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Hydroprocessing to Maximize Refinery Profitability

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Abstract

Refineries are continuously challenged to produce more and cleaner products from a broader range of feeds, preferably with limited or no capital investments.

In the short term, changes in spot market prices for both crude oil and products have forced refiners to reevaluate their process options and planned investments in search of higher operational flexibility. This has led to investments in hydrocracking, for hydrocrackers are often a key factor in achieving greater refinery agility and in staying in sync with market fluctuations so as to maximize refinery margins.

In the medium term the global demand for refined products continues to grow at about 1.4% per annum, and the demand for refined products continues to shift from gasoline to middle distillates. This reinforced a drive to invest in hydrocracking, for hydrocrackers are capable of processing a wide variety of feedstocks and of producing environmentally benign products, particularly clean diesel.

We show that low-cost changes in catalyst systems can significantly enhance operational flexibility and increase returns on investment. Clearly catalyst system selection is more important than ever before, because it is critical to proper unit utilization and profit maximization.

This paper discusses recent examples of refinery margin enhancements that were achieved through the judicious deployment of CLG processes and catalysts. In keeping with a tradition spanning over half a century, CLG development and commercialization continue to meet the refining industry's needs. Commercial data illustrate the competitive advantage that ISOCRACKING processes and ISOCRACKING[®] catalysts can bring to your refinery today.

ISOCRACKING History and Factors Affecting Refining Industry

History

The history of ISOCRACKING dates to the late 1950s, when the modern hydrocracking process was developed by the California Research Corporation, a research division of the Standard Oil Company of California (this later became the Energy Technology Company of Chevron Corporation). Soon after that, numerous ISOCRACKING units were licensed worldwide. The first ISOCRACKING plant licensed to a U.S. refinery was started up in 1962. Today ISOCRACKING technology is licensed by Chevron Lummus Global LLC (CLG), a joint venture of Chevron and Lummus Technologies utilizing industry-leading operating and design experience of both companies.

Most of the hydrocracking units licensed in the United States during the 60s through 90s have been designed for production of motor gasoline (mogas). This design allowed refiners to produce large quantities of heavy naphtha that was further reformed into gasoline and hydrogen. Because the light naphtha produced in these mogas mode hydrocracking units using Chevron catalyst contained unusually high quantities of isoparaffins in relationship to normal paraffins (providing high octane values), the hydrocracking process was given its unique name – ISOCRACKING. While the U.S. market favored gasoline, the international market demanded more middle distillates. Responding to that market need, many ISOCRACKING units maximizing middle distillates have been licensed.

Factors Affecting Refining Industry

Since the initial inception of hydrocracking, the technology has expanded to cover a broad range of feedstocks, products and process configurations to meet market and customer requirements. These hydrocrackers are optimized to maximize profits for the refiner. Today, refiners are faced with new challenges based on ever-stricter product environmental regulations, higher throughput and poorer feed quality.

Increased Demand, Shift to Diesel

Despite fluctuating oil prices the global consumption of petroleum products continued to grow throughout the first decade of the 21st century (overall consumption in U.S. and Europe has not increased). The growing market demand has been dictated by expanding Asian economies. Economic development in China and India has resulted in an increased number of cars and trucks, causing escalating demand for gasoline and diesel.

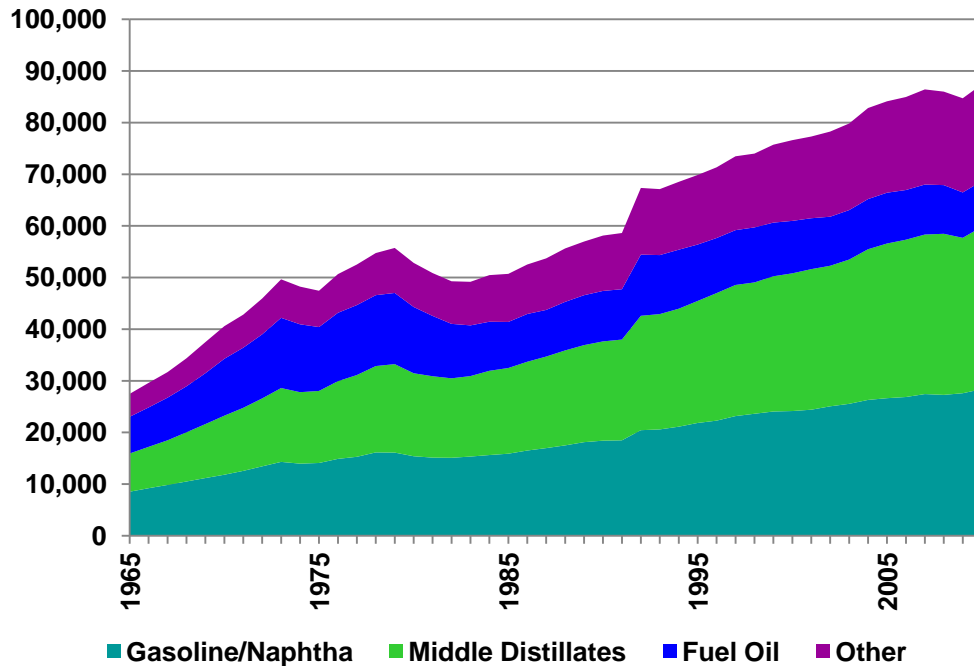


Figure 1 – World consumption growth, 1000 barrels per day. The dramatic increase in consumption in 1993 is an artifact as a result of a change in data administration in the former Soviet Union.

Source: BP World Statistical Review of World Energy, 2011¹

In early 2000, greatly influenced by European markets, global product demand has shifted towards middle distillates. In the late 1990s Europe led an effort to reduce greenhouse gas emissions. The automotive industry has signed a voluntary agreement with the European Commission to reduce CO₂ emissions. This, in turn, led to a shift from gasoline- to diesel-fueled vehicles. Aside from seasonal market fluctuations at times requiring more gasoline, from 2005 the differential between demand for middle distillates versus gasoline has been overwhelmingly in favor of middle distillates. Figure 2 shows the dominance of middle distillate demand in Europe and Asia and the rapid growth of middle distillates in Europe.

