L. R. Groeneveld, T. Maesen and D. Torchia, Chevron Lummus Global,
focus on maximising hydrocracker economics with proper catalyst selection.

One of the toughest challenges refiners face today is how production of cleaner products from a broad range of feeds can be optimised at their refinery in these days with limited or no CAPEX. The demand for refined products, on a worldwide scale, is predicted to increase at a growth rate of approximately 1.4 - 1.5%/y and, since the economies in the Asia Pacific region are continuously expanding, the largest volume of growth is expected to emerge in that area. Furthermore, it is foreseen that the global refined product slate will experience a significant change from gasoline to diesel during the next decade(s). Obviously, the latter in combination with margin fluctuations, i.e. diesel versus gasoline, has forced refiners to reevaluate their process operations to assess the ability to shift production towards middle distillates at the cost of gasoline.

Continuous tightening of regulations and legislation, i.e. product specifications, has put refiners in an even more challenging market environment in their struggle to remain profitable. The presence of a versatile operating process option such as a hydrocracker makes these challenges more bearable as they generally have amongst the highest refinery base margins and usually the highest incremental margins. The built in operating flexibility to process a wide variety of feeds and to produce an assortment of very high quality, environmentally sound products make it a useful asset for improving refinery economics. As the above mentioned trends are expected to continue, each for its own reasons, catalyst system selection and/or optimisation has become more important now than ever before as it is the key to proper unit utilisation and maximum profit realisation. Flow schemes and process parameters may vary from one hydrocracker to another; however, most of the key drivers are similar and can be significantly influenced by catalyst selection, e.g. product selectivity, activity, etc.

Chevron Lummus Global (CLG) finds itself uniquely positioned to address these challenges as one of its parent companies, Chevron, also requires state of the art catalysts and processes and, consequently, works closely with CLG to formulate new catalysts and to improve existing or develop new hydroprocessing technologies. In order to stretch the flexibility of the hydrocracking process even further, Chevron formed another partnership with Grace Davison, Advanced Refining Technologies (ART), particularly focusing on hydrotreating and resid catalyst development. Enhanced hydrotreating of refractory feeds prior to processing over a conversion catalyst will allow the refiner to improve product quality and simultaneously improve on the operational economics resulting from for example a lower required weighted average bed temperature (WABT).

Through reference to CLG's experience and catalyst know how, this article focuses on operational benefits that can be achieved by optimisation of the catalyst system in relation to unit design and/or refinery objectives and, more specifically, the impact on the hydrocracker economics. In addition, the development and commercial experience with CLG's latest ISOCRACKING® catalysts in combination with state of the art pretreat catalysts, providing both a yield and economical surplus to its customers, will also be described. Payback areas such as longer cycles, yield stability, and increased throughput, and their subsequent estimated benefits will be further discussed. Contrary to popular opinion, these are often not mutually exclusive and can be achieved simultaneously and, therefore, can change the merit of a premature catalyst replacement from an investment cost into an added value profit, compared to continuing operation with a non-optimised catalyst system.

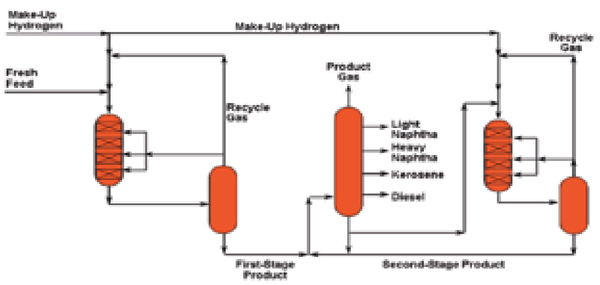

Figure 1. TSR ISOCRACKING simplified process flow sketch.

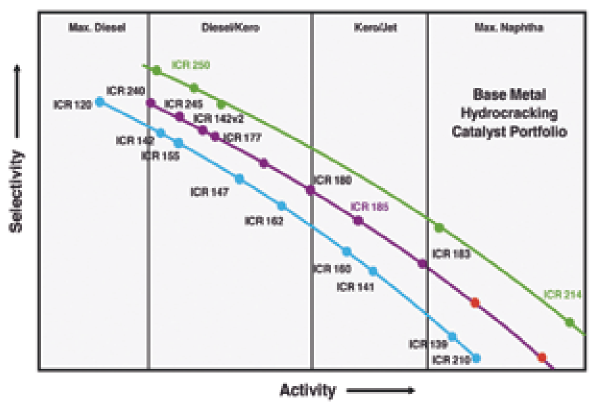

Figure 2. ISOCRACKING catalysts portfolio summarised.

