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HYDROCRACKING CATALYST DEVELOPMENTS AND INNOVATIVE PROCESSING SCHEME

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By

R. Wade, J. Vislocky, T. Maesen, and D. Torchia

Introduction

Refiners currently find themselves in a challenging environment as regulations continue to increase demands on refining processes, while high quality refining feedstocks become scarcer and consequently more expensive. This combination of increasing raw material cost (usually of lesser quality), coupled with more stringent finished product quality requirements, emphasizes the need to utilize the latest technology to remain competitive and maintain safe unit operation. Additionally, recent world events have resulted in reduced capex and thereby increased focus on catalyst and know-how solutions.

Chevron Lummus Global (CLG) finds itself uniquely positioned to address these competitive challenges as we work closely with our parent company, Chevron, to invent new catalysts and processes that provide the technological edge needed to remain the leader in this competitive refining market.

CLG is committed to improve all of its hydroprocessing catalyst technology offerings through the operation of dozens of pilot plants and micro units. We have annual programs for each of our hydroprocessing technologies (Resid Hydrotreating, LC-FINING, ISOTREATING, ISOCRACKING, ISODEWAXING, and ISOFINISHING) that focus on catalyst improvements and process improvements, along with optimizing catalyst offerings for existing customers. The process we employ is straightforward; we work closely with customers to clearly identify market requirements, and tailor our development programs to achieve real world solutions which are reflected in our proposals.

This paper will continue the catalyst discussion begun by my colleagues, Jim Vislocky and Dave Krenzke [1], and follows the development and commercialization of five recently developed CLG ISOCRACKING® catalysts. In addition, this paper will provide updates to CLG's recently introduced Single-Stage Reverse-Staging (SSRS) process [2] by reviewing a recent startup of a new SSRS unit in mainland China, and by reviewing a recent revamp design using SSRS technology in Malaysia. Both units benefited from our most advanced generation of catalysts.

History

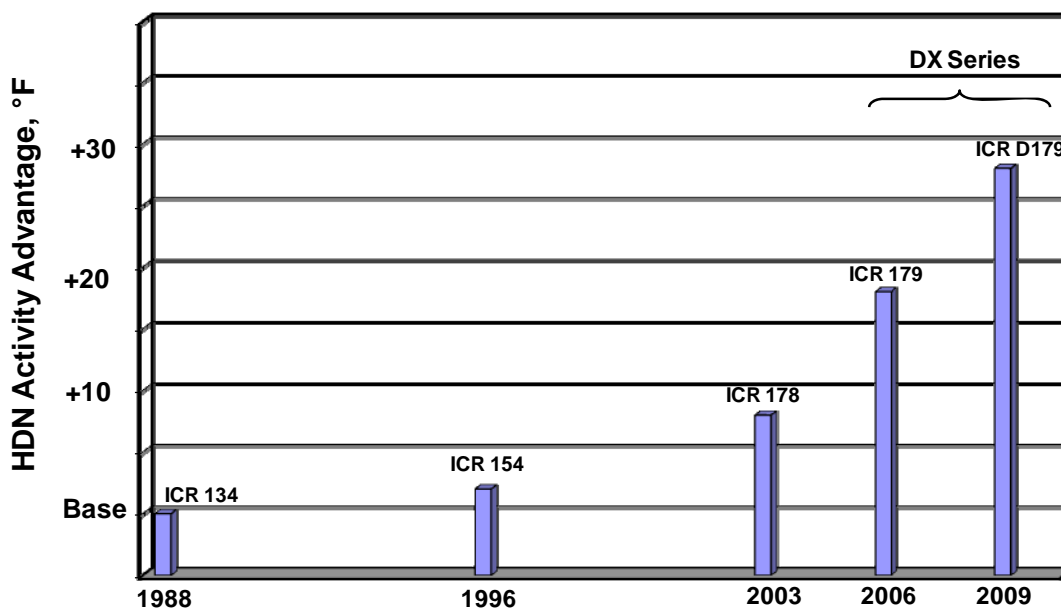
Chevron invented the modern hydrocracking process in 1959. The first licensed unit started up in 1962, and the first commercialized ISOCRACKING process within Chevron's own system at Pascagoula refinery in 1963. Three years later, a two-stage ISOCRACKING plant was commissioned at its Richmond, California, refinery to upgrade VGO to naphtha and jet fuel. At the same time a Single-Stage Once-Through (SSOT) unit was also commissioned at the Richmond refinery to hydrocrack DAO. These early hydrocracking projects added 10 high pressure reactors to the Richmond refinery.

ISOCRACKING technology was further applied by Chevron with a second unit at its Pascagoula, Mississippi, refinery in 1969, and one at its El Segundo, California, refinery in 1971.

Hydrotreating Catalyst Design

It is well understood that the support and active metals are two key ingredients critical to optimizing performance for any hydroprocessing catalyst. These key ingredients determine the density of active sites and the pore size distribution. The optimum activity is achieved by maximizing the density of active sites while maintaining access for the critical molecules of a particular feed [1]. This optimum will be different for the larger molecules in a VGO feed than for the smaller molecules in a diesel feed. CLG has focused on improving hydrotreating catalysts tailored to full range VGO hydrocracking service. Figure 1 shows the relative HDN activity advantage on a full range VGO for the latest version, ICR D179, along with its predecessors.

Figure 1. Significant Recent Advances in CLG Hydrocracking Pretreat Catalyst Technology



The activity gains shown for ICR 134 to ICR 154 and ICR 154 to ICR 178 were achieved through the optimization of support and active site density as described above. Greater than 10°F gains shown for ICR 178 to ICR 179 and ICR 179 to ICR D179 were achieved through the use of a novel process that increases the density of the more active (Type 2) catalyst sites [1].

Hydrocracking Catalyst Design

The principles for optimizing hydrotreating catalyst design extend to hydrocracking catalyst design. As compared to hydrotreating catalysts, hydrocracking catalysts exhibit a larger fraction of active sites that selectively reduce the average size of the feed

molecules to shift the boiling range of the feed into the desired product boiling range. Balancing the density and accessibility of these so-called cracking sites with that of the hydrogenation sites is critical to manufacturing fuels with the lower levels of sulfur, nitrogen, and aromatics required to meet or exceed current and future standards.