¹ Source: BP World Statistical Review of World Energy June 2011
http://www.bp.com/assets/bp_internet/globalbp/globalbp_uk_english/reports_and_publications/statistical_energy_review_2011/STAGING/local_assets/pdf/statistical_review_of_world_energy_full_report_2011.pdf

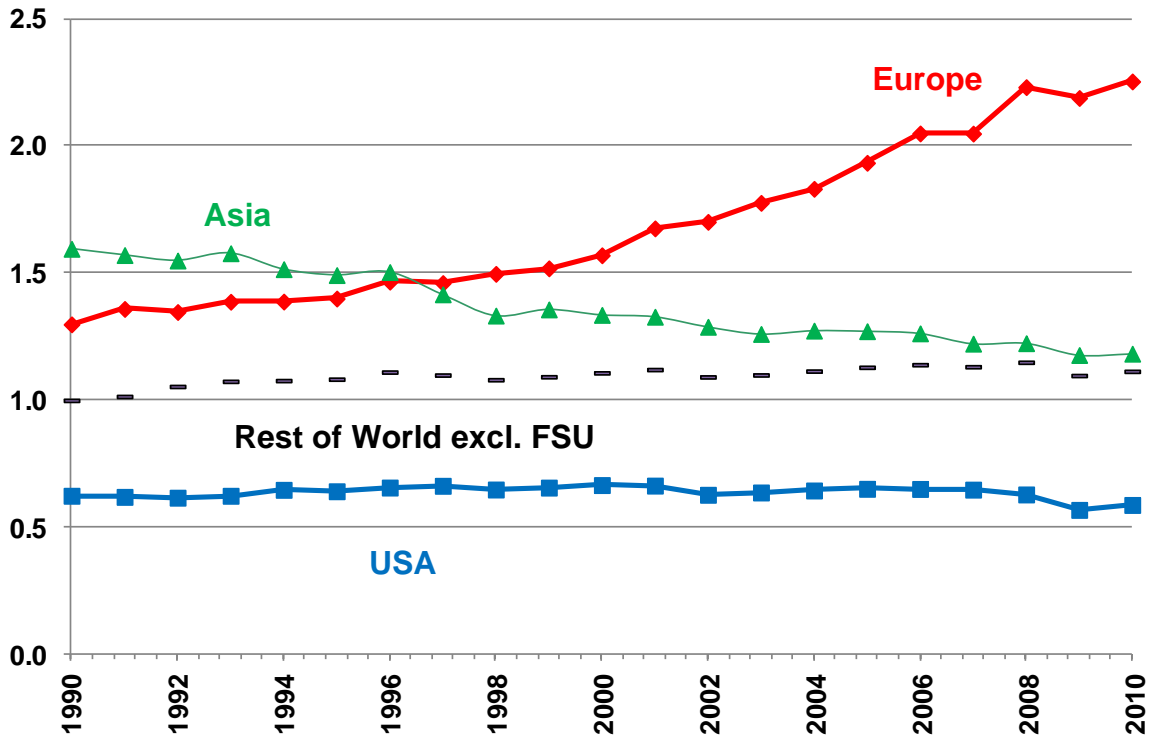


Figure 2 – Ratio of the demand for middle distillates/gasoline and naphtha per region

Source: BP World Statistical Review of World Energy, 2011¹

U.S. refiners, whose hydrocracking processes were primarily designed for mogas, had to adjust to the new reality of growing demand for middle distillates. On the other hand, European refiners, who already owned and operated middle distillate-maximizing technologies, had to quickly increase production using existing facilities. What is the least expensive way for a refiner to adjust to the changing market demand: invest in a new technology or modify an existing process? This article will show how one U.S. refiner found an optimal solution.

New Unconventional Crude Sources

Rising oil prices and shrinking profit margins have forced refiners to look for more economic crude sources. What may not have been economic a decade ago has become profitable today. Now refiners are presented with a variety of unconventional crude sources:

- Bitumen
- Extra Heavy Oil
- Biofuel
- CTL
- GTL
- Oil Shale

Each refinery situation is somewhat different and so is the crude source used there. The CLG ISOCRACKING process is versatile and offers a variety of configurations that can be customized to a particular crude composition and product specifications.

ISOCRACKING Innovations to Improve Profitability

Generally, options for enhancing the product slate or the productivity of a hydrocracker are more attractive the smaller the size of the required capital investment. This part of the paper focuses on options that enhance the desired product make with only a minimum or no investment of capital, and preferably with a concomitant reduction in operating costs.

A change in reactor temperature is the most straightforward option to achieve a shift in product slate or in production rate. An increase in temperature increases the conversion of both the original feed molecules and the initial product molecules. The cracking of the initial (diesel or middle distillate boiling range) product molecules shifts the product slate toward lighter products (naphtha, liquefied petroleum gas). Mild or partial conversion single-stage once-through hydrocrackers are particularly amenable to operating at a higher temperature, for they generally run far from full conversion. In two-stage hydrocrackers, a change in temperature affords shifting conversion from the first to the second reactor (or vice-versa), which shifts functionality largely from hydrotreating-based to hydrocracking-based catalysts.

A change in recycle cut point in either a single-stage recycle or a two-stage recycle hydrocracking configuration affords shifting the operation towards heavier or lighter products in response to market demands. A typical two-stage recycle configuration will even allow toggling between a jet/naphtha and a diesel mode of operation provided the downstream fractionation section can harvest the products. Modification of the combined fresh and recycle feed rate will impact the per-pass conversion in either a single-stage or two-stage recycle hydrocracker, and, therefore, the hydrocracker's product slate. Naturally, all of the operational options for modifying the product slate described thus far require robust catalysts that can withstand dramatic changes in operating conditions.

Catalysts play a key role in the manufacture of hydrocracking product slates that remain commensurate with the demand from the refined oil product market. They afford this desired flexibility at no capital investment through either a change in catalyst or through the use of a catalyst that affords operating in one regime when the demand for naphtha or jet drives the refinery margin and in another regime when the demand for middle distillates dominates. Normally, such a 'flexible' catalyst system will not be able to do as well as a dedicated naphtha or middle distillates catalyst system, but it can afford an excellent compromise when market conditions fluctuate frequently. Figure 3 illustrates that CLG's well-established catalyst portfolio provides a wide range of solutions to meet such product selectivity and product quality targets. The performance of CLG's world-class catalysts provides a clear competitive edge to its customers. Table 1 lists applications of CLG catalysts, along with estimated benefits, to demonstrate the high returns that you can realize from your investment in CLG catalysts. It should be noted that the benefits listed can be additive and are frequently accomplished at the same time. Thorough evaluation and tailoring of the catalyst system toward satisfying specific refinery needs often allows multiple benefits to be realized at the same time — greatly enhancing refinery profitability. In many cases it is actually possible to simultaneously reduce unwanted products, reduce hydrogen consumption and increase cycle length.

