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Dewaxing Challenging Paraffinic Feeds in North America

Presented By:

Renata Szynekarczuk
Criterion Catalysts &
Technologies
Alberta, Canada

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by

Renata Szynekarczuk – Presenter
Criterion Catalysts & Technologies

Michelle Robinson
Laurent G. Huve
Shell Global Solutions International B.V.

Abstract

With more difficult and highly paraffinic feedstocks entering the market as well as increasingly more stringent diesel specifications, there is a growing need to provide alternative opportunities to upgrade diesel quality. Applying specialty catalysts and processes provides cost-effective ways to improve the cold flow properties of diesel ULSD units, giving refineries opportunities to expand market share and increase overall refinery profitability. This paper discusses a range of successfully developed and commercially-proven catalytic dewaxing solutions, some of which have been applied in the last decade in North American units to improve diesel product cold flow properties.

Introduction

Improving the cold flow properties of paraffinic feedstocks in a selective way has become a hot topic during the last decade as refiners search for more effective and cost-efficient ways to achieve cold flow property improvements. The growing trend is to use catalytic dewaxing to limit the use of cold flow additives, reduce kerosene blending requirements, upgrade heavier feedstocks with higher cloud and/or pour points and, consequently, to create more room in the blending pool for heavier feeds.

The increasingly stringent specifications, rise of new types of crudes from different origins or process routes, and desire to sell products while satisfying cold flow properties specifications result in the need to process more challenging types of feedstocks – some of them being heavier, some lighter but of different compositions, and some being significantly more paraffinic.

This paper gives an overview of the possible catalytic dewaxing solutions that can be offered to solve different customers' cold flow property improvement challenges. Advances in catalyst and process development by Shell Global Solutions & Criterion are allowing not only a better understanding of what is achievable in a prescribed set of conditions and constraints but also leading to the development of innovative solutions in a co-creation mode with specific customers.

Examples of research and development carried out in the field of paraffinic feedstocks understanding and processing as well as an illustration of commercial applications of Shell Global Solutions/Criterion catalytic dewaxing for some challenging feedstocks are highlighted in this paper.

Cold Flow Improvement via Catalytic Dewaxing (CDW)

At low temperatures, products with “waxy” components start to crystallize and affect the flow characteristics of the final product. To avoid problems and to ensure that products meet low temperature flow properties, different techniques have been and are being used in the industry, from additization and/or kerosene blending to advanced catalytic dewaxing.

Three main cold flow properties are typically used to characterize a diesel fuel: Cloud Point (CP), the most stringent one; Pour Point (PP); and Cold Filter Plugging Point (CFPP).

For all of these properties there are standard industrial analytical methods prescribed.

Flow improvers modify the wax crystallization process by reducing the crystal size and/or the lattice formation of the solid phases and reduce both the cold filter plugging point and the pour point. However, the cloud point, a property related to individual component characteristics and driven by the heaviest molecules within the feedstock boiling range, is also the most thermodynamically driven property. Consequently, it is also the most difficult to effectively reduce by additization or by cost-effective dilution by kerosene. This becomes a greater challenge when the feeds are becoming more paraffinic in nature with the presence of longer and consequently higher cloud linear alkanes.

On the contrary to Cloud Point, cold flow improvers can significantly reduce Cold Filter Plugging Point and Pour Point.

Cloud Point improvement using additives is typically within a couple of degrees, up to a maximum of 3 to 4°C (5 to 7°F). With hydrotreated kerosene blending, a Cloud Point improvement (reduction) of ~1°C (1.8°F) is typically achieved for every 10% of kerosene added. If a Cloud Point improvement of more than 6-8°C (11-14°F) is desired, then catalytic dewaxing is usually a more long-term economical solution than any other alternative method (additives and/or kerosene blending and /or feedstock boiling range adjustment).

Improving the cold flow properties of any feedstock requires mainly modifying or removing linear alkanes (usually referred to as “paraffins”). This can be achieved by either a physical separation method (extraction) or by different selective chemical reactions (catalytic dewaxing). This paper is focusing on the latter ^[1].

Conversion of linear and/or slightly branched alkanes during catalytic dewaxing is typically carried out by a combination of selective cracking and isomerization reactions (Figure 1), the objective being to reduce cold flow properties (represented here by melting point) either by selective cracking to lighter alkanes and iso-alkanes of lower cold flow properties or by isomerization of alkanes to iso-alkanes of similar molecular weight but lower cold flow properties.

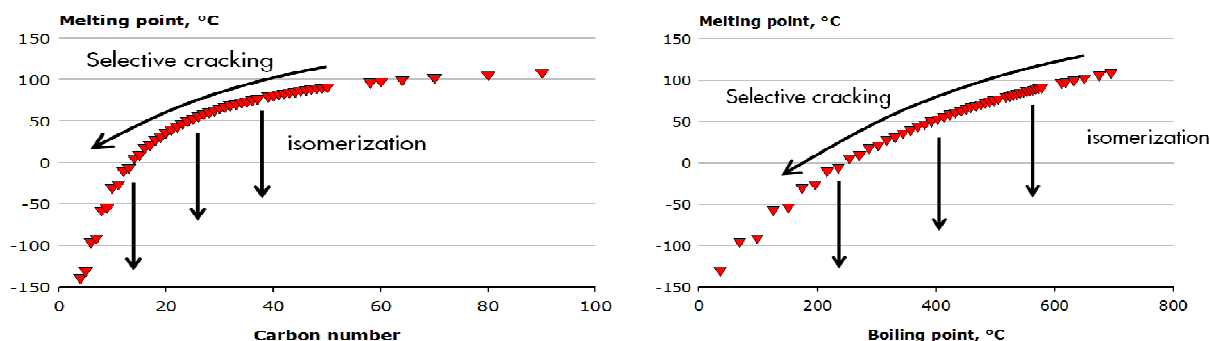


Figure 1: Possible reaction routes to decrease the melting point of a linear alkane of a given carbon number (i.e., a given boiling point). Note the difference between the two routes: selective cracking decreases both the melting point and the boiling point (carbon number), while isomerization mostly affects the melting point leaving the boiling point slightly impacted ^[1] and the carbon number unchanged.

