

Optimising middle distillate production in a hydrocracker

How to maximise middle distillate production and assure product quality from a range of hydrocracking catalysts and processing schemes

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Hydrocracking is one of the key processes of a modern refinery, and a hydrocracking unit is one of the most profitable units in a refinery. Hydrocracking will continue to be a very important process to meet the increased demand for clean transportation fuels. In view of this, new developments in hydrocracking catalysis and process technologies are continuously taking place.

The processing requirements will determine the optimum design of a hydrocracking process and the optimum catalyst selection. This will include the feed rate and feed quality as well as the make-up gas quality and availability. Typical hydrocracker feedstocks are straight-run gas oils, vacuum gas oils (VGO), coker gas oils, fluid catalytic cracking oils, and decant oils as well as mixtures of those. The desired product(s), which may range from liquefied petroleum gas (LPG), naphtha, kerosene, and diesel to unconverted oil (UCO) as well as the required product properties and yield, determine the conversion requirements.

Nowadays, practically all hydrocrackers operate with a pretreatment catalyst for removal of nitrogen compounds in front of the hydrocracking catalyst. Recent developments within NiMo hydrotreating catalyst technologies like the HyBRIM technology invented by Topsoe resulted in a new hydrocracking pretreatment catalyst named TK-611 HyBRIM.¹ This catalyst lifted the activity by 25% compared to the previous generation of commercially available state-of-the-art pretreatment catalysts like the Topsoe TK-609 HyBRIM catalyst. The use of such a catalyst in hydrocracking service adds additional flexibility to the operation of a hydrocracker like

longer catalyst cycles, more throughput, better product qualities, or even the ability to process more severe feedstocks. It also allows the refiner to cut back on pretreatment catalyst volume and to install less active hydrocracking catalysts, resulting in an improved middle distillate selectivity and/or product quality, if this is economically feasible.

Last but not least, optimum operation of a hydrocracker not only requires high performance state-of-the-art pretreatment and hydrocracking catalysts but also well functioning reactor internals and catalyst grading systems. Furthermore, an optimal process scheme should be used. The company developed a full range of proprietary high performance reactor internals. For full conversion hydrocrackers, the build-up of heavy polynuclear aromatic compounds (HPNA) has to be controlled to ensure seamless operation. For hydrocrackers, where HPNA management is needed, Topsoe developed a new technology named HPNA Trim.

Selection of hydrocracking catalysts

When it comes to the selection of the best hydrocracking catalyst system for a given application, many different factors have to be taken into consideration. This is far more complicated than selecting a hydrocracking pretreatment catalyst, where the use of a high activity hydrocracking pretreatment catalyst would be the preferred choice, as this gives additional flexibility in hydrocracking catalyst selection and operation as mentioned above. In the selection of a hydrocracking catalyst system, a very important factor would be the optimisation of the catalyst loading to maximise the profitability of the unit. The

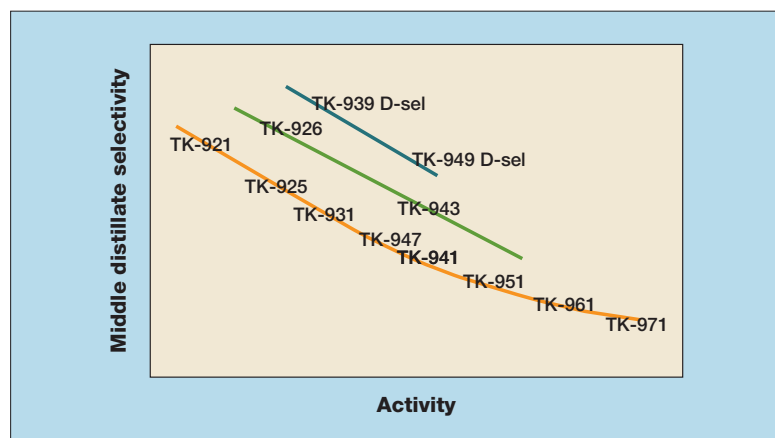


Figure 1 The portfolio of Topsoe base metal hydrocracking catalysts

profitability of the unit is related to the values of the different products from the hydrocracker. For each product, the value is related to the quality of the product. Some hydrocrackers produce mainly naphtha, whereas other units produce mainly middle distillates. For a number of hydrocrackers, the production of UCO for either lube production or for steam cracker feedstock is very valuable. Other hydrocrackers benefit from their ability to shift between the production of mainly naphtha and the production of mainly middle distillates dependent on a change in seasonal demands and/or in the value of products. In some areas, the cold flow properties of the diesel product are very important. For hydrocrackers aiming at production of high quality UCO for use as feedstock for lube dewaxing, the viscosity index of the UCO is a crucial factor. In essence, this means that hydrocrackers have very different processing objectives, and that all hydrocrackers are unique in typical feedstock composition and main objectives.