CLG continues to expand Chevron’s 50 years of know-how in hydrocracking research and development. Commercialization of multiple new generations of hydrocracking catalysts was achieved through optimizing the catalyst formulation, the optimum choice of raw materials, enhanced characterization, more efficient testing techniques, optimized synthesis steps, and improved manufacturing processes. In addition, CLG has been able to include elements of unit operability into catalyst designs, based on feedback from Chevron’s operation of hydrocrackers in many different markets across the globe.

Figure 2. ISOCRACKING® Catalyst Improvements Through Optimization of Formulation

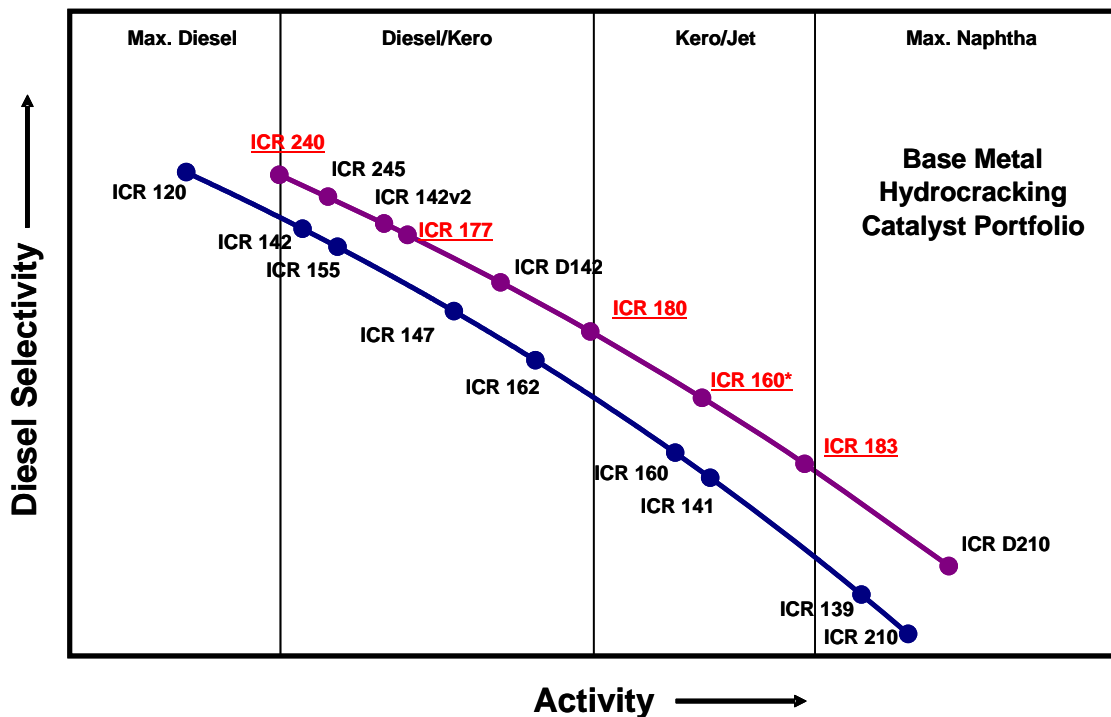


Figure 2 provides CLG’s base metal ISOCRACKING® catalyst portfolio. It covers the full range of hydrocracking applications. The curve represents the tradeoff between activity and selectivity which characterizes a generation of catalysts. The goal of hydrocracking catalyst development is to move to a next generation of catalysts that operate at higher selectivity and activity. Higher selectivity produces more of the desired product while higher activity allows the refiner to extend catalyst run lengths, increase throughput, or process more difficult feeds. The catalysts that are underscored are commercially available and will be discussed in detail here: ICR 177, ICR 180, ICR 160*, ICR 183, and ICR 240.

Figure 3. Higher Activity Zeolites Preferentially Crack Diesel/AGO Range Molecules, Resulting in Loss of Mid-Distillate Selectivity

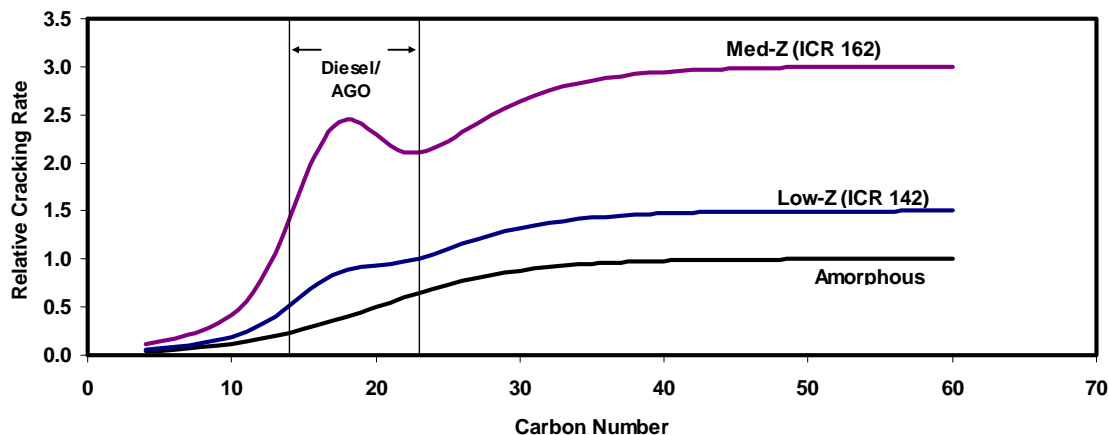
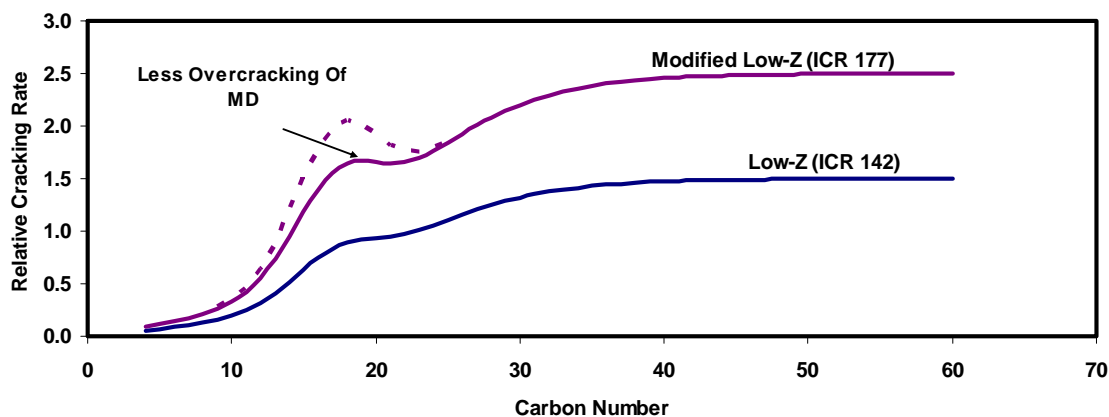