History and hydrocracking background information

ISOCRACKING, CLG's proprietary hydrocracking technology, is ideally positioned to boost bottoms conversion and has been largely used as an upgrading process for poor quality feedstocks since its commercialisation in the late 1950s. The process was utilised for the first time in a licensee refinery in 1962 and has since been commercially available and established due to its many applications in varying novel configurations. Today nearly half of the world's refiners are using CLG's hydrocracking technologies and are producing >2 million bpd of clean fuels while processing low value feedstocks. The continuous growing demand for cleaner and cleaner fuels since the discovery of hydrocracking technology has been an ongoing challenge for refiners. CLG's catalyst

Table 1. Activity gain and shift to heavier products when deploying ICR 180 instead of prior generation ICR 162 at approximately 60% conversion

WBAT, ˚F	-10
C4-, wt%	-0.2
Light naphtha (C5-180 ˚F), LV%	-0.2
Heavy naphtha (180 – 250 ˚F), LV%	-1.5
Jet (250 – 550 ˚F), LV%	-0.7
Diesel (550 – 700 ˚F), LV%	+2.7
Mid distillates (250 – 700 ˚F), LV%	+2.0

Table 2. Improvement in product cold flow properties due to use of ICR 180 instead of ICR 162 at approximately 60% conversion

WBAT, ˚F	-10
Jet/smoke point, mm	Base
Freeze point, ˚C	Base
Heavy diesel/pour point, ˚C	-7
Cloud point, ˚C	-3
Cetane index	Base
UCO N / S, ppm	Base/Base
Pour point, ˚C	-12

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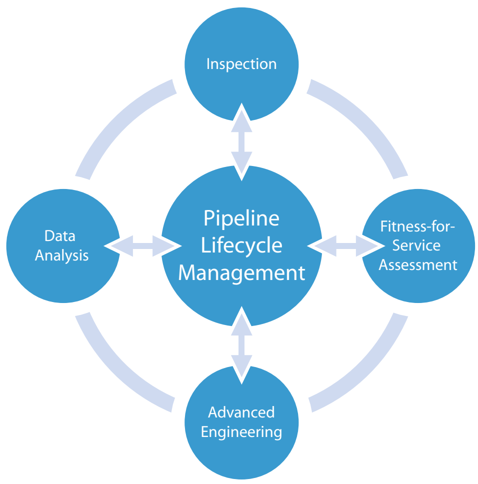

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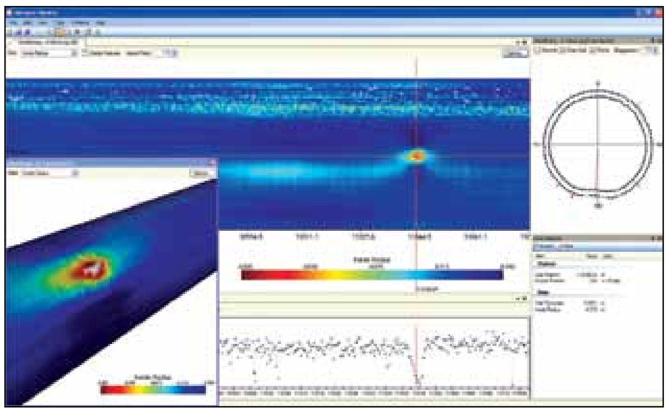


development programmes have been addressing this issue for more than 50 years and the latest catalyst generation(s) will be discussed later in this article.

The majority of existing hydrocrackers can be categorised into two distinctive configurations: single stage (with or without recycle, SSOT and SSREC) or two stage (TSR). A hydrocracker is one of the most technically complex process units in a refinery and yet, with a good design based on operating experience, one of the most reliable. A typical design usually involves multiple reactors, either in series or parallel, each comprised of multiple beds, running in once through or recycle mode of operation, resulting in a feed and product specific configuration that is most likely unique in the world. Obviously, there is not a 'one size fits all' solution for debottlenecking these units in view of catalysts system selection to achieve the highest economical return. Albeit that Chevron and CLG have operated and licensed hydrocracking units of all the aforementioned configurations, CLG's signature and most unique contributions have been in the TSR configuration for which a simplified flow scheme is shown in Figure 1.

