Shell Global Solutions

CRITERION CATALYSTS & TECHNOLOGIES

# Shell Global Solutions Dewaxing Technologies & Catalysts Current Status

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## Summary

Catalytic dewaxing is in use in the refining industry since the end of the seventies when Mobil opened the way with its shape selective ZSM-5-based dewaxing catalyst in Wilhelmshaven refinery in Germany. Since then, some 40 to 50 refineries world wide have applied catalytic dewaxing to improve cold flow properties of diesel fuels. With an increased pressure towards improved product quality in Western Europe and with the opening of third-party markets in former East Europe and Soviet Union countries, new processes combining catalytic dewaxing, hydrodesulphurisation and aromatic saturation have been introduced into the open market.

Shell Global Solutions has recently developed robust hydrodewaxing process routes using breakthrough in dewaxing catalysts (SDD-800 and 801) and is developing / exploring new routes to further improve dewaxing processes at minimum investment costs. The SDD catalysts series is manufactured and marketed by Criterion Catalyst Co. on behalf of Shell Global Solutions.

## 1. Introduction

There are at present two routes for improving the cold flow properties of gas oils (cloud point, pour point or cold filter plugging point) : the addition of kerosene and pour point improvers to the diesel oil pool is the most widely applied route while the second approach is, for a number of refineries, to install a catalytic dewaxing unit. Various technologies or catalysts are already commercially applied, i.e. Mobil Distillate Dewaxing (MDDW) [1], Akzo-Fina Cold Flow Improvement [2,3,4], UOP HC-80 and DW-10 [5], Süd Chemie Hydex-G [6] ; some others were more recently introduced into the market place, e.g. MAKFining MIDW technology [7,8,9]. In all these technologies, pour point/cloud point improvement is achieved by selective hydrocracking/hydroisomerisation of paraffins. In addition to paraffin conversion, most of the new processes claim deep hydrodesulphurisation (HDS) and aromatic saturation (HDA) to meet European diesel fuel standards.

Among the foreseen set of new specifications, the decrease in the end-boiling point of the diesel pool may gradually reduce the need for pour point improvers. With a 10 ppm sulphur specification, kerosene blending may also become limited. Consequently, the need for and the economical attractiveness of a specific dewaxing technology will decrease, at least in Western Europe. On the contrary, the possibility of selective dewaxing as a relatively cheap add-on in existing units or as part of deep HDS/HDA package in newly designed units will increase the flexibility of the refiner operation and give rise to significant savings in additive costs.

The purpose of this paper is to present Shell Global Solutions dewaxing technologies and catalysts marketed by Criterion Catalysts Co., to highlight the potential application of such a technology/catalyst package in modern refinery line-ups and to emphasise on the flexibility offered by the use of improved dewaxing catalysts.

# 2. Catalytic Dewaxing of Diesel fuels

Catalytic dewaxing is used to improve cold flow properties of diesel fuels by selective hydroisomerisation/hydrocracking of normal and slightly branched-paraffins. Normal paraffins have the most detrimental effects on the low-temperature properties of diesel fuels. The high melting points of normal paraffins in the diesel fuel boiling range (Figure 1) is mainly responsible of the high cloud/pour points of heavy gas oils. Even with lower end boiling points as expected for forthcoming specifications in Western Europe, remaining paraffins may still be a problem in reaching acceptable cold flow properties without expensive additivation. This problem becomes even more important in countries where additives package are not commercially an attractive option and where local weather conditions force the use of extreme winter gas oils (arctic) grades. By reducing the amount and/or chain-length of normal and slightly-branched paraffins using catalytic dewaxing, the cold flow properties of diesel fuels strongly improve.