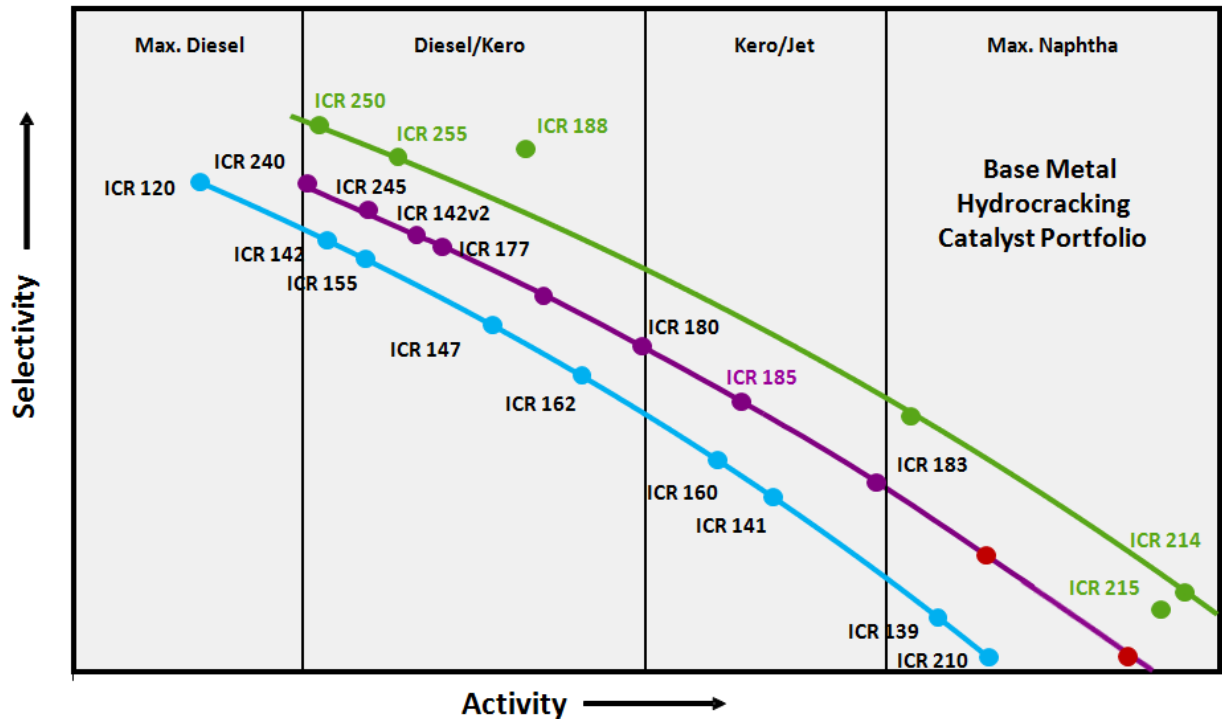


Figure 3 – The ISOCRACKING catalyst portfolio consists of several generations of catalysts. Each newer generation of catalysts lowers the reactor temperature required to achieve conversion target (i.e., extends run length) while maintaining the product slate or—conversely—improves the product yield structure at target activity and run length.

Table 1 – Representative economics of hydrocracker improvements that require little or no capital investments [1]

Item	Result	Estimated Benefits
Longer Catalyst Cycles	Improved Utilization	\$1 MM Maintenance \$2.5 MM Throughput
Increased Throughput	More Valuable Products	\$5.0 MM/Annum
Enhanced Product Properties	Higher Blending Values	\$1 MM/Annum

The first commercial hydrocrackers made extensive use of so-called cogel catalysts which combined amorphous aluminosilicate components with a highly dispersed base metal sulfide component. However, it was soon realized that adding a crystalline aluminosilicate component or “zeolite” offered substantial advantages. One of the major advantages of catalysts containing zeolites is their markedly-reduced coking tendency, which results in significantly improved catalyst stability and run length. This is particularly important when heavy feedstocks are processed, or when high rates of catalyst deactivation are major process constraints. The application of zeolite-based catalysts in Chevron’s refining system has been an important factor in processing increasingly heavier feedstocks and associated economic benefits, while retaining the benefits of the early generation catalysts.

Another important characteristic of catalysts with zeolites, as compared to fully amorphous catalysts, is a high concentration of acid sites, which results in a high activity for hydrocracking. This higher hydrocracking activity indicates that increasing the fraction of USY zeolite activity in a catalyst reduces the required initial reactor temperature. Combined with the reduced rates of coke-induced deactivation inherent to optimized zeolites, this further enhances catalyst life (Figure 4).

