

A Bold Move in Hydrocracking Catalyst Selection Resulted in a Significant Boost in Hydrocracker Margins

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Abstract

A Canadian refinery that had used noble metal based hydrocracking catalyst for over 40 years decided to explore alternative hydrocracking catalyst systems to improve their hydrocracker profitability and provide increased operability to overcome the constraints of the incumbent catalysts. A candid, in-depth dialogue between the customer and Criterion/Zeolyst, utilizing commercial experience and catalyst knowledge, paved the way to design a targeted pilot plant test program. A refinery economic evaluation clearly showed the superiority of a base metal cracking catalyst system compared to the original noble metal catalyst system. This joint effort between the refinery, head office engineering and the catalyst supplier led to the selection of a new base metal catalyst system for the current cycle.

After nearly five years on stream, the customer's commercial data validated the decision to change catalyst systems. This hydrocracker has not only maintained desirable product yields, but has also achieved the desired cycle length while processing more barrels of more difficult and more profitable feed components. All of these positive results translate to an estimated annual benefit of 5 million dollars for this refinery.

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Table of Contents

1	Abstract
2	Introduction
3	Background
4	Catalyst and Reactions
6	Our Case Study
7	Catalyst Selection Considerations
8	Commercial Implementation of Base Metal Cracking Catalyst for Sarnia
9	Commercial Performances and Economic Benefits
11	Conclusions
11	References

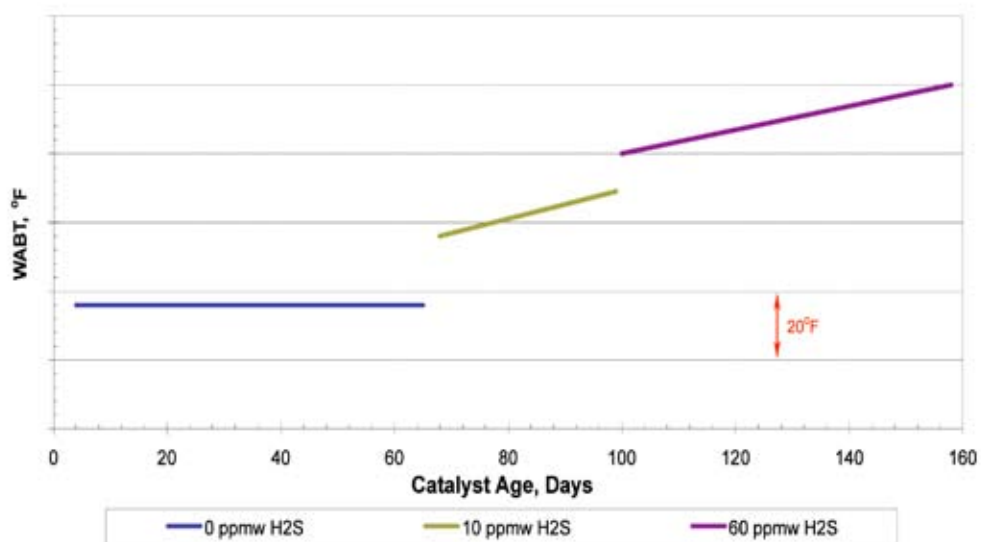


Figure 1: Impact of H₂S on Noble Metal Catalyst Activity

Comparing noble metal catalyst activity in sweet environment: 10 ppmw H₂S can contribute to -20°F activity decline, at 60 ppmw, the additional required operating temperature is 40-50°F, and depending on the user's response to H₂S excursions, the cycle can be seriously shortened by sulfur upsets.

Introduction

Hydrocracking is one of the most important conversion processes in refineries and can have significant impact on the bottom line. Most North American hydrocrackers were originally designed as naphtha selective units, but unit modifications and catalyst developments have allowed operation as intermediate naphtha/jet selective units or as distillate selective units. Depending on seasonal market demand at each refinery location, a hydrocracker may be required to operate in one of the three selective modes. Today, most of the hydrocrackers designed and built 30 to 40 years ago have to adapt to process heavier gas oils from new crudes while also satisfying new product demands and specifications. To meet these needs, revamp of a hydrocracker is possible but requires significant capital and extensive downtime. The more desirable solution is the application of modern catalysts that fit the hardware and require little or no capital investment.