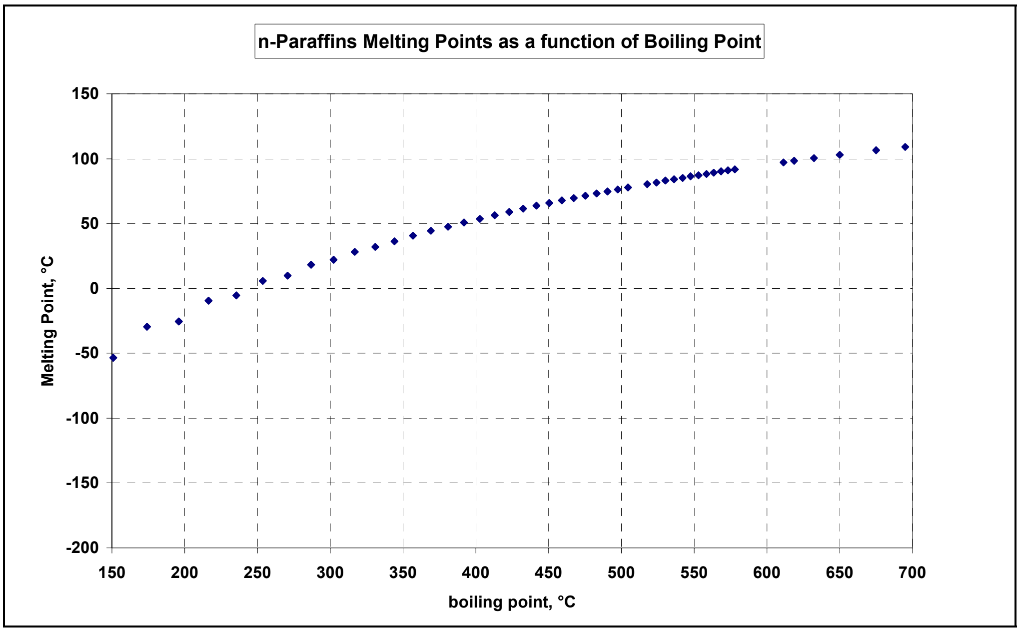


**Figure 1 :** Melting points of paraffins as a function of boiling points and carbon number

## Dewaxing Catalysts

Typically, catalytic dewaxing is carried out on a bifunctional shape-selective zeolitic catalyst under hydrogen flow. Even though recent applications (2$^{nd}$ stage dewaxing) imply noble metal catalysts (platinum, palladium) on medium (ferrierite) or large-pore (beta) zeolites, most of the dewaxing catalysts usually contain a base metal (nickel) supported on a medium-pore zeolite (ZSM-5, silicalite, etc.) and an alumina binder and are used under 1$^{st}$ stage conditions. Medium-pore zeolites are particularly suitable for high selectivity even though for highly paraffinic feeds (paraffin content above 25%), larger pore structures may be preferred.

## Reaction pathway

The waxy molecules which are responsible for the poor cold flow properties of diesel fuels (normal and slightly-branched paraffins), enter the pore structure of zeolites and are isomerised and/or cracked into iso or lower molecular weight molecules. The bulky non-waxy molecules bypass the internal pore structure of the zeolites (Figure 2). For medium pore zeolites, deactivation occurs mainly from coke build-up on the external surface of the crystallites and at the pores' mouth (pore mouth plugging).

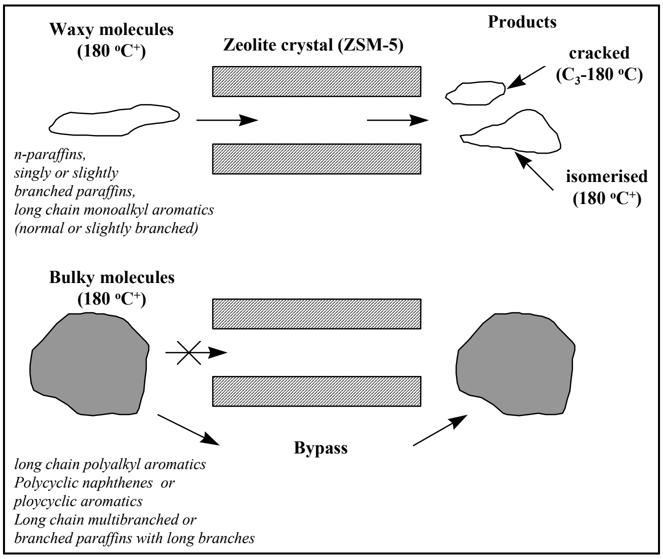


**Figure 2** : Shape-selectivity of medium-pore zeolites

The decrease in n-paraffin content in gas oil during the catalytic dewaxing process can be recorded by standard liquid chromatography as illustrated in Figure 3.