Figure 4. Modified Low-Z Catalyst Improves Activity at Similar Mid-Distillate Selectivity Through Modification of Acid Function



Figures 3 and 4 illustrate how improved catalytic performance is achieved through modification of the cracking (acid) function. These figures show the relative cracking rate constant as a function of carbon number for catalysts of varying activity.

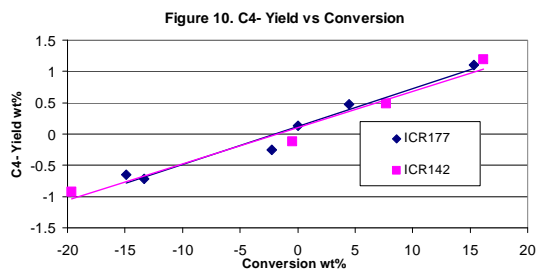
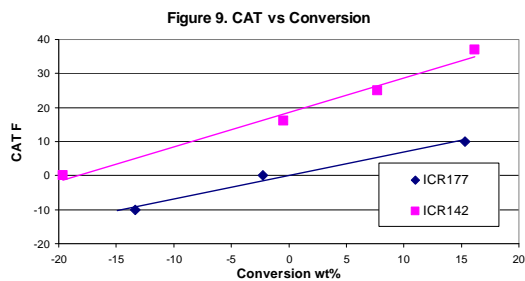
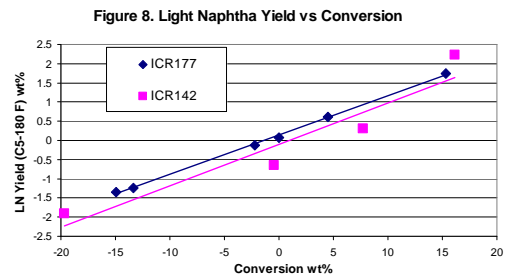
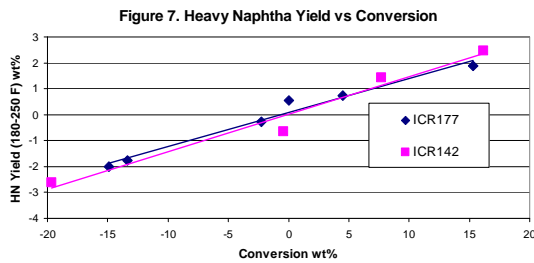
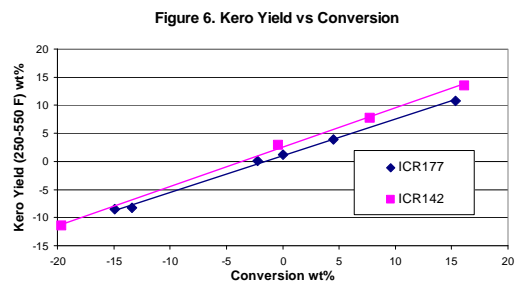
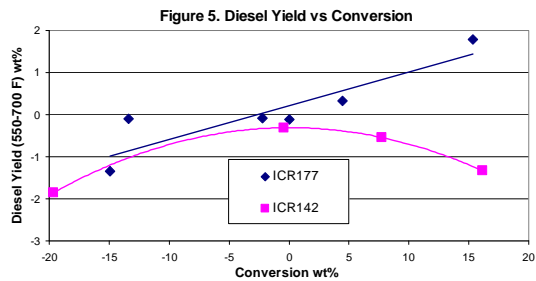
Figure 3 shows that with an increase in activity of the cracking component of the catalyst, the cracking rate constant for molecules in the middle distillate boiling range increases considerably faster than that for molecules in the VGO boiling range. Thus, the middle distillate product molecules are preferentially adsorbed and overcracked, resulting in the selectivity decline with increasing cracking activity shown in Figure 2.

Figure 4 shows how the accessibility to the cracking function can be modified to reduce the amount of overcracking which results in a catalyst with higher activity while maintaining mid-distillate selectivity – yes, it is possible! CLG has recently developed three new catalysts that have been modified to attenuate overcracking of AGO and increase diesel yield selectivity in this fashion. The formulation of each of these catalysts retains the best characteristics of their respective predecessor with the addition

of performance enhancements that increase diesel selectivity by attenuating AGO overcracking.

ICR 177 and ICR 142

Chevron has long been a world leader in hydroprocessing technology for lubricant base oil production and mid-distillate hydrocracking technology. For many years ICR 142 has been the catalyst of choice for both maximum bottoms V.I. and maximum mid-distillate production. As feeds become more difficult, and process severity increases, the need for a more active catalyst to replace ICR 142 has become apparent, hence the advent of ICR 177. Figures 5 through 8 show a significant increase in diesel yield as conversion is increased, without reducing kerosene, and naphtha selectivity. Figures 9 and 10 show that ICR 177 is 10°F more active than ICR 142 over the conversion range considered, with no increase in light gas make.