Utilising two separate stages, each loaded with a conversion catalyst (could be the same, or could be different), will enable refineries to more easily 'swing' product yields from gasoline to diesel and vice versa not only by adjusting the recycle cut point (RCP), the combined feed rate (CFR), but also by moving conversion from first to second stage or the reverse. In other words, a TSR will allow refineries to better take advantage of feed and product price fluctuations and market demands. The TSR design by far will provide the highest operational flexibility; however, the refinery layout and market requirements will dictate which design is the best choice in terms of economics for a particular refinery.

Production can be further optimised through layering of one or more hydrotreating (HDS, HDN and HDA) and hydrocracking catalysts, thereby creating a catalyst system unique to the operating environment and processing objectives. CLG can design blended catalyst systems if the changes in chemical properties along the reaction pathway require this. In order to fully benefit from such tailored catalyst systems, utilisation should be maximised by installation of state of the art distributors such as the company's ISOMIX® reactor internals. Complete catalyst wetting and uniform gas and liquid distribution throughout the reactor and extreme low radial temperature spreads will enhance overall unit performance, thereby improving economics.

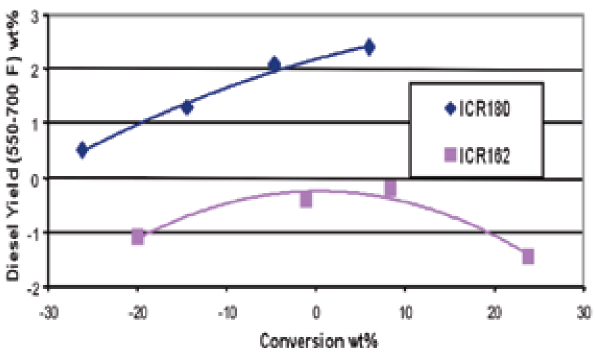


Figure 3. Diesel yield versus conversion.

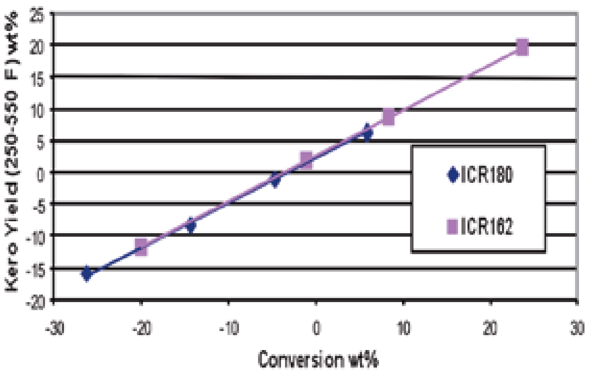


Figure 4. Kerosene yield versus conversion.

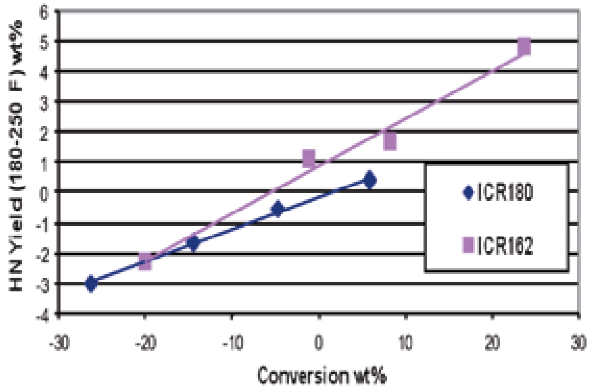


Figure 5. Heavy naphtha yield versus conversion.

Catalyst portfolio and developments

The level of 'forgiveness' of the incumbent catalyst system will determine whether a refiner can 'freely' change the product palette and/or increase the throughput for his hydrocracker without too much pain. Chevron and its affiliates, ART and CLG, have been active in the development of a wide array of hydroprocessing catalysts for many years. While early generations of ISOCRACKING catalysts were, for example, based on proprietary cogel technology, innovations in material science related to improve raw materials quality (amorphous and zeolitic) and improvements in catalyst characterisation and manufacturing techniques have resulted in the commercialisation of multiple ISOCRACKING catalysts. These catalysts are not only being used by Chevron refineries and CLG technology licensees, they are increasingly being used in non-licensed units as well. Figure 2 provides CLG's current base metal ISOCRACKING catalysts portfolio. These catalysts combine the best features of amorphous and zeolite technologies and span the full range of hydrocracking applications.