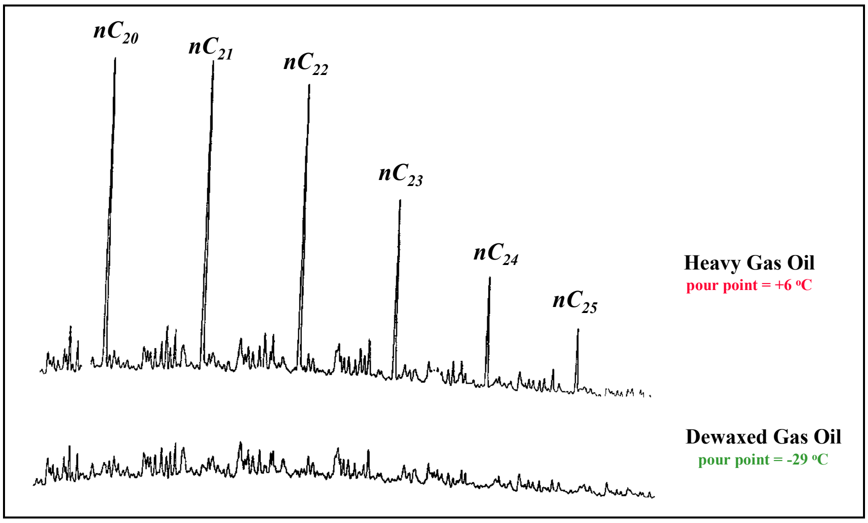


**Figure 3 :** Selective removal of n-paraffins in gas oil dewaxing

Usually catalytic dewaxing of gas oil is carried out in series-flow configuration where hydrotreating of the gas oil is carried out prior to dewaxing. Such processes involves base metal dewaxing catalysts usually in sandwich configuration, the dewaxing catalyst being used under severe conditions, i.e. in the presence of $H_2S$, ammonia, unconverted organic sulphur- and nitrogen-containing molecules.

Alternative processes, i.e. two-stage unit, involve higher isomerisation/cracking ratio in the second stage where dewaxing reactions takes place on noble-metal-containing catalysts and usually requires very clean 2nd stage feeds, i.e. extremely low in nitrogen and sulphur (ppm levels). Typically, second stage dewaxing results in higher yields of dewaxed gas oils than first stage.

# 3. Shell Global Solutions Dewaxing Catalysts

## 3.1. Background

The development of Shell catalytic dewaxing technologies for gas oils and base oils was initiated in the early eighties. This programme resulted first in the commercialisation of Shell 776 dewaxing catalyst in the late eighties.

Shell 776, a commercial noble metal catalyst on medium pore zeolite was used in Shell Oil's Wood River (USA) for dewaxing of light base oil grades.

In the mid-nineties, a major breakthrough in catalyst formulation / preparation was successfully adapted to dewaxing catalysts. The creation of Shell Global Solutions in the late nineties pushed the development of adequate technologies to be added to the commercial portfolio of the new organisation. In the the diesel area, this technology push resulted in the development of the Shell Distillate Dewaxing (SDD) proprietary catalysts series, SDD-800 and -801.

SDD-800 and SDD-801 belong to a family of dewaxing catalysts based on an original proprietary Shell concept developed in catalyst formulation / preparation which results in :

- an improved tolerance to sulphur- and nitrogen-containing organic molecules,
- an overall improved yield profile (Figure 3) and product slate,
- a superior catalyst stability (Figure 4).

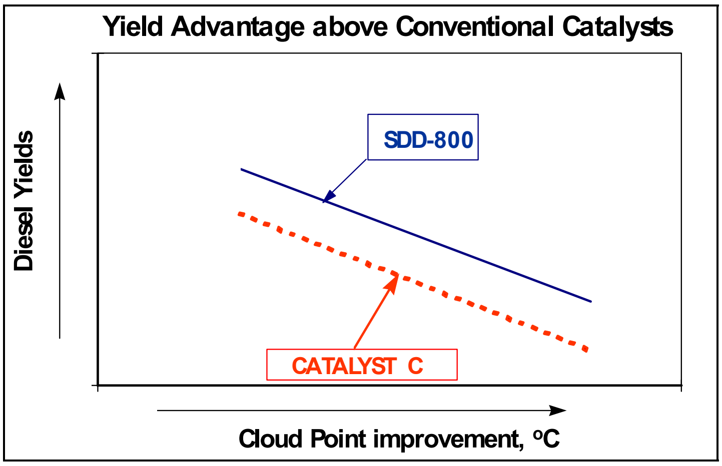


**Figure 3 :** Yield advantage of SDD-800 base metal catalyst over conventional dewaxing catalyst in 1st stage diesel fuel dewaxing application