To meet different processing objectives, a broad portfolio of hydrocracking catalysts for different applications is a must. The portfolio of base metal hydrocracking catalysts offered by Topsoe is shown in **Figure 1**. It is well known that low activity hydrocracking catalysts have a high selectivity towards middle distillate production, whereas high activity hydrocracking catalysts exhibit a lower middle distillate selectivity. Topsoe offers three series of hydrocracking catalysts, which cover a wide activity range. The red series is for applications where maximum product hydrogenation is required. The blue series is for applications where the improvement of

cold flow properties of diesel is important. The catalyst belonging to the D-sel series is used to maximise the middle distillate yield. In many cases, the use of more than one hydrocracking catalyst in a given unit is the optimal choice. It is possible to combine, for example, a hydrocracking catalyst from the red series with a hydrocracking catalyst from the blue series to tune the properties of the produced diesel, so that good cold flow properties and an excellent cetane number are obtained at

the same time. This loading solution was successfully used by a handful of commercial units.

In the following, three cases will be discussed, which illustrate how the selection of catalysts and the use of different process schemes can result in a maximisation of middle distillate production and of the product quality of diesel.

Catalysts for maximising middle distillate production in single stage and two stage units

Traditionally, hydrocracking process configurations are classified by four basic process schemes: single stage hydrocracking with recycle, once-through hydrocracking, two stage hydrocracking, and separate hydrotreat hydrocracking. The most common design is the single stage system.

A simplified process scheme for single stage and two stage hydrocracking is shown in **Figure 2**. In single stage hydrocracking, the fresh feedstock and UCO are treated with surplus hydrogen over a hydrocracking pretreatment catalyst followed directly by a hydrocracking catalyst system. In many cases, two reactors are used, one for the hydrocracking pretreatment catalyst including catalyst grading and one for the hydrocracking catalyst system. The product is fractionated into light ends, naphtha, kerosene, diesel, and UCO. The UCO can be recycled back to the reactor. It is an option to let the UCO recycle pass a HPNA Trim unit for removal and management of HPNA compounds before it is recycled back to the reactor. Once-through hydrocracking is without liquid recycling. For simplicity's sake, the high pressure separator as well as the recycle compressor were omitted

from the process scheme shown in **Figure 2**. In the two stage process, the hydrocracking pre-treatment of the feedstock and part of the hydrocracking are carried out in the same way as during the single stage process. The product from the first cracking stage is fractionated in the same fractionation system as mentioned above, and the UCO is passed to an additional reactor loaded with a hydrocracking catalyst system. As mentioned before, it is in this case also an option to let the UCO recycle pass a HPNA Trim unit. In the two stage process, the hydrocracking in the second stage can take place in the absence of ammonia and in a sulphur-free atmosphere (sweet operation), or in a sulphur containing atmosphere (sour operation). In case a sweet operation is desired in the second stage, this can be carried out with two separate gas recycle loops or with a common recycle gas that has been amine treated. In the single stage process, hydrocracking is carried out in the presence of ammonia and hydrogen sulphide (sour operation). The activity and selectivity of a hydrocracking catalyst are very dependent on the amount of ammonia present in the treat gas. The presence of ammonia passivates the acidic sites typically provided by the silica alumina and/or zeolite compounds present in the hydrocracking catalyst support. A small bleed of the recycle oil is normally taken out for HPNA management. The HPNA Trim technology is a versatile tool for minimising the bleed rate.

For many hydrocrackers, the main objective is maximisation of middle distillate production. In this case, a hydrocracking catalyst system with a high middle distillate selectivity should be selected. As can be seen in **Figure 1**, the natural choice would be to use the Topsoe catalyst TK-939 D-sel. Due to the lower activity of TK-921, TK-925, and TK-926, these catalysts would be less attractive to use in existing single stage hydrocrackers. In the absence of ammonia it was demonstrated in dedicated pilot testing that TK-921 can have a better middle distillate selectivity than TK-939 D-sel in two stage hydro-

