Dewaxing challenging paraffinic feeds

Catalytic dewaxing using recent developments in dewaxing catalysts provides an alternative method for cold flow improvement in diesel and lube oil

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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 improvements in cold flow properties. 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.

Increasingly stringent specifications, the rise in new types of crude from different origins or process routes, and the desire to sell products that meet cold flow property 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 article gives an overview of the possible catalytic dewaxing solutions that can be offered to solve different challenges in improving cold flow properties. Advances in catalyst and process development by Shell Global Solutions and Criterion enable not only a better understanding of what is achievable in a prescribed set of conditions and constraints but are also leading to the development of innovative solutions in association with customers.

Examples of research and development carried out in understanding and processing paraffinic feedstocks, as well as an illustration of commercial applications of Shell Global Solutions' and Criterion's catalytic dewaxing for some challenging feedstocks, are highlighted here.

Cold flow improvement via catalytic dewaxing

At low temperatures, products with 'waxy' components start to crystallise 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 the use of additives and/or kerosene blending to advanced catalytic dewaxing.

Three main cold flow properties are typically used to characterise a diesel fuel: cloud point, the most stringent property; pour point; and cold filter plugging point. Standard industrial analytical methods are prescribed for each of these properties.

Flow improvers modify the wax crystallisation 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 additives or by cost-effective dilution with kerosene. This becomes a greater challenge when feeds are becoming more paraffinic in nature, with the presence of longer and consequently higher cloud, linear alkanes.

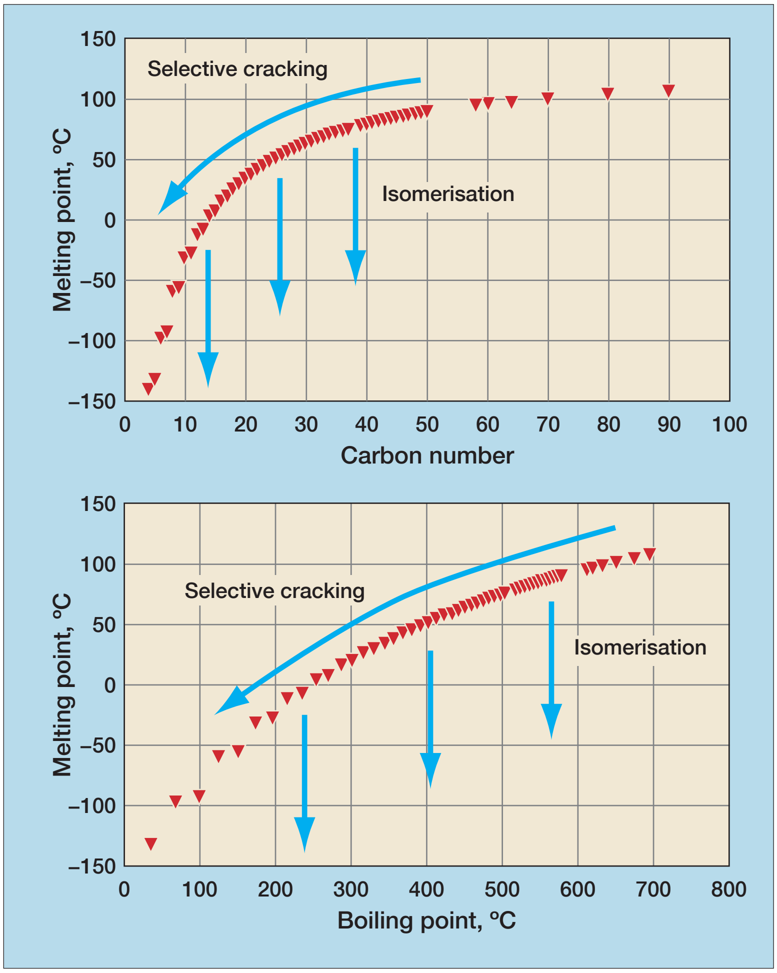

Figure 1 Possible reaction routes to decrease the melting point of a linear alkane of a given carbon number (that is, a given boiling point). Note the difference between the two routes: selective cracking decreases both the melting point and the boiling point (carbon number), while isomerisation mostly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

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 3-4°C (5-7°F). With hydrotreated kerosene blending, a cloud point 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 economical long-term solution than any 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 either by a physical separation method (extraction) or by different selective chemical reactions (catalytic dewaxing). This article focuses 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 isomerisation reactions (see **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 with lower cold flow properties or by isomerisation of alkanes to iso-alkanes with similar molecular weights but lower cold flow properties.

