psia H_2) and high-pressure (1,400–1,500 psia H_2) FCC pretreating. At both pressures, improved FCC performance is readily apparent. For low pressure (LP) hydrotreating, a significant conversion increase is observed, and there is a large increase in FCC-gasoline yield with corresponding decreases in light-cycle oil (LCO) and bottoms yields.

TABLE 2. Typical HCGO/VGO feed properties

API	17–22
S, wt %	2.0–2.5
N, ppm	1,700–2,500
Boiling range, °F	700–1,000

TABLE 3. Typical feed properties for DAO/heavy SR VGO feeds

API	14–16
S, wt %	>2.0
N, ppm	2,200–2,600
Concarbon, wt %	6-8
Ni + V, ppm	>20
Boiling range, °F (ASTM D2887)	700–1,350

TABLE 4. Integrated hydrotreater upgrades bitumen-derived AGO/LVGO blends

Stream	Resid derived LGO	External SR gasoils	HDT blend
Boiling range, °F	250–800	200–900	200–900
N, ppm	1,600–2,000	400–700	>1,000
S, wt%	0.2–0.5	2.0–2.5	1.0–1.5

The high pressure (HP) case shows even higher conversion levels, a greater gasoline yield and much reduced LCO and bottoms yields as compared to the LP case. Table 1 summarizes selected properties of the FCC feeds from this study, along with some FCC product properties. These data clearly demonstrate that hydrotreating FCC feed has a significant positive impact on unit performance in terms of yields and product quality.

An important consideration for optimizing FCC pretreater performance is understanding how the hydrotreating catalyst systems impact the FCC. Fig. 2 is a comparison of three catalyst systems—NiMo, CoMo and combined NiMo/CoMo system—used to hydrotreat a coker-gasoil blend. Fig. 2 shows the relative activity for HDS, hydrodenitrification (HDN) and PNA saturation activity (HDPNA) for the three catalyst systems as well as the FCC gasoline yield from hydrotreated products. The NiMo system has an activity of 100 for HDS, HDN and HDPNA. As expected, the CoMo catalyst provides the highest HDS activity, which is 35% higher than the all-NiMo system. However, the HDN and PNA saturation activities are only 80% of the all-NiMo systems which significantly decreases FCC gasoline yield. Conversely, the combined NiMo/CoMo system has nearly the same HDS activity as the all-CoMo system and has slightly better HDN and PNA saturation activities as the all-NiMo system. The resulting FCC gasoline yield is essentially the same for the combined NiMo/CoMo system as for the NiMo catalyst, confirming that the two systems can provide the same level of FCC feed upgrading.

Combined NiMo/CoMo system for hydrotreating. The versatility of the combined NiMo/CoMo system can also be demonstrated when processing HCGO/vacuum-gas-oil (VGO) blends. Table 2 summarizes typical properties for HCGO/VGO blends. The HCGO/VGO feed blend was tested with each catalyst type separately and then with two different combined NiMo/CoMo systems. The NiMo/CoMo catalyst ratios were varied to determine the effects on HDS and HDN activities. Pressure was also varied to determine the proper ratio for these catalysts for different refining conditions. Figs. 3 and 4 show the results of these studies.

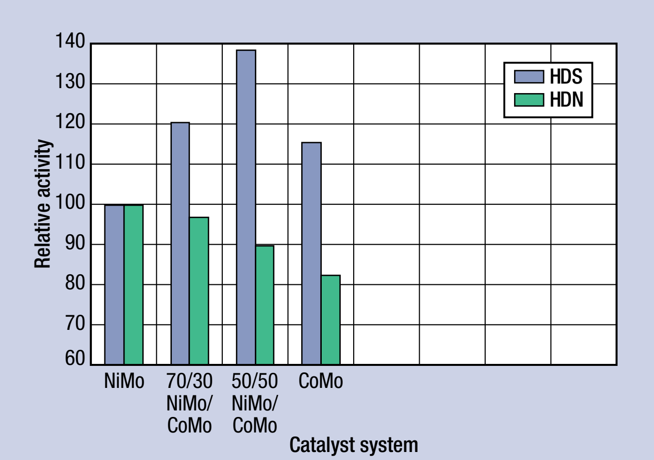

FIG. 4 Activity of using combined NiMo/CoMo catalyst system to hydrotreat HCGO/VGO blends at low pressure system conditions.