1st Stage Cracking Catalyst CAT and NCAT Trends

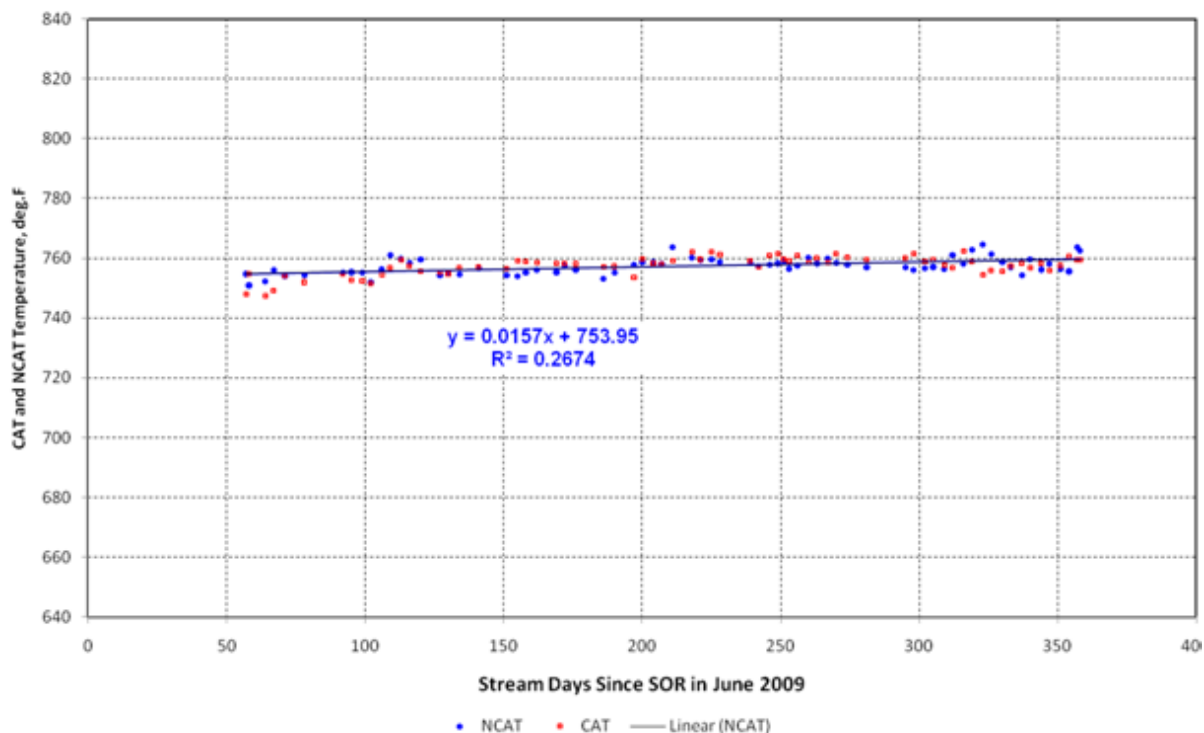


Figure 4 – At one of CLG’s customers ICR 183 has achieved unprecedented operational stability in first stage operation, reducing the activity decline to as little as 0.45°F/month.

Since the acid sites in USY zeolites are located inside of micropores (~1 nm in diameter), catalysts containing USY zeolites preferentially adsorb and convert the hydrocarbon fraction that boils in the 500-850°F range into jet and lighter products [2]. Since the acid sites in amorphous aluminosilicates are located inside of mesopores (~10 nm in diameter), fully amorphous catalysts preferentially adsorb and convert the fraction in the highest boiling range of the feed into middle distillates [2]. This difference in conversion preference implies that increasing the fraction of USY zeolite activity at the cost of the amorphous component in a catalyst shifts the hydrocracking product slate from middle distillates toward naphtha.

Since USY zeolites enhance activity and life at the cost of middle distillate selectivity, there is a tradeoff between activity and life on the one hand and selectivity on the other hand (Figure 3). Which level and flavor of USY zeolite activity is desirable depends on factors such as the

hydrocracker configuration, the hydrocracking process conditions, the way the hydrocracker is integrated into the refinery and the demands for refined products in the relevant markets.

ICR 183 affords an example of a catalyst with a high USY zeolite activity that was developed to improve the activity and stability for processing heavy and difficult feedstocks while maximizing the production of either high quality middle distillates or the production of naphtha. Through its tailored USY zeolite activity this catalyst exhibits great flexibility in operational regime and desired product slate. It has been used in single-stage once-through and recycle operation, and in both stages of a two-stage configuration. Figure 4 demonstrates the impressively low deactivation rate that can be obtained through the judicious use of ICR 183. As expected, the distillate product slate remains as stable as the catalyst activity.

For a duty as demanding as those described for ICR 183 catalyst usage, but for markets like those in Europe and Asia that exhibit a high demand for middle distillates (particularly diesel), a catalyst like ICR 185 is of interest. This catalyst, commercialized in 2011, is the latest member of a new generation of hydrocracking catalysts that tailors the pore size distribution of traditional catalysts and, thereby, introduces a hydrodewaxing capability. Traditional catalysts comprise ~1 nm wide USY zeolite pores, ~10 nm wide amorphous aluminosilicate pores and base metal sulfides. Advanced computational methods have established that wax adsorption and conversion requires zeolite pores about half as wide as those of USY [3]. Replacement of the ~1 nm wide USY zeolite pores with the optimum amount of these narrower pores enables ICR 185 to convert hydrocracking wax into isoparaffins in the middle distillate boiling range. These isoparaffins ensure a diesel (and jet) fraction with significantly improved cold flow properties as compared to the products made with a catalyst without such a dewaxing functionality. The lower USY activity of ICR 185 further enhances the middle distillate (particularly the diesel) yield as compared to ICR 183, at minimal loss of overall catalyst activity (Table 2). The dewaxing functionality in ICR 185 has exhibited a high resistance to fouling in commercial service; even under demanding second-stage recycle conditions. The commercially proven robustness and high distillate selectivity of ICR 185 make this catalyst attractive for refineries that want to improve both distillate yield and distillate cold flow properties.

In locations that exhibit an overriding demand for middle distillates, ICR 240 has been a major success since 2007 when it was put into commercial service. Recently, ICR 240 had to relinquish its position as CLG's most middle distillate-selective catalyst to ICR 250. ICR 250 further enhances the middle distillate yield through an improved base metal sulfide activity. Particularly in recycle operation, this results in a significantly enhanced diesel (and middle distillate) yield (Table 3).

Table 2 – Replacement of USY zeolite with a dewaxing functionality in a traditional catalyst formulation results in ICR 185. As compared to ICR 183, ICR 185 greatly enhances the selectivity toward middle distillates (particularly heavy diesel) (top), and these middle distillates exhibit significantly improved cold flow properties (bottom).

WBAT (°F)	+15
C ₄ - (Wt %)	-0.3
Light Naphtha C ₅ -180°F (Vol %)	-0.8
Heavy Naphtha 180-250°F (Vol %)	-2.7
Kerosene 250-550°F (Vol %)	+0.8
Heavy Diesel 550-700°F (Vol %)	+3.5
Middle Distillates 250-700°F (Vol %)	+4.2

Jet / Smoke Point (mm)	Base
Freeze Point (°C)	-3
Heavy Diesel / Pour Point (°C)	-6
Cloud Point (°C)	-10
Cetane Index	-1
UCO N / S (ppm / ppm)	Base/Base
Pour Point (°C)	-4

Table 3 – Enhancement of the base metal sulfide dispersion in a traditional catalyst formulation results in ICR 250. As compared to ICR 240, ICR 250 greatly enhances the activity and the selectivity toward jet. The enhanced aromatics saturation results 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 unconverted oil.