Influence of Molecular Structure on Cold Flow Properties

A significant amount of research, including the use of modern and recently developed analytical tools, has been carried out in the last 5 to 15 years resulting in a large database aiming at investigating and capturing the influence of molecular structure on cold flow properties.

The studies focused on understanding what type of isomerization and/or selective cracking of linear alkanes had the highest effect on cold flow improvement, what were the governing parameters, and how this knowledge can be used to design catalysts and catalytic systems of superior performance. This allows development of solutions to solve a number of key issues such as achieving deep dewaxing (several tens of °C) of diesels or base oils with limited yield loss and limited gas formation while keeping other properties within agreed specifications or better.

A single methyl group branching of linear alkanes already has a significant impact on the cold flow properties (represented here by melting point as found in literature ^[2] or measured on pure sample).

For example, while nonadecane, the linear alkane with 19 carbon atoms, $\text{CH}_3(\text{CH}_2)_{17}\text{CH}_3$ boiling at 329.7°C (625.5°F) within in the diesel boiling range, has a melting point of +32.1°C (89.8°F), any of its single methyl-branched isomers has a significantly lower melting point, the highest being for the 2-methyl-octadecane with a melting point of +13°C (55.4°F), the lowest for the methyl group located in the middle of the chain, the 9-methyl-octadecane with a melting point of -16.5°C (2.3°F) (Table 1).

But while positioning a methyl group in the middle of the chain is showing the largest melting point improvement, it is also known that a single methyl group is not sufficient when chain length is increasing as illustrated by the comparison of 9-methyl octadecane, 10-methyl eicosane and 13-methyl hexacosane melting points (Table 2, left). Therefore, more branching is required to further decrease the melting point as illustrated with n-triacontane and 2, 6, 10, 15, 19, 23 - hexamethyl tetracosane (Table 2, right).

Table 1: Melting points of the single methyl branched isomers of nonadecane

Methyl position in the chain (C₁₉H₄₀)	Melting point °C (°F)
2-methyl-octadecane	+13.0 (+55.4)
3-methyl-octadecane	+0.5 (+32.9)
4-methyl-octadecane	-1.0 (+30.2)
5-methyl-octadecane	-13.5 (+7.7)
6-methyl-octadecane	-4.0 (+24.8)
7-methyl-octadecane	-16.0 (+3.2)
8-methyl-octadecane	-10.0 (+14.0)
9-methyl-octadecane	-16.5 (+2.3)

Table 2: Melting point comparison for methyl branching of various hydrocarbons with increasing chain length and effect of multi-methyl group branching on melting point and viscosity index for triacontane

Main chain length (carbon number) Methyl group position	Melting point °C (°F)	Formula (C ₃₀ H ₆₂)	Melting point °C (°F)	Viscosity Index
18 / 9 methyl octadecane	-16.5 (+2.3)	n-triacontane (n-C ₃₀ H ₆₂)	+66 (+151)	190
20 / 10 methyl eicosane	-3.8 (+25.2)	2,6,10,15,19,23-hexamethyltetracontane	-38 (-36)	116
26 / 13 methyl hexacosane	+28.9 (+84.0)			

Of course, the more the molecules are isomerized, the more boiling point shift is observed as evidenced with high-resolution, two-dimensional gas chromatography (2xGC) applied to carbon (Figure 2).

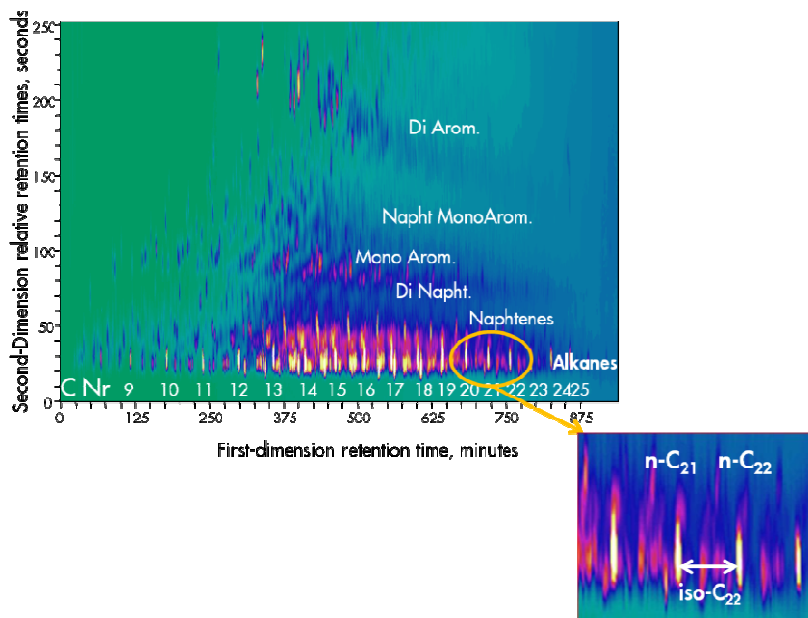


Figure 2: 2xGC carbon - n-alkanes & isomerized alkanes in diesel boiling range (and extract)

The isomers of docosane, n-C₂₂H₄₆, are located between the elution of n-C₂₁ and n-C₂₂.

Some other key properties may also be somewhat affected such as a small decrease of Cetane Index upon isomerization for deeply dewaxed diesel fuels or a decrease in viscosity index for base oil (Table 2, right).

This was of particular interest for Shell as the company was looking to invest significantly in gas-to-liquids (GtL) applications where dewaxing of essentially heavy paraffinic feedstock was targeted. Since then, Pearl Qatar started up smoothly with two trains including catalytic dewaxing of light- and medium-heavy highly paraffinic base oils showing excellent performance of the highly selective isomerization-dewaxing reactors where cloud/pour point improvements as high as 60 to 80°C (108 to 144°F) are achieved on Shell/Criterion dewaxing catalyst SLD-821, leading to ultra-high quality base oils (Table 3 & Figure 3).

