Annual Meeting
March 18-20, 2007
Marriott Rivercenter Hotel
San Antonio, TX

AM-07-62

SOLVING CLEAN FUELS PRODUCTION AND RESIDUUM CONVERSION THROUGH HYDROPROCESSING INTEGRATION

Presented By:

Ujjal Mukherjee
Technology Director
Chevron Lummus Global
Bloomfield, IL

Mohammad Habib
Consulting Scientist
Chevron Lummus Global
Richmond, CA

Art Dahlberg
Research and
Development Manager
Chevron Lummus Global
Richamond, CA

Charles Olsen
Technical Services Manager
Advanced Refining
Technologies
Chicago, IL

National Petrochemical & Refiners Association

1899 L Street, NW
Suite 1000
Washington, DC
20036.3896

202.457.0480 voice
202.457.0486 fax
www.npra.org

NPRA

National Petrochemical & Refiners Association

1899 L Stree
Suite 1000
Washington
20036.3896

SOLVING CLEAN FUELS PRODUCTION AND RESIDUUM CONVERSION THROUGH HYDROPROCESSING INTEGRATION

By
M. Habib, A. J. Dahlberg, U. Mukherjee, Chevron Lummus Global
and
C. W. Olsen, Advanced Refining Technologies

Introduction

Chevron has long been active in the research, development, and commercialization of hydroprocessing catalysts and processes. More recently, Chevron formed two joint partnerships to improve, accelerate, and expand on the applications of these catalysts and processes. Chevron formed a partnership with ABB Lummus (**Chevron Lummus Global** or **CLG**), which has been developing and commercializing new innovations in **ISOCRACKING®** and **ISODEWAXING®** catalysts, along with engineering and licensing all of the different hydroprocessing configurations.

In the area of hydrotreating catalysts for distillates, residuum, and other heavy, difficult feeds, Chevron formed a partnership with Grace Davison (**Advanced Refining Technologies** or **ART**) that handles the research, development, and commercialization of these catalysts.

This paper will discuss the synergy between these technologies and how advanced knowledge and innovative design coupled with experience can be applied to upgrade very refractory, heavy feeds into high-value products. The topics begin with hydrotreating heavy feeds and then shift to more difficult feeds and more complex designs, many of which have been very successful in commercial operation. Most of the catalysts which are discussed come from a new generation that applies the latest improvements in raw materials, characterization, design, and pilot plant testing.

Experimental Systems

When pilot plant data are cited in this paper, they have been generated in state-of-the-art facilities whose results have been shown to correctly predict performance in commercial-scale units. These pilot plants can operate with recycle gas in Single Stage Once-Through mode (**SSOT**) or with gas-and-liquid recycle in Single Stage Recycle (**SSREC**) and Two Stage Recycle (**TSREC**) modes. All the pilot plants are computerized to allow continuous, automatic operation and data collection. Products are fractionated on-line or in separate fractionation systems to obtain selectivity and properties.

ApART Hydrotreating System for FCC Pretreat

Since their inception, CLG and ART have concentrated on developing high-performance catalysts and technologies aimed at helping refiners meet the new challenges of processing increasingly more difficult feeds at very economical costs. This led to the introduction of several new technologies, one of which is the ApART system for pretreating of heavy feeds.

The ApART technology is designed to provide significant improvements in HDS activity and provide significant upgrading of FCC feeds. This technology has enjoyed great success since its introduction just a few years ago with over 18 commercial applications. The performance of the technology is driven by using a staged catalyst system of an improved NiMo catalyst (ICR 175) over a CoMo catalyst (ICR 176), both of which have been specifically designed for heavy feeds hydroprocessing. The technology is one of the results of ART's continuing emphasis on developing a detailed understanding of the reactions and kinetics involved in FCC pretreating and leveraging its relationship with Grace Davison Refining Technologies to develop a better understanding of the impacts of hydrotreating on FCC performance.

One of the primary objectives of FCC pretreating is the removal of sulfur from the FCC feed resulting in lower sulfur FCC products (i.e., gasoline) and lower SO_X emissions. An added benefit is pretreating removes metal contaminants (such as nickel and vanadium) which otherwise poison the cracking catalyst resulting in an increase in gas make and coke yield. Perhaps the most noteworthy influence of hydrotreating FCC feed, however, comes from the fact that nitrogen and aromatics (polynuclear aromatics or PNA's) are removed from the FCC feed. This results in significant increases in FCC conversion and gasoline yield.

Figure 1 summarizes pilot plant work demonstrating the benefits of FCC pretreating discussed above. The chart shows the difference in FCC yields between hydrotreated FCC feeds and non-hydrotreated feed. The work investigated low pressure (800-900 psia H_2) and high pressure (1400-1500 psia H_2) FCC pretreating. At both pressures, the improvements in FCC performance are readily apparent. For low pressure hydrotreating, a significant increase in conversion is observed, and there is a large increase in FCC gasoline yield with corresponding decreases in LCO and bottoms yields. The high pressure case shows even higher conversion, a larger increase in gasoline yield, and a bigger decrease in LCO and bottoms yields compared to the low pressure case.