The blue curve represents CLG's earlier generation of catalysts, many of which are still quite popular. The purple curve represents CLG's next generation of catalysts. Most of these catalysts are already fully commercialised. CLG is already rolling out a new generation of catalysts noted on the green curve. It is of interest to compare the performance between specific catalysts of different generations in more detail.

ICR 180 and ICR 162

ICR 162 was commercialised in 2003. ICR 162 is one of the more frequently deployed mid distillate selective catalysts used widely in first stage SSOT and SSREC units, along with both first and second stages of TSR units. Figure 2 shows that ICR 162 is

much more active than ICR 142 at the cost of some mid distillate selectivity. ICR 180 was developed to improve on both the selectivity and activity of ICR 162 targeting a catalyst closer to ICR142 in selectivity with much better activity. ICR 180 was developed through the addition of a small change in functionality to a current generation catalyst. This enhances activity and mid distillate selectivity (Table 1). In addition, this change results in a product slate that exhibits markedly improved cold flow properties (Table 2).

Figures 3 and 4 show an increase in diesel yield of greater than 2% with no increase in kerosene yield. Figures 5 and 6 show the difference in naphtha selectivity is small at low conversion levels with a decrease of as much as 2% at high conversion levels. Tables 1 and 2 show that ICR 180 provides a 10 ˚F activity advantage over ICR 162 with a reduction in light

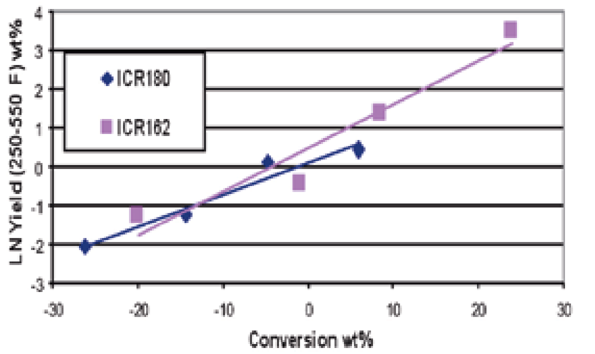


Figure 6. Light naphtha yield versus conversion.

Table 3. Shift to heavier products when deploying ICR 185 instead of prior generation ICR 160 at approximately 60% conversion	
WBAT, ˚F	Base
C4-, wt%	-0.7
Light naphtha (C5-180 ˚F), LV%	-1.1
Heavy naphtha (180 – 250 ˚F), LV%	-0.9
Jet (250 – 550 ˚F), LV%	-0.2
Diesel (550 – 700 ˚F), LV%	+2.2
Mid distillates (250 – 700 ˚F), LV%	+2.0

Table 4. Shift to heavier products when deploying ICR 250 versus ICR 240 in second stage recycle operation	
WBAT, °F	Base
C4-, wt%	-0.7
Naphtha (C5-250 ˚F), LV%	-1.3
Jet (250 – 550 ˚F), LV%	-0.6
Diesel (550 – 700 ˚F), LV%	+2.4
Mid distillates (250 – 700 ˚F), LV%	+1.8

Table 5. Yield shift to heavier products when deploying flexible ICR 183 instead of naphtha selective ICR 210 at approximately 70% conversion	
C4-, wt %	-2.1
Naphtha (C5-250 ˚F), LV%	-3.4
Mid distillates (250 – 650 ˚F), LV%	+8.4

gas make. Overall the company's objectives were achieved in the formulation of ICR 180, and it is currently being used successfully in one of Chevron's joint venture hydrocrackers that maximises mid distillate make.

ICR 185 versus ICR 160

ICR 160 was first commercialised in 2002. This catalyst was developed to maximise the kerosene yield for processing refractory feeds 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. What this plot does not show is that ICR 160 also has significantly lower light naphtha and gas make as compared ICR 141.

ICR 185 was developed to improve on both the selectivity and activity of ICR 160. Like ICR 180, ICR 185 was developed by a minor modification of the formulation of its predecessor. This results in a marked improvement in mid distillate yield (Table 3).