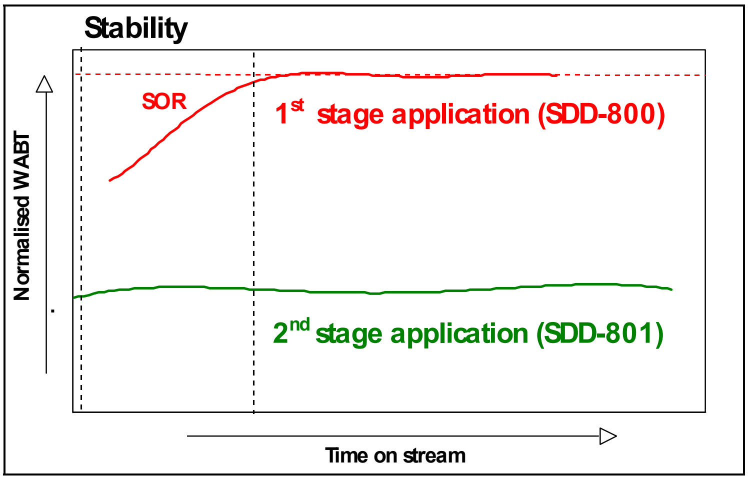


**Figure 4 :** Improved stability of SDD-800 and SDD-801 in 1st and 2nd stage duty respectively for similar cloud point improvement

During the development phase, extensive pilot plant tests were carried out on several members of the family including :

- feedstock sensitivity scouting on various feedstocks under most severe conditions (low pressure).
- feedstocks contaminants levels ranging from 3 ppmw to 3% sulphur and from < 1 to more than 1000 ppm w nitrogen.
- extensive stability testing in deep dewaxing mode under severe conditions (low pressure, high space velocity).

Deactivation rates range from less than 0.5 to less than 2.0 °C/1000 hours depending on feedstocks, operating conditions, catalyst bed configurations and dewaxing depth.

Base and noble metal versions have been further optimised for 1st and 2nd stage diesel fuel dewaxing applications, respectively. Beginning 1999, a commercial trial run on the 1st member of the family was successfully carried out. Since then, upon customer request, SDD-800 and SDD-801 have been tested on a number of gas oil and hydrocracker feedstocks and marketed for cold flow improvement of diesel fuels in 1st and 2nd stage application by Criterion Catalyst Co.

SDD-800 is a sulphur- and nitrogen-tolerant base metal dewaxing catalyst with improved stability and yields, specifically targeting 1st stage dewaxing operation under severe conditions, i.e. high sulphur and nitrogen environment.
SDD-801 is a noble metal dewaxing catalyst combining hydrodewaxing and hydrogenation and targeting 2nd stage dewaxing.

SDD-800 and SDD-801 are suited for the following applications :

- ***conventional diesel fuels dewaxing to deep dewaxing (Arctic grade production) in 1st and 2nd stage applications***
- ***in combination with high-pressure hydrocracking or mild hydrocracking catalyst package***
- ***mild hydrocracker bottoms pour point reduction for storage and transportation.***

The first commercial application of one of the member of the SDD catalyst family in late 2000 and its excellent behaviour after several months of operation fully confirm expectations.

## 4. Process line-ups

Due to their original design and their high tolerance towards poisons, the Shell Distillate Dewaxing catalysts offer a wide range of possibilities for use in existing or new hydrotreating units (Figures 5 to 7).

For economical reasons, the main application of catalytic dewaxing shifts from standard stand-alone unit towards integration of dewaxing catalysts within hydroprocessing reactors catalyst package, or towards new process line-ups (two-stage units) and new modes of operation (counter-current) for product quality and/or flexibility reasons. While the first approach is mainly directed to existing units and require sulphur- and nitrogen-tolerant catalysts, i.e. base metal, the second approach may offer advantages for new unit design or in case of severe constraints on product properties (European aromatics and sulphur specifications for 2005 and beyond). It allows the use of powerful hydrogenating noble metal-based catalysts (high hydrogenation) and/or noble metal dewaxing catalysts (higher isomerisation/cracking ratio and hydrogenation).

