



Don't be  
medieval,  
make more  
diesel!





**Bi-Zeng Zhan and Theo Maesen, Chevron Lummus Global, USA, Jay Parekh and Dan Torchia, Advanced Refining Technology, USA, describe how catalyst technology approaches and processing tactics can be used to optimise hydrocracker unit operation in order to meet the future needs for diesel and gas oil production.**

In a world of ever tighter fuels specifications and ever fewer ways to process poor quality feedstocks, hydrocracking has become firmly entrenched as the lead refinery conversion process. Over the course of the last decade, hydrocrackers have been asked to produce greater volumes of distillate, including ultra low sulfur diesel (ULSD), and at higher levels of operating severity including increased throughput. If one currently has a hydrocracker, one is probably running well over original design capacity and at considerably higher operating severity than that of the original design. Few refinery units can accommodate such a large variation in feeds, products, and throughputs while continuing to manufacture environmentally friendly products.

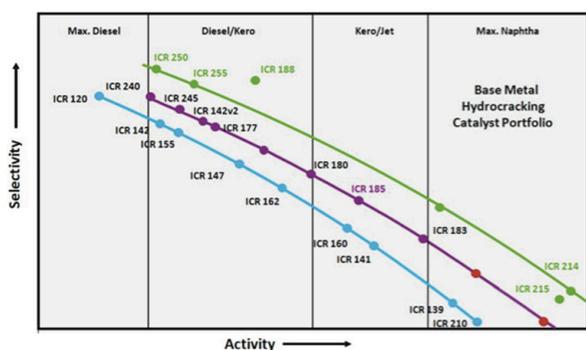
At the heart of a hydrocracker is the catalyst system. This typically consists of several carefully optimised individual catalysts working closely together. This article will describe how some of these maximum middle distillate catalysts are developed, selected, and how they maximise value in commercial operation.

In early 2013, Advanced Refining Technology (ART) and Chevron Lummus Global (CLG) announced an agreement in which

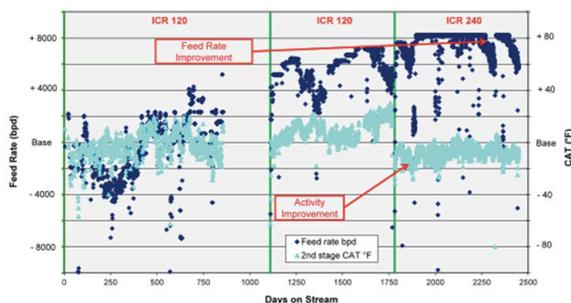
ART has an exclusive right to sell CLG's hydrocracking and lubes hydroprocessing catalysts to petroleum refiners worldwide for unit refills while CLG continues to sell them in licensed units as first fills. This agreement establishes ART as a single point of contact for all hydroprocessing catalyst needs, which dramatically streamlines hydroprocessing catalyst supply and the technical service focus for refining customers. CLG's depth of technical expertise remains available for the refiner who requires process technology. As an illustration of the retained synergies between ART and CLG, this article addresses catalyst technology approaches and processing tactics that optimise hydrocracker unit operation in order to meet the future needs for diesel and gas oil production.

### **Increased demand, shift to diesel**

Despite fluctuating oil prices the global consumption of petroleum products continues to grow, particularly as a result of the expanding Asian economies. Economic development in China and India has resulted in an increased number of cars and trucks, escalating the demand for transportation fuel.



**Figure 1.** Each newer generation catalyst lowers the reactor temperature required to achieve conversion target (i.e. extends run length).



**Figure 2.** Improved activity with ICR 240.

**Table 1.** Advanced performance of ICR 250 over ICR 240 for high aromatics feed in cycle operation

WBAT, °F	-20
C <sub>4</sub> , Wt%	-0.7
Naphtha (C <sub>5</sub> - 250 °F), Wt%	-0.9
Kerosene (250 - 250 °F), Wt%	+1.2
Heavy diesel (550 - 700 °F), Wt%	+0.3
Total distillates (250 - 700 °F), Wt%	+1.5
H <sub>2</sub> consumption, ft <sup>3</sup> /bbl	-50
Kerosene freeze point, °C	Base
Heavy diesel cetane point, °C	Base
Heavy diesel cloud point, °C	Base
Dewaxed UCO VI	+4

As the inventor of the modern hydrocracking process, Chevron was the first global operating company to provide catalysts, hardware, or both that afforded shifting existing hydrocracking units from maximum naphtha production to maximum middle distillate production. Since the 1980s Chevron has been a market leader in developing catalysts for maximum middle distillate production (especially diesel) as the demand for these distillate fuels expanded in Europe, the Middle East, China, and India. Since the 1990s CLG has been a market leader in licensing new hydrocracking units geared toward maximum middle distillates production, being awarded more than 50% of the new licensed units. Key to Chevron's early leadership in maximum middle distillate production was amorphous catalysts made by the so

called cogelation technique (e.g., ICR 106, ICR 120). For many years these cogel catalysts were the premier catalysts of choice in the industry for high quality middle distillate production.