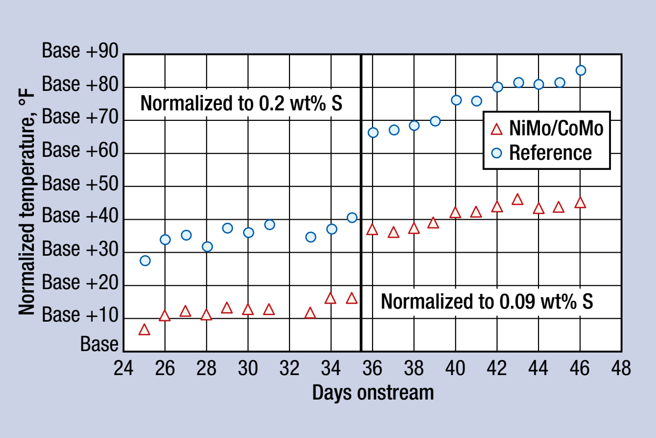

FIG. 5 Hydrodesulfurization activity for of the NiMo/CoMo catalyst system treating a DAO containing feed.

At the higher pressure, the CoMo catalyst gave lower HDN activity than the NiMo catalyst and the combined NiMo/CoMo systems. Also, the data show the same trends for the HDS activity (Fig. 3). At the lower pressure (Fig. 4), the CoMo catalyst provided better HDS activity than the NiMo catalyst, but lower HDS activity relative to the combined NiMo/CoMo catalyst systems. The combined NiMo/CoMo systems also offered improved HDN activity over the CoMo-only catalyst.

Combined NiMo/CoMo system for DAO pretreating. The combined NiMo/CoMo system was successfully applied to processing a refractory deasphalted oil (DAO) feed blend, which has a high concentration of metals and concarbon. Table 3 lists the typical feed properties for DAO and straight-run (SR) VGO blends. Again,testing results compared an industry standard hydrotreating catalyst and the combined NiMo/CoMo system.

Fig. 5 shows the normalized temperature required for HDS activity. The large advantage for the combined NiMo/CoMo system, as compared to the neat NiMo standard catalyst, is shown in Fig. 5. Fig. 6 graphs the normalized temperature required for HDN. The combined NiMo/CoMo system shows activity essentially the same as that of the neat NiMo catalyst.

Example. When a large US refiner wanted to improve its DAO processing, similar testing on available catalyst systems was conducted. The refiner elected to use the combined NiMo/CoMo system. More importantly, the combined NiMo/CoMo system could tolerate more metals and still offer high HDN and HDS activities. **Result:** The combined NiMo/CoMo system could offer higher stability and longer service life, which translates into better performance for the refiner.

Integrated resid hydrotreating process. A major refiner selected hydroprocessing technology to upgrade vacuum residuum derived from Athabasca bitumen into clean products.[1] The upgrader, which is part of the Athabasca Oil Sands Project, uses a unique design. The hydroprocessing unit is integrated with a close-coupled hydrotreater (Fig. 7). The design conversion of the vacuum residuum is nearly 80 wt%.

The integration of the hydrotreater provides many advantages. The close-coupled hydrotreater processes both distillates produced in the hydroprocessing unit and external refinery distillate feeds. The equipment-piece count for the reaction section of the integrated hydrotreater is 50% less than for a standalone unit. The hydroprocessing and hydrotreating reactors share the same HP loop, and the hydrotreater uses excess hydrogen from the hydroprocessing effluent. While some fractionation is common for both sections, the upgrader is very energy efficient due to increased heat integration.