WBAT (°F)	-20
C ₄ - (Wt %)	-0.7
Naphtha, C ₅ -250°F (Vol %)	-0.6
Jet, 250-550°F (Vol %)	1.1
Diesel, 550-700°F (Vol %)	Base
Mid-Distillates, 250-700°F (Vol %)	1.1

Jet / Smoke Point (mm)	-4
Freeze Point (°C)	Base
Heavy Diesel / Pour Point (°C)	Base
Cloud Point (°C)	Base
Cetane Index	Base
UCO Dewaxed VI	+4

Clean Fuels Project at U.S. Refinery A

This Clean Fuels Project at Refinery A is an excellent example of using hydroprocessing knowledge and ingenuity rather than large outlays of capital to address changes in product specifications and, at the same time, increase refinery profitability. Figure 5 shows the configuration of Refinery A prior to implementing the Clean Fuels Project. The heart of the residue conversion capability at Refinery A is the coker. Hydroprocessing units were installed upstream and downstream of the coker. The residuum hydrotreater removed sulfur and carbon residue from part of the feed to the coker. This severe hydrotreating caused a reduction in the amount of coke produced by the coker (thereby increasing the liquid volume yield of the refinery), ensured that the coker would produce sponge coke and reduced the sulfur content of the sponge coke produced (thought to be important at the time to find a ready market for the refinery's coke). The coker gas oil hydrotreater removed nitrogen and sulfur from the fluid catalytic cracking (FCC) feed which included straight-run vacuum gas oil (VGO) and heavy coker gas oil streams to meet then-current product specifications. VGO product from the residuum hydrotreater was also sent as feed to the FCC.

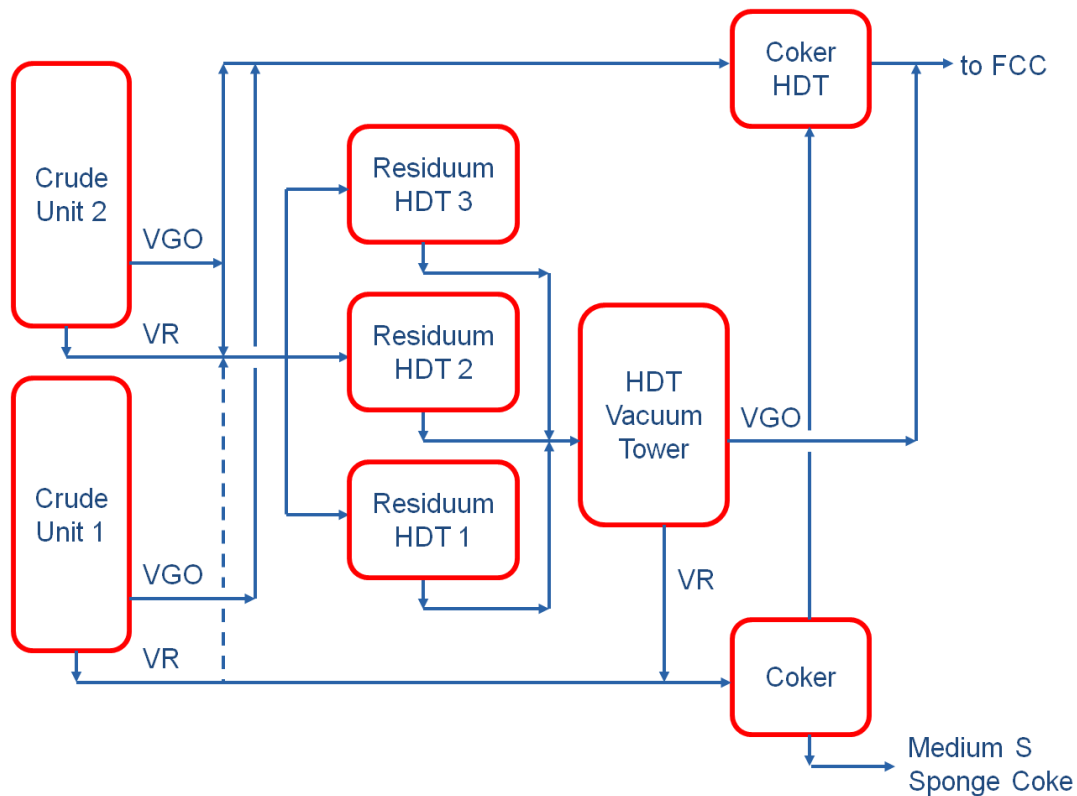


Figure 5 – Configuration before Clean Fuels Project

In the early 2000s, refiners became aware of the severe tightening in on-road diesel maximum sulfur from 500 ppm to 15 ppm by mid-2006 to produce ultra-low sulfur diesel (ULSD). Motor gasoline sulfur limits were also being decreased from almost 200 ppm to less than 30 ppm. In order to meet the coming requirements for making ULSD, many refiners built for-purpose diesel hydrotreaters. Instead, Refinery A decided to take advantage of its large hydroprocessing capacity as well as recent advances in coker technology. The flow scheme for the refinery after

the Clean Fuels Project is shown in Figure 6. As part of the Clean Fuels Project, a vacuum tower was constructed and one was modified to increase the VGO cut point from the crude units and the heavy vacuum residue was sent directly to the debottlenecked coker without pretreating (by the residue hydrotreater). This was accommodated in the coker by moving to shorter, 12-hour, coke drum cycles and to the production of high sulfur shot coke. This allowed the refinery to free up the entire residue desulfurizer capacity to hydrotreat straight-run VGO and heavy coker gas oil to feed the FCC. A new gas oil filter was added at the coker to keep from overwhelming the feed filters in the downstream residue desulfurizer. This move freed up the gas oil hydrotreater to severely hydrotreat light gas oils and naphthas from the crude units and the conversion units to produce ULSD and low sulfur mogas.