Most of the process licensors focus on 2$^{nd}$ stage options arguing that hydroisomerisation on noble metal dewaxing catalysts provide better yields. This is true since it is well known that noble metal dewaxing catalysts require lower temperatures to effectively provide higher yields than conventional cracking catalysts at a given cold flow property improvement. But this is only achievable at the expense of a more severe pre-treatment of the feedstock to ensure a minimum nitrogen and sulphur slips to the 2$^{nd}$ stage and intermediate stripping of $H_2S$ and $NH_3$. To date, there is no noble metal catalyst able to tolerate high sulphur levels, i.e. exceeding a few hundred ppm, and keeping its hydrogenation power, or a noble metal dewaxing catalyst able to tolerate more than a few ppm nitrogen without a significant shift in its operating window. The severity prior to the second stage may require the addition of expensive equipments/catalyst volume resulting in an overall less attractive economics than a first stage dewaxing option despite a potential better yield profile.

SDD-801 is significantly less sensitive to these poisoning effects and therefore could be use in less constraining environment.

SDD-800 (base metal) and SDD-801 (noble metal) are suited for use in the following configurations and process line ups :

## 4.1. Stand Alone Dewaxing

***Stand-alone dewaxing*** used a single stage dewaxing reactor for post dewaxing of diesel. In such a configuration where the diesel to be dewaxed has been already fully hydrotreated, the dewaxing catalyst, i.e. usually base metal loaded, provides a very significant pour and cloud point improvement at still relatively moderate temperature. In extreme cases when deep HDS/HDN prior to dewaxing has been carried out, a noble metal catalyst can be used. Such a combination is usually used in base oil hydroprocessing where dewaxing is carried out in blocked modes operation (per grade).

## 4.2. 1$^{st}$ Stage Dewaxing

• ***Combination of dewaxing with conventional HDS*** (Figure 5) : depending on catalyst configuration (a sandwich configuration is usually recommended), such an approach is rather flexible and operates independently in summer (HDS only) or winter modes (HDS and dewaxing). In both modes, the unit can be operated at rather high space velocities (space velocities on dewaxing bed in the range 3 to 7 t/m$^3$.h are not unusual). The position of the dewaxing catalyst in the reactor is a key factor in achieving the required duty. It is mainly determined by the feedstock characteristics, i.e. wax content and nature, boiling range, unsaturates content, nitrogen and sulphur contents, etc. The exotherm from the desulphurisation reactions, the constraints in operating window and overall catalyst package deactivation pattern dictate the location and required volume of dewaxing catalyst. When the right balance between the various catalysts has been derived from the correct evaluation of feed characteristics, the dewaxing function can be switched off during the summer by simply lowering the temperature and consequently maximising diesel yields when dewaxing is not required (summer mode). Since in Europe, sulphur specification becomes tighter and tighter (50 ppm in 2005, already 10 ppm mandatory or strongly supported in Sweden, Germany and Austria), 1$^{st}$ stage dewaxing approach may become less interesting as an add-on, although, for new unit design, this remains an attractive option. The increased severity required for HDS may reduce the existing flexibility between summer and winter modes of operation. Consequently, this will favour two-stage options where cold flow improvement (if still required) and additional hydrogenation may take place.