Figure 1 - Benefits of FCC Pretreating

Note: Delta yields are the hydrotreated yields minus the non hydrotreated yields

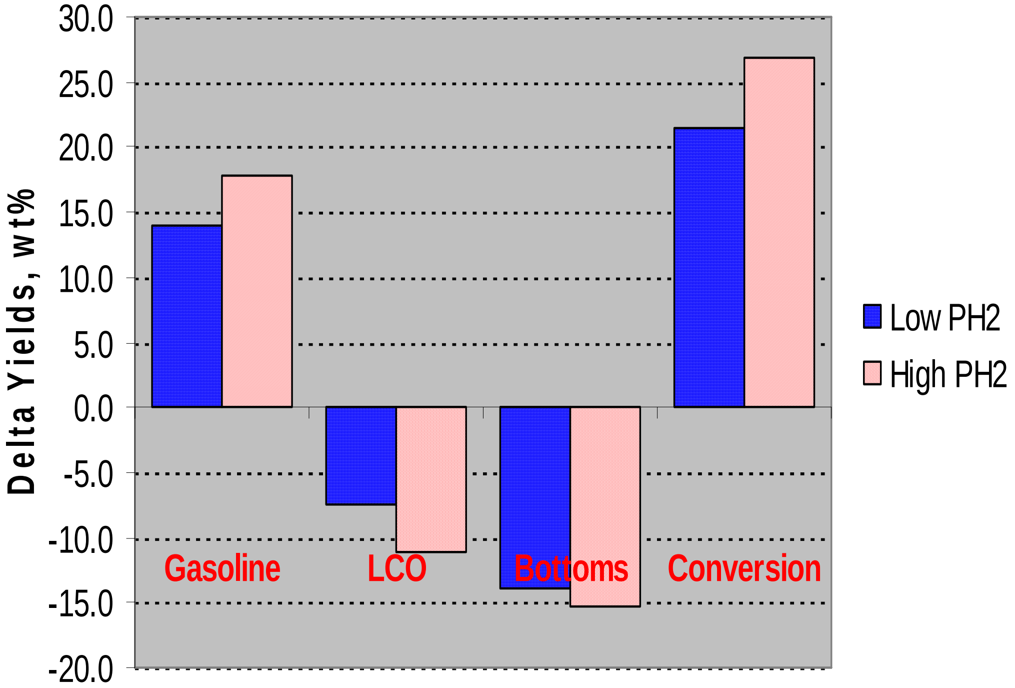


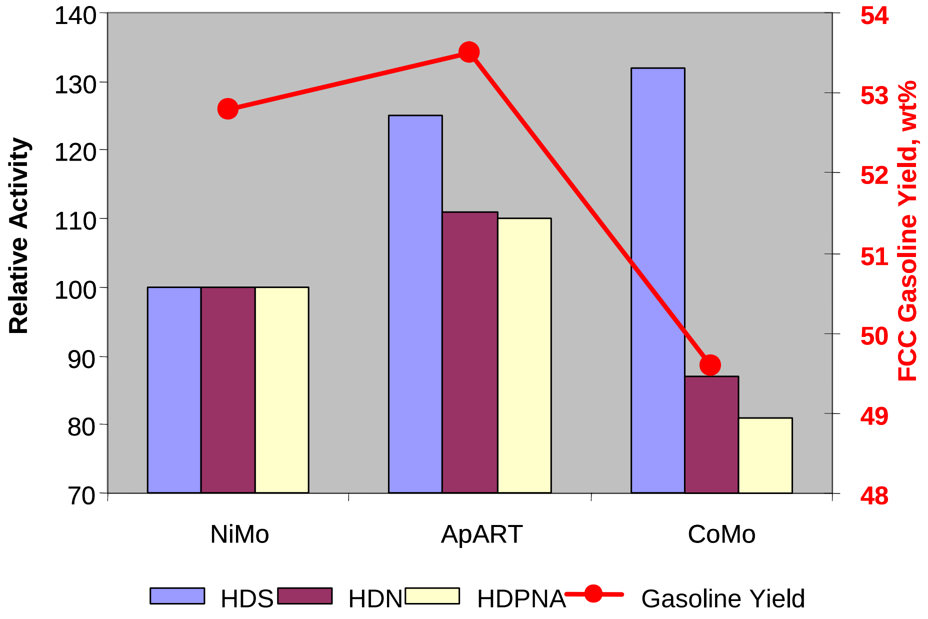
Table 1 summarizes selected properties of the FCC feeds from this study, along with some properties of the FCC products. Hydrotreating FCC feed not only increases gasoline yield, but also preserves gasoline octane while at the same time making it less olefinic. These data clearly demonstrate that hydrotreating the FCC feed has a significant positive impact on FCC performance in terms of both yields and product quality.