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 five to 15 years, resulting in a large database for investigating and capturing the influence of molecular structure on cold flow properties.

These studies focused on understanding what type of isomerisation and/or selective cracking of linear alkanes had the greatest 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 enables the development of solutions to a number of key issues such as achieving deep dewaxing (by several tens of degrees) of diesels or base oils with limited yield loss and limited gas formation while keeping other properties within agreed specifications or better.

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

For example, while nonadecane, the linear alkane with 19 carbon atoms, boiling at 329.7°C (625.5°F) within 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 2-methyl-octadecane with a melting point of +13°C (55.4°F), the lowest for the isomer with a methyl group located in the middle of the chain, 9-methyl-octadecane, with a melting point of -16.5°C (2.3°F, see **Table 1**).

Melting points of single methyl branched isomers of nonadecane

Methyl position in the chain ($C_{19}H_{40}$)	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 1

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

Melting points comparison for methyl branching of various hydrocarbons with increasing chain length and the 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-hexamethyltetracosane	-38 (-36)	116
26/13 methyl hexacosane	+28.9 (+84.0)			

Table 2

Of course, the more the molecules are isomerised, the greater the boiling point shift observed; this is illustrated by high resolution, two-dimensional gas chromatography (2xGC) applied to carbon (see **Figure 2**). The isomers of docosane, n-$C_{22}H_{46}$, are located between the elution of n-C_{21} and n-C_{22}.

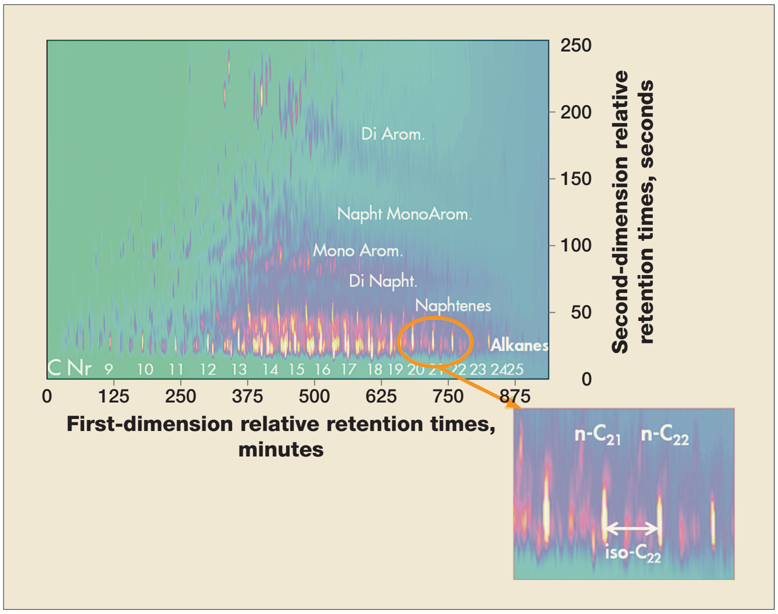

Figure 2 2xGC carbon - n-alkanes and isomerised alkanes in the diesel boiling range (and extract)

Some other key properties may also be affected, for instance a small decrease in cetane index upon isomerisation for deeply dewaxed diesel fuels, or a decrease in viscosity index for base oil (see **Table 2**, right).