Significant progress has been made in hydrocracking catalyst development and refineries have been able to increase hydrocracking performance and flexibility with the use of more active and more selective catalysts. Products from a hydrocracker are expected to be of superior quality. The light gasoline is often blended directly into the gasoline pool. Therefore, it must have a high octane number (RON) from the isoparaffin content. The heavy gasoline should have high naphthene content

for use as reformer feedstock in order to produce high-octane reformat or to produce BTX aromatics for petrochemical feedstock. Jet fuel must have low aromatic content in order to have high smoke point and desirable cold flow properties such as low freeze point. As we enter the ULSD era, in addition to high cetane index and good cold flow properties for diesel fuel, the sulfur content must also be <10 ppmw such that it can be directly blended into the ULSD pool.

Due to the importance of the hydrocracker in the refinery profitability equation, the complexity of unit and stringent demand on product quality, the catalyst selection must be made carefully. An error in catalyst selection can detrimentally affect the profit margin of the hydrocracker and the profitability of the refinery. Therefore, highly effective cooperation between the refinery and the catalyst supplier is very important in order to identify the appropriate catalyst solution for each hydrocracker. Understanding process limitations is essential. As a major hydrocracking catalyst supplier, Criterion/Zeolyst have been able to quickly respond to the needs of our customers by prioritizing our R&D efforts to commercialize new catalysts with improved activity, stability and product yields. This paper documents the joint effort between Shell Canada Sarnia Refinery and Criterion/Zeolyst devoted to the selection of the catalyst system for the current cycle hydrocracker operation along with the actual benefits realized after nearly five years of operation.

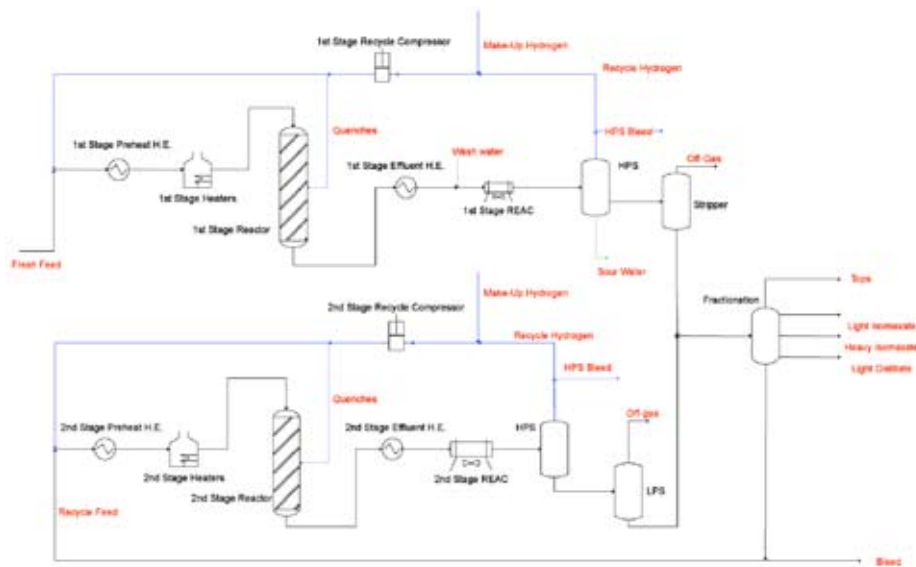


Figure 2: Shell Sarnia HCU Simplified PFD

A two-stage hydrocracker with a common fractionation section is illustrated. The second stage is designed for noble metal catalyst: separate recycle gas circuit, low H₂S metallurgy and no water wash of the reactor effluent stream.

Background

The first commercial hydrocracking technology was developed in the early 1900s in Germany to convert coal into liquid fuel. The hydrocracking process to convert heavy petroleum fraction into lighter fuels was later developed in the 1920s through collaboration between I.G. Farbenindustrie in Germany and Standard Oil in New Jersey (1). Tungsten sulfide and nickel on amorphous silica-alumina were among the earliest catalysts to be successfully implemented. In the early 1960s, hydrocracking became a commercial reality with several technology licensors. Hydrocracking also became popular in the 1960s because of major shifts in the transportation industries that increased the demand for higher quality of all fuel types. The automobile industry started manufacturing high-performance cars that required high-octane gasoline. The railroad industry moved from steam to diesel engines. The introduction of commercial jet aircraft in the 1950s further increased the demand for diesel fuel, especially jet fuel with a low freezing point. With the flexibility of the newly developed hydrocracking processes, refiners were

able to keep up with the new market demand and to continue to gain profitability by producing lighter fuels from heavier feedstocks. From the mid-1960s through the 1970s, hydrocracking technologies matured and continued to grow moderately. In the 1980s and 1990s, slow growth was observed in the US while hydrocracking continued to grow in other parts of the world still under industrial development, such as Asia-Pacific, and in Europe, due to the demand for more diesel fuel. Since the beginning of the 2000s, the product slate in North America has trended towards increased distillate production. New hydrocrackers are coming on-line both outside and inside the US. The emphasis will continue to be on increased production of middle distillates. Since 2006, nearly 70 new hydrocrackers worldwide are in various stages of construction and planning through 2012.

