Hydrocracking catalyst and processing developments

Improvements to hydrocracking catalyst activity and selectivity at various operational and feedstocks conditions are discussed

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R efiners 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, emphasises the need to utilise 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 hydrocracking catalyst and know-how solutions. In this effort, Chevron Lummus Global (CLG) is involved in operating dozens of pilot plants and micro units. There are also annual programmes in progress for each of the following proprietary hydroprocessing technologies: Resid Hydrotreating, LC-Fining, Isotreating, Isocracking, Isodewaxing and Isofinishing. These programmes focus on catalyst improvements and process improvements, along with optimising catalyst offerings for existing customers.

Chevron invented the modern hydrocracking process in 1959. The first licensed unit started up in 1962, followed by the first commercialised Isocracking process within Chevron's own system at the Pascagoula, Mississippi, refinery in 1963. Three years later, a two-stage Isocracking plant was commissioned at its Richmond, California, refinery to upgrade vacuum gas oil (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 deasphalted oil (DAO). These early hydrocracking projects added ten high-pressure reactors to the Richmond refinery. Isocracking technology was further applied by Chevron with a second unit at its Pascagoula refinery in 1969, and one at its El Segundo, California, refinery in 1971.

Hydrotreating catalyst design

It is well understood that support and active metals are two key ingredients critical to optimising performance for any hydroprocessing catalyst. These key ingredients determine the
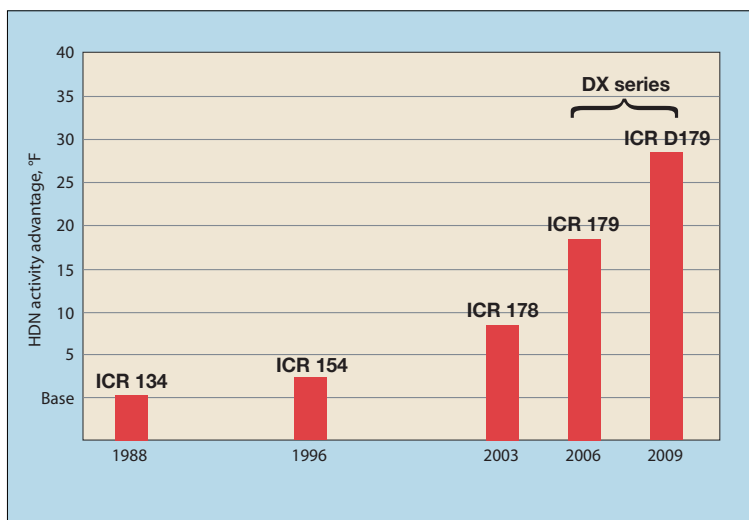

Figure 1 Significant recent advances in CLG hydrocracking pretreat catalyst technology
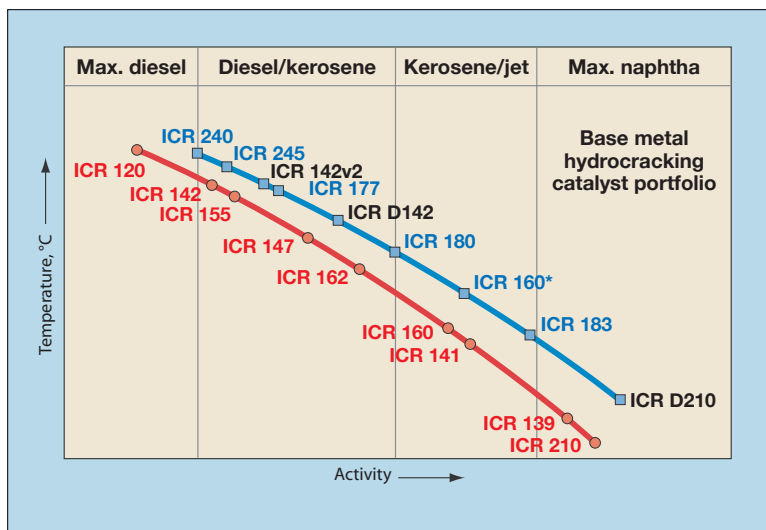
Figure 2 Isocracking catalyst improvements through optimisation of formulation

density of active sites and pore size distribution. The optimum activity is achieved by maximising 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 a full-range VGO hydrocracking service. Figure 1 shows the relative hydrodenitrogenation (HDN) activity advantage on a full-range VGO for the latest version, ICR D179, along with its predecessors.