This was of particular interest to Shell as the company

Shell GTL base oils quality and main characteristics

Shell GtL base oils	**4 cSt**	**5 cSt**	**8cSt**
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

Table 3

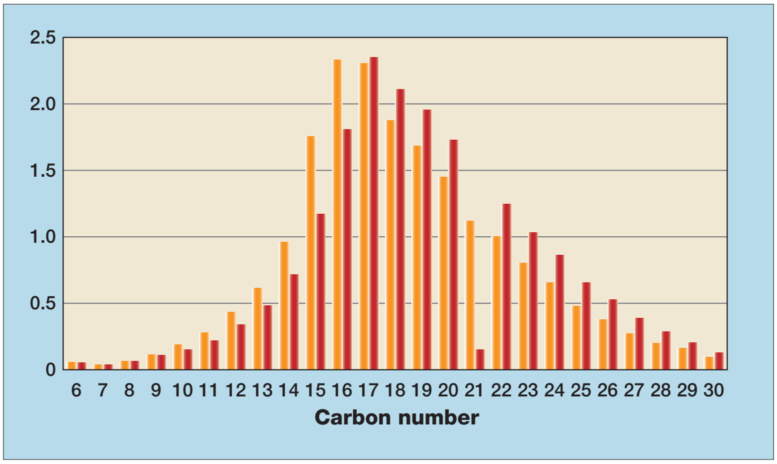

Figure 3 Comparing two feedstocks of very similar bulk properties but somewhat different distributions of n-alkanes

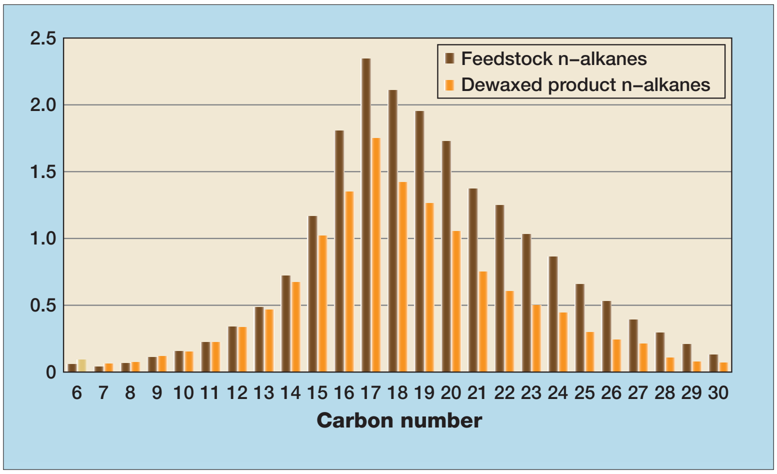

Figure 4 Comparing feedstock and dewaxed product for linear alkanes content and distribution

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

Influence of boiling range distribution of n-alkanes on cold flow properties and dewaxing

On top of molecular structure and molecule re-arrangement (via isomerisation) playing a significant role in cold flow properties improvements, the distribution of linear alkanes and their relative amounts also significantly influences the dewaxing process and its outcome. This is illustrated by comparing two feedstocks very similar in overall bulk properties but differing in a subtle way in their distribution and relative amounts of linear alkanes (see **Figure 3**). The two feedstocks contain 19.4 and 20 wt% n-alkanes respectively, quantitatively measured by 2xGC carbon. But the first feedstock (in red) contains 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 influence the outcome of the dewaxing process when a given improvement is targeted.

Examining the details of what typically happens in selective cracking-dewaxing with a highly selective catalyst from the Shell/Criterion dewaxing catalyst portfolio is revealing (see **Figure 4**).

To be efficient in improving cold flow, catalytic dewaxing must target the heaviest linear alkanes; this can be seen in a detailed characterisation of feed and products (see **Figure 5**).

The higher the proportion of linear alkanes above C_{16}, the more conversion is needed and, as a consequence, the higher the possible yield loss (as 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.