	Straight-run Heavy Diesel	Atmospheric Gas Oil	Light Vacuum Distillate	Cat Cracker Light Gas Oil
API Gravity	30.5	27.6	27.6	16.3
Nitrogen, ppmw	247	562	389	840
Sulfur, wt%	0.923	1.05	1.52	1.62
D-2887 Distillation, wt% (°F)				
IBP	417	215	331	285
50%	623	697	612	527
90%	678	785	733	646
FBP	739	874	858	739

Figure 3: Typical Feed Component Properties

The most difficult feed component and most valuable for upgrading is the Cat Cracker Gas Oil. The second most difficult feed component is the Atmospheric Gas Oil, followed closely by the Light Vacuum Distillate. The easiest feed component is the Straight-run Diesel.

Catalyst and Reactions

In hydrocracking, there are two major reactions: hydrocracking and hydrogenation-dehydrogenation. Hydrocracking occurs on acidic sites while hydrogenation-dehydrogenation occurs on metallic sites. Therefore, a hydrocracking catalyst must be dual-functional. For modern hydrocracking catalysts, the hydrocracking function is provided by an acidic support such as alumina, amorphous silica-alumina (ASA), zeolite or a mixture of all of these. Directionally, the cracking activity of the three catalyst support materials is ranked in order of decreasing acidity as follows:

Zeolite > amorphous silica-alumina (ASA) > alumina

The naphtha product yield selectivity follows the same order. Therefore, for a high severity and maximum naphtha selective hydrocracker, a high zeolite containing catalyst with up to 80% zeolite should be applied. On the other hand, to increase distillate yield, the zeolite content can be reduced. For distillate selective catalysts, the zeolite content can be as low as 0 to 10% with a mixture of ASA and alumina as the main support material. For example, commercially applied amorphous silica-alumina (ASA) is used for mild hydrocracking to maximize production of middle distillate or conversion to lube oil.

The hydrogenation-dehydrogenation function occurs on the metal surface of noble metals such as platinum (Pt) or palladium (Pd) or on a non-noble (base) metal surface such as tungsten (W) or molybdenum (Mo) promoted by nickel (Ni). A hydrocracking catalyst with a good hydrogenation function generally leads to better distillate quality, less gas make and often better stability. Nevertheless, the cracking and hydrogenation functions need to be properly balanced and the ratio of acidity and metallic sites must be carefully adjusted for optimal activity and selectivity.

It is well known that noble metal catalysts with platinum or palladium are more active for hydrogenation than Ni/W followed by Ni/Mo catalysts. One of the major differences between noble metal and base metal catalysts is that the noble metal catalyst needs to be kept in the reduced metal state to retain most of its catalytic function and noble metals lose activity in the presence of sulfur. This is in contrast to the base metal catalysts, which are active in the sulfided state. Figure 1 depicts the impact of H₂S on noble metal catalyst activity. At the sulfur levels illustrated and higher, a base metal hydrocracking catalyst exhibits no deficit in performance.

Today, the majority of hydrocrackers employ base metal hydrocracking catalysts. However, there are a few hydrocrackers in North America designed in the

	Zeolyst Noble Metal Catalyst	Zeolyst Base Metal Catalyst
NWABT for 65% Conversion (°F)	Base	Base + 1.5
Gas (C1-C4) Make, vol%	Base	Base + 1.1
Light Naptha (C5-180 °F), vol%	Base	Base + 1.4
Heavy Naptha (180-375 °F), vol%	Base	Base + 1.6
Total Jet + Diesel (375-500 °F), vol%	Base	Base - 4.6
Hydrogen Consumption, SCF/BBL	Base	Base - 100

Figure 4: Product Yields Comparison

As expected, the noble metal catalyst is more active and consumes more hydrogen at the same conversion. However, heavy naphtha selectivity is higher with the base metal catalyst.

1950s and 60s that are still in service with noble metal catalyst. Historically, North American hydrocrackers were designed to hydrocrack FCC cycle oil, coker gas oil, and straight-run atmospheric heavy distillate to produce gasoline. During the 1950s and '60s, noble metal catalyst was viewed to be the most active and to produce a better quality of naphtha. To accommodate noble metal catalysts, hydrocrackers were specifically designed for a sweet environment where almost no organic sulfur or H₂S were present. Not only must nearly all of the feed sulfur be removed in the pretreat section, the recycle gas must also be free of H₂S. Only in hydrocracking units with a separate recycle system can the second stage be H₂S-free. Even in an environment with less than 100 ppm H₂S, noble metals can still react to form corresponding sulfides rendering the metal sites inactive and/or less selective. Furthermore, it is challenging to operate the pretreat stage such that there is little or no sulfur and nitrogen slip to the cracking stage throughout a cracking stage operating cycle.