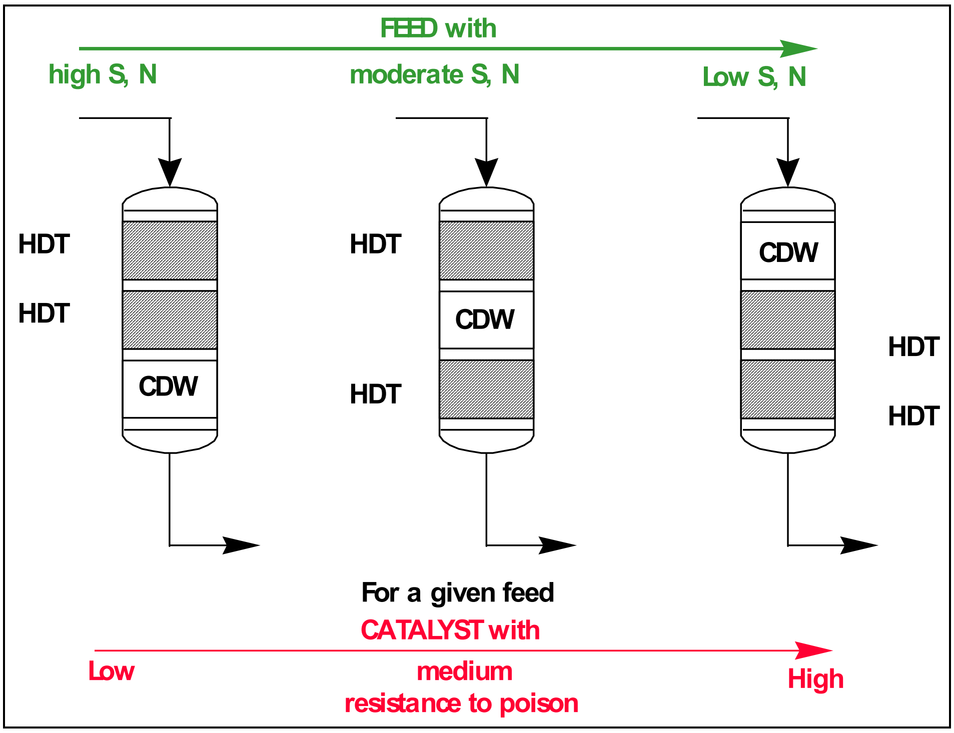


**Figure 5 :** 1st stage application of SDD catalyst in combination with (deep) HDS

- ***Combination with 2nd stage HDA*** (Figure 6) : if high aromatics saturation is required, combination with a 2nd stage hydrofinisher may be envisaged either after a stripping of ammonia and $H_2S$ on the full range of liquid products, or after fractionation, on the diesel fraction only. Such a combination gives a high flexibility between several modes of operation, i.e. summer and winter mode, with or without deep hydrogenation.

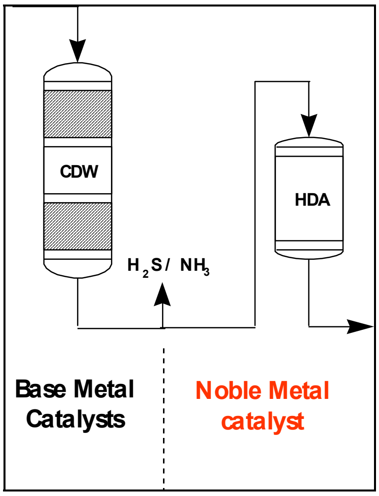


**Figure 6 :** 1st stage application of SDD catalyst
in combination with HDS and 2nd stage hydrogenation

### 4.3. 2nd Stage Dewaxing

• ***2nd stage dewaxing*** (Figure 7) : Depending on customer requirements, unit constraints, product properties, desired flexibility or for new units, it can be advantageous to select a two-stage option which can ideally combine deep desulphurisation in 1st stage and selective dewaxing in the 2nd stage. Such an option allows the use of noble metal selective dewaxing (SDD-801) in 2nd stage which results in lower temperature window, better yield profile and longer cycle length. In addition, the noble metal dewaxing catalyst may provide additional hydrogenation.

• ***Combination with hydrogenation of aromatics*** (Figure 7) : If severe aromatics' hydrogenation becomes the main driver, the 2nd stage could contain either stacked-beds of dewaxing and hydrogenation catalysts or specifically designed bi-functional catalysts. The choice between the two options being directed mainly by the desired flexibility between the different modes of operation (decoupled dewaxing / HDA activity).