The commercialisation of ICR 240 in the early 2000s marked the completion of a portfolio of catalysts that represent a dramatic improvement over the cogel catalyst technology. With the completion of the portfolio many improvements came to full fruition, comprising innovations to both the crystalline and the amorphous parts of the catalysts, innovations to the base metal emplacement process, and enhanced quality control.

Since the early 2000s new generations of catalyst have been added. The current CLG-ART portfolio of catalysts affords fully optimising a hydrocracking unit from maximum middle distillates production to maximum naphtha production within the unit's operational envelope to meet the changing demands from the pertinent transportation fuels markets.

In the remainder of the article the authors will cover the technical developments that led to the creation of ICR 240 as the maximum distillate selective catalyst of choice by over a dozen commercial units to maximise distillate production as well as the latest generation of maximum middle distillate catalyst, ICR 250.

## Diesel selective hydrocracking catalysts

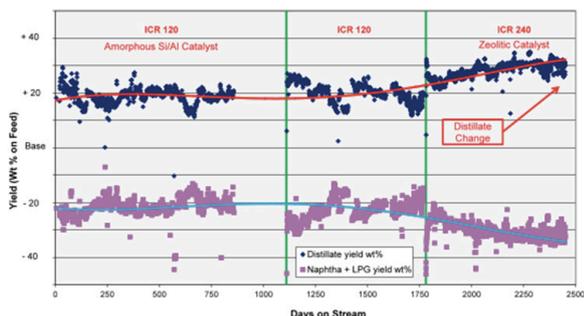
Hydrocracking catalyst design involves the careful tuning of at least two key catalyst functionalities, a (de)hydrogenation function and a cracking and isomerisation function. The metallic active sites afford hydrogenation and dehydrogenation. These base metal sulfide sites are located in the approximately 10 nm pores of the bulk of the catalyst. The acidic sites afford cracking and isomerising of hydrocarbons. These sites are located both in the approximately 1 nm pores of the zeolites and in the approximately 10 nm pores of amorphous silica alumina components. Optimising and varying the combination of these acidic catalyst components provides a tunable acidic strength and a tunable pore size for meeting a wide spectrum of fuels production of different molecular sizes (e.g., naphtha, jet, diesel, lube oil, and their combination) to meet the need of the dynamic world market.

Balancing the metal and acid activities, i.e., the hydrogenation and the cracking activities, respectively, is the key to tailoring a catalyst for the desired product slate. Ideally a hydrocracking catalyst preferentially converts heavier hydrocarbons to primary cracked products and avoids secondary cracking of the primary cracked products to undesirable lighter products. Ideal hydrocracking catalysts favour isomerising paraffinic intermediates and retaining paraffinic branches of naphthenic components for improved cold flow properties of both middle distillates and unconverted oil (UCO). UCO can be utilised as a superior base oil feedstock for lubricant oil production.

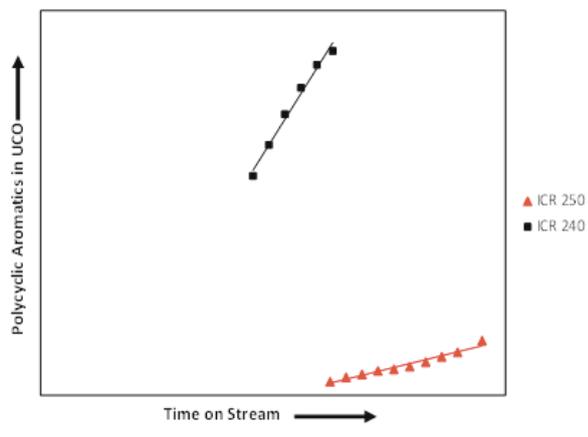
The strength of the acidic sites and the pores that surround them, particularly the confined environments of zeolites and of amorphous silica aluminas offer controllable scission locations to tune the reactants and products at a molecular level. With decades of research experience in zeolite synthesis and application, Chevron were able to control the location and strength of the acid sites, so as to minimise undesirable secondary cracking. The development of the diesel selective hydrocracking catalyst ICR 240 is a demonstration of this breakthrough technology to convert heavy vacuum gas oil very selectively into diesel. The