Table 3: Shell GtL Base Oils Quality & main characteristics ^[3]

Shell GTL Base Oils	4 cSt	5 cSt	8 cSt
Vk100 °C (cSt)	3.8-4.2	4.8-5.4	7.5-8.5
Vk40 °C (cSt)	-	-	-
Viscosity Index	135	145	150
VdCCS, -30 °C	1000	1860	5300
Pour Point, °C	< -30	< -24	< -15
Noack Volatility, %m	12	9	2
Flash Point, °C (D-93)	215	232	240

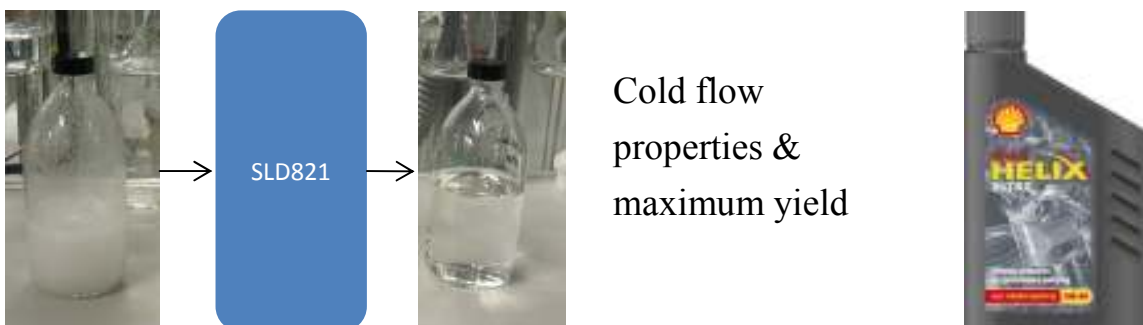


Figure 3: Heavy paraffins mixture dewaxing for producing high-quality base oil for Shell lubricants

Influence of Boiling Range Distribution of n-Alkanes on Cold Flow Properties & Dewaxing

On top of the molecular structure and molecule re-arrangement (i.e., via isomerization) playing a significant role in cold flow properties improvements, the linear alkanes distribution and their relative amounts is also significantly influencing the dewaxing process and its outcome. This is illustrated when comparing two very similar feedstocks in overall bulk properties but differing in a subtle way by their linear alkanes distribution and relative amounts (Figure 4). The two feedstocks represented do contain 19.4 and 20 %wt n-alkanes, respectively, as quantitatively measured by 2xGC carbon. But the first feedstock (in red) does contain almost 15% of C_{17}^{+} n-alkanes and less C_{16}^{-} n-alkanes while the second feed (in yellow) contains only 12.5 %wt of C_{17}^{+} n-alkanes and more C_{16}^{-} . Such differences do influence the outcome of the dewaxing process when targeting a given improvement.

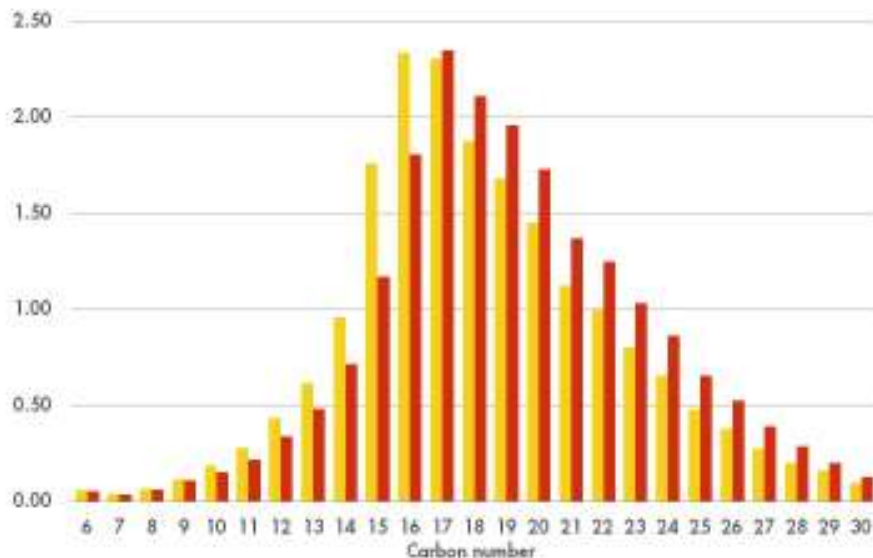


Figure 4: Comparing two feedstocks of very similar bulk properties but somewhat different n-alkanes distribution.

Examining details in what is typically happening in selective cracking dewaxing with highly selective catalyst for Shell/Criterion's dewaxing catalyst portfolio is revealing (Figure 5).

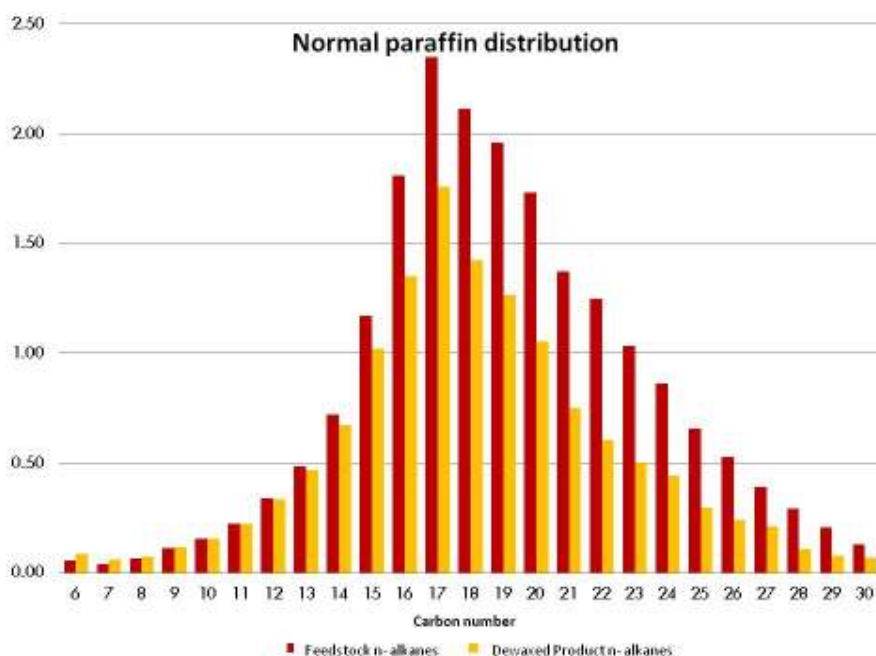


Figure 5: Comparing feedstock and dewaxed product for linear alkanes content & distribution.