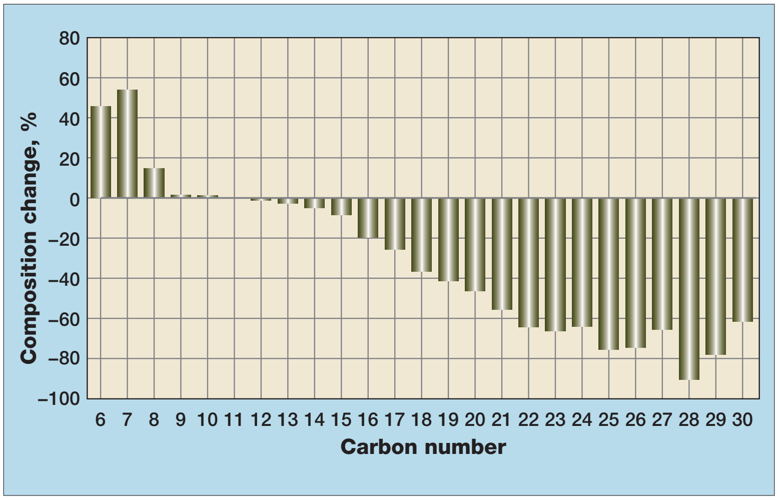

Figure 5 Change in n-alkanes composition between feedstock and dewaxed product for a given day of operation

Dewaxing catalysts selectivity

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

Both catalysts have extensive commercial application in units worldwide. SLD-821, a base oil counterpart dewaxing catalyst, was developed using the same principles and is currently applied in units processing highly paraffinic feedstocks.

Typically, a selective dewaxing catalyst converts exclusively linear alkanes ('waxes'), which typically represent 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 (see **Figure 6**). On the contrary, the larger the amount of linear alkanes present, the deeper the conversion will be, resulting in both molecular rearrangement and boiling point shift due to isomerisation and some cracking, albeit selective, into lighter molecules.

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

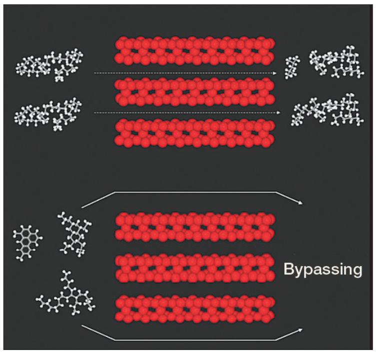

Figure 6 Illustration of reactant shape selectivity in zeolite containing dewaxing catalyst

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 maximised in the acidic zeolite, and conversion (isomerisation or cracking) is carried out at acidic catalytic centres. 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. Poisoned adsorption is usually reversible when properly controlled.

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. The reactivity of feedstock mole-

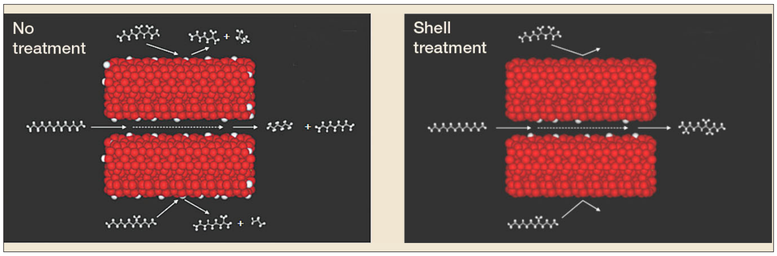

Figure 7 Reactivity (cracking) on the outer surface of untreated dewaxing catalyst compared to no activity after Shell's passivation treatment

cules is based upon their shape such that linear and branched molecules can react within the pore structure of the zeolite while the other, more bulky molecules are untouched. Therefore, dewaxing catalysts presenting a well-controlled outer surface composition are used for dewaxing by selective cracking and/or isomerisation.

To make the outer surface of a catalyst inactive, it is necessary to chemically passivate the surface. A number of outer surface passivation methods are described in the literature, such as impregnation by inert organic oxides, sublimation, or by inorganic or organic agents binding with the acidic centres 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 on the outer surface, while they cannot easily enter and/or diffuse within the smaller pore structure (see **Figure 7**).

A carefully selected zeolite type and controlled acidity during synthesis before embedding the crystals in a carrier, as well as surface passivation that eliminates 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 when compared to conventional dewaxing catalysts used in diesel or base oil dewaxing applications (see **Figure 8**).