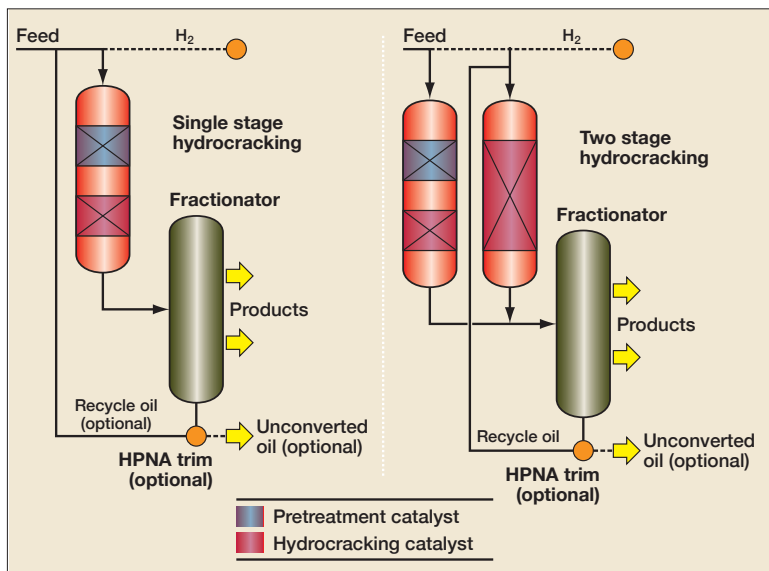


Figure 2a Single stage hydrocracking unit; **2b** Two stage hydrocracking unit

cracking. From a process point of view, the lower activity of TK-921 is not an issue in this sweet environment, as the required reactor temperature will be significantly lower than 400°C. When the ammonia concentration in the treat gas of the second stage becomes higher, it becomes attractive to use the more active TK-939 D-sel catalyst.

Based on these findings, the optimal catalyst loading for a single stage unit and a two stage unit aiming at maximising the middle distillate yield from a VGO feedstock was studied in pilot plant testing. A single stage catalyst loading using the TK-609 HyBRIM pretreatment catalyst in front of the TK-939 D-sel hydrocracking catalyst was compared with a two stage loading consisting of the pretreatment catalyst TK-609 HyBRIM and the TK-939 D-sel hydrocracking catalyst in the first stage and the TK-921 hydrocracking catalyst in the second stage. The yields of kerosene (160-285°C), heavy diesel (285-370°C), and a wide boiling middle distillate cut (>160°C) for the two process schemes are shown in **Figure 3**. The combined feed ratio (CFR) is the amount of combined feed (fresh and recycle oil) relative to the fresh feed rate. For the single stage process, the results obtained for two different CFR cases are given. The middle distillate yield obtained in the two stage process was higher than that found for the single stage process. The middle distillate yield decreases in the single stage process, when the CFR is decreased. For a typical single stage operation, the oper-

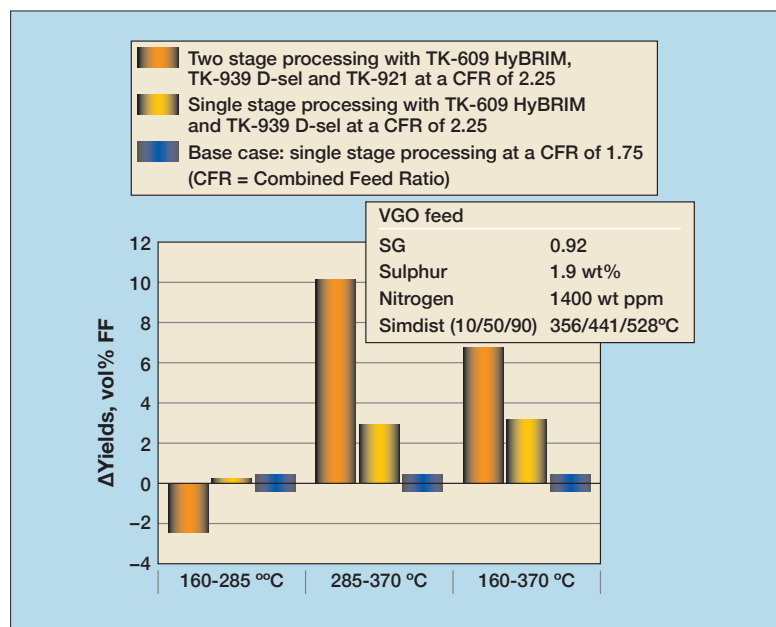


Figure 3 Middle distillate yields for single and two stage processing

Product quality from single and two stage processing at a CFR of 2.25				
		Two stage	Single stage	
Kerosene/160-285°C	Mono-aromatics, wt%	10.6	14.2	
	Smoke point, mm	27	25	
Heavy diesel/285-370°C	Mono-aromatics, wt%	8.4	10.5	
	CCI (ASTM D 4737)	>70	>70	
	Cloud point, °C	-12	-8	

Table 1

ating CFR is in the range 1.3-1.6, so the middle distillate yield from a typical commercial single stage operation is in fact lower than that shown in **Figure 3**. The CFR used in the two stage test, however, is quite typical of industrial applications. This example clearly illustrates that a two stage process gives a higher middle distillate yield than a single stage process for hydrocracking of VGO. It also illustrates that the use of two hydrocracking catalysts in the same unit can be beneficial. When it comes to product quality, the kerosene and heavy diesel cuts produced from a two stage process are of a better quality than those obtained from processing in a single stage process as shown in **Table 1**. The aromatic content in the kerosene and diesel cut is found to be lower in the two stage process. The best kerosene smoke point is obtained in two stage processing. The heavy diesel cloud point is lower in two stage processing than in single stage processing.