To be efficient in cold flow improvement, catalytic dewaxing must target the heaviest linear alkanes and this is what can be seen when using detailed characterisation of feed and products (Figure 6).

The more linear alkanes above C₁₆, the more the conversion needed and, as a consequence, the higher the possible yield loss (i.e., naphtha make). These observations are key factors in developing optimal technical solutions with customers that have one or more of these challenging paraffinic crudes to be dewaxed in their pool.

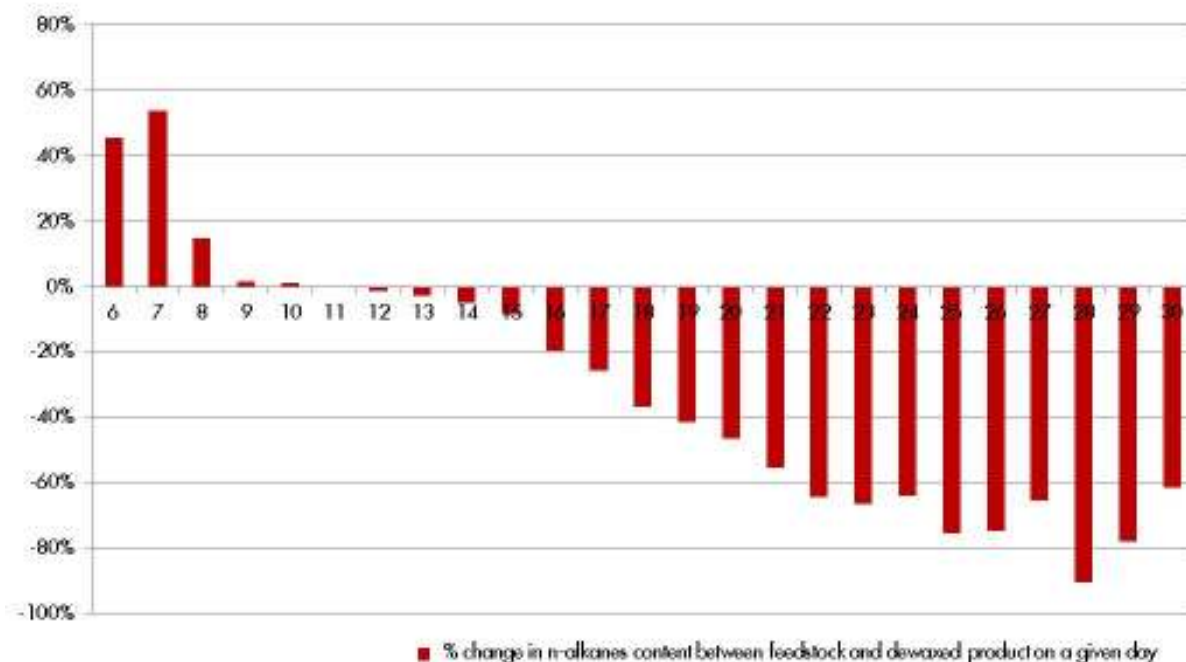


Figure 6: Change in n-alkanes composition between feedstock and dewaxed product for a given day of operation.

Dewaxing Catalysts Selectivity

Shell Global Solutions and Criterion have developed state-of-the-art selective cracking (SDD-800) and isomerization (SDD-821) dewaxing catalysts for distillate applications. A number of the previously mentioned findings were incorporated into their developments.

Both of these catalysts have extensive commercial experience in various units worldwide. SLD-821, a base oil counterpart dewaxing catalyst, was developed along the same lines of thoughts and is currently applied in different, highly paraffinic feedstock units.

Typically, a selective dewaxing catalyst converts exclusively linear alkanes (“waxes”), which are typically representing a maximum of 10-15% of standard feedstock molecules. In the absence of linear and/or slightly branched alkanes that can be converted within the catalyst pore structure; no reaction will take place with these types of catalysts as shown in Figure 7. On the contrary, the larger the amount of linear alkanes present, the deeper the conversion will be, resulting in both molecule re-arrangement, boiling point shift due to isomerization and some cracking, albeit selective, into lighter molecules.

For well-balanced dewaxing solutions, a specialty dewaxing catalyst is typically installed at the back- end of the process lineup, where all other required properties of the targeted product have been already met. To prevent yield loss, medium-pore zeolites, as an active acidic catalyst component, are used in combination with a binder to selectively crack or isomerize linear and slightly branched alkanes present in the feed and are thus limiting the cold flow properties.

For catalytic dewaxing, reactant-shape selective conversion of linear paraffinic molecules theoretically describes the required catalyst selectivity. The reactant-shape selectivity concentration of linear alkanes is maximized in the acidic zeolite, and conversion (isomerization or cracking) is carried out at acidic catalytic centers. In commercial applications, the effectiveness of catalyst selectivity can be inhibited by adsorbing poisons on the acidic site, leading to blocking of catalyst active sites. Poison adsorption is usually reversible when properly controlled.