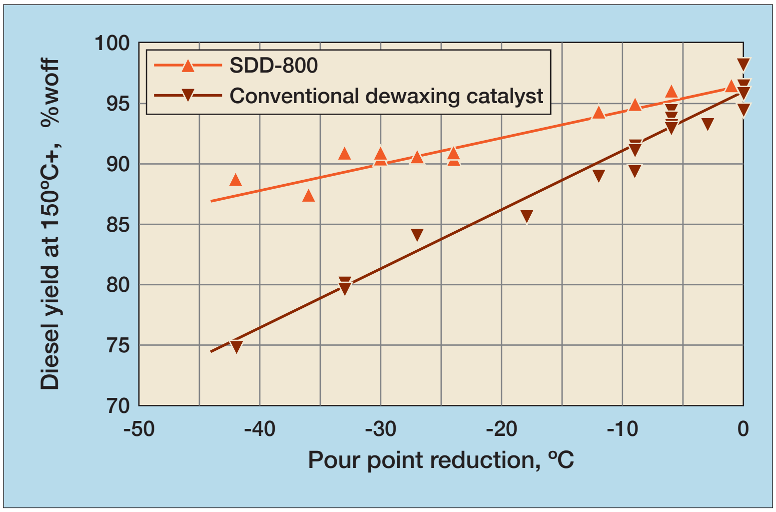

Figure 8 Performance comparison of Shell SDD-800 and a conventional dewaxing catalyst

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

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 a temporary decline in activity, but the catalyst can fully recover after nitrogen levels are reduced to allowable levels. Tempering dewaxing catalyst activity is used in commercial units that operate in winter (dewaxing) and summer (ULSD) modes, allowing the flexibility to switch the dewaxing catalyst on or off on demand. During summer mode, when dewaxing is not needed, the dewaxing catalyst is dormant in the reactor and has negligible dewaxing activity and consequently delivers marginal yield losses. During winter mode, the dewaxing catalyst is turned on by desorbing the nitrogen adsorbed onto the catalyst during the summer mode months. In winter mode, the activity of the dewaxing catalyst can be tuned to the desired levels of cold flow improvement by adjusting the temperature of the dewaxing catalyst bed.

First versus second stage dewaxing

Depending on unit capability, targets and choice of dewaxing catalyst, Shell/Criterion dewaxing technology can be applied in a first or second stage dewaxing configuration (see **Figure 9**).

In a 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 ammonia that could adsorb onto the dewaxing catalyst's acidic sites and inhibit catalyst performance. Organic sulphur slip and/or hydrogen sulphide 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 a second stage configuration, a minimum of two reactors with stripper in between is required. Feedstock is hydrotreated in the first reactor and hydrogen sulphide and ammonia are stripped from the liquid before it is dewaxed in a dedicated, clean environment second reactor, allowing the use of highly selective, noble metal-based isomerisation-dewaxing catalysts.

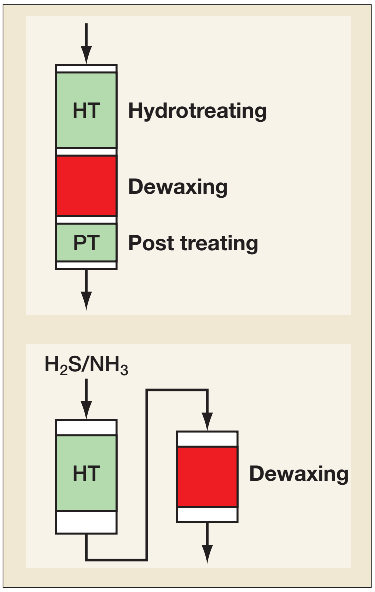

Figure 9 First and second stage dewaxing catalyst configuration

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

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

The following section illustrates the development of Shell/Criterion dewaxing solutions from pilot plant confirmation testing to commercial implementation.