Even when the hydrocracker is designed for a sweet environment, the noble metal cracking catalyst is still at risk from sulfur compounds. It is common for an operational upset or operating error to lead to high S slip or high H₂S in the cracking stage recycle gas. If the cracking catalyst were non-noble metal, this event would be minor at most. Possibly the sulfur in the diesel product would increase. Once the operational problems are identified, normal operation is resumed with no harm done to the base metal cracking catalyst. However, if the cracking catalyst utilized is noble metal, this minor event may permanently damage the noble metal sites and will at the least reduce the cycle length.

Adsorption of sulfur on platinum may be reversible or irreversible. Sometimes, sulfur can be readily desorbed using high temperature hydrogen stripping with feed removed from the unit. However, when sulfur strongly interacts with the metal, the adsorption of sulfur may be irreversible. In this case, the activities of the metal sites are permanently reduced and the cycle life is drastically shortened.

Since base metals must already be in sulfided states to be active, base metal catalysts are more resilient in units prone to operational upsets or units with economic incentive to feed heavier, higher sulfur feedstocks. High-activity base metal catalysts such as Zeolyst Z-863 were designed for these operations. The Z-863 was even designed for better resistance to nitrogen compounds that can occasionally slip through due to abnormal operation in the pretreat stage or more refractive nitrogen compounds found in the heavier feeds.

	Zeolyst Base Metal Catalyst			Zeolyst Noble Metal Catalyst		
	LN	HN	Jet & Diesel	LN	HN	Jet & Diesel
Cut (°F)	C5-158	158-338	338-500			338-500
Cetane Index D976			37			39
Cetane Index D4737			39			41
Smoke Point, mm			23			24
Naphthenes, wt%		42.3			44.2	
Aromatics, wt%		8.2			0.5	
N+2A		58.6			45.3	

Figure 5: Product Properties Comparison

Distillate cetane is slightly lower with base metal catalyst but N+2A is higher in heavy naphtha, thus having better reformability. Incremental hydrogen production increase from the reformer equates to higher throughput in the hydrocracker.

Our Case Study

Originally built in 1952 by Canadian Oil Companies Limited, Shell's Sarnia Manufacturing Centre (SMC), also referred to as Shell's Corunna Refinery, is located about 10 kilometers south of Sarnia, Ontario. The refinery became part of Shell's operations when Shell purchased Canadian Oil in 1963. This 75,000 barrels-per-day refinery processes raw crude oil into a range of petroleum products such as gasoline, diesel, jet fuel and various petrochemicals such as benzene, toluene and xylene.

The 10,000 barrels per day hydrocracker is one of the key processes for the Sarnia refinery to produce ultra-low sulfur gasoline and ultra-low sulfur diesel.

The Sarnia hydrocracker is a two-stage hydrocracking process with one hydrotreating reactor, one hydrocracking reactor and a common fractionation section in between the two stages (Figure 2). The first stage reactor effluent is fractionated with the hydrocracked unconverted oil from the second stage reactor.

The hydrotreated effluent from the first stage reactor is sent to separation for H₂S removal and then to the fractionation section. The fractionation section consists of a Stabilizer where LPG is removed and sent to the depropanizer. The bottom product of the Stabilizer is routed to a Splitter to fractionate out the Light hydrocrackate, Heavy hydrocrackate and Distillate products. The unconverted oil product bottom of the

Splitter is recycled to the second stage reactor. The unit was originally designed for a 48-month cycle. The second stage has a separate recycle gas circuit to maintain an H₂S-free environment thus the low H₂S metallurgy and no water-wash. The reformers were originally the only source of hydrogen and other units have fixed demand. The HCU rate depends on hydrogen availability and the hydrogen consumption of the HCU determined the maximum throughput. Since the reformer hydrogen production also depends on the HCU naphtha production and quality, a vicious cycle was created.