The properties of the naphtha cuts are similar. The improved product qualities obtained in two stage processing do not result in an overall higher hydrogen consumption as compared with that of single stage processing due to the fact that a lower amount of light ends and naphtha cuts are formed. The hydrogen is consumed in a more intelligent way.

For new hydrocrackers aiming at maximising middle distillate production, it is highly relevant to consider a two stage design rather than a single stage design. A revamp of once-through hydrocrackers and single stage hydrocrackers to two stage hydrocrackers can be a very attractive way to boost production of middle distillates.

How to produce ultra low aromatics diesel from a feedstock rich in LCO

Cracked products such as light cycle oil (LCO) have a considerably lower cetane value than straight-run distillates. LCO is a poor diesel fuel blending component due to its poor engine ignition performance and its high sulphur content. In a clean fuels refinery, LCO can be an issue. Many North American refiners have historically routed their LCO to a hydrocracker in order to crack it into naphtha and lighter products. The produced naphtha product quite often requires catalytic reforming before it is blended into the gasoline pool. With the increased demand for diesel that has to meet, for example, demanding sulphur, cetane, and aromatic specifications, new ways to upgrade LCO to high quality diesel are of profound interest. Up to now it has been a challenge to produce diesel meeting the low diesel aromatic content as specified by some countries and regions (for example, 10% in California and 5% in Sweden) when processing LCO in a hydrocracking unit. In fact, the dream scenario was to find a way to produce a diesel product with less than 5% aromatics. By performing pro-

ponent due to its poor engine ignition performance and its high sulphur content. In a clean fuels refinery, LCO can be an issue. Many North American refiners have historically routed their LCO to a hydrocracker in order to crack it into naphtha and lighter products. The produced naphtha product quite often requires catalytic reforming before it is blended into the gasoline pool. With the increased demand for diesel that has to meet, for example, demanding sulphur, cetane, and aromatic specifications, new ways to upgrade LCO to high quality diesel are of profound interest. Up to now it has been a challenge to produce diesel meeting the low diesel aromatic content as specified by some countries and regions (for example, 10% in California and 5% in Sweden) when processing LCO in a hydrocracking unit. In fact, the dream scenario was to find a way to produce a diesel product with less than 5% aromatics. By performing pro-

cess modifications and by using existing catalysts in new ways, it is now possible to produce high quality, low aromatic diesel from LCO that by far meets the diesel aromatic target.

Industrial processing of LCO alone or in combination with a gas oil is practised in various hydrocracking process layouts. These include single stage and two stage process designs as shown in **Figure 2**. With a LCO feedstock, the recycle oil is a diesel boiling material. Since there is now also an interest in co-production of middle distillates, it is desirable if the middle distillates can be routed to the diesel pool without any further upgrading. It is not a challenge to meet the diesel sulphur specification. However, in both single stage and two stage processing mode it is difficult to produce high cetane or low aromatic diesel from LCO. In a typical two stage design, the diesel product is a blend of diesel produced in the first stage and in the second stage. In general, the diesel product from the first stage has a high aromatic content, which cannot meet a 10% diesel aromatic target.

In the early days of hydrocracking, one of the first process layouts used in the industry was the so-called separate hydrotreat process (see **Figure 4a**). In essence, this process is a two stage operation, where no hydrocracking catalyst is used in the first step. Only a hydrocracking pretreatment catalyst is used in the first stage. In this process, part of the hydrotreated feed from the first stage ends up in the diesel product.