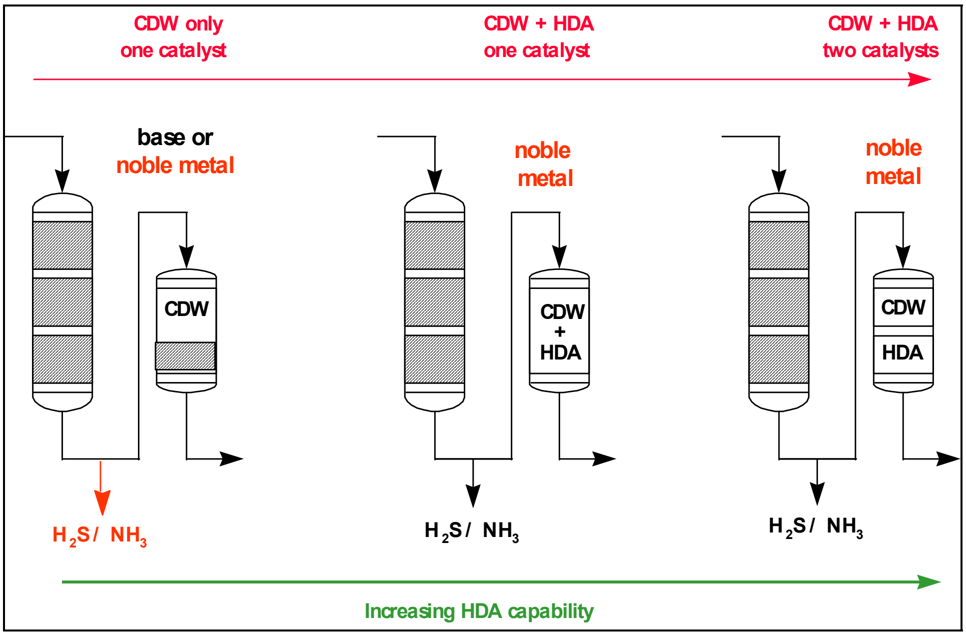


**Figure 7 :** 2nd application of SDD catalyst in combination with deep HDS and hydrogenation

## 5. Feedstock Effects

A number of factors determine the configuration / process line-up to be used for a specific duty and the overall performance of the process in terms of dewaxing capabilities, temperature requirement for a given duty, flexibility (winter/summer mode, dewaxing and aromatics'hydrogenation), catalyst deactivation, etc. The most important factors to be considered are listed as follows :

• Feedstock characteristics (sulphur, nitrogen, aromatics content, boiling range, wax content and nature, etc.)

• Product properties requirement (depth of dewaxing, HDS, hydrogenation, etc.)

• Hydrogen availability

• Targeted production and modes of operation

• Catalyst package selection and synergies

• Catalyst loading scheme and unit constraints.

Feedstock characteristics and catalyst package cost/performance ratio are usually the main drivers in gas oil catalytic dewaxing application. Nowadays, although cost efficiency remains an important factor, the prevailing factors in catalyst package and process line-up selections are mainly product quality requirements and flexibility between modes of operation to maximise the economics of the overall unit and its integration in the refinery line-up.

For locations which are not constrained by end-boiling point specification, the dewaxing process makes also possible a significant increase in diesel yield by extending the diesel end point.

## 6. Case Studies

This section describes three case studies that were completed in response to specific client needs. These studies illustrates the capabilities and options available within Shell Global Solutions/Criterion Catalyst Co. using Shell proprietary dewaxing catalysts of the SDD series.

### *Case Study 1 - Deep dewaxing of low pour gas oil*

This project was targeted the production of desulphurised winter grade diesel products from a low pour point straight run gas oil stream using an existing conventional HDT. The objective was to process the feedstock indicated in Table 1 to produce diesel fuels meeting the following requirements :

- diesel fuel "Winter" grade (pour point = -35 °C, cloud point = -25 °C, sulphur < 350 ppm w)

- diesel fuel "Winter" grade (pour point = -45 °C, cloud point = -35 °C, sulphur < 350 ppm w)

On the basis of the information provided by the client, it was assumed that the required product objectives can be achieved using the existing reactors although consideration needs to be given to ancillary equipment such as the downstream fractionator as product slates resulting from the deep dewaxing implementation will differ from standard hydrodesulphurisation.

**Table 1 :** Main characteristics of feedstock - Case study 1

| Properties | Case Study 1 - Design Case |
|---|---|
| Density @ 15 °C | 0.852 |
| Cetane Index | 52 |
| Sulphur, %wt | 0.75 |
| Nitrogen, ppmw | 121 |
| Cloud point, °C | -6 |
| Distillation, °C | ASTM D-86 |
| 10 vol. % | 233 |
| 50 vol. % | 288 |
| 90 vol. % | 353 |

Catalyst choice and catalyst bed configuration / volumes were mainly directed by the following considerations :

- the configuration was tuned to cold flow improvement assuming that an HDS conversion above 95 % is a standard duty for Criterion HDS catalysts under hydrotreating conditions (unit total pressure was max. 35 bar).

- a sandwich configuration was preferred.

From the existing hydrotreating and dewaxing catalysts portfolio, Criterion's DN-190 and Shell's SDD-800 were selected as the optimal solution to meet both customer requirements and cost efficiency. A pilot plant test was carried out at Shell Research & Technology Centre, Amsterdam to support yield and operating window estimates and to assess product quality under operating conditions. Table 2 summarises some key outcomes of this study.