The main unit objective for the hydrocracker at Shell Sarnia is to optimize hydrogen uptake in order to maximize volume gain subject to LPG production constraints. Low fuel gas make and minimal heavy bleed are always beneficial. During the winter operation, cold flow properties of diesel can be a constraint and improvement is of economic value. Improvement in N+2A of Heavy hydrocrackate adds to better reformability of this feed to the reformer. Thus higher quality and higher quantity of Heavy hydrocrackate have greater economic value for higher hydrogen availability and higher hydrocracker feed rate. Figure 3 describes each feed component's properties. The feed for the unit is a mixture of atmospheric distillates (straight-run heavy diesels and atmospheric gas oils), vacuum distillate and FCCU cycle oil. The cat cracker light gas oil is the most difficult feed due to its heaviness, high nitrogen content and high sulfur content. The atmospheric gas oil is also a difficult, low value stream with high nitrogen content and high back-end distillation. The light vacuum distillate has

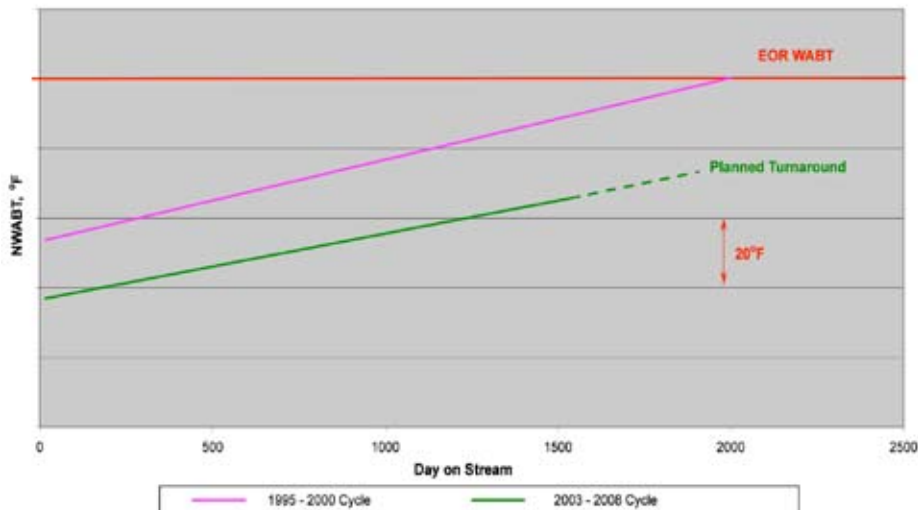


Figure 6: Normalized WABT Pretreat Stage

The pretreat stage with stacked bed system in the current cycle is more active and more stable, matching the stability of the cracking stage even with more difficult feed blends.

lower nitrogen content and lower back-end distillation than the atmospheric gas oil but it is a more difficult feed than the straight-run heavy diesel. Maximizing cat cracker light gas oil, atmospheric gas oil and light vacuum distillate streams in the fresh feed means that lower value streams can be upgraded to higher value streams for a better profit margin.

The high-activity noble metal catalyst in the second stage had provided long cycle length for the Sarnia hydrocracker. High hydrogenation activity also meant consistently good distillate product qualities. Shell Sarnia, however, observed several disadvantages with noble metal catalyst usage. High hydrogen consumption can lead to a hydrogen/naphtha imbalance. The noble metal catalyst has limited ability to process difficult feeds due to high hydrogen consumption. Another disadvantage that Sarnia experienced is the poor resistance to sulfur and nitrogen of the noble metal catalyst. In 2000, shortly after startup, the refinery experienced a first stage breakthrough resulting in the loss of about 1/2 of the expected catalyst cycle life in the noble metal cracking catalyst. The resulting loss of cycle life helped convince Shell Sarnia that a more robust system would help increase catalyst reliability in addition to an improvement in unit margins.

Catalyst Selection Considerations

Criterion and Zeolyst had been working closely since 1997 with Shell Sarnia to try to implement base metal catalyst in the second stage reactor. Preliminary economic evaluation showed that Shell Sarnia would only save approximately \$200,000 with base metal catalyst. Shell Sarnia evaluated other benefits that base metal catalyst would bring, such as the stability and robustness of the base metal system that would allow the refinery to improve operability, hydrogen utilization and naphtha yields, while maintaining distillate quality, and more flexibility in processing difficult feed components. Criterion submitted performance estimates that included activity, deactivation rate, yields, product qualities and yield declines for both noble metal and base metal catalyst systems. Pilot plant programs validated the yield estimates. Shell Sarnia also performed a cash-flow model for each option, taking into consideration catalyst management costs, turnaround costs and yield declines.