TABLE 5. Integrated hydrotreater performance

- Commercial HDT catalysts
- Two-year cycle length
- Product properties

	Diesel	VGO bottoms
API gravity	34	26
N, ppm	<10	<100
S, ppm	<100	<200
Cetane index	45	–

TABLE 6. Hydrocracking technology and advanced catalyst systems can successfully upgrade Hamaca bitumen feed

Feed	Typical Hamaca HCG/HVG
API gravity	12–14
N, ppm	3,000–3,500
S, wt %	3–4
Polyaromatic indicator, ppm	6,500–7,500
Ni + V, ppm	≥2

TABLE 7. New-generation of catalysts can maximize processing of Hamaca HCG/HVG feeds

Catalyst system	Combined NiMo/CoMo with hydrocracking catalysts
Syncrude product properties	
Diesel	44 Cetane index
VGO	
API gravity	34
N, ppm	0.2
S, ppm	7

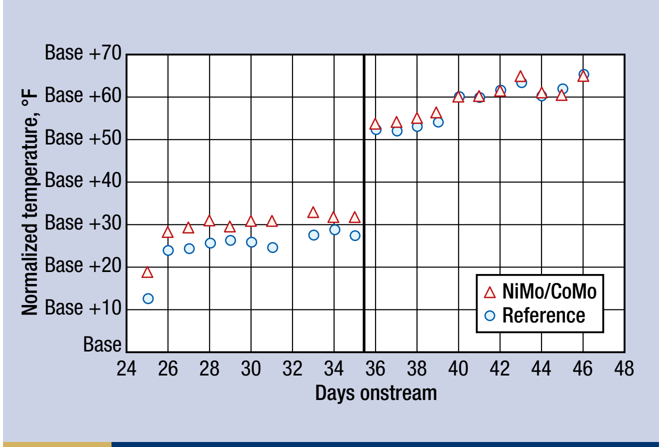

FIG. 6 Hydrodenitrification activity of the NiMo/CoMo catalyst system treating a DAO containing feed.

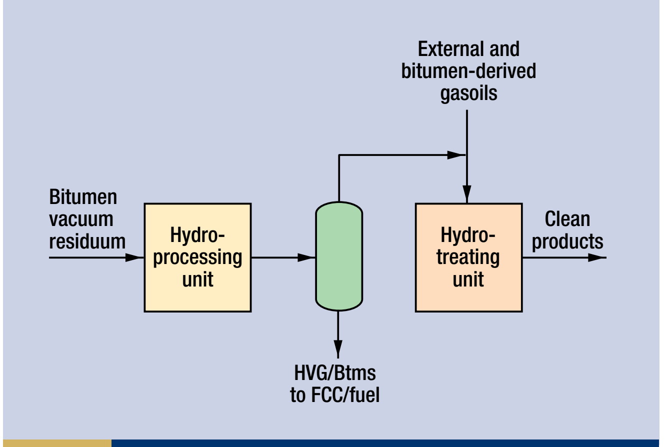

FIG. 7 Integrated hydroprocessing/HDT scheme to upgrade Alberta bitumen.

Table 4 lists the inspections of a typical feed blend for the integrated hydrotreater. The hydrotreating feed has a broad boiling range and contains more than 1,000 ppm N and 1.0–1.5 wt% S. Table 5 indicates that commercial hydrotreating catalysts can achieve a two-year cycle and generate high-quality, saleable fuels or intermediate products. The innovative synergy of the design lowered capital investment and reduced operating costs. The upgrader has been operating at 10% above design since its successful startup in 2003.