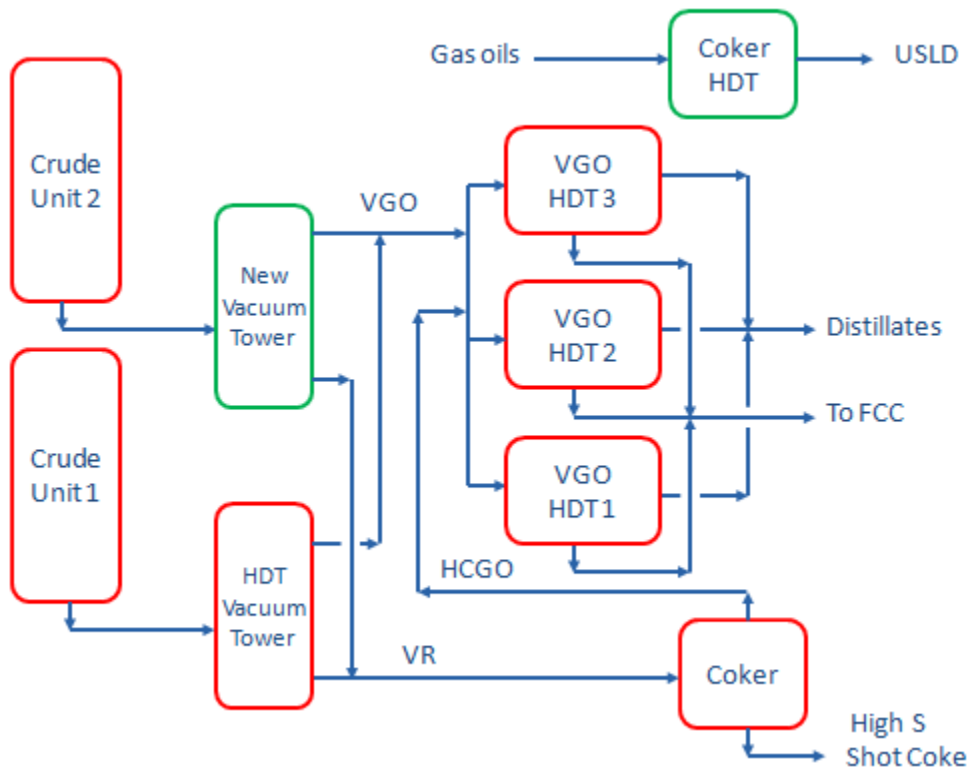


Figure 6 – Configuration after Clean Fuels Project

Changes to the residue hydrotreater are listed in Table 4. In each of the residue desulfurizer modules the reactors were originally piped in a parallel configuration consisting of two parallel reactors with multiple beds. Because of the lower viscosity of VGO feed compared to the heavy residuum that the hydrotreaters were designed for, and to take advantage of more catalyst beds and quench points, the parallel reactors in each module were repiped to be in series with a quench point added between reactors. Reactor internals were slightly modified to allow for the higher throughput per reactor cross-section area. Of course, the catalyst was changed from residuum hydrotreating catalyst to VGO hydrotreating catalyst of a slightly larger diameter (to accommodate the higher throughput per reactor area). Modifications were also made to the product fractionator and product handling areas of the former residuum hydrotreater.

Table 4 – Significant residuum hydrotreater modifications

- Change piping to parallel reactors to connect them in series
- Modify reactor internals to allow higher liquid flux rates (increase hole areas and replace mesh screens with Johnson Screen)
- New gas oil filter installed in the coker
- Improve feed filter elements for better filtration for feed from tankage
- Add quench line and flow controller to add quench gas between series reactors
- Improve reactor effluent air cooler (REAC) metallurgy
- Modify product fractionator for higher liquid rates

The modifications to the coker gas oil hydrotreater were less significant, as shown in Table 5. Here the reactor internals were modified to the then state-of-the art reactor internals because of the great impact that any reactor bypassing would have when producing 5 ppm sulfur diesel from feed containing over 1 wt % sulfur. Product fractionation and product handling sections were also modified to meet the new service and the catalyst type was changed to high activity diesel HDS catalyst. Table 6 shows the resulting feed and product inspections.

Table 5 – Significant coker gas oil hydrotreater modifications

- Update reactor internals with “Nautilus”
- Increase quench gas line as required
- Increase fractionator overhead condenser duty
- Install new heavy stripper reboiler on sidecut stripper
- Change piping to route diesel to existing salt driers
- Increase fractionator bottoms line size
- Change fractionator pumparound steam generators to cool diesel rundown

Table 6 – Yields and product qualities from converted coker gas oil hydrotreater

Product	Vol %	API	Sulfur, ppm
Gasoline	6.9	55.0	1
Diesel	97.0	40.7	10

The reconfiguration and debottlenecking was more capital efficient than constructing a dedicated diesel hydrotreater.

European Refiner Improves Margins

In anticipation of the robust demand for distillates, the Northern European refiner in this example had already invested in a relatively large hydrocracker in late 1990s. The product slate, as shown in Figure 7, was already moderately weighted toward distillates. The hydrocracker was the main conversion unit in the refinery, as well as the main profit driver.