Table 1 - FCC Feed and Product Properties

	Base Case	Low Pressure	High Pressure
FCC Feed Sulfur, Wt %	2.28	0.13	0.07
FCC Feed Nitrogen, ppm	1890	860	320
FCC Feed PNA, %	19.6	10.9	5.4
FCC Products			
Gasoline Octane	83.8	84.1	84.2

One of the most important considerations for getting the most out of the FCC pretreater is a thorough understanding of how the hydrotreating catalyst system impacts the FCC. Figure 2 is a comparison of three catalyst systems, ICR 175 (NiMo), ICR 176 (CoMo), and an ApART system, in the hydrotreating of a coker gas oil blend. It shows the relative activity for HDS, HDN, and HDPNA for the three systems as well as the FCC gasoline yield resulting from an ACE study on the hydrotreated products. ICR 175 has an activity of 100 for HDS, HDN, and HDPNA on this chart. As expected, the CoMo catalyst, ICR 176, provides the highest HDS activity which is 35% higher than the all NiMo system. The HDN and PNA saturation activities, however, are only 80% of the all NiMo system, which results in a significant decrease in FCC gasoline yield. The ApART system, on the other hand, has nearly the same HDS activity as the all CoMo system and has slightly better HDN and PNA saturation activity than the all NiMo ICR 175 system. The resulting FCC gasoline yield is essentially the same for the ApART system as for ICR 175, confirming that the two systems give the same level of FCC feed upgrading.

Figure 2 - ApART Hydrotreating of Coker Gas Oil in FCC Pretreat Application



ApART for Heavy Coker Gas Oil Blend HDT

The versatility of the ApART system can also be demonstrated when processing a HCGO/VGO blend, typical properties of which are shown in Table 2.

Table 2 - Typical HCGO/VGO Feed Properties

API	17-22
Sulfur, Wt %	2.0-2.5
Nitrogen, ppm	1700-2500
Boiling Range, °F	700-1000

This feed blend was hydrotreated at several pressures using each catalyst type separately along with two ApART systems. The NiMo/CoMo catalyst ratio in the systems was varied to demonstrate the effects on HDS and HDN activity. Some of the results are summarized in Figures 3 and 4.

Figure 3 - ApART Hydrotreating of HCGO/VGO Blend at High Pressure

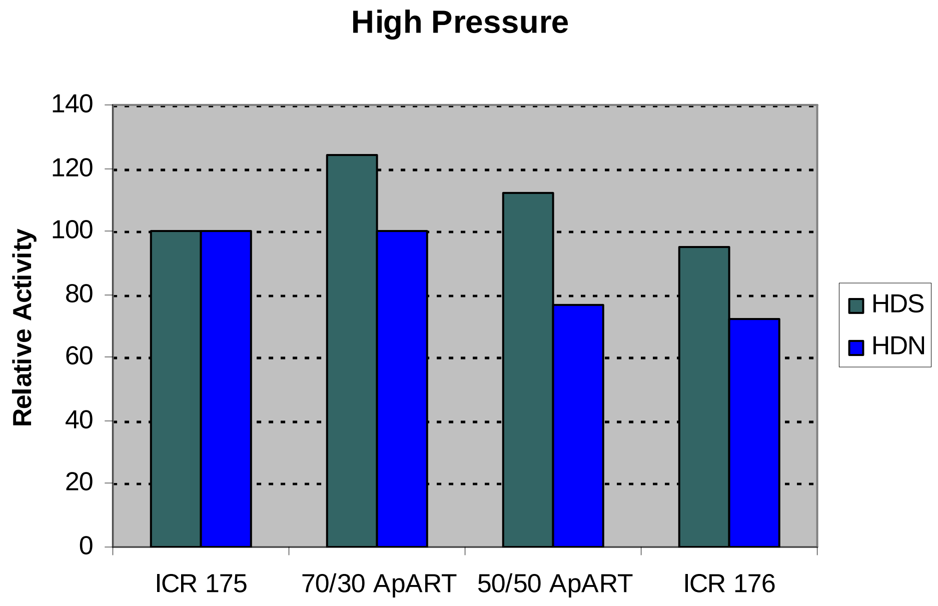
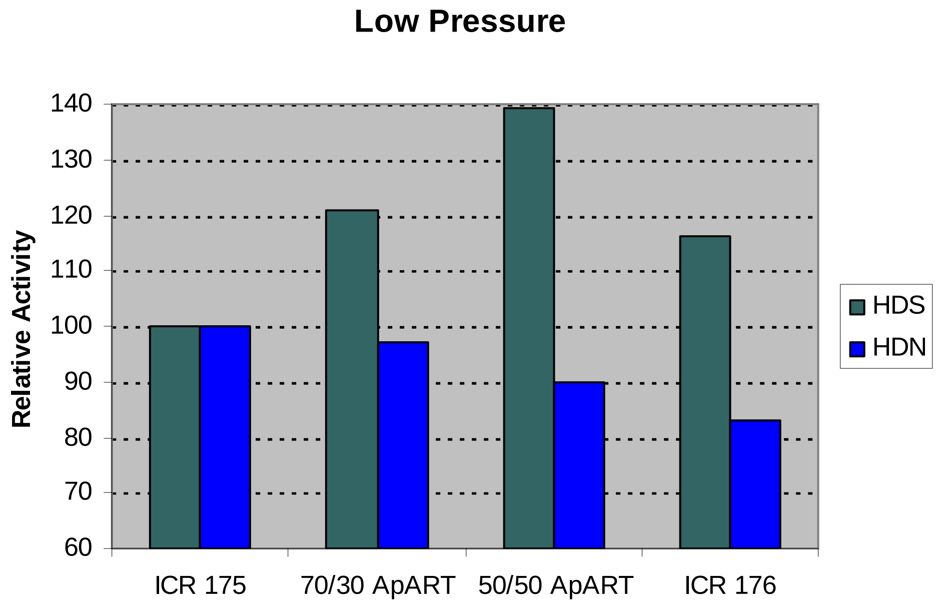


Figure 4 - ApART Hydrotreating of HCGO/VGO Blend at Low Pressure



At higher pressure (Figure 3), the 70/30 ApART system shows the highest HDS activity while also providing the same HDN activity as the neat NiMo system.