**Table 2 :** Summary of Operating Cases - Case Study 1

| **Operating Modes** | **Summer** | **Winter Grade 2** |
|---|---|---|
| Targeted functions | HDS | HDS<br>CDW |
| Catalyst Package | DN-190<br>SDD-800 | DN-190<br>SDD-800 |
| Liquid Yield ($C_5^+$), % vol. | > 100 | > 100 |
| Diesel Yield (150 $^oC^+$), % vol. | > 100 | > 90 |
| Product Properties | | *(no additive)* |
| Sulphur, ppmw<br>Nitrogen, ppmw<br>Cloud Point, $^oC$<br>Pour Point, $^oC$ | <50<br>< 1<br>-6<br>-9 | <50<br>< 1<br>**-35**<br>**-45** |

### *Case Study 2 - Dewaxing of straight run gas oil - Performance of SDD-800 in 1st stage top bed operation*

This study aimed at qualifying the sulphur- and nitrogen-tolerant, recently developed SDD-800 for 1st stage dewaxing operation under unfavourable conditions (top bed dewaxing). One of the advantage of SDD-800 is its ability to perform in top bed operation. This allows the removal of the dewaxing catalyst from the system without unloading other catalysts and add to the flexibility of the overall operation. A test was carried out on an untreated straight run gas oil (Table 3) and compared with a similar test carried out on a conventional 1st stage dewaxing catalyst.

**Table 3 :** Main characteristics of feedstock - Case study 2

| **Properties** | **Case Study 2** |
|---|---|
| Density @ 20 °C<br>Sulphur, %wt<br>Nitrogen, ppm | 0.854<br>1.44<br>157 |
| Aromatics (UV) | |
| mono., mmol/100g<br>di., mmol/100 g<br>poly., mmol/100g | 74<br>36<br>14 |
| Distillation | ASTM D-86 |
| 10%vol.<br>50%vol.<br>90% vol. | 258<br>305<br>357 |
| Cold Flow Properties | |
| Pour Point, °C<br>Cloud Point, °C | -3<br>+3 |

The production of dewaxed diesel fuels with cloud point in the range -10 to -20 °C was targeted.

- For the same dewaxing depth, SDD-800 was found 3 times more stable than the reference catalyst but also consistently 2 to 3 % wof more diesel selective (Figure 3).

- Deactivation rate, under such conditions (top bed dewaxing), was estimated to be less than 2 °C / 1000 h.

This translates in an average 2.5 % higher diesel yield on a three times longer cycle without intermediate regeneration(s).

### *Case Study 3 - 2nd stage dewaxing / hydrogenation on SDD-801*

The objective here was to process a first-stage effluent feedstock, i.e. low in sulphur and nitrogen (Table 4), to produce, during winter time (about 3 month/year), a diesel product (177 °C+ fraction) with low aromatics and improved cold flow properties. An additional target was to ensure a substantial cycle length of the 2nd stage catalyst package.

**Table 4 :** Main characteristics of feedstock - Case study 3

| **Properties** | **Case Study 3** |
|---|---|
| Density @ 20 °C<br>Sulphur, ppmw<br>Nitrogen, ppm | 0.843<br>20<br><1 |
| Total Aromatics, %w | 7 |
| Simulated Distillation | TBP-GLC |
| 10%<br>50%<br>90% | 227<br>325<br>391 |
| Cold Flow Properties | |
| Cloud Point, °C | +9 |

Table 5 summarises the targeted product specifications.

**Table 5 :** Product specifications - Case study 3

| **Property** | **Customer target** |
|---|---|
| Cetane Index<br>Cloud point, °C<br>Aromatics conversion, %wt | 49 min.<br>-8 max.<br>60% min. |

These product objectives were addressed with a single bed of SDD-801, a bi-functional noble metal dewaxing catalyst from Shell Global Solutions portfolio. This catalyst provides a stable dewaxing operation on clean feedstocks together with a significant hydrogenation of aromatics. Developed for its improved stability, cycle lengths as long as 3 to 5 years can be targeted for such a duty. Table 8 summarises the performance of SDD-801 as measured in a dedicated pilot plant testing.

Under constant operation and design process conditions, catalyst deactivation was found to be about 1±1 °C/1000 h for cold flow improvement and somewhat higher, i.e. 2±1/1000 h for hydrogenation.

On the basis of the unit 2nd stage operating window, a catalyst life of minimum 4 years is foreseen.

**Table 6 :** Summary of SDD-801 behaviour in 2nd stage duty - Case Study 3

| | **SDD-801** |
|---|---|
| **Reactor Yields** | |
| 177 °C+ (diesel), %w | 92.0 |
| **Product properties** | |
| Diesel cloud point, °C<br>Aromatic hydrogenation, %<br>Cetane Index | -8<br>> 70<br>> 60 |

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