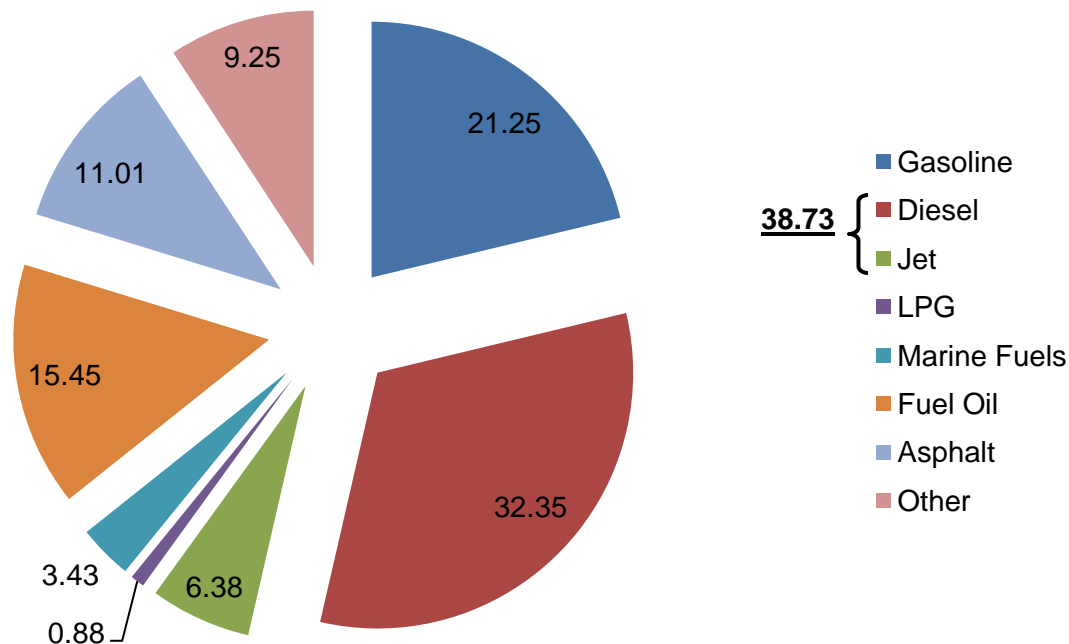


Figure 7 – Refinery product slate in 2006

The simplest and the fastest way to meet the rapidly-rising demand was to build more topping capacity. However, the economics on this investment was marginal. Taking real advantage of the market change and increasing the profitability of the refinery required a new conversion unit along with additional topping capacity. But, with limited capital at the time, funding both the topping project and a conversion project was deemed by the refiner to be beyond its reach. Instead, a refinery optimization study was initiated which identified that debottlenecking the hydrocracker combined with topping capacity addition was the highest return project.

As with many, this hydrocracker was already running at 110% throughput and was near 100% utilization. As such, the LPG and gasoline handling capability in the unit was limiting any further increase in production. Hardware solutions required large investment as well as costly downtime.

The refinery staff and CLG engineers and scientists reviewed the constraints and concluded that a catalytic solution, along with some operational changes, was quite feasible to achieve refinery objectives of higher throughput and higher distillate yields. Two steps were taken:

- The first-stage hydrocracker catalyst was switched out with a new generation, more active and distillate-selective type of catalyst to enable increased throughput and conversion without cycle length reduction. The fractionator operating targets were changed to draw the products to their appropriate (maximum and minimum) quality specifications.
- The second-stage catalyst in the hydrocracker was switched out from a largely amorphous catalyst type to a new generation zeolitic catalyst to further increase the distillate yield, reduce LPG and gasoline make, and improve cycle life.

The second change required a lot of convincing, both internally and externally, since the concept of zeolitic catalyst being more distillate-selective than amorphous catalyst had many

skeptics. However, success in the first step above and successful pilot plant tests at CLG laboratory convinced the refinery management to approve the implementation of the second step.

The end result is summarized in Figure 8 and Figure 9. The dramatic increase in distillate production is apparent from cycle to cycle as the improvements are implemented. The implementation of the first step around 1100 days after initial startup yielded an almost 8,000 barrel per day improvement in throughput while the distillate selectivity was maintained. The implementation of the second step around 1800 days after initial startup yielded roughly 10 % gross increase in distillate selectivity.