At lower pressure (Figure 4), the CoMo catalyst performs better than the NiMo catalyst for HDS as expected, but it is not as good as the ApART systems. The ApART systems also provide better HDN performance compared to the CoMo, and approach that of the neat NiMo catalyst.

ApART for DAO Feed Pretreating

The ApART system was successfully applied to processing a refractory DAO feed blend, which has relatively high concentration of metals and concarbon. Typical feed properties are shown in Table 3. In this test, the appropriate ApART catalyst system was compared to an industry standard hydrotreating catalyst.

Table 3 - Typical DAO/Heavy SRVGO Feed Properties

API	14-16
Sulfur, Wt %	>2.0
Nitrogen, ppm	2200-2600
Concarbon, Wt %	6-8
Ni + V, ppm	>20
Boiling Range, °F (ASTM D2887)	700-1350

Figure 5 shows the normalized temperature required for HDS activity. The large advantage for the ApART system, compared to the neat NiMo standard catalyst, is clear.

Figure 5 - HDS Activity Comparison on DAO Feed

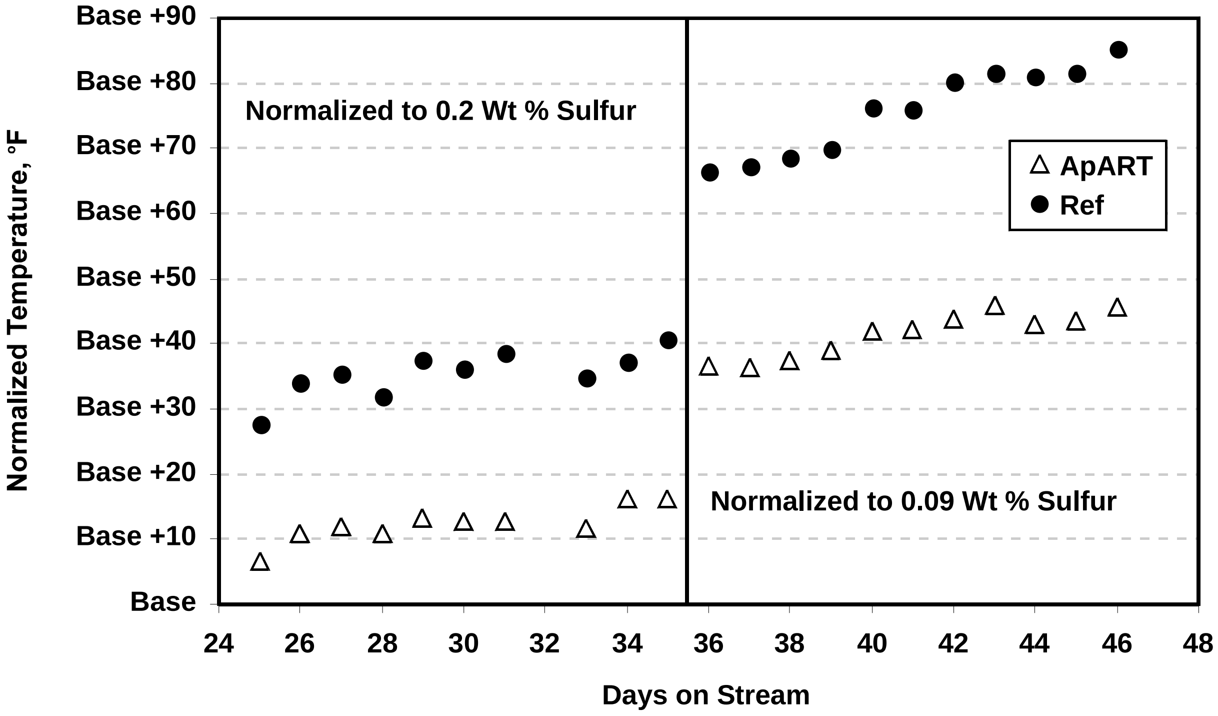
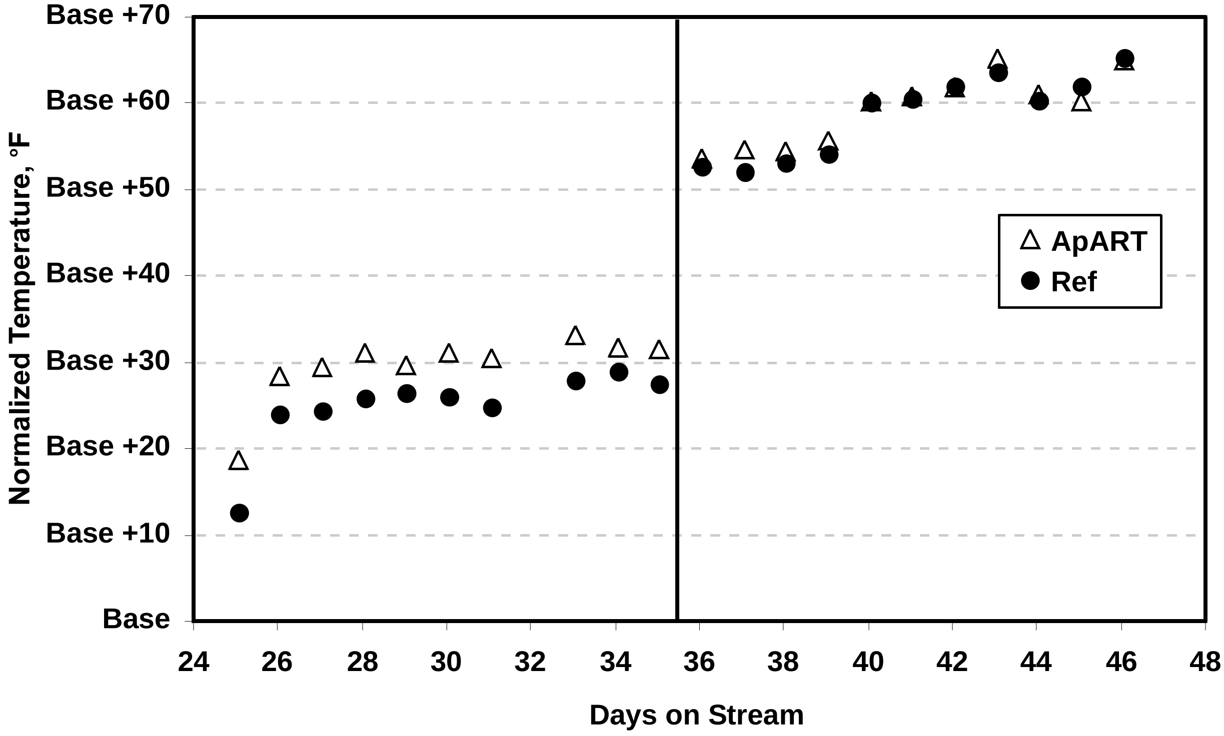