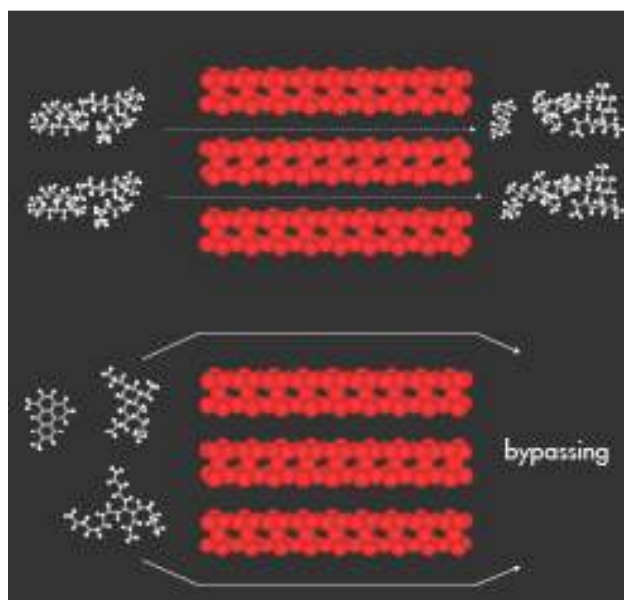


Figure 7: Illustration of reactant shape selectivity in zeolite containing dewaxing catalyst

The level and type of inhibitors or catalyst poisons will have an impact on the choice of a dewaxing solution and its related catalyst selection. Highly selective dewaxing is possible if no acidic function is present on the “outside” of the zeolite pores and channels. Reactivity of feedstock molecules is based upon their shape such that the linear and branched molecules can react within the pore structure of the zeolite while the other more bulky molecules stay untouched. Therefore, dewaxing catalysts presenting a well controlled outer surface composition are used for dewaxing by selective cracking and/or isomerization.

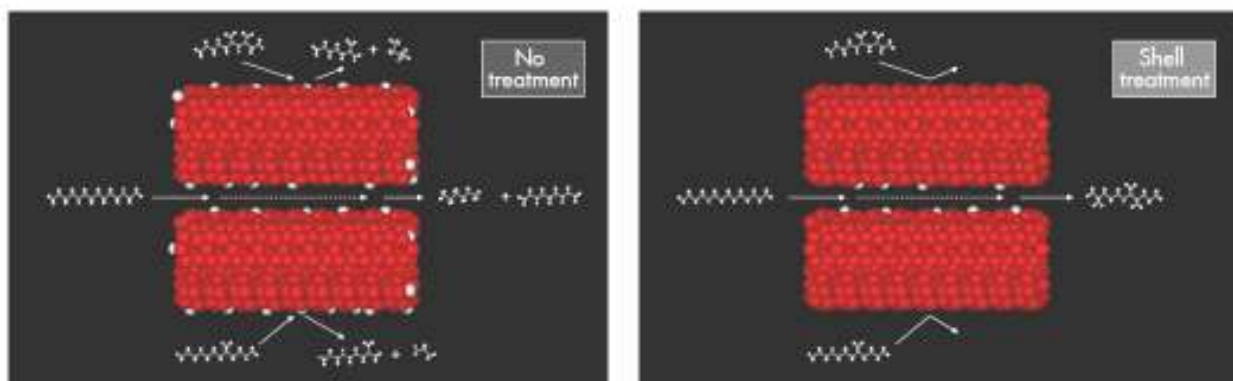


Figure 8: Reactivity (cracking) on outer surface of untreated dewaxing catalyst compared to no activity after Shell's proprietary passivation treatment

To make the outer surface of a catalyst inactive, it is necessary to chemically passivate the surface. There are a number of outer surface passivation methods described in open literature such as impregnation by inert organic oxides, sublimation, or inorganic or organic agents binding with the acidic centers on the outer surface of a zeolite. All approaches, as well as Shell's proprietary surface passivation treatment, use reactant shape selectivity and passivation agents with a size that limits their effects to the outer surface, while they can't easily enter and/or diffuse within the smaller pore structure (Figure 8).

A carefully selected zeolite type and controlled acidity during synthesis before embedding the crystals in a carrier, as well as the proprietary surface passivation that eliminates the catalytic activity on the outer surface of the embedded zeolite crystals, delivers superior performance in term of yields and resistance to deactivation by coke formation as compared to conventional dewaxing catalysts used in diesel or base oil dewaxing applications (Figure 9).

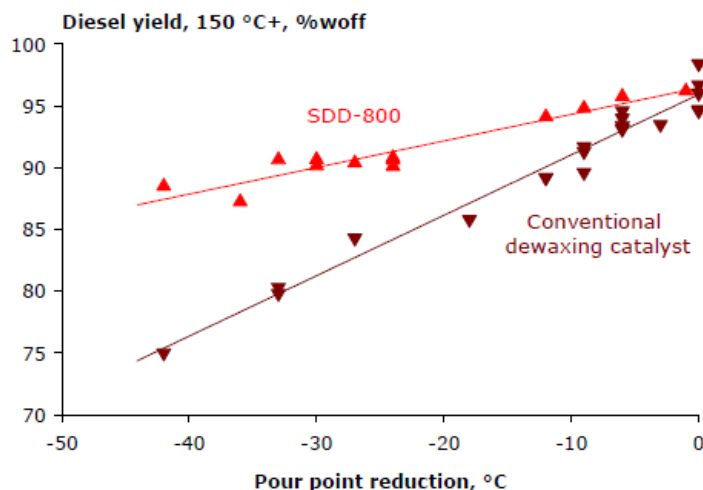


Figure 9: Performance comparison of Shell SDD-800 and a conventional dewaxing catalyst.

Exceptional diesel yields are achieved with SDD-800 as a function of pour or cloud point reduction as compared to the lesser results found when using a conventional dewaxing catalyst. Outside surface passivation clearly improves diesel yields and is a key part of the successful application of Shell/Criterion dewaxing catalyst technology solutions to challenging paraffinic cases where improvement can be seen with any conventional technology. In addition, the Shell/Criterion dewaxing catalysts surface treatment acts as a protection against coke and results in extended life; commercial operation of up to 7 years without reactivation or regeneration have been reported ^[1].