ICR 250 and ICR 240

ICR 240 was commercialised in 2007 as CLG's most mid distillate selective catalyst. ICR 240 can process a large variety of feedstocks such as process vacuum gas oil (VGO), light cycle oil (LCO) and coker gas oil (CGO) while maximising the kerosene and diesel yield. Even though it was originally formulated for use in the second stage it is also effective in first stage operations. ICR 240 allows a refiner to produce high distillate yields, excellent distillate properties, at low bleed requirements and at low gas make.

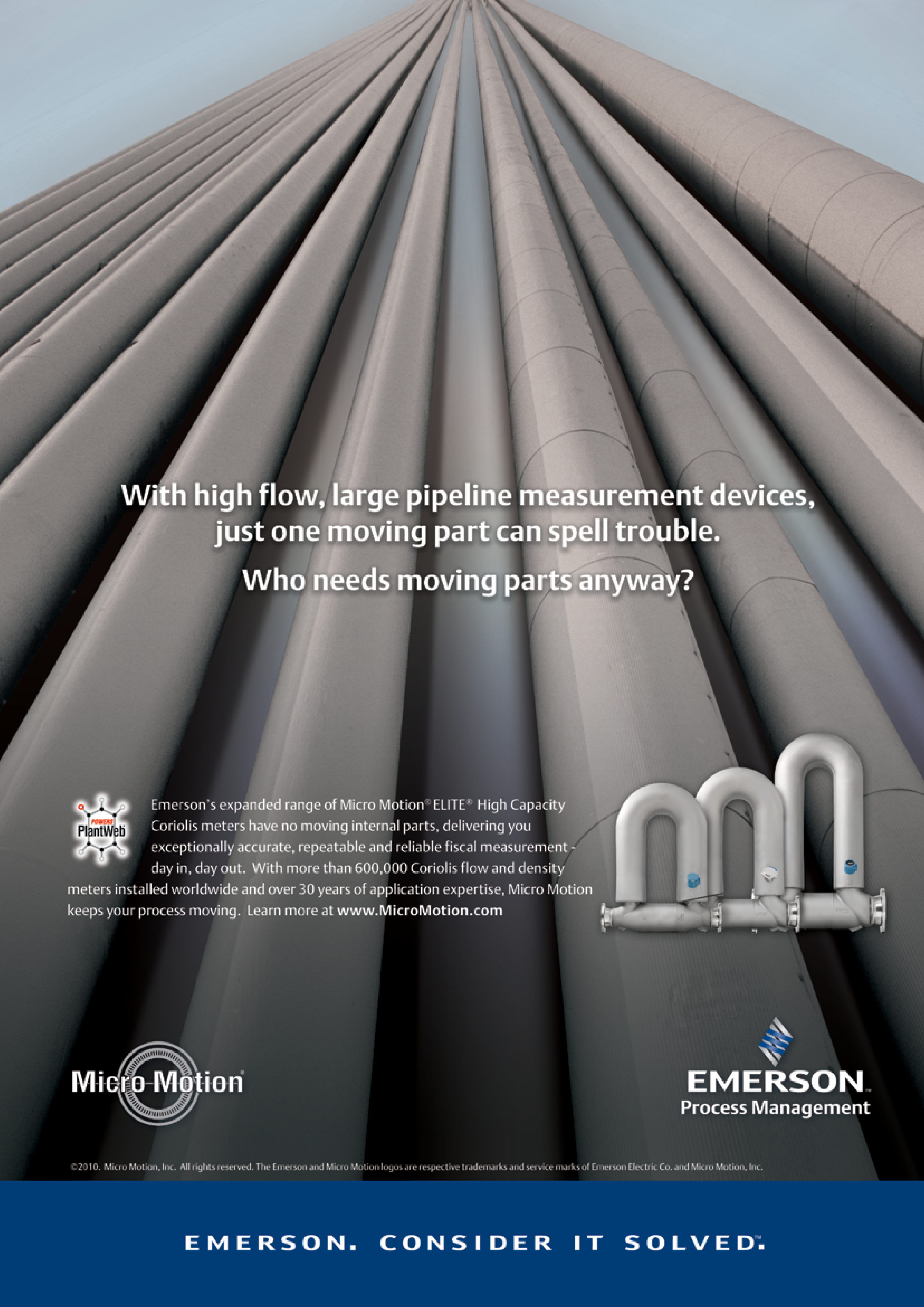
ICR 250 was designed to further improve the mid distillate yield of ICR 240. This was achieved through improving the hydrogenation functionality of the catalysts. Particularly in recycle operation this results in a significantly enhanced diesel (and mid distillate) yield (Table 4).