Figure 6 shows the normalized temperature required for HDN. The ApART system shows activity very close to that of the neat NiMo catalyst.

Figure 6 - HDN Activity Comparison on DAO Feed

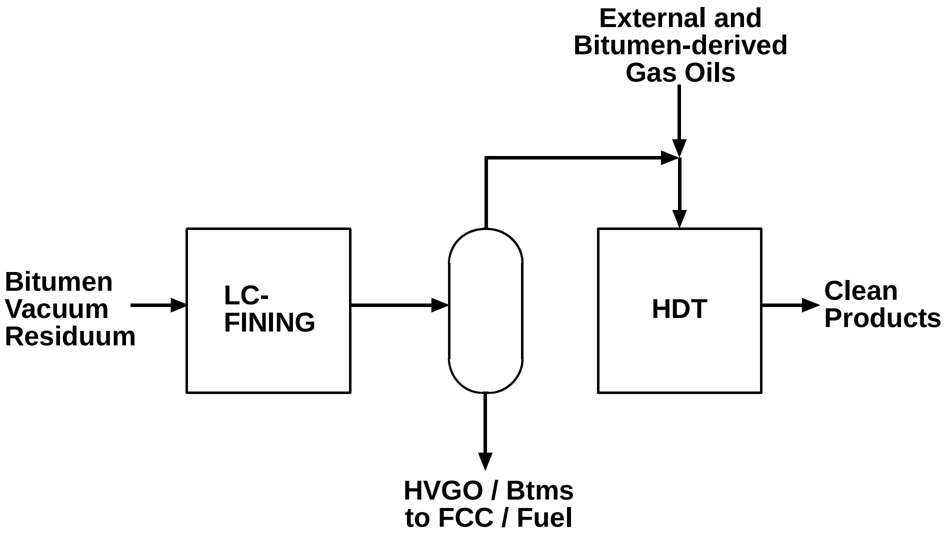


When a large U.S. refiner wanted to improve its DAO processing, other vendors also carried out similar tests using their best catalyst systems. The customer chose the ApART system based on its performance. More importantly, the ApART system can tolerate more metals than other catalysts in its class and still offers high HDN and HDS activities. This means that the ApART system offers higher stability and longer life, which translates into better performance for the refiner.

Integrated LC-FINING/Hydrotreating Process

A major refiner selected CLG's LC-FINING technology to upgrade the vacuum residuum derived from Athabasca bitumen into clean products.[1] The upgrader, which is part of the Athabasca Oil Sands Project, employs a unique design in which the LC-FINING unit is integrated with a close-coupled hydrotreater (Figure 7). The design conversion of the vacuum residuum is nearly 80 wt %.