The proprietary surface treatment also helps the catalyst to resist poisoning. For Shell/Criterion dewaxing catalysts, most of the poisoning effects are fully reversible. Nitrogen slip to the dewaxing catalyst can cause temporary activity decline, but the catalyst can fully recover after nitrogen levels are reduced to allowable levels. This possibility of tempering the dewaxing catalyst activity is used in commercial units that operate in winter (dewaxing) and summer (ULSD) modes allowing flexibility to switch on/off the dewaxing catalyst on demand. During summer mode, when dewaxing is not needed, the dewaxing catalyst is dormant in the reactor and has a negligible dewaxing activity and consequently marginal yield losses. During winter mode, the dewaxing catalyst is turned on by desorbing the nitrogen adsorbed on the catalyst during the summer mode months. In winter mode, the activity of the dewaxing catalyst can be tuned to the desired cold flow improvement levels by adjusting the temperature of the dewaxing catalyst bed.

First versus Second-Stage Dewaxing

Depending on unit capability, targets and dewaxing catalyst choice, Shell/Criterion dewaxing technology can be applied in first- or second-stage dewaxing configuration (Figure 10).

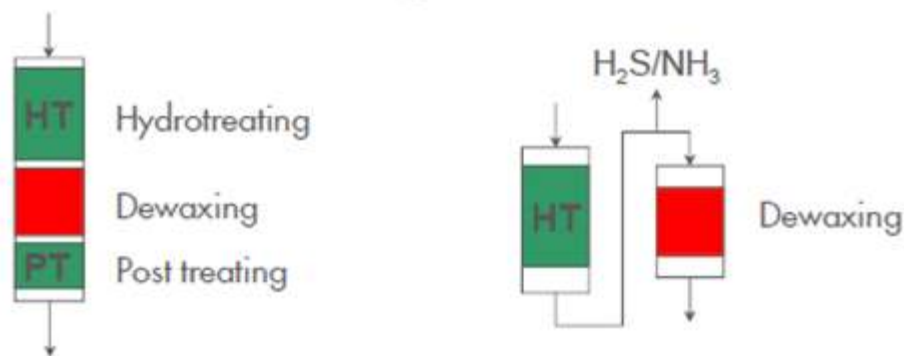


Figure 10: First and second-stage dewaxing catalyst configuration.

In first stage configuration, the dewaxing bed is part of the hydrotreating section in the so-called “drop in” solution. As a result, the nickel-based dewaxing catalyst is exposed to organic nitrogen slip and NH_3 that could adsorb on dewaxing catalyst acidic site and inhibit catalyst performance. Organic sulphur slip and/or H_2S have no effect on first-stage dewaxing catalyst activity or selectivity.

First-Stage Dewaxing can provide a reasonably low cost “drop in” solution in existing hydrotreaters.

In second stage configuration, a minimum of two reactors with stripper in between is required. Feedstock is hydrotreated in the first reactor and the H_2S and ammonia is stripped from the liquid before it is dewaxed in a dedicated clean environment second reactor allowing the use of highly selective noble metal based isomerization-dewaxing catalysts.

As a result, the cost of implementation is expected to be somewhat higher than a first-stage dewaxing solution; however, compared to first-stage dewaxing, noble metal isomerization-dewaxing delivers superior distillate yields and products.

To avoid mercaptan formation, the dewaxing catalyst is followed by a small post-treating bed to ensure that product color properties are met.

The next section illustrates the development of Shell/Criterion dewaxing solutions, step improvement and way forwards from pilot plant confirmation testing to commercial implementation.

Developing Solutions for Deep Dewaxing of Highly Paraffinic Feedstocks

As with other technology solution applications, the deep dewaxing of highly paraffinic feedstocks can be developed in several steps depending on the requirements, market drivers, level of equipment available and/or re-usability, and amount of investment that can be justified for the economical viability of the project. Three typical steps are considered (Figure 11): sweating the asset, where a catalytic solution is implemented with minimum modification/impact on the existing unit; revamp where a number of key modifications are required to adopt a better solution; and, finally, the development of a new solution aimed at breakthrough performance but with a significant investment required. These three steps have been developed for catalytic solutions and implemented successfully in a number of commercial operations or in final phase of development when targeting specifically deep catalytic dewaxing of highly paraffinic feedstocks. The main three steps will now be illustrated with key examples and on-going developments.

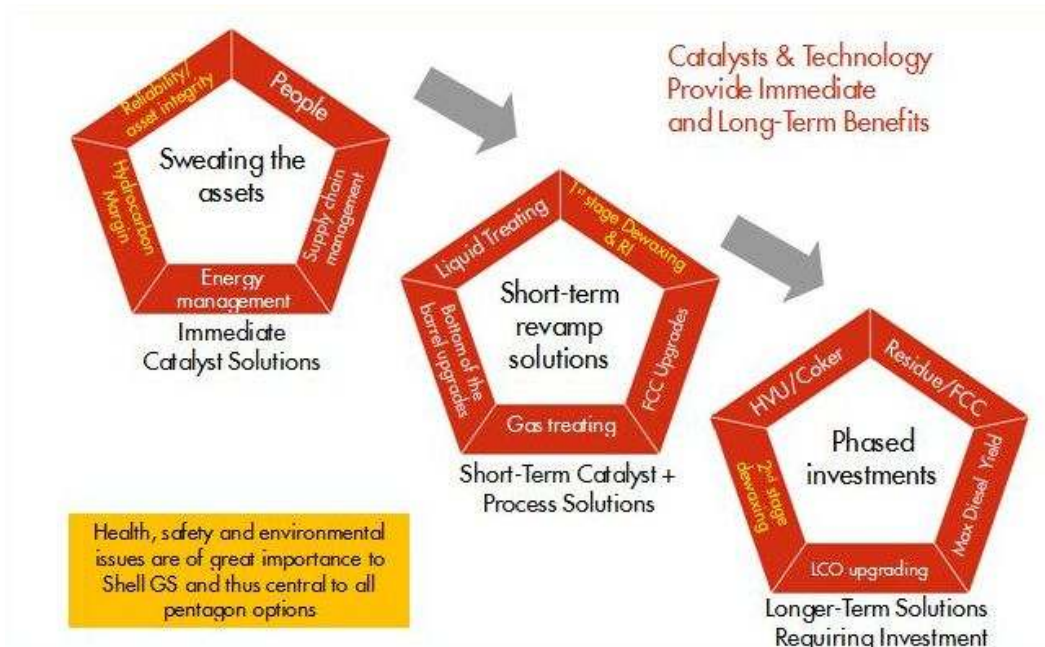


Figure 11: The pentagons - From sweating the asset to short-term catalyst & process solutions to longer-term solutions requiring investment