ICR 183

ICR 183 was commercialised in 2008. ICR 183 was developed to improve the activity for processing heavy and difficult feedstock while maximising the production of high quality naphtha or kerosene. ICR 183 can process VGO, LCO and CGO feeds with nitrogen concentrations in excess of 3000 wppm. ICR 183 can be used in an SSOT, SSREC, as well as both the first and second stage of a two stage configuration. ICR 183 can be run in either a naphtha or distillate mode. Table 5 shows the difference in overall yields between a naphtha selective (ICR 210) and mid distillate selective catalyst in the second stage of a two stage hydrocracker unit. In addition, ICR 183 has shown good operating stability with these cracked feeds.

Hydrocracking pretreating catalyst design

It is well understood that the support texture and the dispersion and interaction of the active metals are critical to optimising the performance for any hydroprocessing catalyst. The catalyst support determines the number of active sites, the surface area, and the size distribution. The optimum activity is achieved for a given feed by maximising surface area while favouring access to the active sites for the target boiling range fraction of a particular feed. A VGO with large heteroatom molecules requires a carefully optimised pore size gradient. In addition, the level of metals should be optimised, for an excess of metals tends to reduce pore diameter and thereby decrease the average boiling temperature of the targeted feed fraction. CLG has been working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on an improved hydrotreating catalyst that has been tailored for full range VGO hydrocracking service. Figure 7 shows the relative HDN activity advantage on a full range VGO for the latest version, ICR 511, along with its predecessors. ICR 511 was commercialised in early 2010. It is approximately 10 ˚C more active than its predecessor and appears to be 30 - 50% more stable in its first commercial duty, as shown in Figure 8.

Improved economics

Looking at the options for changing the product palette and/or the amount of materials produced by a hydrocracker, these can be split into three main groups: no CAPEX, low CAPEX, and high CAPEX. Taking into account the current economic environment the main focus will be on the no CAPEX and enhanced profit options, preferably even resulting in a reduced OPEX solution.

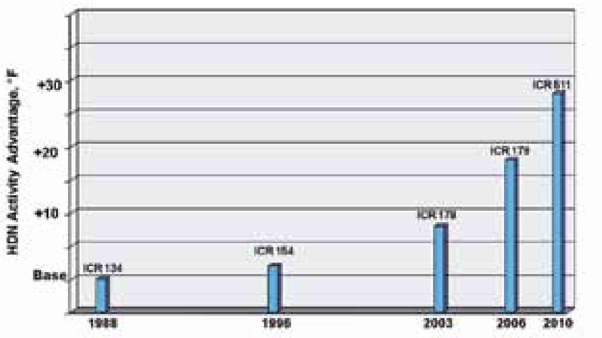

Figure 7. Improvement of hydrocracking pretreat catalysts with time.

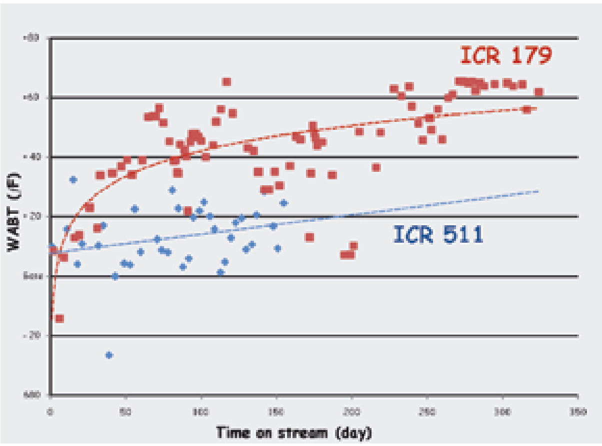

Figure 8. Improvement of ICR 511 over ICR 179 in commercial operation.