TABLE 8. Properties of extract/visbreaker GO/SR VGO feed for two-step, mild hydrocracking process

API gravity	18–20
N, ppm	1,800–2,100
S, wt%	2.4–2.7
Polyaromatic indicator, ppm	2,000–2,500

TABLE 9. MHC generates high-quality products from extract/visbreaker GO/SR VGO blend

MHC yields, LV %	
Naphtha	8–10
Middle distillates	30–40
FCC feed	60–70
Product properties	
Kerosine smoke point, mm	≥20
Diesel	
S, ppm	<10
Cetane index	≥45
FCC feeds	
API gravity	≥32
S, ppm	10–20
N, ppm	1-2

TABLE 10. Typical properties of Mexican HCGO/HVGO/ FCC LCO feed blend

API gravity	13–15
N, ppm	2,500–3,000
S, wt%	3.0–3.5
Polyaromatic indicator, ppm	7,000–8,000

Hydrocracking Hamaca bitumen feed. With the continuing popularity of delayed coking as an inexpensive solution for fuel-oil reduction, refiners are faced with the issue of treating greater amounts of coker gasoils with high levels of N and S. This was particularly evident for a refiner who wanted to upgrade Hamaca bitumen. A pilot-plant study was conducted using a Hamaca HCGO/HVGO blend. Table 6 summarizes the results of this study. While both HCGO and HVGO are high in N (>3,000 ppm) and S (>3 wt%), the HCGO is extremely refractory due to its high concentration of polyaromatics. In fact, the polyaromatic indicator value of approximately 13,000 for the Hamaca HCG places it at the top end of the database for petroleum-derived VGOs without residuum entrainment.

The combined NiMo/CoMo system and new-generation hydrocracking catalysts can provide the capability to upgrade the Hamaca HCGO/HVGO blends as listed in Table 7. The combination NiMo/CoMo with advanced hydrocracking catalysts yields an innovative catalyst system that can generate a single-stage, once-through (SSOT) mode with a 45% conversion level at a reasonable start-of-run temperature. The products are high-value, ultra-low-S (ULS) gasoil streams.

Mild hydrocracking options. In the last decade, mild hydrocracking units (MHCs) have become the preferred option to improve FCC feed quality and to debottleneck refineries. Mild hydrocracking converts excess VGO. Many units operate at low pressures, thereby limiting product upgrade and catalyst cycle length. As mentioned earlier, with most fuel-oil-reduction processes, refiners also must treat incremental gasoils with high N and S contents. By using a new two-step, mild-hydrocracking process scheme, refiners can upgrade middle distillates while retaining the capital incentives of lower-pressure mild hydrocracking conditions.[2] Additional external distillates in the refinery can also be upgraded at the same time.

Fig. 8 shows the process flow diagram for the two-step, mild hydrocracking scheme. This processing option involves flashing reactor effluent from the MHC unit in a hot HP separator (HHPS). Vapor from the hot separator is cooled to hydrotreating conditions by adding cold, external distillate feeds such as FCC LCOs and atmospheric gasoils (AGOs), which also require treatment to produce ULS diesel. The

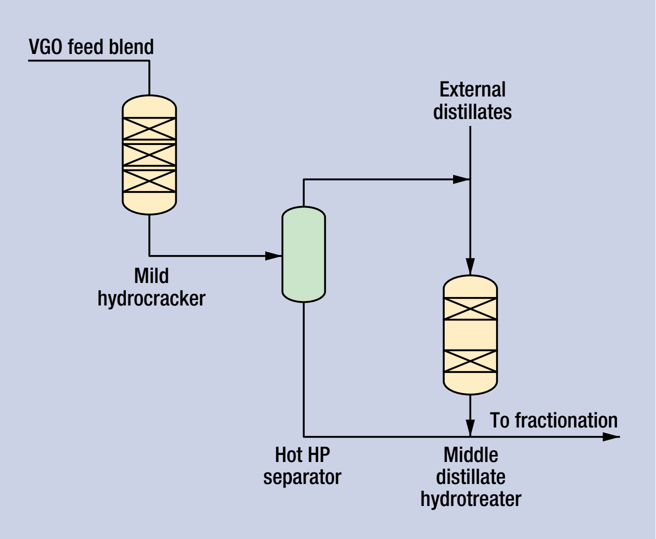

FIG. 8 The two-step mild hydrocracking process and middle-distillate hydrotreating process.