ICR 180 and ICR 162

ICR 162 was first commercialized in 2003. ICR 162 is one of our workhorse mid-distillate selective catalysts used widely in first-stage SSOT and SSREC units, along with both first and second stages of the Two-Stage Recycle (TSR) units. Figure 2 shows that ICR 162 is more active than ICR 142 at the cost of mid-distillate selectivity. ICR 180 was developed to improve on both the selectivity and activity of ICR 162, targeting a catalyst closer to ICR 142 in selectivity while improving on ICR 162 activity.

ICR 180 was developed by a slight modification to the formulation of its predecessor ICR 162. Figures 11 and 12 show an increase of diesel yield in excess of 2% with no increase in kero yield. Figures 13 and 14 show the difference in naphtha selectivity is small at low conversion levels, with a decrease of as much as 2% at high conversion levels. Figures 15 and 16 show that ICR 180 provides a 10°F activity advantage over ICR 162 with a reduction in light gas make. The innovation objectives were achieved, and ICR 180 currently maximizes mid-distillate yield in one of Chevron's JV hydrocrackers.

Figure 11. Diesel Yield vs Conversion

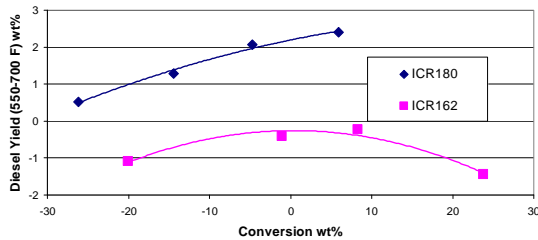


Figure 12. Kero Yield vs Conversion

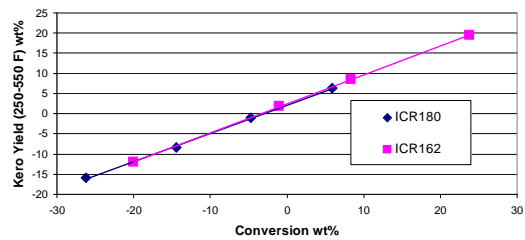


Figure 13. Heavy Naphtha Yield vs Conversion

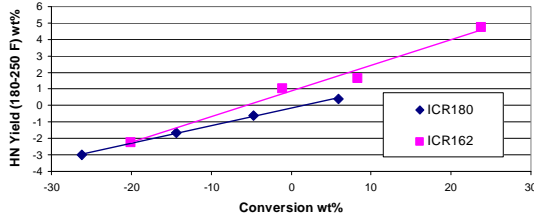


Figure 14. Light Naphtha Yield vs Conversion

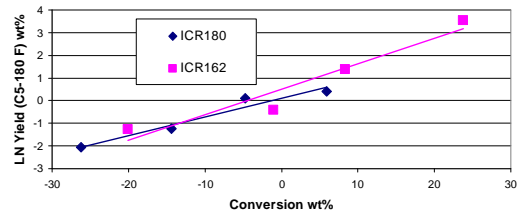


Figure 15. CAT vs Conversion

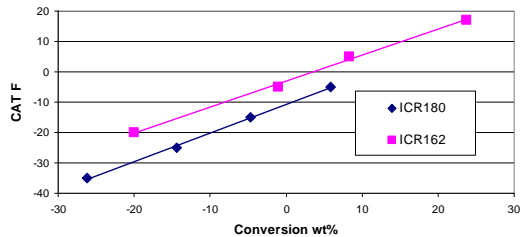
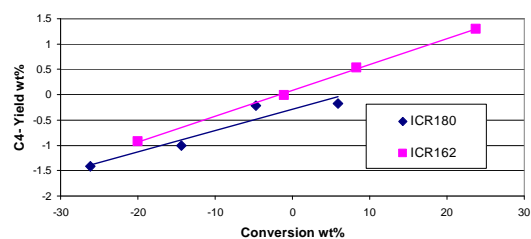


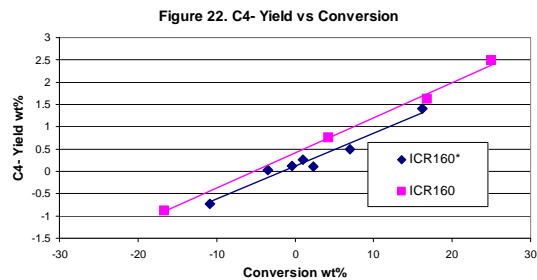
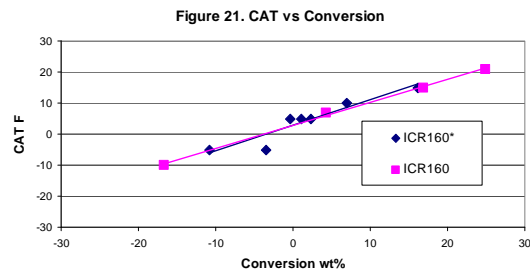
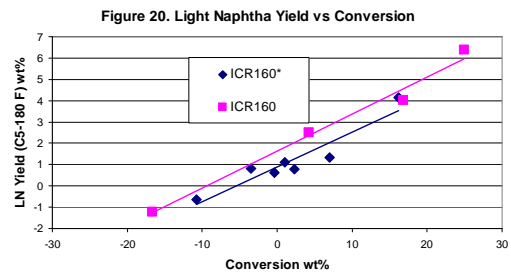
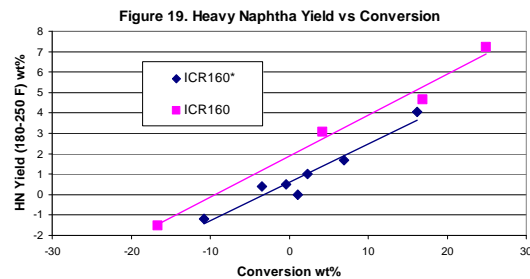
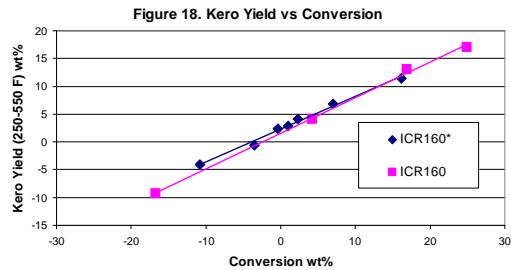
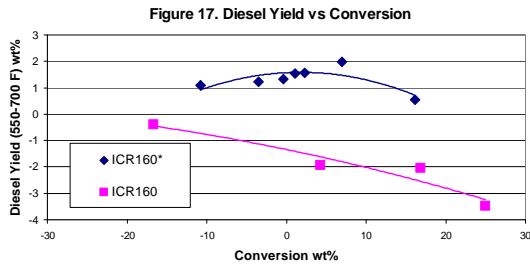
Figure 16. C4- Yield vs Conversion