Table 6. Potential hydrocracker benefits

Item	Result	Estimated benefit
Longer catalyst cycles	Delay or eliminate turnarounds and associated costs	~ US$ 1 million maintenance ~ US$ 2.5 million throughput ~ Lower catalyst costs
Increased throughput	Improved utilisation	US$ 4.5 million/y
Improved yield stability	More valuable products	US$ 1.5 million/y
Enhanced product properties	Higher blending values	US$ 1 million/y

One of the simplest ways to adjust the product slate in a hydrocracker and/or the amount being produced is by adjustment of the reactor temperatures, which will increase total conversion and, due to higher operating temperatures, will shift the yields to produce more lighter materials. The latter will especially apply for those units that are not yet running at full conversion such as, for example, mild and partial conversion SSOT hydrocrackers. Adjusting the RCP in either a SSREC or a TSR hydrocracking configuration will allow the refiner to shift operation towards production of heavier or lighter materials, depending on the market demands and what unit design permits. A typical TSR configuration will even allow the refiner to switch from a jet/naphtha to a diesel mode of operation within the downstream limitations of the fractionation section. Last but not least, modification of the CFR will impact the conversion per pass in either a SSREC or a TSR, thereby changing the selectivity pattern achieved by the hydrocracker. Obviously, all the above described operational solutions for adjusting the product palette of a hydrocracker will have considerable wear and tear on catalyst fouling rate and, therefore, cycle length achievement.

A non-process parameter that can conspicuously change the production pattern of a hydrocracker unit, at no CAPEX, is the flexibility of the incumbent catalyst system and/or alternative catalyst systems that are readily available and exhibit product slates that fit market needs much better. Normally, the 'flexible' catalyst system will not be able to maximise extremes when market conditions change, but can be a very good compromise in case of frequent fluctuating markets. As shown in Figures 2 - 8, CLG's catalyst portfolio is well established in providing a wide range of solutions to meet product selectivity and product target qualities. CLG's latest pretreat and hydrocracking catalysts provide both a yield and economical surplus for its customers. Payback areas and some estimated benefits that can be achieved are listed in Table 6. It should be noted that these items are not necessarily mutually exclusive but can be achieved concurrently. Thorough evaluation, followed by tailoring of the catalyst system and, of course, good unit operation will make it possible to achieve multiple benefits at a time which can lead to astronomical profits.

Improvement of catalysts is ongoing but in today's environment of more stringent product specifications while processing tougher feeds, and at higher throughputs, 100% catalyst utilisation becomes critical to maximise value but also to assure safe operating practice. Numerous external and internal factors significantly affect 'overall' unit performance such as, for example, catalyst selection (i.e. type, quality and size), internals efficiency, catalyst loading and unit startup. Catalyst loading especially is often taken for granted and done the way it has always been done. Once improperly loaded, the system will prevent the unit from performing to its fullest extent and negate the effects of superior catalyst system. For example, inconsistent densities due to small errors in loading can cause channelling within a catalyst bed, high radial temperature differences or hot spots. In extreme cases, a significant portion of the catalyst will either never or only marginally be exposed to the hydrocarbons being processed in the unit or, even worse, will lead to a condition where the unit has to operate at the edge of the safety limits.

Commercial successes

A commercial example illustrating the above statements is shown in Table 7, representative of catalyst agglomeration found in the first stage of a hydrocracker after the second run. Peak and delta bed temperatures approached the maximum allowable with radial spreads approaching 55 ˚C. It is noteworthy that the reactor internals were very successful in bringing the inlet radials back to within expected design variance; however, operating severity was limited due to radial variances at different heights in some of the catalyst beds as shown.

One of the corrective actions taken by CLG in order to prevent recurrence was the selection of a highly experienced catalyst loading company to assure proper inspection, loading and accounting of loaded catalysts. Properly done, this need not take any additional time and can often be done in less time than historic for any particular unit. After the unit was restarted, significant improvements in reactor performance became obvious, as shown in Table 7. As a result, this unit was successfully operated for almost 26 months at or above target.

Another commercial example showing the economic benefits of working close with a licensor/catalyst supplier, which can be achieved by a refinery, is shown hereafter. A full conversion two stage ISOCRACKING unit was started up in 2000 and has since, met or exceeded processing objectives and provided the refinery a great degree of flexibility. The crude slate is comprised of ≥90% Urals while the feed to the hydrocracker consists of a mixture of LVGO, VGO, as well as some high end point/high aromatic extracts. The original design catalyst system, amongst others, comprised ICR 120, which is an amorphous catalyst made by cogellation technique and for years was considered the premier second stage catalyst in the industry for middle distillate production. Early perception was that difficult feeds (ex-Russian origin) would result in high PNA buildup rates and accelerated catalyst deactivation. However, the selection of a tailored catalyst system by CLG has shown that stable operation, i.e. constant product yields and qualities and low deactivation rates are feasible. Limitations in the light ends recovery section, most of the time caused by feed composition, initiated the desire to switch to a higher middle distillate selective catalyst system in order to reduce naphtha production. After an intermediate step up in the first stage treating/cracking catalyst system, the ICR 120 was replaced by the earlier discussed ICR 240, which is a mild zeolite second stage cracking catalyst. Since that change, commercial performance has exceeded expectations, with significant improvements in product selectivity as shown in Figure 9. Since extended cycle length is considered at least as important by the refinery, the higher overall activity and lower deactivation rate has allowed the refinery to increase throughput as shown in Figure 10, or to run longer cycles.