The Criterion/Zeolyst pilot plant program was carried out to confirm the cracking activity, yields performance and each product's properties for two commercial catalysts. One system was Zeolyst noble metal that has already been determined to have similar activity and yield performance as the catalyst loaded in the second stage reactor at the end of year 2000. The second catalyst system was a Zeolyst base metal catalyst. The base metal

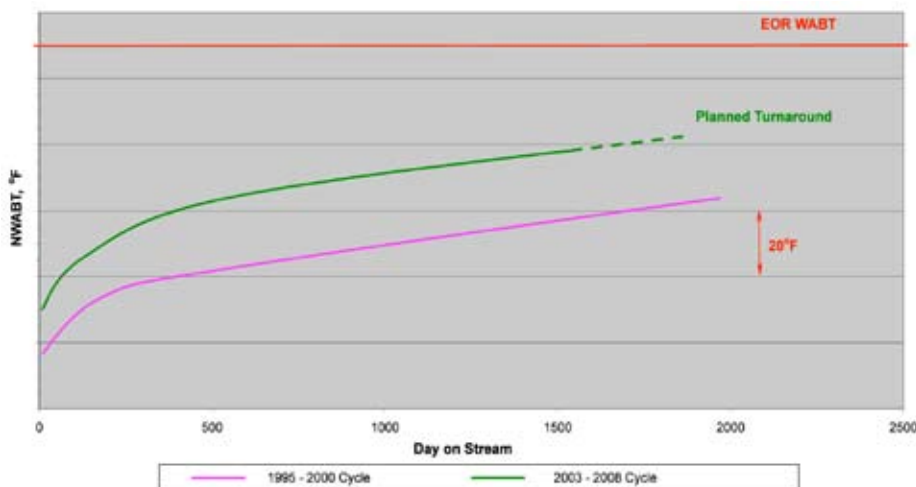


Figure 7: Normalized WABT Cracking Stage

Base metal system requires higher WABT at the same conversion. However, the base metal catalyst is stable through several upsets during the cycle while processing more difficult/heavier feed blends.

catalyst tested was the latest high-activity, nitrogen tolerant cracking catalyst from Zeolyst. It is a rugged second-generation catalyst that provides superior activity and stability based on the proven technology. Despite the very high zeolite content for maximum cracking activity, it was loaded with high amounts of Ni/W using an improved metal impregnation technique that significantly boosted the hydrogenation activity of the catalyst.

Both pilot tests were conducted with the second stage feed collected from the commercial unit in 1999. The conversion target was for 65% conversion per pass similar to the commercial unit target and at equivalent unit conditions of LHSV, hydrogen partial pressure and an H₂S-free environment for the noble metal catalyst. Both tests were conducted for approximately 1000 hours to let both systems stabilize such that the results could be accurately interpreted.

Comparisons of product yields and product properties are presented in Figures 4 and 5.

Pilot test results in Figure 4 show that the noble metal catalyst system is 15°F more active at the same 65% conversion. However, even at higher WABT, the gas make in the base metal system is only 1 wt% higher. The heavy naphtha selectivity increases with the base metal catalyst. Hydrogen uptake with the noble metal catalysts was higher due to higher hydrogenation for aromatic removal as reflected in the cetane Index values in

Figure 5. It should also be noted that under a sour recycle gas system, pilot plant data had shown the base metal catalyst to be more active than the noble metal catalyst due to H₂S poisoning of the noble metal catalyst.

For this unit, aromatic specifications are not limiting. Since the cetane index and smoke point values of the distillate products are virtually the same with both catalyst systems, the product properties from the base metal systems are fully competitive. Additionally, N+2A of heavy naphtha was higher with base metal catalyst thus improving reformability of this stream.

Given that the base metal catalyst tested was a commercially proven catalyst, the data showed that Shell Sarnia would still be able to achieve a 48-month cycle in spite of the higher WABT requirement. In fact, the forecasted EOR for this current cycle with base metal cracking catalyst is greater than 5 years.

Commercial Implementation of Base Metal Cracking Catalyst for Sarnia

In the third quarter of 2003, as a result of the demonstrated performance during the pilot test program, Shell Sarnia replaced the noble metal cracking catalyst in the second stage with the base metal catalyst. Additionally, Shell Sarnia replaced the pretreat catalyst system with a stacked bed pretreat/mild hydrocracking