ICR 160* and ICR 160

ICR 160 was first commercialized in 2002. This catalyst was developed to replace ICR 141 for the increasingly difficult to process feeds where maximum kero/jet is desired. ICR 160 may also be used in first-stage SSOT and SSREC units, along with both first and second stages of TSR units. Figure 2 shows that ICR 160 is slightly less active than its predecessor ICR 141 with a gain in selectivity. ICR 160 also yields significantly less light naphtha and gas make as compared to ICR 141 (not shown).

ICR 160* was developed to improve both selectivity and activity of ICR 160. Like ICR 177 and ICR 180, ICR 160* was developed through a slight modification to the formulation of its predecessor. Figures 17 and 18 show diesel yield was improved by 1% to almost 3% without decreasing kero selectivity. Figures 19 and 20 show that naphtha yield was decreased by about 1.5%, and Figures 21 and 22 demonstrate that activity is similar for both catalysts with a slight decrease in gas make for ICR 160. Additional testing is planned on a similar feed to fully understand the potential benefit for ICR 160*.



ICR 183 and ICR 160

ICR 183 was commercialized in 2008. This catalyst was developed to improve the activity of ICR 160 for difficult to process feed applications where maximum jet and naphtha production is desired. ICR 183 exhibits a high tolerance for organic nitrogen. It can be used in first-stage SSOT and SSREC units, along with both first and second stages of the TSR units. Figure 2 illustrates that ICR 183 exhibits considerably more activity than ICR 160 while increasing the naphtha selectivity.

ICR 183 was developed by increasing the cracking site density of ICR 160. This higher cracking site density makes this catalyst more tolerant to organic poisons and significantly improves activity for jet and heavy naphtha operations. Figure 23 shows the increase in activity reduces diesel yield by 2%. Figure 24 shows no change in kero yield. Figure 25 shows a 1.5% increase in heavy naphtha yield and Figure 26 shows a gain of 1% to 2.5% light naphtha. Figures 27 and 28 show that ICR 183 is 30°F more active than ICR 160 with no increase in light gas make. ICR 183 has proven itself in multiple head-to-head pilot plant testing at both CLG and customer locations. Because of its excellent performance ICR 183 was recently commercialized by a U.S. customer and is slated for use for a rapidly expanding list of additional U.S. customers.

Figure 23. Diesel Yield vs Conversion

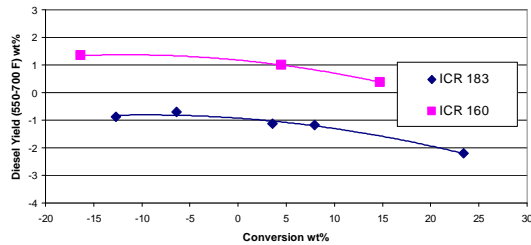


Figure 24. Kero Yield vs Conversion

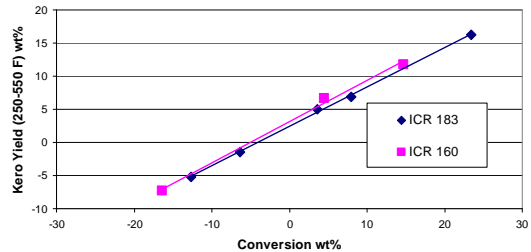


Figure 25. Heavy Naphtha Yield vs Conversion

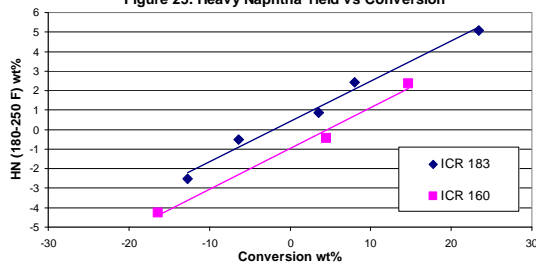


Figure 26. Light Naphtha Yield vs Conversion

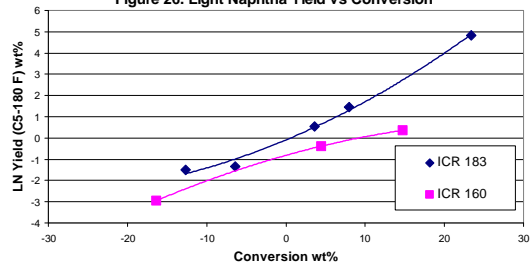


Figure 27. CAT vs Conversion

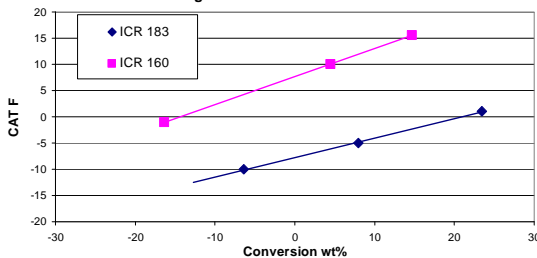
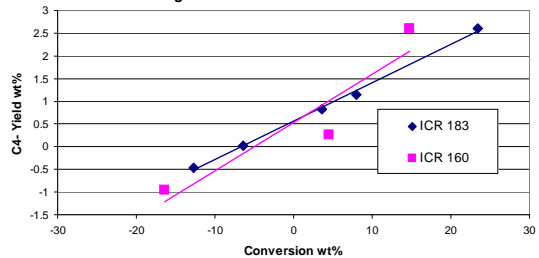