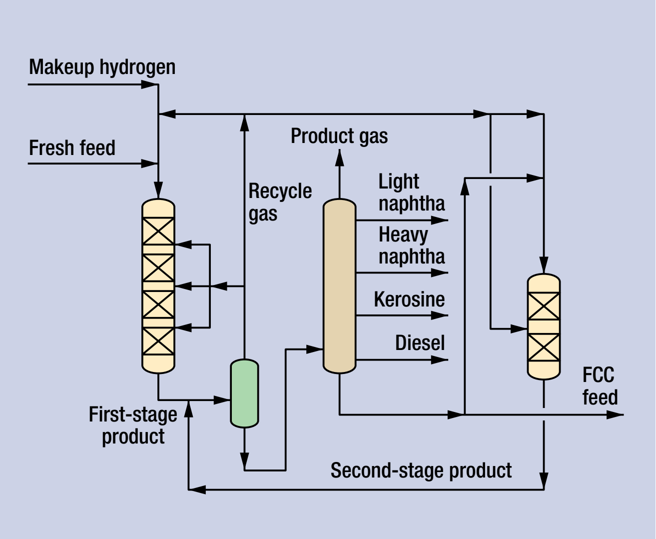

FIG. 9 Optimized partial-conversion hydrocracking process for heavy feeds—HCGO/HVGO/FCC LCO blends.

combined feed stream is pumped to the middle-distillate hydrotreater where final desulfurization and aromatic saturation occur. This two-step, mild hydrocracking scheme can provide several processing advantages:

The process can upgrade a wide range of feedstocks

- Split-feed configuration permits treating each feed stream over the most effective catalyst system.
- Hydrogen consumption is minimized because unconverted oil is removed from the reaction system immediately after the mild hydrocracking-conversion step.
- There is independent control of each reaction sequence.
- Optimal conversion and high selectivity are achieved with the minimum pieces of equipment.

Examples of this two-step, mild hydrocracking scheme and mild hydrocracking process can be found in Tables 8 and 9. A refiner with lube-extraction facilities and a visbreaker operation wanted to upgrade VGO intermediates and a combination of high-S AGOs and LCO in a commercial two-step, mild hydrocracking system. The mild HCR unit will process a VGO blend containing approximately 2,000 ppm N and approximately 2.5 S wt% at approximately 35% conversion. The resulting MHC VGO will be an excellent feedstock for an FCC unit, and the product distillates will be ultra-low in S and have excellent burning properties.

Optimized partial conversion hydrocracking. Many existing refineries with SSOT hydrocrackers are looking for revamp options to meet more stringent fuels specifications, to increase feed flexibility or to increase throughput. Conventional wisdom suggests adding catalyst volume in series or adding a product-saturation reactor if improved product quality is desired.

An innovative solution is less expensive and more flexible than either of the above options.[3] A small reactor is added upstream of the existing reactor, converting the SSOT unit into a partial-recycle or two-stage recycle (TSREC) configuration. Because the added reactor operates in a "clean" second-stage environment, less than one-half of additional catalyst volume is needed as compared to conventional solutions (Fig. 9). This new approach was proven at a US refinery. Feed for this hydrocracker (Table 10) is a blend of HCGO, SR VGO and FCC LCO derived from Mexican crude. The HCGO is very difficult to hydrocrack due to its high N and polyaromatic contents. Compared to a conventional design, the required catalyst volume, hydrogen consumption and product qualities all benefited from the new TSREC design. Additional capital was also saved by integrating the first and second stages into the same recycle-gas loop. This approach takes advantage of first-stage processing conditions to produce excellent FCC feed with minimum hydrogen addition. The partial-conversion hydrocracking process also utilizes the "clean" second stage

TABLE 11. Typical partial-conversion, two-stage hydrocracking yields from Mexican HCGO/SR VGO blend

Naphtha, LV%	25–35
Middle distillates, LV%	40–45
Bottoms, LV%	30–40

TABLE 12. Typical product qualities in partial-conversion mild hydrocracking of Mexican HCGO/SR VGO blend

Reformer naphtha	
N + 2A, LV%	70–80
Bottoms	
N, ppm	5–20
S, ppm	50–100

TABLE 13. Properties of Venezuelan HCGO blend for two-stage hydrocracking operation

API gravity	15–18
N, ppm	3,400–3,800
S, wt%	3.0–3.5
Polyaromatic indicator, ppm	5,000–6,000

Continued

very effectively, with low-reactor temperatures and higher space velocities generating high-quality fuels.