Another variation of the separate hydrotreat process includes a stripper after the first stage reactor, which removes the hydrogen sulphide and ammonia from the liquid product (see **Figure 4b**). The stripped, deeply hydro-treated liquid product from the first stage can then be routed to the second stage reactor and processed essentially in the absence of ammonia. As mentioned in the previous example, this allows for the use of low activity and high selectivity hydrocracking catalysts. In this case, where hydrogenation of the LCO aromatics was needed, a natural catalyst choice would be a

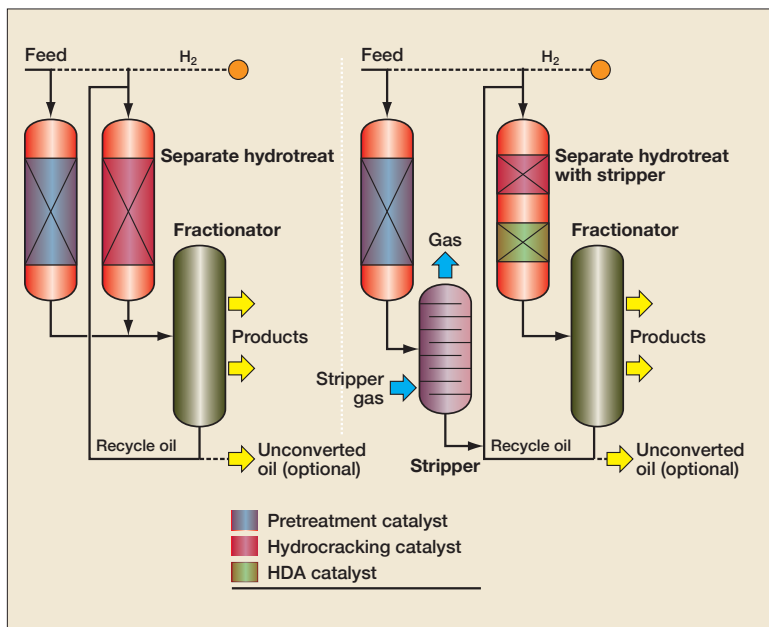


Figure 4a Separate hydrotreat; **4b** Separate hydrotreat with stripper

hydrocracking catalyst from the red series (see **Figure 1**) to get as much hydrogenation and ring opening as possible. Since co-production of diesel was also required, a hydrocracking catalyst of moderate activity with good middle distillate selectivity like the Topsoe hydrocracking catalyst TK-931 would seem to be a suitable choice. However, it turned out that the aromatic saturation activity of TK-931 was not sufficient to give a diesel aromatic content below 10%. In order to produce lower diesel aromatics, it was decided to introduce a noble metal hydro dearomatisation (HDA) catalyst after the hydrocracking catalyst.

Topsoe developed a range of noble metal HDA catalysts and a two stage process for diesel dearomatisation to be able to meet the Swedish diesel specification of maximum 5% aromatics and the Californian specification of maximum 10% aromatics. This technology is already being used by several operators in stand-alone aromatics saturation units. The present Topsoe HDA catalyst portfolio includes TK-907, TK-911, and TK-915. TK-915 is the most active of these catalysts and has the best tolerance towards hydrogen sulphide and ammonia. TK-915 was tested in combination with TK-931 for LCO upgrading, as illustrated by the following example.

The hydrocracking pretreatment catalyst TK-609 HyBRIM was loaded in the first stage

Properties of the feedstock, first stage product, and final jet and diesel product

	Feedstock	First stage product	Jet product	Diesel product
SG (D 4052)	0.929	0.893-0.897	0.83-0.84	0.850-0.865
S, wt ppm (D 4294)	4200	25-35	<0.2	<0.3
N, wt ppm (D 4629)	1018	1-2	<0.2	<0.2
Aromatics (D 6591)				
Mono, wt%	21.6	50.4-53.0	<0.5	<0.7
Di, wt%	30.0	2.0-2.3	<0.1	<0.1
Tri+, wt%	5.9	0.2-0.3	<0.05	<0.05
Sim. Dist. (D 7213C)				
10 wt%	218	206-208	178-180	231-242
50 wt%	281	269-270	207-208	271-274
90 wt%	348	336-338	222-230	337-341
Cetane Index (D 4737)	26	32-33	-	45-52
Smoke point, mm (D 1322)	-	-	22-24	-