Figure 28. C4- Yield vs Conversion



ICR 240

A schematic of CLG's two-stage hydrocracker design is shown in Figure 29. Gas oil conversion to products is conducted in two sequential stages. The first stage performs pretreat in the top stages followed by hydrocracking to moderate conversion (40-60 LV %) in the lower beds. First-stage effluent is sent to a fractionator along with the effluent from the second stage. The fractionator bottoms are sent to the second stage where it is further cracked to full or partial conversion. Since the fractionator removes the H_2S and NH_3 produced in the first stage, the second stage operates in a 'clean' environment, which significantly enhances the kinetics thereby reducing the required reactor temperature and size. In addition, the products from the second stage are of extremely high quality. The proper formulation of cracking catalyst is critical for optimum performance in the second-stage reaction environment. Particular attention has to be paid to the acid function to minimize overcracking of the higher value products. For years, Chevron's ICR 120 catalyst, an amorphous catalyst made by proprietary cogellation technique, was the premier second-stage catalyst in the industry for mid-distillate production. CLG has recently developed ICR 240, a mild zeolite second-stage catalyst to replace ICR 120. Commercial performance has exceeded expectations, with significant improvements in product selectivity as shown in Figures 30 and 31. In fact, the shift in product slate has been so dramatic that the refiner reported very significant operational improvements. ICR 240 has completely removed the light ends recovery bottleneck in the plant which has allowed the refiner to increase throughput to 115% of design. The plant is now actually limited by its ability to recover mid-distillate! In addition, the impact from the hydrocracker has been so significant that total refinery throughput has increased several percent. The overwhelming success of ICR 240 is an excellent example of the large impact that a catalyst improvement can have on refining economics.

Figure 29. TSR ISOCRACKING

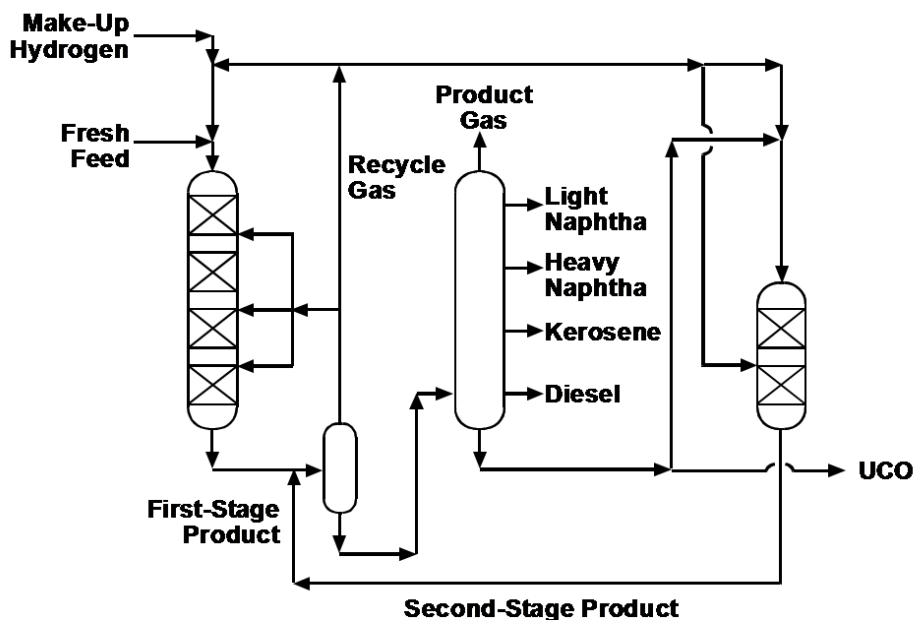


Figure 30. Yields

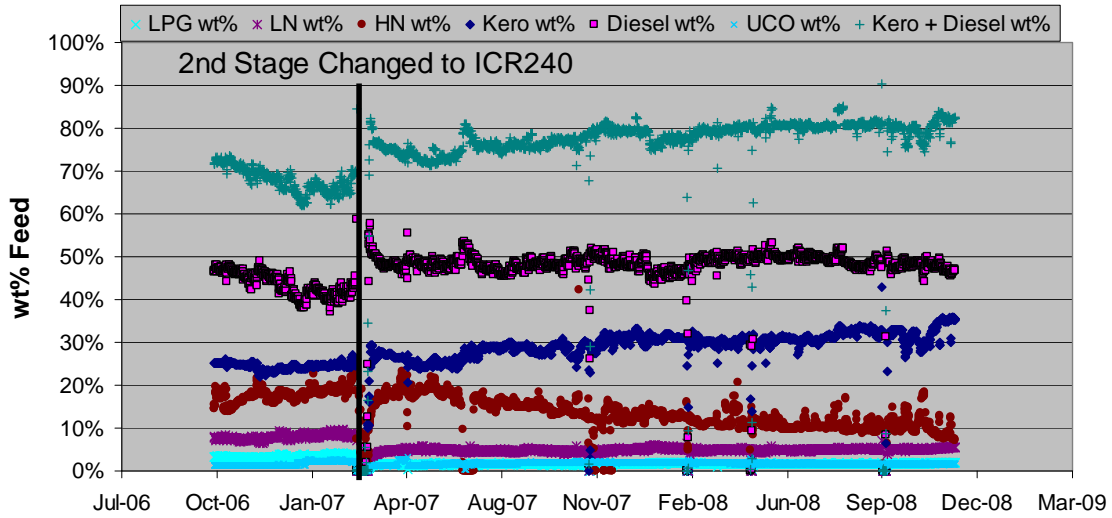
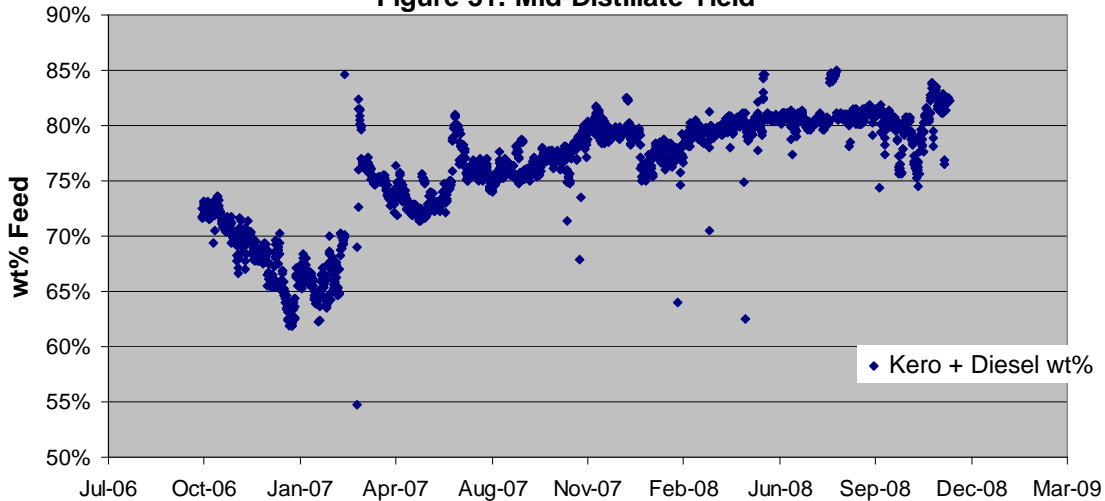