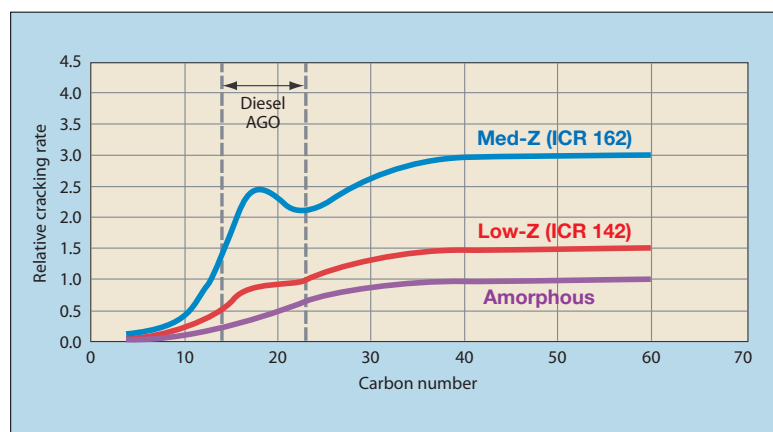The activity gains shown for ICR 134 to ICR 154 and ICR 154 to ICR 178 were achieved through the optimisation of support and active site density, as previously described. Greater than 10°F gains shown for ICR 178 to ICR 179 and ICR 179 to ICR D179 were achieved through the use of a process that increases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

Hydrocracking catalyst design
The principles for optimising 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 sulphur, nitrogen and aromatics required to meet or exceed current and future standards.

Commercialisation of multiple new generations of hydrocracking catalysts has been achieved through optimising the catalyst formulation, optimum choice of raw materials, enhanced characterisation, more efficient testing techniques, optimised 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 its operation of hydrocrackers in many different markets across the globe.

Figure 2 shows CLG's base metal Isocracking catalysts, covering the full range of hydrocracking applications. The curve represents the trade-off between activity and selectivity, which characterises 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

Figure 3 Higher activity zeolites preferentially crack diesel/AGO range molecules, resulting in loss of mid-distillate selectivity

desired product, while higher activity allows the refiner to extend catalyst run lengths, increase throughput or process more difficult feeds. The catalysts that are commercially available and discussed in further detail include ICR 177, ICR 180, ICR 160*, ICR 183 and ICR 240.

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. 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.

Bottoms cracking and distillate production

For many years, ICR 142 has been the catalyst of choice for both maximum bottoms cracking 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 became apparent; hence, the advent of ICR 177. ICR 177 provides a significant increase in diesel yield as conversion is increased, without reducing kerosene and naphtha selectivity. ICR 177 is 10°F more active than ICR 142, with no increase in light gas make.
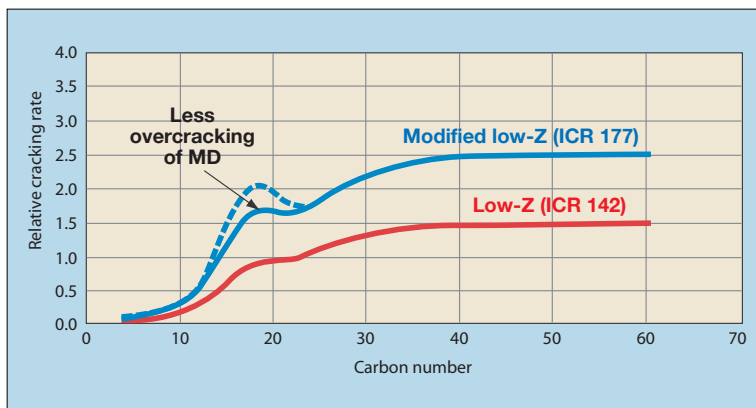

Figure 4 Modified low-Z catalyst improves activity at similar mid-distillate selectivity through modification of acid function

Improved selectivity and activity for mid-distillate service

ICR 162 was first commercialised in 2003. It has been a primary mid-distillate selective catalyst used widely in first-stage SSOT and single-stage recycle (SSREC) units, as well as both the first and second stages of 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 ICR 162 predecessor. When comparing the two formulations, an increase in diesel yield in excess of 2% has been shown for ICR 180, with no decrease in kero yield. For both catalysts, the difference in naphtha selectivity is small at low conversion levels, with a decrease of as much as 2% at high conversion levels. ICR 180 provides a 10°F activity advantage over ICR 162, with a reduction in light gas make. ICR 180 currently maximises mid-distillate yield in one of CLG's JV hydrocrackers.