Case study 1: A customer was looking at applying a deep catalytic dewaxing solution in an existing unit while minimizing any investment and maintaining the same depth of hydrodesulphurisation. With targeted pour and cloud point improvements of 10 to 45°C (18 to 81°F) and starting from a feedstock containing between 20 and 30% of heavy paraffinic components, only a first-stage dewaxing solution was possible. By adjusting smartly the location of the dewaxing catalyst bed, using SDD-800 and the right combination of HDS/HDN hydrotreating catalysts, it was possible to develop a solution that was compatible with the capability of the existing unit and for cycles as long as 5 years, without having to rejuvenate, regenerate or change the dewaxing catalyst. With the new catalytic system in place and with the right catalyst configuration and process conditions applied, it was possible to obtain deep to very deep dewaxing (20 to 45°C (36 to 81°F) improvement) while maintaining dewaxed diesel yields between 90 and 86 %wt on feed, by combining selective cracking and isomerization on SDD-800 (Figure 12).

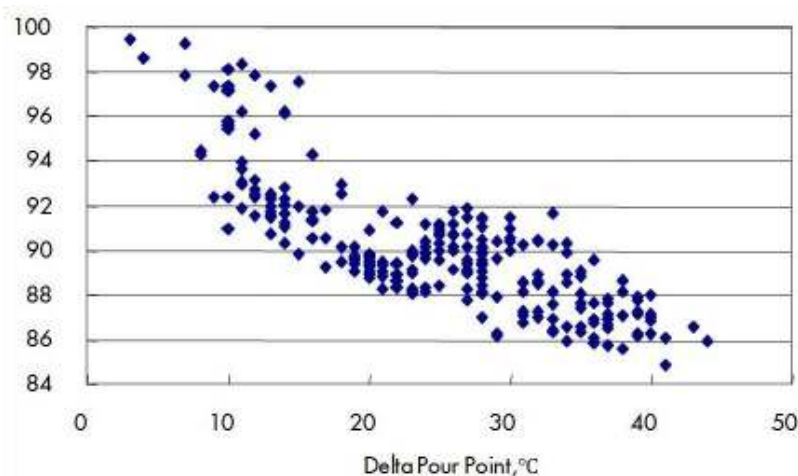


Figure 12: Dewaxed diesel yield as a function of delta pour point in commercial operation

Case studies 2 & 3: The challenge becomes significantly larger when even more paraffinic feedstocks have to be considered. The first approach is to study whether or not a first-stage dewaxing option is possible and, if not applicable in a straightforward way, how to adjust it to make it possible, at least temporarily, to achieve very deep dewaxing at still acceptable yield loss.

This was extensively studied by Shell Global Solutions and Criterion on highly paraffinic feedstocks of different origins comparing an adapted first-stage dewaxing solution and a second-stage option in the presence of limited amounts of poison (namely sulphur).

Case study 2: The first option considered was an adapted first-stage dewaxing solution with bed-to-bed temperature control on the dewaxing catalyst to ensure a stable operation throughout the cycle, avoiding uncontrolled deeper dewaxing than required and consequently more yield loss than suitable at any point of the cycle.

This resulted in a rather controlled operation with very deep dewaxing achievable albeit at the expense still of yield loss (Figure 13). It was proven possible, within the unit constraints, to achieve depth of dewaxing as high as 60°C (108°F) while maintaining a stable unit operation and sufficiently high yield of good quality deeply dewaxed diesel and gasoline.

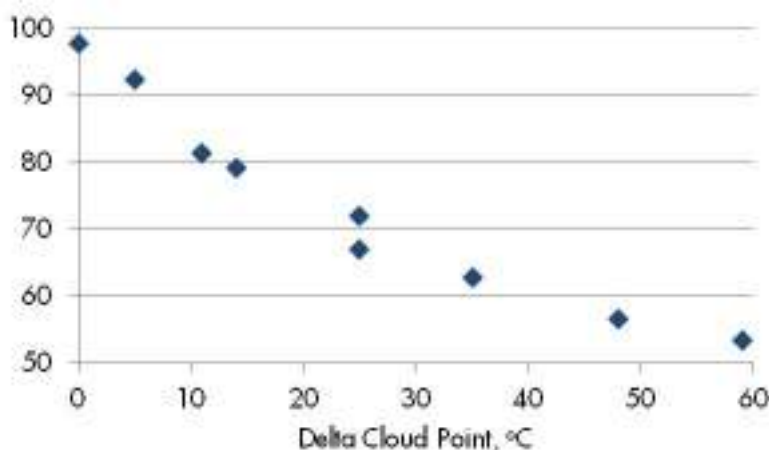


Figure 13: Very deep dewaxing of highly paraffinic feedstock (selective cracking)

Case study 3: The next step in developing adequate solutions for such a challenging type of highly paraffinic feedstock (containing up to 90-95 %wt of paraffinic components) is to consider a complete revamp of an existing unit into a two-stage dewaxing application. Shell Global Solutions International has extensively studied such an option, starting from paraffinic feedstocks with pour point as high as 40 to 45 °C (104 to 113°F) aiming at reaching cloud point and/or pour point improvement as high as 70 to 75°C (126 to 135°F)! One of the key challenges in such an operation is the remaining presence of poisons, mainly sulphur and nitrogen that may hamper the activity and selectivity of isomerization-dewaxing noble metal dewaxing catalysts.