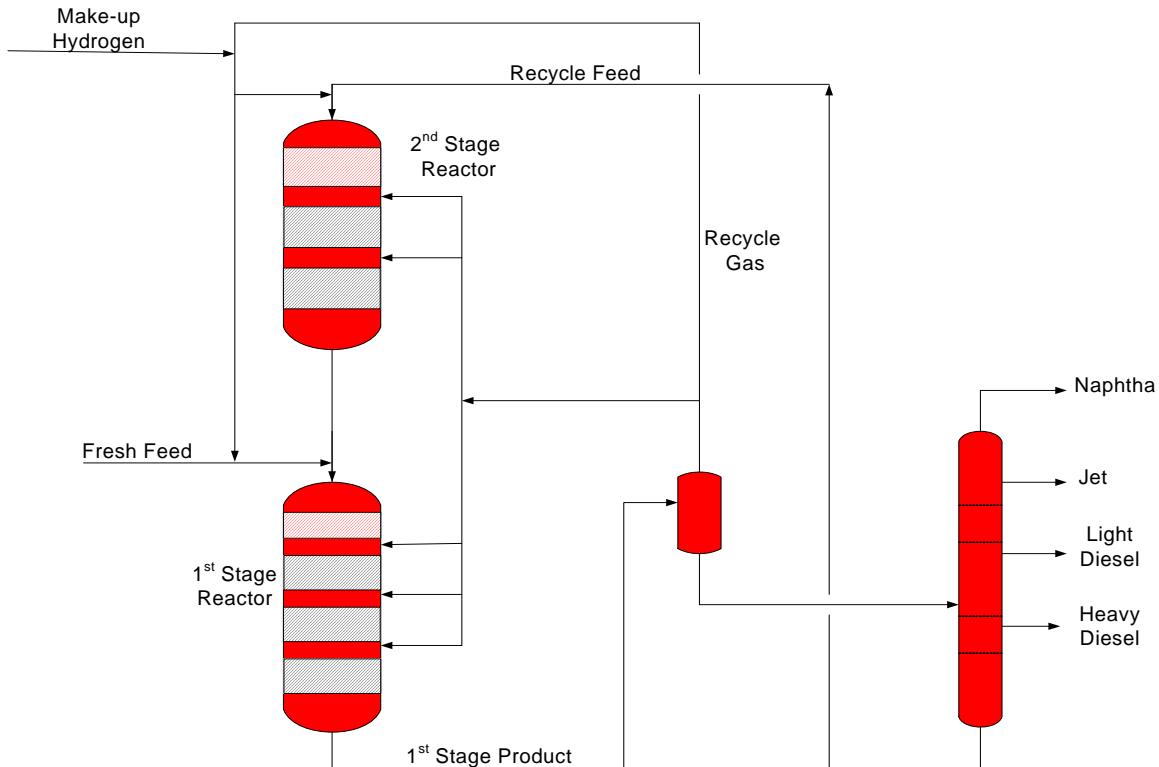
Figure 31. Mid-Distillate Yield



The SSRS Process

The SSRS process was first publically introduced by CLG at the NPRA Annual Meeting in March 2005 by Ujjal Mukherjee [2]. Mr. Mukherjee mentions in his review that a major refiner in China was scheduled to start up the first SSRS unit. This paper will quickly review the key SSRS processing benefits, and share typical product qualities reported from the first guarantee test run of this unit. In addition we will also discuss the most recent application of this process for a CLG licensee who is utilizing this technology to revamp its existing TSR unit to increase throughput and extend run length.

Figure 32. SSRS ISOCRACKING



Key SSRS Process Benefits

A schematic of CLG's SSRS flow scheme is shown in Figure 32. This second-stage process, like a TSR, also takes advantage of a clean second-stage environment with overall rate constants much greater than the rate constants from the first stage. This clean environment allows the user to achieve full conversion of difficult feeds with less than half the reactor volume needed compared to an SSOT or SSREC. The obvious difference between the TSR configuration shown in Figure 29 and the SSRS configuration shown in Figure 32 is the effluent from the second stage flows directly to the inlet of the first stage, which provides the following benefits over a conventional TSR configuration:

1. Effluent from the second stage provides a heat sink for the first stage, reducing first-stage quench gas demand typically by 40%.
2. Unused hydrogen from the second stage is used to supplement G/O requirement for the first stage.
3. The combination of items 1 and 2 reduces the overall recycle gas compressor load typically by 70%.
4. Only one reactor furnace is required.