Maximum kero/jet from difficult feedstocks

The ICR 160 catalyst, first commercial-ised in 2002, 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, as well as both the 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
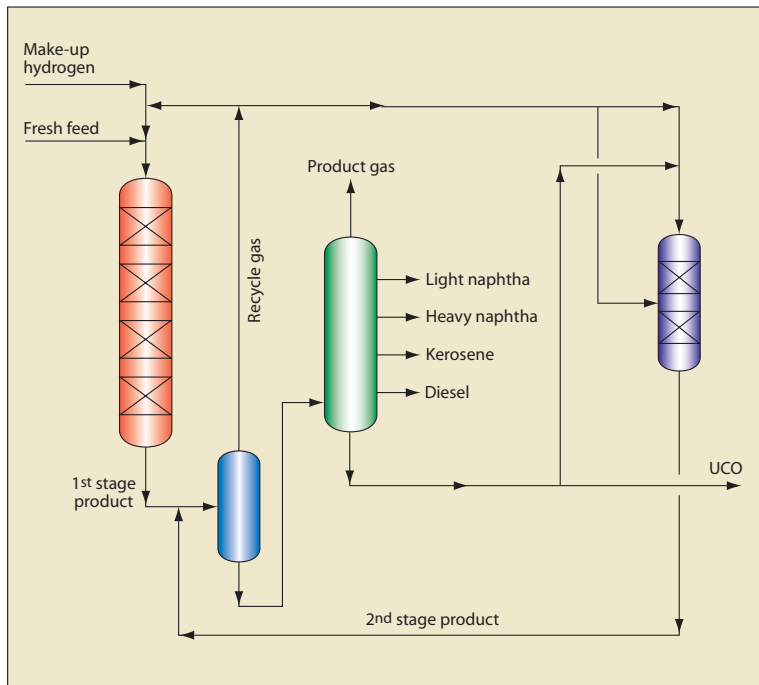
Figure 5 TSR Isocracking

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. This increase in activity reduces diesel yield by 2%, while no change in kero yield is observed for either catalyst. When comparing the two formulations, ICR 183 showed a 1.5% increase in heavy naphtha yield and a gain of 1–2.5% in light naphtha. 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. It was recently commercialised by a US refiner.

A schematic of CLG's two-stage hydrocracker design is shown in Figure 5. 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 they are 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 minimise overcracking of the higher value products. For years, CLG's ICR 120 catalyst, an amorphous catalyst made by proprietary cogellation technique, was the primary 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 expecta-

in selectivity. ICR 160 also yields significantly less light naphtha and gas make than 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, improving diesel yield by 1% to almost 3% without decreasing kero selectivity. In addition, naphtha yield was decreased by about 1.5%. 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 of ICR 160*.

Maximum jet and naphtha

ICR 183 was commercialised 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, as well as both the first and second stages of 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

tions, with significant improvements in product selectivity. In fact, the shift in product slate has been so dramatic that the refiner reported 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 per cent. The overwhelming success of ICR 240 is an excellent example of the large impact that a catalyst improvement can have on refining economics.

The single-stage reverse-staging (SSRS) process was first publicly introduced by CLG at the NPRA Annual Meeting in March 2005 by Ujjal Mukherjee.[2] Mukherjee mentions in his review that a major refiner in China was scheduled to start up the first SSRS unit. The following discussion is a succinct review of the key SSRS processing benefits and typical product qualities reported from the first guarantee test run of this unit. In addition, the most recent application of this process for a CLG licensee who is utilising this technology to revamp their existing TSR unit (to increase throughput and extend run length) is discussed.