Figure 7 - Integrated LC-FINING/HDT Process Scheme Upgrades Alberta Bitumen



The integration of the hydrotreater provides many advantages for the refiner. The close-coupled hydrotreater processes both the distillates produced in the LC-FINING unit and external distillate feeds in the refinery. The piece count for the reaction section of the integrated hydrotreater is 50% less than that of a stand alone unit. The LC-FINING and hydrotreating reactors share the same high pressure hydrogen loop, and the hydrotreater utilizes the excess hydrogen remaining in the LC-FINING effluent. While some fractionation is common for both sections, the upgrader is very energy efficient because of increased heat integration.

Table 4 lists the inspections of a typical feed blend for the integrated hydrotreater. The hydrotreater feed has a broad boiling range and contains more than 1000 ppm nitrogen and 1.0-1.5 wt % sulfur.

**Table 4 - Integrated Hydrotreater Upgrades
Bitumen-Derived AGO/LVGO Blend**

Stream	LC-FINING LGO	External SR Gas Oils	HDT Blend
Boiling Range, °F	250-800	200-900	200-900
Nitrogen, ppm	1600-2000	400-700	>1000
Sulfur, Wt %	0.2-0.5	2.0-2.5	1.0-1.5

Table 5 indicates that commercial hydrotreating catalysts achieve a 2-year cycle and generate high quality, saleable fuels or intermediate products.

Table 5 - Integrated Hydrotreater Performance

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

	Diesel	VGO Bottoms
API Gravity	34	26
Nitrogen, ppm	<10	<100
Sulfur, ppm	<100	<200
Cetane Index	45	--

The innovative synergy of the design has resulted in lower capital investment and reduced operating costs. The upgrader has been operating at 10% above design since its successful startup in 2003.

ISOCRACKING Hamaca Bitumen Feed

With the continuing popularity of delayed coking as a relatively inexpensive solution for fuel oil reduction, refiners are faced with the issue of treating an increasing amount of coker gas oils with high levels of nitrogen and sulfur. This was particularly evident for a client who wanted to upgrade Hamaca bitumen. CLG conducted a pilot plant study using a Hamaca HCGO/HVGO blend (Table 6). While both the HCGO and HVGO are high in nitrogen (>3000 ppm) and sulfur (>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 HCGO places it at the top end of the Chevron database for petroleum-derived VGOs without residuum entrainment.

Table 6 - ISOCRACKING Process Technology and CLG/ART Catalyst Systems Can Successfully Upgrade Hamaca Bitumen Feed

Feed Stream	Typical Hamaca HCGO/HVGO
API Gravity	12-14
Nitrogen, ppm	3000-3500
Sulfur, Wt %	3-4
Polyaromatic Indicator, ppm	6500-7500
Ni + V, ppm	≥2

The combination of the ApART catalyst system and a new generation of ISOCRACKING catalysts provides the capability to upgrade the Hamaca HCGO/HVGO blend (Table 7). Named ICR 175/ICR 176 and ICR 160, respectively, the catalyst system generated a SSOT conversion of 45% at a reasonable start-of-run temperature. The products are high value, ultra-low-sulfur gas oil streams.

Table 7 - New Generation of Catalysts Maximizes Ability to Process Hamaca HCGO/HVGO Feed

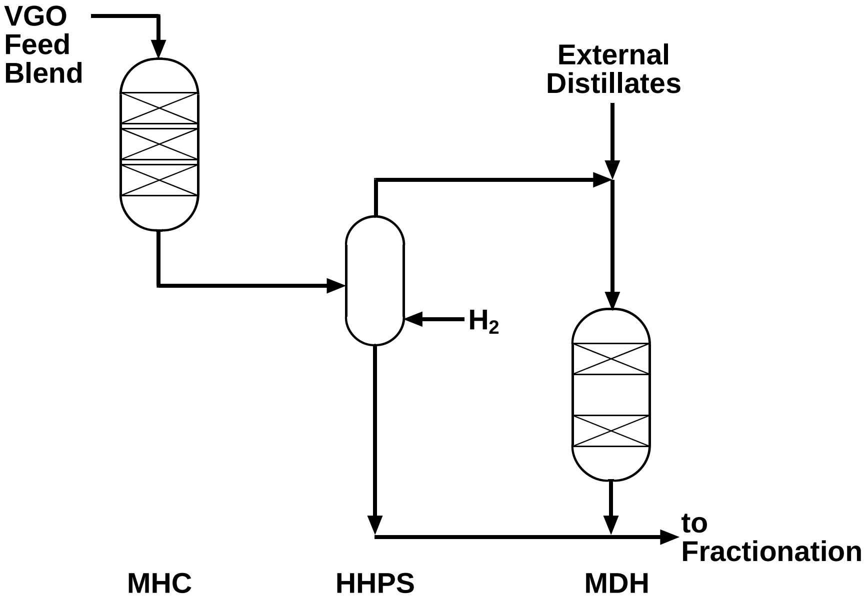
Catalyst System	ICR 175/ICR 178/ICR 176/ICR 160
Syncrude Product Qualities	
Kerosene	15 mm Smoke Point
Diesel	44 Cetane Index
VGO	
API Gravity	34
Nitrogen, ppm	0.2
Sulfur, ppm	7

ISOFLEX for Mild Hydrocracking

In the last decade, mild hydrocracking units have become a preferred option to improve FCC feed quality and to debottleneck refineries by converting excess VGO. Many of these units operate at relatively low pressures, thereby limiting product upgrade and catalyst cycle length. As mentioned above, with most fuel-oil-reduction processes, refiners also must treat incremental gas oils with high nitrogen and sulfur contents. By utilizing one of CLG's ISOFLEX process schemes,[2] the refiner can upgrade the middle distillates from a mild hydrocracker while retaining the capital incentives of lower pressure mild hydrocracking conditions. Additionally, external distillates in the refinery can also be upgraded at the same time.