First Commercial SSRS Unit

In addition to the four advantages presented, the overall product qualities achieved by the first SSRS unit are very similar to those expected for a TSR unit (product quality was the primary concern for those considering this novel technology).

Table 1 summarizes the test run results from the 2007 startup of the first SSRS unit. This table clearly shows that pristine mid-distillate products may be made from a SSRS unit. The feed from this unit was a full range Middle Eastern VGO. The unit runs in maximum mid-distillate mode and normally achieves >90% mid-distillate yield. The catalyst system used in this unit is ICR 162 in the first stage and ICR 180 in the second stage, both of which were described earlier in this paper.

Table 1. 2007 SSRS Unit Startup Test Run Results

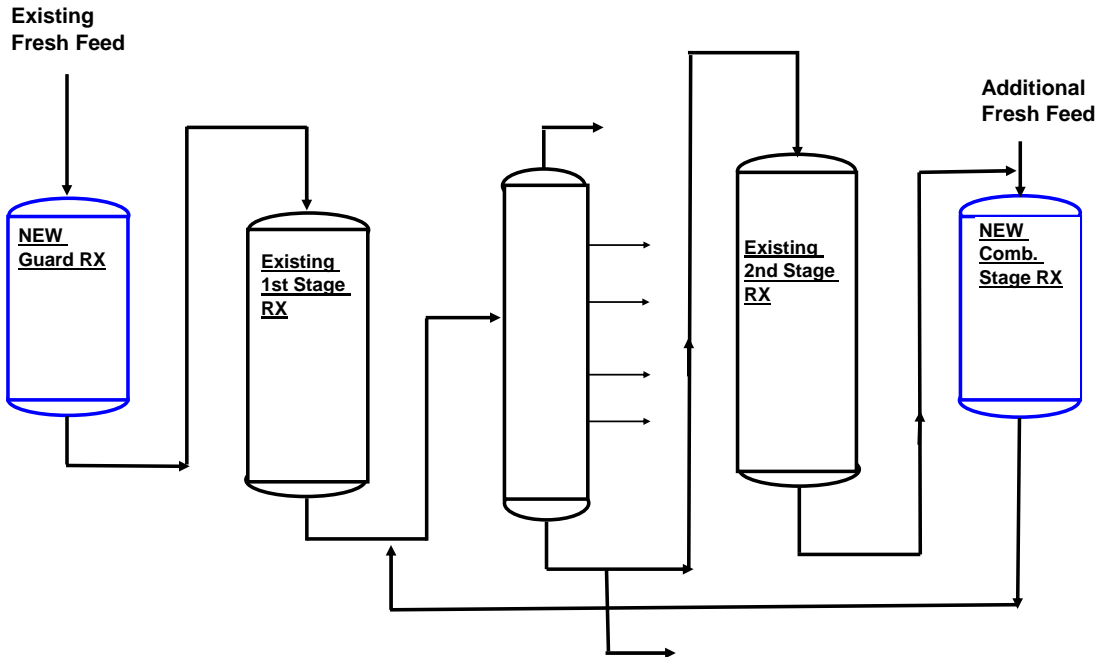
Parameters	Guarantee	Test Run Results
Feed Capacity, MBPD	31-34.5	31
Chemical Hydrogen, Wt % FF	2.29	2.19
Mid-Distillate Yield, Wt % FF (Jet + Diesel)	81.5	81.9 (92 LV %)
Product Properties		
Jet Smoke Point, mm	25	28.8
Jet Freeze Point, °F	-53	-67
Jet Flash Point, °F	100	112
Diesel Sulfur, ppmw	30	<3
Diesel Flash Point, °F	154	186
Diesel Cetane Number	55	61

SSRS Revamp Application

High pressure hydroprocessing revamp economics are largely influenced by recycle gas compressor costs. The SSRS flow scheme is ideal for revamp consideration due to the small incremental load on the recycle gas compressor. This is fairly intuitive for consideration of a SSOT or SSREC revamp to a two-stage unit, but less intuitive for a TSR revamp. Figure 33 shows a TSR configuration with a guard bed added to the first stage, and an additional first-stage reactor added between the second-stage effluent and the product fractionator. The guard reactor was added to increase demetallation and overall first-stage reactor volume to extend catalyst run length. The unit (pre-revamp) is currently running at 133% of original design capacity. The addition of the two new reactors will allow the unit to increase throughput by another 42% to a total of 175% of original design and extend run length by 30%. This will allow a 228% increase in processed barrels per catalyst fill compared to the original design, and will all be achieved using the existing recycle gas compressor. This project is in its final stages of construction and is scheduled to start up in the fourth quarter of this year. In this revamp design it is critical to use catalysts with the proper balance of activity and selectivity in each of the reaction zones. The hydrocracking catalysts that will be used for this unit

are ICR 177 in the existing first stage, ICR 240 in the second stage, and ICR 162 in the combined stage. The unit will continue to run in a maximum mid-distillate mode.

Figure 33. Revamp Configuration Using Reverse Staging



Summary

Leveraging 50 years of hydrocracking catalyst and process technology know-how, combined with hands-on day-to-day operating experience, CLG continues to meet difficult commercial and environmental challenges. CLG is well positioned to assist its clients with both process and catalyst solutions. At CLG we strive to improve both our process and catalyst offerings so Chevron remains a leader in refining and CLG remains the technology company of choice. Novel unit revamps and new unit designs such as SSRS in combination with advanced catalysts can achieve amazing results at capex well below traditional levels.

Let CLG's extensive background and ingenuity work for you – Experience the Difference!

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2. Mukherjee, U., Dahlberg, A. J., and Kemoun, A., "Maximizing Hydrocracker Performance Using ISOFLEX Technology," NPRA, Annual Meeting, March 13-15, 2005.