**Table 2. Advanced performance of ICR 250 over ICR 240 for high paraffin feed in recycle operation**

WBAT, ° F	-20
C <sub>4</sub> -, Wt%	+0.2
Naphtha (C <sub>5</sub> - 290 °F), Wt%	-2.3
Kerosene (290 - 700 °F), Wt%	+2.0
Diesel properties	
Viscosity @ 40 °C	Base
Cloud point, °C	-4
Density, g/mL	Base



**Figure 3.** Improved distillate yield with ICR 240.



**Figure 4.** Advanced hydrogenation performance of ICR 250 over ICR 240 in polycyclic aromatics saturation for high aromatics feed in recycle operation.

introduction of a tuned zeolite and a tuned amorphous silica alumina to a hydrocracking catalyst significantly enhanced catalyst activity, life, and diesel selectivity in comparison with its predecessor catalyst, ICR 120. It is worth noting that the high diesel selectivity achieved with ICR 240 is without the requirement, hassle, and safety concerns around ammonia titration throughout the operating cycle.

Results in Figures 2 and 3 illustrate the benefits of utilising ICR 240 in a commercial unit. As is typical, this hydrocracker was running at 110% throughput of the original design and it was near 100% utilisation. As throughput increased over design rates, LPG and gasoline handling capability in the unit became the

bottleneck limiting any increase in production. The replacement of the second stage hydrocracking catalyst ICR 120 by ICR 240 reduced the yield of LPG and naphtha by 10%. The implementation around 1800 days after initial startup yielded roughly 10 wt% gross increase in distillate yield.

Recently, a new technology was introduced for manufacturing Chevron ISOCRACKING® catalysts. This technique allows optimising the size, location, and dispersion of the base metal sulfide nano particles. This advance resulted in commercialisation of a new hydrocracking catalyst, ICR 250, in the early 2010s with further performance enhancements.

Results in Table 1, Table 2, and Figure 4 demonstrate that ICR 250 provides many advantages over ICR 240 including activity and distillate selectivity, aromatics saturation (particularly polycyclic aromatics saturation), and controlled hydrogen addition to desired products.

As compared to ICR 240, ICR 250 greatly enhances the activity and the selectivity toward mid distillate in the second stage hydrocracking application for high aromatics feed (Table 1). ICR 250 enhances aromatics saturation resulting in an improved smoke point of the jet and a markedly improved stability of the viscosity (quantified by a higher viscosity index or VI) of the UCO.

ICR 250 allows control of hydrogenation performance and manages where the hydrogen addition occurs and to what extent. It minimises hydrogen addition to low value products such as LPG and naphtha and provides value to product upgrade or UCO. ICR 250 further enhances hydrogenation of polycyclic aromatics to prevent their accumulation in UCO. The accumulation rate of polycyclic aromatics of ICR 250 was reduced by more than 80% versus ICR 240 (Figure 4). This is particularly important in recycle operation, resulting in improved catalyst life, and reduced bleed rate of the recycle stream, resulting in higher conversion. As a result, ICR 250 consumes significantly less hydrogen and provides for a longer operating cycle.

The enhanced activity and mid distillate selectivity of ICR 250 was also demonstrated with highly paraffinic feed, as shown in Table 2. The increased selectivity indicates that ICR 250 tends to not overcrack long chain paraffins and/or to retain paraffinic branches of naphthenic components. It enhanced intermediate isomerisation to improve diesel cold flow properties quantified by diesel cloud point lowered by 4 °C. Results of diesel density and viscosity, and comparable carbon number distribution (not given) support that the improved cold flow properties illustrate that the diesel maintains its boiling range.

## Conclusion

Deployment of a combination of an optimum catalyst system with major process design changes epitomises how a combination of ART catalyst know how and of CLG process knowledge represents a unique value proposition. In the Chevron tradition, ART continues to expand the ICR catalyst portfolio. ICR 250 is the latest addition to the portfolio. Through its careful design, this robust catalyst further enhances middle distillate yield and enhances run length at optimum hydrogen consumption. 

## References

1. KODACHENKO, N., YOON, A., MAESEN, T., TORCHIA, D., BROSSARD, D., AM-12-41 'Hydroprocessing to Maximize Refinery Profitability', AFPM Annual Meeting, March 11 - 12, 2012.