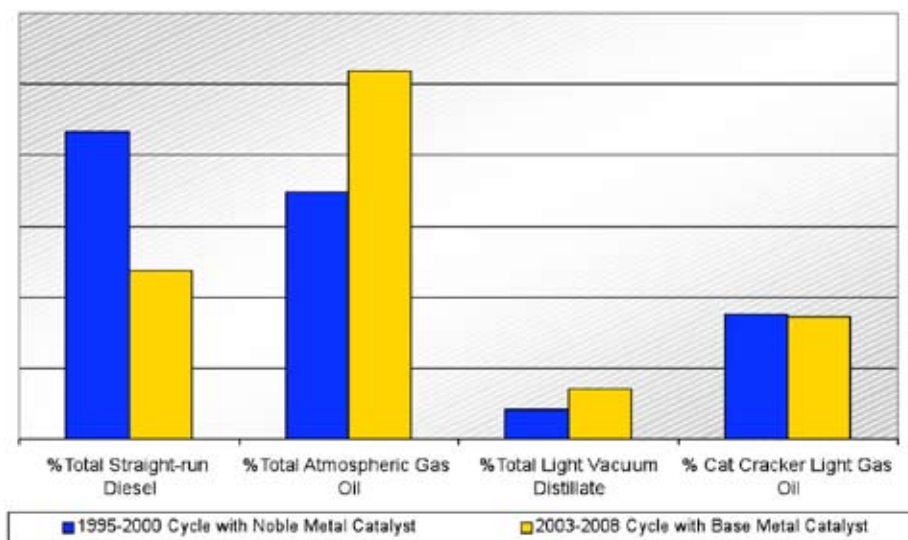


Figure 8: Shell Sarnia Average Feed Components

The current cycle has processed the same amount of total feed but with higher amounts of the more difficult feed components. The total amount of straight-run diesel has been reduced by ~50% and replaced by the atmospheric gas oil and the light vacuum gas oil.

catalyst system for additional activity and stability in the first hydrotreating stage. At the time of this writing, the hydrocracker continues to perform as predicted with significant economic improvements.

Challenges in switching from noble metal to base metal catalyst came from the fact that the second stage reactor and recycle system were designed for noble metal catalyst. The second stage metallurgy only allows a maximum of 50 ppmw H₂S in the recycle gas. On the other hand, H₂S is required to maintain base metal catalyst in a sulfided state. Detailed operating guidelines were developed and implemented for Sarnia. Typically, 20 to 50 ppmw H₂S will be sufficient depending on reactor temperature. There are several options for controlling H₂S concentration. One is to increase the sulfur slip from the first stage to the second stage. The second solution is to route a sour gas stream from the first stage to the second stage, and the third solution is to inject a sulfiding agent. Shell Sarnia decided to apply the third option for positive sulfur control. A small metering pump was installed to inject DMDS in the second stage. The H₂S concentration is measured on each shift and the metering pump stroke is adjusted to control the H₂S concentration required at the specific maximum reactor temperature for the current condition of the cycle.

Additionally, since the second stage has been operating at higher temperatures, there will be changes in metallurgy during the next turnaround. During a brief outage in the summer of 2007, the equipment in the second stage circuit was scanned. It was determined that some Carbon ½ Moly equipment and piping will require upgrading in order to operate at high temperatures for the next cycles. The cost of these upgrades will be approximately \$700K.

There are capital changes required in implementing base metal catalyst in a unit designed for noble metal catalyst. However, the economic benefit of such implementation has been proven to be significant to the bottom line of Shell Sarnia.

Commercial Performances and Economic Benefits

As a result of the replacement of the pretreat catalyst system, the performance of the first stage pretreatment has remarkably improved. The pretreating stage activity data for the 1995-2000 cycle and the 2003-2008 cycle are shown in Figure 6. The data in pink represent commercial data from the 1995-2000 cycle. The data in green are from the current 2003-2008 cycle.

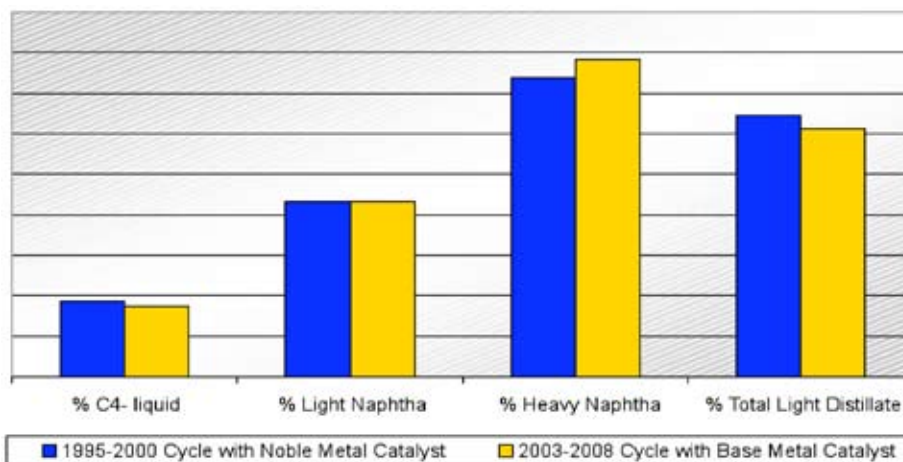


Figure 9: Shell Sarnia Average Yields

With base metal catalyst, the gas make is slightly lower while the light naphtha yield is equal. The heavy naphtha and distillate yields with base metal system are also better than expected.