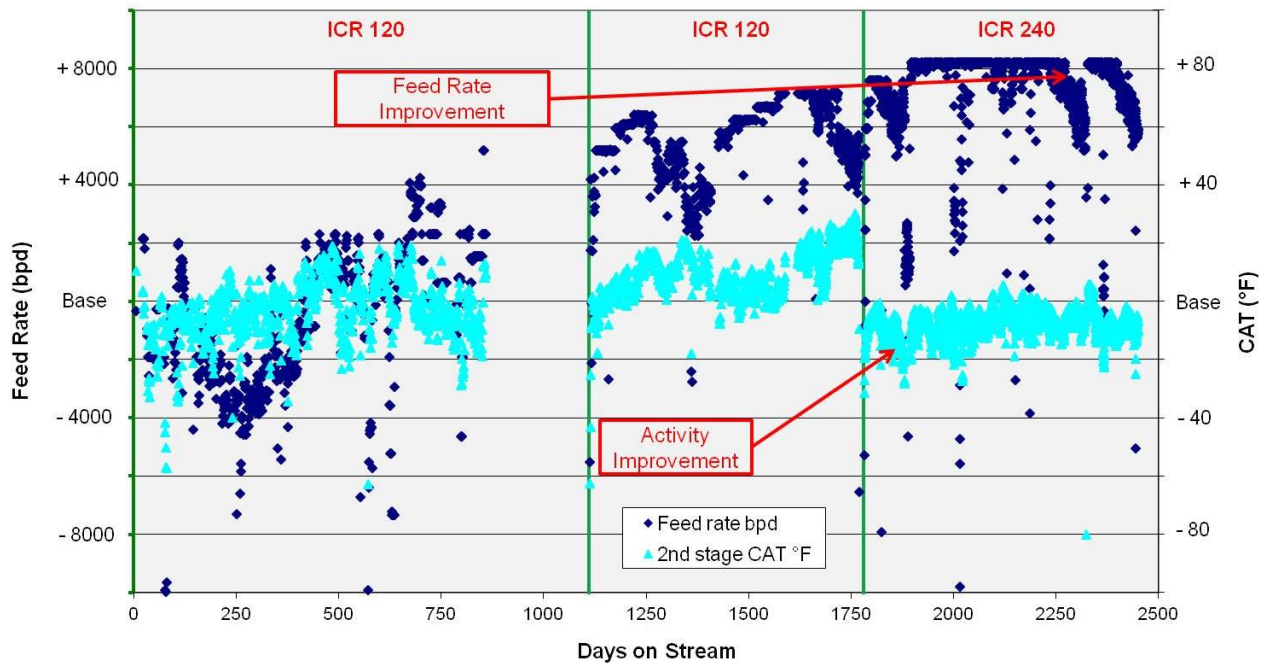


Figure 8 – Improved feed rate without cycle length reduction

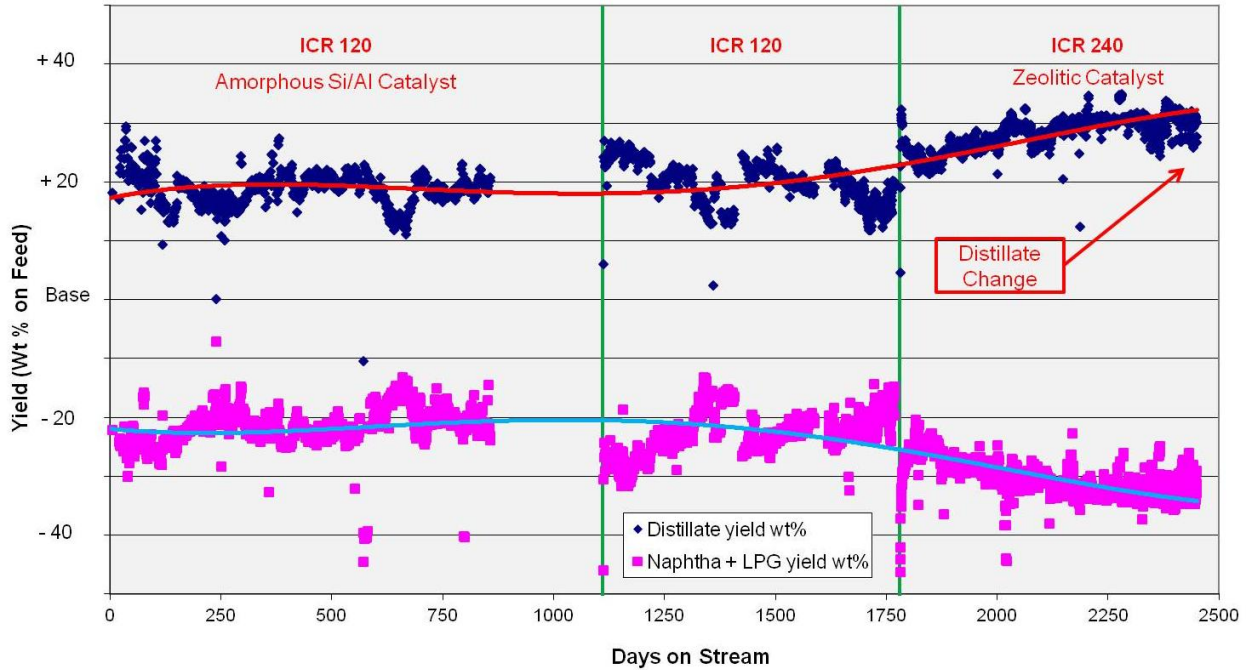


Figure 9 – Improved distillate selectivity

The gross margin improvement for the refinery was well north of \$50 million per annum, at \$10 per barrel crack spread and \$4 per barrel product differential. In summary, the catalyst solution achieved an almost 10% increase in the middle distillate product slate at this refinery as shown in Figure 10 to enable it to take full advantage of the shift in product demand.

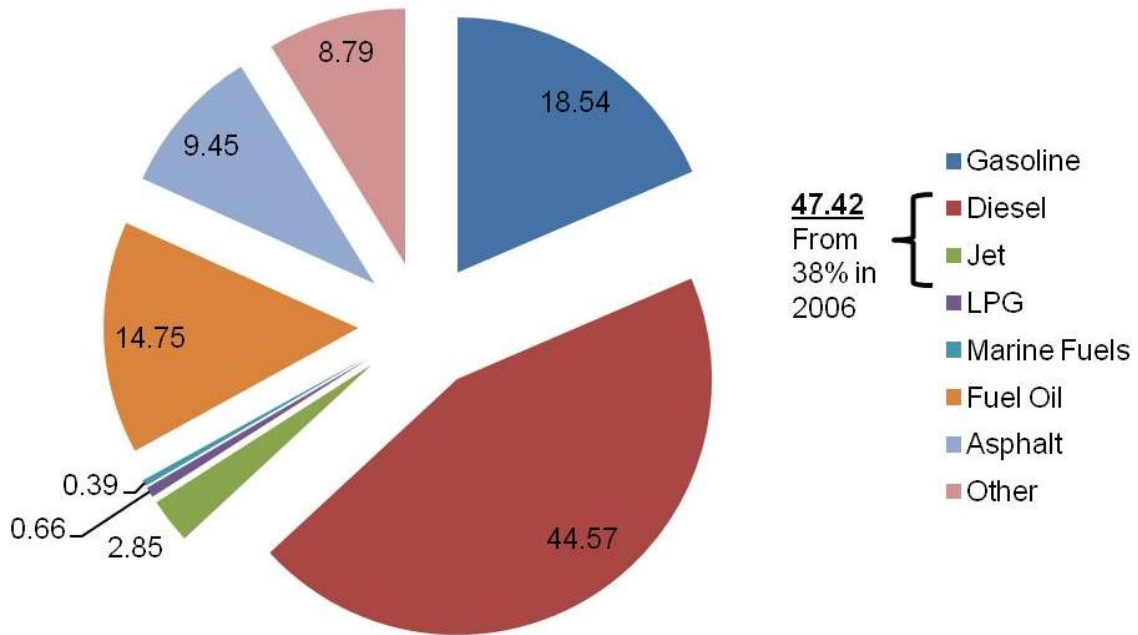


Figure 10 – Refinery product slate in 2010

Summary and Conclusions

Hydroprocessing has served our industry for well for over half a century and has been rapidly on the rise. As illustrated in the above examples, hydroprocessing has enabled greater refinery utilization by way of revamps or often simply by a catalyst change. Hydroprocessing units have enabled compliance with the ever-tougher product specs over the last several decades and often allowed for avoidance of large capital expenditures. Hydrocrackers and ULSD units make only the highest quality products available today, destroy non-saleable feedstocks in the process and produce volume gain as well. It almost seems too good to be true! Continued environmental pressure as well as the pressures of increased operating profit will ensure a prominent place for hydroprocessing well into the 21st century.

References

1. Groeneveld, L. R.; Maesen, T.; Torchia, D., Hydrocarbon Engineering (2010), 15(11), 39-40, 42, 44, 46-47.
2. Krenzke, Dave; Vislocky, Jim, Hydrocarbon Engineering (2007), 12(11), 57-58, 60-63.
3. Smit, Berend; Maesen, Theo L. M., Nature (London, United Kingdom) (2008), 451(7179), 671-678.