Very long duration tests (>15000 hours (~ 21 months)) were carried out in a large pilot plant to develop in detail the understanding around such a challenging operation by looking at various paraffinic feedstock poisoning levels (from under detection limit to as high as 19 ppmw sulphur) and at varying space velocities.

To make it comparable, the same product quality was targeted –a product having a pour point of -30 °C (-22°F), starting from feedstock pour point ranging between 40 and 45°C (104 to 113°F). While it is more than beneficial to process feedstock as clean as possible from poisons, the presence of limited amount of sulphur does not prevent reaching the same high quality product albeit at somewhat higher temperature

(Figure 14). Yield-wise, it was proven that dewaxed yield as high as 80-87 %wt of feed can be achieved even at the deepest dewaxing depth achieved.

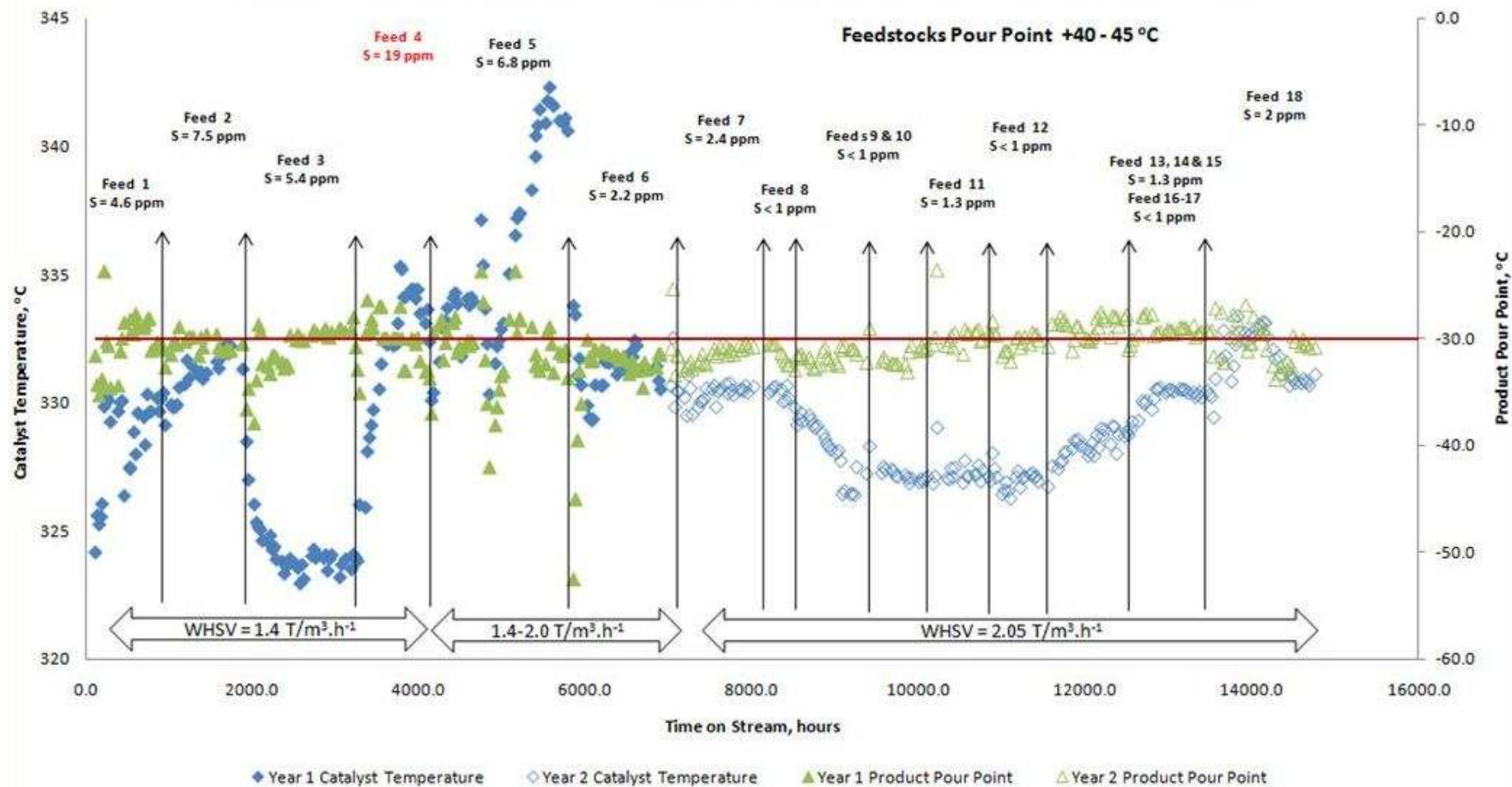


Figure 14: Extensive pilot plant testing of several highly paraffinic feedstocks containing various amounts of sulphur and processed under different process conditions (WHSV & temperature) for deep dewaxing

Conclusions

Catalytic dewaxing provides an alternative method for cold flow improvements of diesel and lube oil that cannot be met to a significant level by more conventional methods. The latest generation of dewaxing catalysts is specifically tailored to the application and feedstock type by utilizing shape selective zeolites to preserve maximum distillate yields. Shell/Criterion's dewaxing catalysts superior selectivity is ensured by a proprietary outer surface passivation method. With the current increase of heavy paraffinic material on the market, refiners must adapt their processing facilities to meet these new challenges.

The development of light tight oils (LTO) in North America, as well as the presence of some local highly paraffinic crudes in former Soviet Union, China and North America, is now opening the route to an increase in applications of dedicated catalytic dewaxing solutions in refineries.

With a long history in gas-to-liquid technology development, ability to create or co-create, develop and implement integrated solutions including process and catalyst aspects, Shell Global Solutions and Criterion, together with their partners, are opening a new way to the future of refining.

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