Table 2

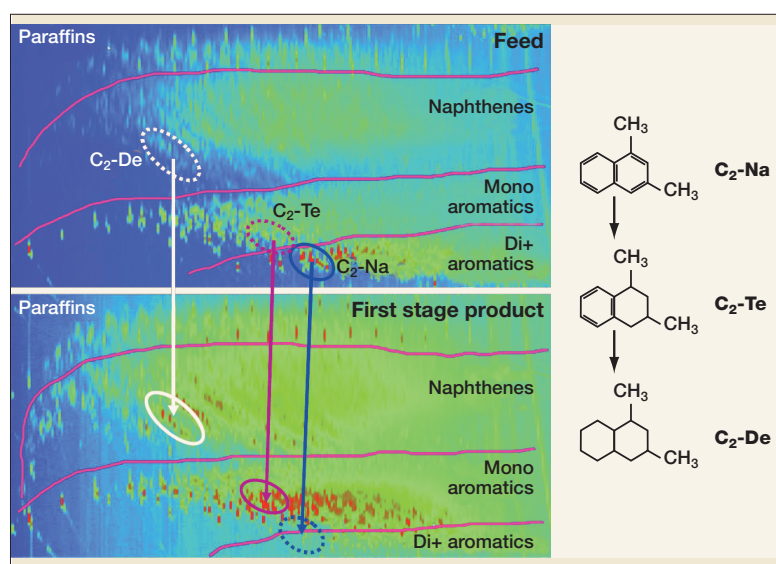


Figure 5a GCxGC chromatogram of feed for dearomatisation; 5b GCxGC chromatogram of first stage product

reactor. In the second stage, the red series hydrocracking catalyst TK-931 was loaded on top of the noble metal HDA catalyst TK-915. Each stage was operated at a pressure of 105 barg. The testing took place in a modified two stage pilot unit able to simulate the process shown in Figure 4b. The feedstock was a mixture of gas oil and LCO with the properties given in Table 2. The testing lasted more than 2000 hours. The first stage reactor was operated at a temperature of about 350°C, whereas the second stage reactor was operated in the range 307-335°C.

The properties of the hydrotreated product from the first stage is shown in Table 2. The product sulphur level was below 35 wtppm, and most

of the di- and tri+-aromatics were converted into mono- aromatics. The feedstock and first stage products were also analysed by the so-called GCxGC gas chromatography technique, which in a three dimensional plot gives a classification of the hydrocarbon species present (see Figure 5). Access to such information is crucial to understand the fundamental chemistry of the different catalysts. The first dimension of the GCxGC chromatogram is similar to that of a normal GC chromatogram, where increasing retention time is proportional to increasing boiling point. Adding a second dimension with separation according to polarity makes a much more detailed compositional analysis of the complex oil samples possible. In this case, the least polar compounds (paraffins) appear in the top of the chromatogram, and the more polar compounds (aromatics) are found near the bottom of the chromatogram. Figure 5 shows the chromatogram of the feed (top) and the first stage product (bottom). The most important trend is a shift along the ordinate, which represents a decrease in polarity. This decrease in polarity occurs

as the di- and tri+-aromatics are saturated into mainly mono-aromatics but also to a lesser extent into naphthenes. To further illustrate this reaction, the fate of a dimethyl-substituted naphthalene was tracked. The C_2 -diaromatic (C_2 -Na) was very abundant in the feed but was not found in the product. The C_2 -Na can be partly saturated into a C_2 -tetralin (C_2 -Te) or be fully saturated into a naphthene (C_2 -De). Neither of these saturation products were abundant in the feed, but they could easily be identified in the first stage product. This finding is in agreement with the HPLC based aromatic analysis results shown in Table 2.

The first stage product was combined with the recycle oil before it was routed to the sec-

ond stage reactor. The combined feed had a content of about 32% mono-aromatics. The aromatics content was about 15% mono-aromatics after treatment with TK-931. Further treatment with the HDA catalyst TK-915 resulted in a dramatic reduction in the diesel aromatics (see **Table 2**). The diesel product contained less than 1 wt% aromatics, which is outstanding, and less than 1 wtppm sulphur. The cetane index was higher than 45. The produced diesel will be excellent as a diesel blendstock. The jet fuel was also extremely low in aromatics, resulting in a high smoke point. The density of the jet was relatively high, but by adjusting the kerosene/diesel cut point it was possible to produce a jet product meeting the Jet-A1 specifications.

The chemistry occurring in the second stage reactor was also studied by GC×GC (see **Figure 6**). TK-931 has a dual purpose in this configuration. The high hydrogenation capacity enables further conversion of mono-aromatics into naphthenes, but the cracking function also plays a very important role in this process. Instead of undergoing the saturation reaction described above, the C_2 -Te can also undergo a ring opening reaction into a one ring aromatic compound C_6 -Bz (see **Figure 6b**). The benefit of this type of reaction is the fact that the density is lowered without removing the compound from the diesel boiling range, which results in a significant cetane boost. In order to saturate the remaining aromatics, TK-915 HDA catalyst is used. As can be seen from **Figure 6c**, it is not possible to detect any aromatic compounds in the reactor effluent by GC×GC chromatography.