Tables 11 and 12 show typical yields and product properties obtained with partial-conversion hydrocracking. The yield structure is directed at maximizing gasoline production in the refinery, and the distillate products are ULS and highly valued. To gain aromatic saturation of the kerosine and to produce more naphtha during gasoline season, a kerosine recycle feature can also be implemented.[3,4]

Two-stage hydrocracking for Venezuelan HCGO. A study was conducted for a Venezuelan refiner to produce middle distillates from a coker gasoil blend. With a variety of coking facilities, the refiner wanted the maximum upgrade of a neat HCGO blend to premium-quality middle distillates. The feedstock was composed of three different HCGO components as shown in Table 13, including as a blend of which contained greatest N levels and a high concentration of polyaromatics. A two-stage, recycle hydrocracking configuration, using a base-metal-zeolite catalyst in the first stage and a noble-metal-zeolite catalyst in the second stage, was developed.

The catalyst system provided high yields of excellent-quality middle distillates from the refractory feed (Table 14). The total distillate yield of approximately 85 LV% is split between kerosine and diesel. The burning characteristics of the distillates are excellent (25-mm smoke-point kerosine and 52 cetane-index diesel), while the bottoms is a premium FCC feedstock.

Improved reactor internals. To take advantage of the rapid development in processing schemes and high-activity catalyst systems, a new class of reactor internals for fixed-bed hydroprocessing reactors are being developed. These new internals are applicable to both new reactor designs and reactor retrofits.

The new internals allow new and retrofitted reactors to successfully apply high-activity catalysts with a low risk of reactor temperature maldistribution and hot spots often associated with high-activity catalysts. The internals provide nearly complete mixing and equilibration of reactants between catalyst beds, correcting any temperature and concentration maldistributions, with LP drop while using minimal reactor volume.

One of the key components of the new internals is a collector tray with a large, centrally located bubble cap. Special baffles surround the bubble cap. Cold-quench gas is introduced above the collection tray and is thoroughly mixed with the hot gas and liquid mixture entering the inter-bed zone from the bed above. All streams flow through the baffles in a way that induces swirling and mixing of the cold and hot gases and liquid. The well-mixed gas and liquid enters the centrally located bubble cap. There are also baffles inside and outside the riser to further aid in mixing. A special weir around the bubble cap is used to break up and dissipate the angular momentum of the swirling liquid.

The second key component of the new design is the mixing-flow nozzles. These high-efficiency spray nozzles provide a uniform distribution of gas and liquid to the catalyst bed over a wide range of gas and liquid feedrates. In addition to providing even distribution of feed to a catalyst bed, they provide good gas-liquid mixing and heat exchange. The even-flow distribution across the flow nozzles is also much more tolerant to distributor tray out-of-levelness.

An added benefit of the design is that mixing and redistribution are achieved with virtually no increase in pressure drop and in less reactor-shell length. Since the flow nozzles provide a sustained spray of the gas-liquid mixture, catalyst efficiency and utilization will also be higher.

The new reactor internals have been demonstrated in various hydrocracking and hydrotreating units. Elements can be retrofitted in existing reactors, even for fixed-bed residuum applications. In hydrocracking applications, significant improvements in yields and catalyst average temperatures have been observed. **HP**

TABLE 14. Product properties from hydrocracking Venezuelan HCGO blend

Kerosine	
Smoke point, mm	25
Freeze point, °C	– 67
Diesel	
Cetane index	52
Cloud point, °C	–19

ACKNOWLEDGMENT

Revised and upgraded from an earlier presentation from the 2007 NPRA Annual Meeting, March 18–20, 2007, San Antonio, Texas.

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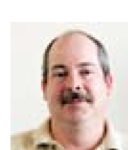

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