Key process benefits

A schematic of CLG's SSRS flow scheme is shown in Figure 6. 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 for an SSOT or SSREC. The obvious difference between the TSR configuration shown in Figure 5 and the SSRS configuration shown in Figure 6 is the effluent from the second stage flows directly to that the inlet of the first stage, which provides the following benefits over a conventional TSR configuration:
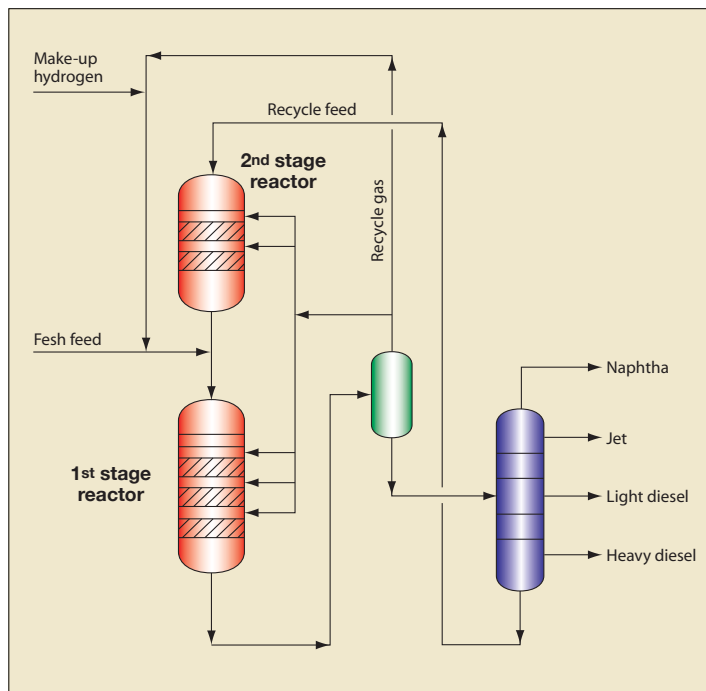

Figure 6 SSRS Isocracking

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

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 summarises 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 article.

| 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 sulphur, ppmw	30	‹3
Diesel flash point, °F	154	186
Diesel cetane number	55	61

Table 1
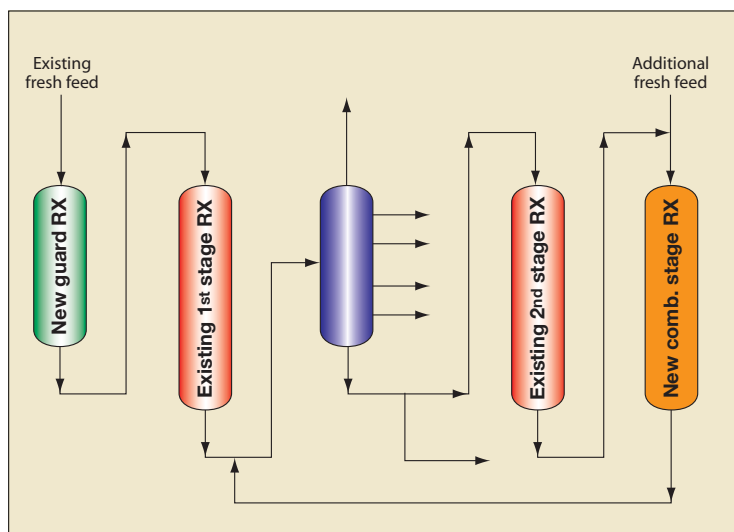
Figure 7 Revamp configuration using reverse staging

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 7 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.

Conclusion

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.

This paper is a modified version of a more detailed paper with 33 graphs and presented at the March 2009 NPRA Annual Meeting in San Antonio, Texas. It is a continuation of catalyst discussions initiated by CLG's Jim Vislocky and Dave Krenzke,[1] and follows the development and commercialisation of five recently developed CLG Isocracking catalysts.

Resid Hydrotreating, LC-Fining (LC-FINING), Isotreating (ISOTREATING), Isocracking (ISOCRACKING), Isodewaxing (ISODE-WAXING), Isofinishing (ISOFINISHING), TSR, SSOT, SSREC and SSRS are marks of Chevron Lummus Global.

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