This example clearly illustrates that it is possible to upgrade LCO to a high yield of low aromatic, high cetane diesel by combining process technologies with innovative catalyst loading schemes involving a HDA catalyst in combination with a hydrocracking catalyst in a separate hydrotreat two stage process with a stripping of

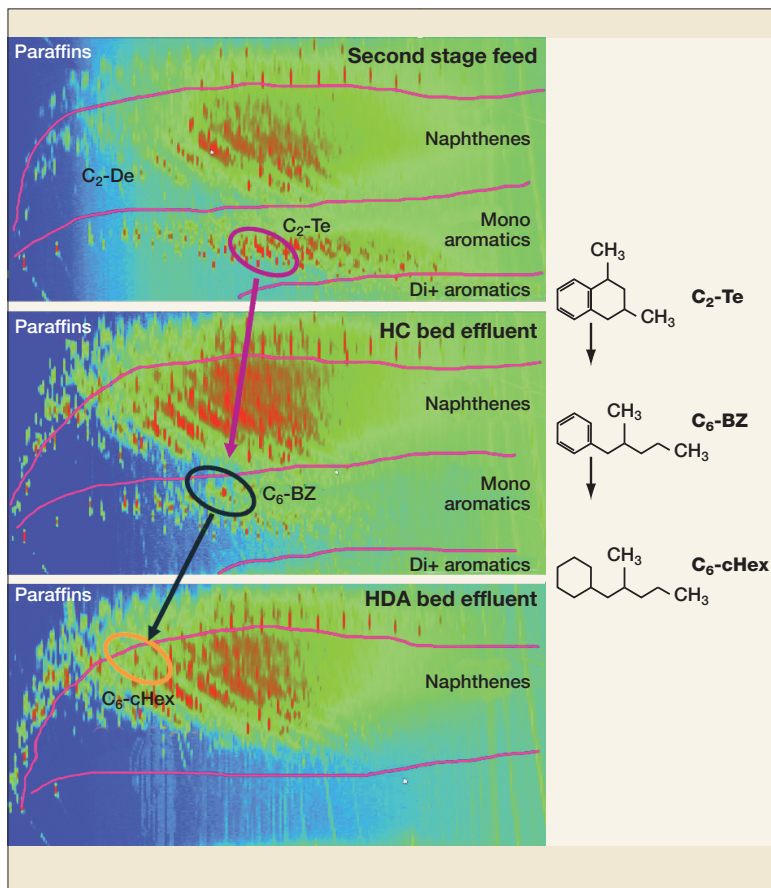


Figure 6a Second stage feed; **Figure 6b** HC bed effluent; **Figure 6c** HDA bed effluent

the first stage effluent between the two stages.

A more active hydrocracking catalyst than TK-931 can be used in case a higher naphtha production is desired. In fact, it is also possible to exclude the hydrocracking catalyst and only use a HDA catalyst in the second stage reactor. This will result in less ring opening, and the produced jet and diesel will end up having a higher density than that found when a hydrocracking catalyst is used in front of the HDA catalyst.

Is full conversion in a once-through unit possible?

Normally, a recycle unit (single stage or two stage process layout) will be the route to take to achieve full conversion. In some cases, however, it is possible to achieve full conversion in a once-through hydrocracker by adjusting the properties of the feedstock, so that no UCO is produced. As no UCO is produced, a dedicated costly distillation column separating the UCO from the other products is no longer needed.