Developing solutions for deep dewaxing of highly paraffinic feedstocks

The deep dewaxing of highly paraffinic feedstocks can be developed in several steps, depending on requirements, market drivers, level of equip-

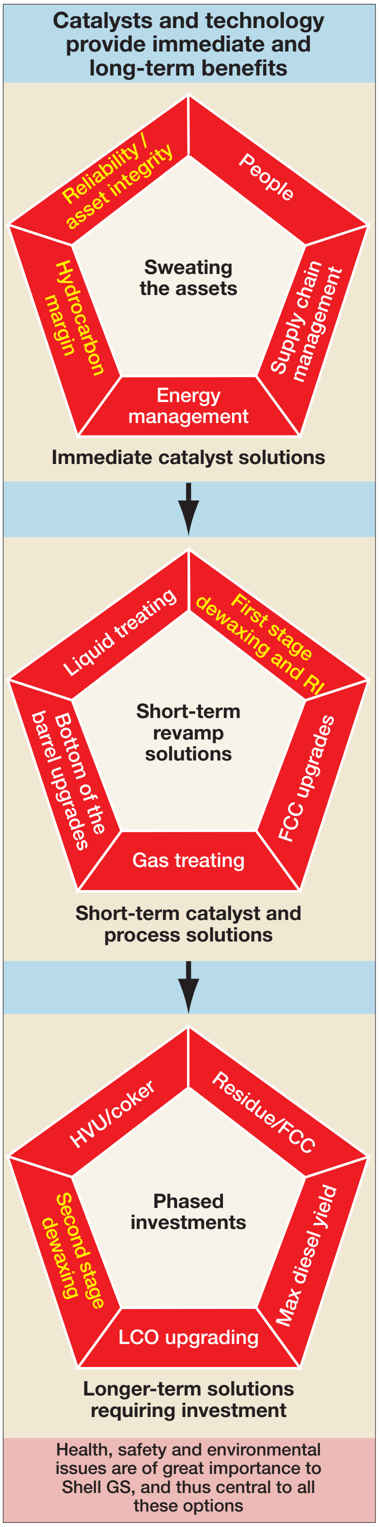

Figure 10 The pentagons: from sweating the asset to short-term catalyst and process solutions, to longer-term solutions requiring investment

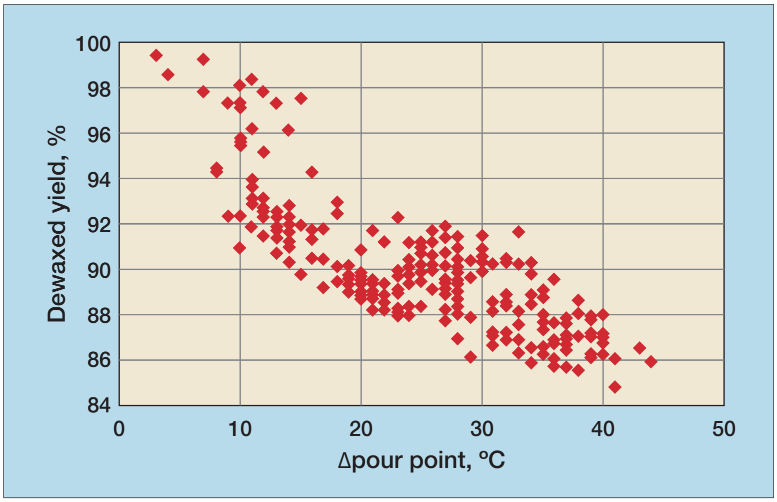

Figure 11 Dewaxed diesel yield as a function of delta pour point in commercial operation

ment available and/or re-usability, and the amount of investment that can be justified for the economic viability of the project. Three typical steps are considered (see **Figure 10**): sweating the asset, where a catalytic solution is implemented with minimum modification to, or impact on, the existing unit; revamp where a number of key modifications are required to adapt 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 are implemented successfully in a number of commercial operations or in the final phase of development when targeting specifically deep catalytic dewaxing of highly paraffinic feedstocks. The three main steps will be illustrated with examples and on-going developments.