Figure 8 depicts an ISOFLEX process for mild hydrocracking. The scheme involves flashing the reactor effluent from the MHC unit in a hot high pressure separator (HHPS). Vapor from the hot separator is cooled down to hydrotreating conditions by addition of cold, external distillate feeds such as FCC light cycle oils and atmospheric gas oils, which also require treatment to produce ultra-low-sulfur diesel. The combined feed stream is pumped to the middle distillate hydrotreater where final desulfurization and aromatic saturation take place.

Figure 8 - Schematic of ISOFLEX Process for Mild Hydrocracking and Middle Distillate Hydrotreating



The ISOFLEX process in this case offers many process advantages:

- The process can upgrade a wide range of feedstocks.
- The 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 HCR conversion step.
- There is independent control of each reaction sequence.
- Optimal conversion and high selectivity are achieved with the minimum pieces of equipment.

An example of ISOFLEX mild HCR processing can be found in Tables 8 and 9. A refiner with lube extraction facilities and a visbreaker operation will upgrade these VGO intermediates and a combination of high-sulfur atmospheric gas oils and light cycle oil in a commercial ISOFLEX system. The mild HCR unit will process a VGO blend containing 2000 ppm nitrogen and 2.5 wt % sulfur 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 sulfur and have excellent burning properties.

Table 8 - Properties of Extract/Visbreaker Gas Oil/SR VGO Feed Blend for ISOFLEX Mild HCR Processing

API Gravity	18-20
Nitrogen, ppm	1800-2100
Sulfur, Wt %	2.4-2.7
Polyaromatic Indicator, ppm	2000-2500

Table 9 - MHC Generates High-Quality Products From Extract/Visbreaker Gas Oil/SR VGO Blend

MHC Yields, LV %	
Naphtha	8-10
Middle Distillates	30-40
FCC Feed	60-70
Product Properties	
Kerosene Smoke Point, mm	>20
Diesel	
Sulfur, ppm	<10
Cetane Index	≥45
FCC Feeds	
API Gravity	≥32
Sulfur, ppm	10-20
Nitrogen, ppm	1-2

Optimized Partial Conversion (OPC) ISOCRACKING

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 to add catalyst volume in series or to add a product-saturation reactor if improved product quality is desired.

CLG’s innovative solution is less expensive and more flexible than either of these options.[3] A small reactor is added upstream of the existing reactor, converting the SSOT unit into a partial-recycle, TSREC configuration. Because the added reactor operates in a “clean” second-stage environment, less than one-half of the additional catalyst volume is needed compared to conventional solutions (Figure 9). This approach was proven in its application at a U.S. refinery. The feed for this hydrocracker (Table 10) is a blend of HCGO, SRVGO, and FCC LCO derived from Mexican crude. The HCGO is very difficult to hydrocrack due to its high nitrogen and polyaromatic contents. Compared to a conventional design, the required catalyst volume, hydrogen consumption, and product qualities all benefited from CLG's OPC solution. Additional capital was also saved by integrating the first and second stages into the same recycle gas loop. The OPC approach takes advantage of first-stage processing conditions to produce excellent FCC feed with minimum hydrogen addition to this stream. The approach also utilizes the "clean" second stage very effectively, with relatively low reactor temperatures and higher space velocities generating high-quality fuels.