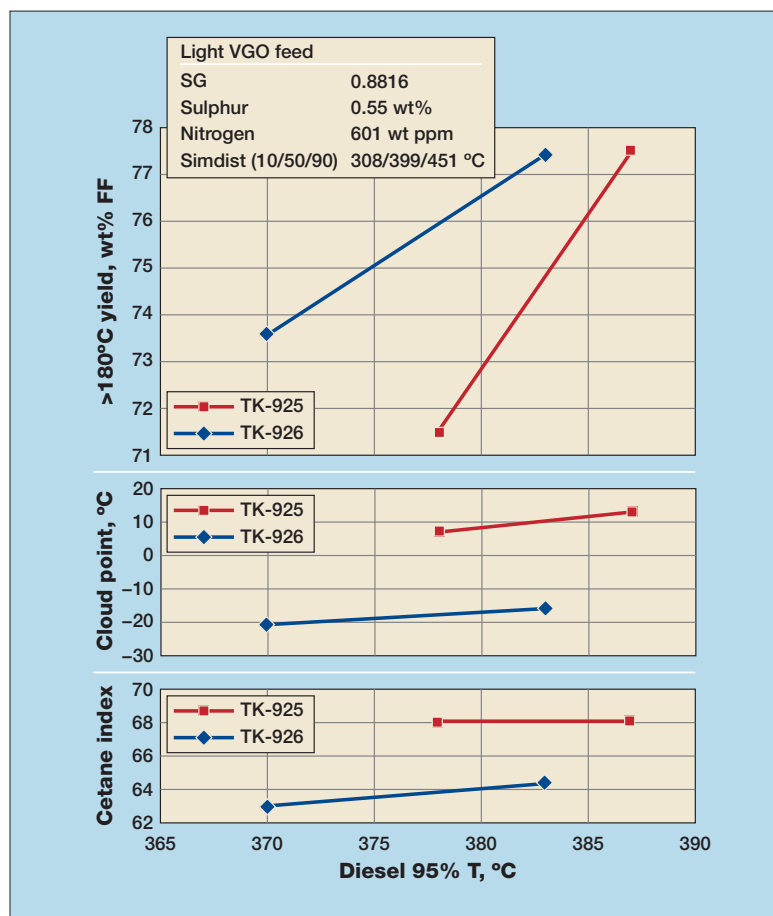


Figure 7 Once-through pilot testing: middle distillate yield (>180°C product), cloud point and cetane index vs ASTM D86 95% temperature

Two Topsoe hydrocracking catalysts, TK-925 and TK-926, were compared in once-through pilot testing using a light vacuum gas oil. The objective of the test was to maximise the production of a full range diesel (>180°) and to identify operating conditions eliminating the production of UCO. The results of the testing are summarised in **Figure 7**.

The yield of the full range diesel (>180°C) is shown in **Figure 7a** for both catalysts as a function of the ASTM D86 95% boiling point of the full range diesel. The D86 95% boiling point will decrease with increasing reactor temperature, and a specified D86 95% temperature for the full range diesel can be obtained by adjusting the reactor temperature. The obtained D86 95% temperatures were within the accepted range. TK-926 gave a better diesel yield than TK-925. With regard to diesel properties, the cloud point obtained with TK-926 was much lower than

that obtained with TK-925 (see **Figure 7b**). The highest cetane index (+4 to 5) was as seen in **Figure 7c** obtained with TK-925 due to its high hydrogenation activity. The cetane index obtained with TK-926 was very satisfactory. This case clearly illustrates that high amounts of diesel with good properties can be produced without co-production of UCO. Commercially, this approach was used successfully.

Other tests showed that the diesel yield can be further improved by the use of TK-939 D-sel. In a particular case with a slightly heavier feedstock (SG: 0.8937, S: 0.32 wt%, N: 1138 wt ppm, SimDist 10/50/90%: 382/421/471°C), the yield of a full range diesel (>145°C) with a requested D86 95% diesel boiling point of 360°C was 12 wt% FF higher with TK-939 D-sel than with TK-926. The cloud point of the diesel was found to be -30°C with the TK-939 D-sel catalyst and -48°C with the TK-926 catalyst.

For a given application, the optimum catalyst system including a high activity pretreatment catalyst can be tailor-made to give the desired diesel quality (D86 95% T, cloud point, and cetane index). The requested front end temperature of the full range diesel will also vary depending on the flash point specification. The obtainable yield of the full range diesel depends on the quality and nature of the feedstock, on the specified front end and back end diesel temperatures, as well as on the diesel cold flow requirements. If boosting the cetane index is required, a catalyst from the red series can be part of the loading. Some refiners may have a light vacuum gas oil or a heavy gas oil that can be upgraded to high quality diesel by installing a simple once-through hydrocracker without a UCO distillation unit.

For a traditional once-through hydrocracker, a catalyst system can also be tailor-made to give the requested yield structure and diesel quality.

In many cases, this will require that more than one hydrocracking catalyst is loaded.

Conclusion

A major factor in maximising the profitability of a hydrocracker is to choose a catalyst system that can give the highest possible combined value of products. In all cases, this will call for the use of a high activity hydrocracking pretreatment catalyst like Topsoe TK-611 HyBRIM. When it comes to selection of the hydrocracking catalyst system, it is far more challenging to select the best system as many factors have to be considered. What is the optimal product yield structure? What are the optimal properties of each of the produced products? What is the value of each product related to the product quality? All of these factors are refinery specific, and it is a complicated analysis to determine the best product structure with the optimal product quality.

This article demonstrates how to maximise middle distillate production and how to impact product quality, for instance cold flow properties, by the use of hydrocracking catalysts from different catalyst series and by the use of different processing schemes. A new way to produce

very low aromatic, high cetane diesel from LCO feedstock with a high selectivity to diesel is presented. This process includes the innovative use of a hydrocracking pretreatment catalyst, a hydrocracking catalyst, and a hydro dearomatisation catalyst.

HyBRIM, D-sel and HPNA Trim are trademarks of Haldor Topsoe.

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