A lower overall pretreat WABT is required in the current cycle. As the catalyst activity in the first stage diminished, EOR for the 1995-2000 cycle was reached at approximately 1900 days on stream. The pretreat catalyst data for the 2000-2003 period is excluded here since that cycle life was shortened due to the reduced activity of the cracking catalyst after start-up. For this current 2003-2008 cycle with the pretreat/mild hydrocracking stacked system, activity and stability improvements have been demonstrated. The deactivation slope for the normalized WABT trend for the current cycle is lower indicating that the stacked bed system is more active and more stable even with heavier feeds throughout the cycle. The current cycle pretreat stage is expected to perform well until the turnaround in May 2008.

The cracking base metal catalyst was expected to be ~15°F less active than the noble metal catalyst. Figure 7 shows that even though the base metal catalyst system is less active, it is as stable as the noble metal system even with much more difficult feed blends processed during this cycle.

The new stacked pretreat catalyst and the base metal catalyst in the current cycle have processed the same total feed throughput but with higher amounts of more difficult feed components. The cumulative amounts of the atmospheric gas oil and light vacuum distillate streams processed have already exceeded those processed in the previous healthy cycle but in a shorter cycle time.

Figure 8 represents the average percentage of each feed component from the two cycles comparing the noble metal system in the 1995-2000 cycle to the current base metal system. In the current cycle, the easiest straight-run distillate streams were reduced by nearly half and replaced mainly by the more difficult, higher value gas oil and light vacuum distillate streams. The %volume of the cat cracker light gas oil processed is similar in both cycles.

Even with the much more difficult feed blends, the yield pattern remains healthy as shown in Figure 9 and summarized in Figure 10. Light gas make is less in the current cycle. The light naphtha yield is comparable in both cycles. The heavy naphtha gain is higher than predicted and the distillate yield reduction is less than expected. The improvement in yields for base metal catalyst was better than that projected using pilot plant data.

The improved performance of the base metal catalyst in the current cycle has allowed Shell Sarnia to have robustness to unit upsets and to process more difficult, lower value feeds. Base metal catalyst usage also makes catalyst management a more simple process. The ability to process more difficult feeds while maintaining desired product slates translates to a significant boost in profit margin for this refiner. Using a simple economic calculation of the additional margin from the incremental atmospheric gas oil processed during the current cycle, Shell Sarnia has benefited approximately 5 million dollars US annually since the replacement of noble metal catalyst with base metal catalyst in the hydrocracker.

	Commercial Data	Pilot Data
Gas(C1-C4) Make, vol%	Competitor Noble Metal -0.6	Zeolyst Noble Metal +1.1
Light Naptha (C5-180 °F), vol%	Competitor Noble Metal +0.0	Zeolyst Noble Metal +1.4
Heavy Naptha (180-375 °F), vol%	Competitor Noble Metal -2.3	Zeolyst Noble Metal +1.6
Total Jet + Diesel (375-500 °F), vol%	Competitor Noble Metal -1.6	Zeolyst Noble Metal -4.6

Figure 10: Product Yields Comparison Pilot vs. Commercial

Conclusions

Through close communication and cooperation between Shell Sarnia and Criterion/Zeolyst from 1997 to 2003, we were able to conduct a detailed evaluation that included kinetic modeling, pilot testing program and a thorough economic evaluation to compare the base metal catalyst system versus the noble metal catalyst system. This joint effort was the key to the confident selection of an appropriate and more economical catalyst solution for this unit.

In commercial operation with the selected base metal catalyst, Shell Sarnia has achieved the desired product yields and properties while maximizing more difficult feed streams, thus increasing the profit margin. This bold move resulted in the benefit of an additional 26 million dollars over the past 5 years for Shell Sarnia. Additionally, the base metal catalyst system is more resilient and has performed through several unexpected unit upsets and shutdowns during this cycle. The base metal catalyst system has been observed to be as stable as the noble metal catalyst system but with more robustness. The base metal catalyst system has processed much more difficult feed blends while compensating for any unit upsets. The more robust base catalyst system has helped increase catalyst reliability in addition to an improvement in unit margins for this refinery. For the next cycle starting in May 2008, Shell Sarnia has again selected Criterion base metal catalyst for the second stage cracking reactor. Additionally, new reactor internals from Shell Global Solution will be installed for optimal catalyst utilization (2).

With confidence in the results of our pilot plant programs and a track record of proven commercial success, Criterion/Zeolyst have been able to aid other customers' decisions to replace their noble metal catalyst systems with base metal catalyst systems.

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