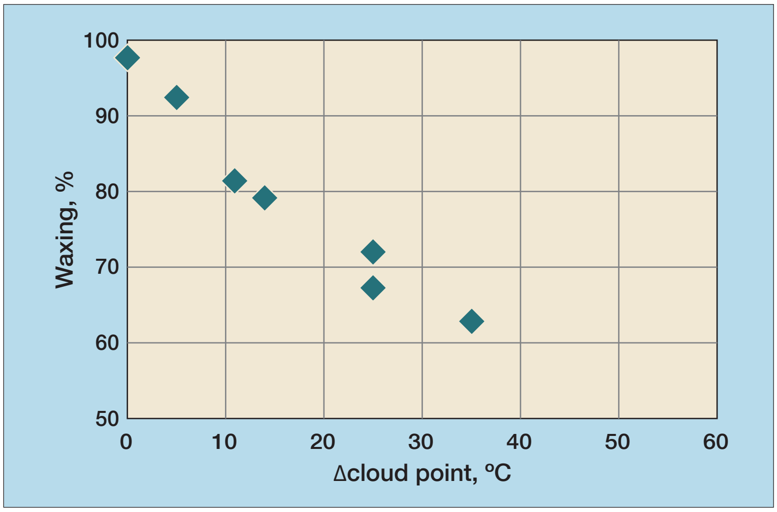

Figure 12 Very deep dewaxing of highly paraffinic feedstock (selective cracking)

Case study 1

A customer wanted a deep catalytic dewaxing solution in an existing unit with minimum investment and the same depth of hydrodesulphurisation. With targeted pour and cloud point improvements of 10-45°C (18-81°F) and starting from a feedstock containing 20-30% of heavy paraffinic components, only a first-stage dewaxing solution was possible. By adjusting 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 five 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 (20-45°C, 36-81°F improvement) while maintaining dewaxed diesel yields between 90 wt% and 86 wt% on feed, by combining selective cracking and isomerisation on SDD-800 (see **Figure 11**).

The challenge becomes significantly greater 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 it is not applicable in a straightforward way, how to adjust it to make it possible, at least temporarily, to achieve very deep dewaxing for a still-acceptable yield loss.

This was extensively studied by Shell Global Solutions and

Criterion on highly paraffinic feedstocks of different origins by comparing an adapted first stage dewaxing solution and a second stage option in the presence of limited amounts of poison (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 stable operation throughout the cycle, avoiding uncontrolled, deeper dewaxing than required and consequently more yield loss than desired at any point of the cycle.

This resulted in a rather controlled operation with very deep dewaxing achievable, albeit at the expense of yield loss (see **Figure 12**). It proved possible, within unit constraints, to achieve a depth of dewaxing as high as 60°C (108°F) while maintaining stable unit operation and a sufficiently high yield of good quality, deeply dewaxed diesel and gasoline.

Case study 3

The next step in developing an adequate solution for such a challenging, 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 40-45°C (104-113°F), with the aim of reaching cloud point and/or pour point improvement as high as 70-75°C (126-135°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 isomerisation-dewaxing with noble metal dewaxing catalysts.

Very long duration tests (>15 000 hours) were carried out in a large pilot plant to develop detailed understanding of such a challenging operation by looking at various paraffinic feedstock poisoning levels (from below the detection limit to as high as 19 ppmw sulphur) and at varying space velocities.

To make the exercise comparable, the same product quality was targeted: a product with a pour point of -30°C (-22°F), starting from a feedstock pour point of 40-45°C (104-113°F). While it is more than beneficial to process feedstock as free of poisons as possible, the presence of a limited amount of sulphur does not prevent reaching the same high quality product, albeit at higher temperature (see **Figure 13**). It was shown that a dewaxed yield as high as 80-87 wt% of feed can be achieved, even at the deepest dewaxing depth achieved.

Conclusions

Catalytic dewaxing provides an alternative method for cold flow improvement in 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 application and feedstock type by utilising shape selective zeolites to preserve maximum distillate yields. Superior selectivity in Shell/Criterion's dewaxing catalysts is ensured by a proprietary outer surface passivation method. With the current increase in heavy paraffinic material on the market, refiners must adapt their processing facilities to meet these new challenges.

The development of light tight oils in North America and the presence of highly paraffinic crudes in the former Soviet Union, China and North America are opening the way to an increase in applications of dedicated catalytic dewaxing solutions in refineries.

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