As a result of replacing the ICR 120 with ICR 240, the light ends recovery bottleneck in the plant was completely removed and the operation is now limited by its ability to recover the mid distillate! Throughput has been increased to ≥115% of design and, in combination with the significant change in mid distillate selectivity, the total distillate yield increased by close to 10%. Assuming a 30 000 bpd hydrocracker this would imply an extra 3000 bpd of middle distillates, which at an upgrading value of approximately US$ 4/bbl would generate an extra profit of more than US$ 4.5 * 10^6/y (the latter depends on local costs and product values). In addition to the aforementioned, the impact of the hydrocracker performance has been so significant that total refinery throughput has also increased by a few percent. The above described success related to catalyst system optimisation is an example of the impact that fine tuning of such a system can result in and the effect it can have on refining economics.

Conclusion

It is evident that each factor on its own (i.e. unit design, operating conditions, catalyst selection, loading, and startup) plays a crucial role in the ability of a specific refiner to satisfy regulative demands, produce materials on spec, be responsive to changing market demands and still make some money. Any hiccup in one of the above mentioned elements can easily result in a sudden, huge loss. Through the use of state of the art hydrocracking catalyst systems, refiners have been able to increase unit revenue and reduce costs by longer cycles and/or less downtime. The combination of higher feed rates and longer cycle lengths or improved product properties is especially important in times of lower margins or during cost reduction pressures.

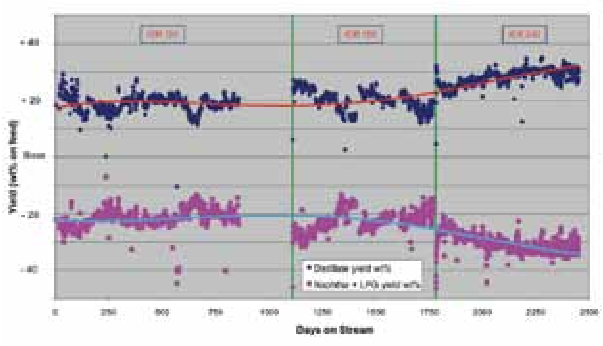

Figure 9. Middle distillate yield improvement versus catalyst system.

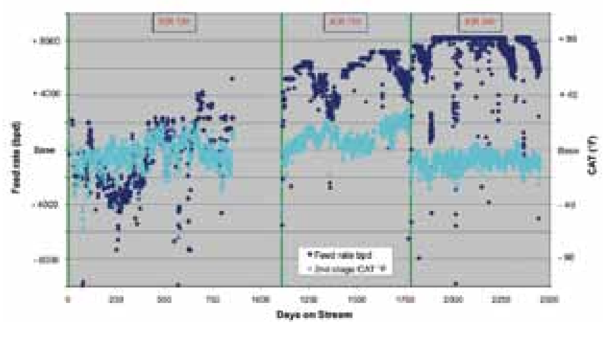

Figure 10. Feed rate and second stage CAT versus catalyst system.

Table 7. Operating conditions of the hydrocracker

Operating cycle	Feed rate	Radials	Yields	Peak catalyst temperatures	Other
Run 2	Limited to 88 – 90% as the run progressed. Could not run light feed (LGO, LCGO).	Up to 55 ˚C	Unable to achieve full yield slate due to axial temperature restrictions (55 – 58 ˚C).	440 ˚C+, as had one runaway in Bed 4 (R-1000). Restricted temperature to 427 – 432 ˚C max.	R_x unresponsive to quench moves in Beds 2 - 4.
Run 3	Able to achieve 100%+.	< 6˚C	Normal yields achievable.	433 ˚C in lower beds depending on feed.	R_x responsive to quench moves.