Figure 9 - Optimized Partial Conversion (OPC) ISOCRACKING

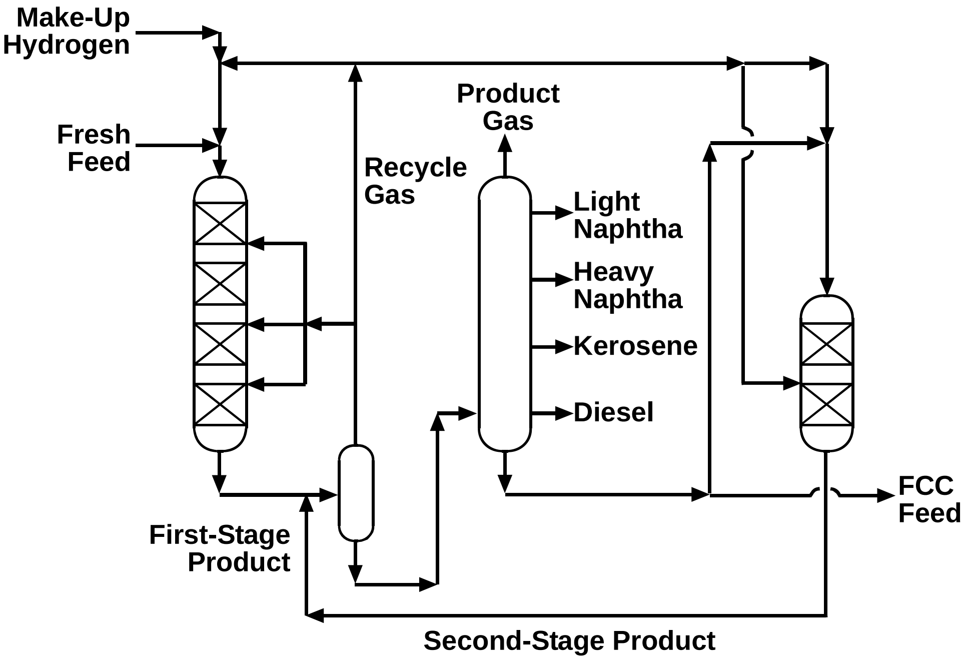


Table 10 - Typical Properties of Mexican HCGO/HVGO/FCC LCO Feed Blend

API Gravity	13-15
Nitrogen, ppm	2500-3000
Sulfur, Wt %	3.0-3.5
Polyaromatic Indicator, ppm	7000-8000

Tables 11 and 12 show typical yields and product properties obtained at the OPC unit. The yield structure is directed at maximizing gasoline production in the refinery, and the distillate products are ultra-low-sulfur and highly valued. To gain aromatic saturation of the kerosene and to produce more naphtha during gasoline season, a kerosene recycle feature was also implemented at the plant. This innovation has been discussed previously.[3,4]

Table 11 - Typical OPC Two-Stage ISOCRACKING Yields
Mexican HCGO/SR VGO Blend

Naphtha, LV %	25-35
Middle Distillates, LV %	40-45
Bottoms, LV %	30-40

Table 12 - Typical Product Qualities in OPC HCR of Mexican HCGO/SR VGO Blend

Reformer Naphtha	
N + 2A, LV %	70-80
Bottoms	
Nitrogen, ppm	5-20
Sulfur, ppm	50-100

Two-Stage ISOCRACKING of Venezuelan Heavy Coker Gas Oil Blend

CLG conducted a study for a Venezuelan refiner involving the production of middle distillates from a coker gas oil 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 (Table 13), the blend of which contained a large amount of nitrogen and a relatively high concentration of polyaromatics. CLG proposed a two-stage, recycle ISOCRACKING configuration, using a base-metal-zeolite catalyst in the first stage and a noble-metal-zeolite catalyst in the second stage.

Table 13 - Properties of Venezuelan Heavy Coker Gas Oil Blend for Two-Stage ISOCRACKING

API Gravity	15-18
Nitrogen, ppm	3400-3800
Sulfur, Wt %	3.0-3.5
Polyaromatic Indicator, ppm	5000-6000

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 kerosene and diesel. The burning characteristics of the distillates are excellent (25 mm smoke point kerosene and 52 cetane index diesel), while the bottoms is a premium FCC feedstock. The study demonstrated the robustness and selectivity of the CLG catalyst system when processing a difficult, neat HCGO feed blend.

Table 14 - Product Properties From ISOCRACKING of Venezuelan HCGO Blend

Kerosene	
Smoke Point, ,mm	25
Freeze Point, °C	-67
Diesel	
Cetane Index	52
Cloud Point, °C	-19

Summary

Chevron has been actively introducing novel hydroprocessing catalysts and process schemes for over 50 years. In the last 10 years, these activities have accelerated through joint ventures with ABB Lummus (CLG) and Grace Davison (ART). The synergies brought about by the joint ventures have resulted in further catalyst and process advances, many of which have been cited in this paper. The superior technology has enabled refiners to upgrade heavy refractory feeds into high-value products with minimal capital expense and operating costs. The performance of commercial units applying these innovations has met or exceeded expectations, based on pilot plant results. Consequently, our technology and catalysts have captured a large share of recent refinery expansion and revamp business. We will continue to work with refiners to develop state-of-the-art solutions to meet their needs.

References

1. Spieler, S., Mukherjee, U., and Dahlberg, A. J., “Upgrading Residuum to Finished Products in Integrated Hydroprocessing Platforms -- Solutions and Challenges,” NPRA Annual Meeting, March 20, 2006, pp 3-5.

2. Mukherjee, U., Dahlberg, A. J., Mayer, J., and Kemoun, A., “Maximizing Hydrocracker Performance Using ISOFLEX Technology,” NPRA Annual Meeting, March 4, 2005, pp 8-9.

3. Papon, J. M., Parekh, J., Yoon, H. A., and Dahlberg, A. J., “Premcor Heavy Oil Upgrade Project,” NPRA Annual Meeting, March 18, 2002, pp 4-8.

4. Mukherjee, U., Dahlberg, A. J., Mayer, J., and Kemoun, A., “Maximizing Hydrocracker Performance Using ISOFLEX Technology,” NPRA Annual Meeting, March 4, 2005, pp 2-3.

:kad/070009