Hydrocracking catalysts

A hydrocracker is one of the most profitable units in a refinery, partly due to the volume swell, and partly because it converts heavy feedstocks to lighter and more valuable products such as naphtha, jet fuel, kerosene and diesel. The unconverted oil may be used as feedstock for FCC units, lube oil plants and ethylene plants. Any improvement in the hydrocracking unit operation significantly improves overall refinery economics.

The proper selection of hydrocracking catalysts offers a great potential for enhancing the performance of the hydrocracking unit with respect to yield structure, product properties, throughput and cycle length.

For optimum performance of a hydrocracking catalyst, it is important to have a high-activity hydrotreating catalyst in front of it to convert organic nitrogen and heavy aromatic compounds to low levels. Topsøe offers a complete catalyst solution, comprising hydrotreating and hydrocracking catalysts as well as grading and guard catalysts.

Maximum middle distillate hydrocracking catalysts

For hydrocracking catalysts, there is often a trade-off between catalyst activity and product selectivity. There can furthermore be a trade-off between the various product properties such as the smoke point of the jet fraction, the cetane number and cold flow properties of the diesel fraction and the viscosity index of the unconverted oil.

At the same time, the refiner is often interested in limiting hydrogen consumption. The tools that catalyst developers have at hand to address these various requirements are balancing the hydrogenation function with the acidic function and modifying the two functions.

As a result of extensive R&D efforts, Topsøe has developed and commercialised two series of hydrocracking catalysts which, in combination with the appropriate Topsøe pretreater catalyst from the BRIM™ series, have shown to provide a step-out performance compared to existing hydrocracking catalysts in the industry.

The RED hydrocracking catalyst series provides exceptional middle distillate yields combined with excellent product properties including high cetane number for diesel, high smoke point for kerosene and high viscosity index for unconverted oil.

- TK-925
- TK-931
- TK-941
- TK-947
- TK-951

The BLUE hydrocracking catalyst series provides an even better middle distillate yield with superior cold flow product properties compared to the RED series.

- TK-926
- TK-933
- TK-943
The RED series
TK-925 is a maximum distillate catalyst. Its main objective is to maximise high-quality diesel yield while producing unconverted oil with excellent qualities for lube oil plants or for FCC units.

TK-931 is a middle distillate catalyst designed to produce very high yields of premium-quality diesel, jet fuel and lube oil base stocks. Specifically, this catalyst gives a high smoke point for jet fuel, an excellent cetane number for diesel fraction and a high viscosity index (VI) for lube base oils.

TK-941 and TK-951 are the recommended catalysts when both high activity and high yield are important. TK-951 is more active than TK-941, and both provide excellent middle distillate yields with efficient hydrogen utilisation.

TK-947 is optimised for units operating at high space velocity and/or low unit pressure. TK-947 has shown excellent performance in both catalyst activity and stability and in product yields and properties.

The BLUE series
TK-926 has a high selectivity for diesel production. The acid function of TK-926 has been modified to enhance the isomerisation reactions and improve the cold flow properties of the products.

TK-933 and TK-943 are medium-activity catalysts to be used in services, where very high middle distillate yields, very good cold flow properties and optimised hydrogen consumption are a must. The diesel cloud point is typically 10-20°C (18-36°F) lower than that obtained with other catalysts.

A special acid function modification is used to improve the isomerisation activity and the middle distillate selectivity. TK-943 is more active than TK-933.

Mild hydrocracking applications
Many hydrocrackers in the refineries operate in mild hydrocracking mode. For these units, the main objectives are to obtain a certain minimum conversion as well as to meet specific product properties such as sulphur content, density and cetane number. Typical pressures are in the 60-110 bar (850-1560 psig) range. Typical conversion is 10-20% for lower pressure units and 30-50% for higher pressure units.

Meeting the product objectives under such conditions can be challenging. Very often the cycle length is determined not by decline in conversion, but by failure to meet a product property such as sulphur content in the diesel fraction. Our catalysts exhibit an excellent nitrogen tolerance, resulting in very stable HDS and HDN activities throughout the cycle. The optimal catalyst or combination of catalysts depends on feed quality and available hydrogen.

Hydrocracker pretreatment
The pretreatment stage in a hydrocracker has the primary objective of removing organic nitrogen, particularly basic nitrogen compounds and aromatics in the feed. Nitrogen compounds have a significantly negative impact on the activity of the hydrocracking catalyst and consequently on the performance of the hydrocracker.
The growing interest in processing heavy oils with high nitrogen content has created a need for pretreatment catalysts with an even higher HDN activity. Depending on the specific needs, Topsoe has developed two catalysts for this service. The catalysts are prepared with the proprietary BRIM™ technology, resulting in high activity for both HDS and in particular HDN. In addition, due to the better utilisation of the active metals and modified carriers, the high activity BRIM™ catalysts have attractive filling densities.

**TK-607 BRIM™** exhibits a very high HDN activity and an excellent stability for high-pressure hydrocracker services. Sulphur and nitrogen removal are significantly improved with TK-607 BRIM™ compared to previous generation catalysts TK-605 BRIM™ and TK-565.

**TK-561 BRIM™** is a catalyst where the activity for nitrogen removal has been maximised while maintaining a high HDS activity. TK-561 BRIM™ is the perfect choice for mild hydrocracking applications where stability and conversion activity are main objectives, and product sulphur is the limiting factor.

**Cold flow properties**

Cold flow properties are strongly related to the content of normal and near normal paraffins present in the diesel. The more highly branched paraffins that are present in the diesel, the better the cold flow properties. Catalysts from our **BLUE** series of hydrocracking catalysts in combination with our pretreatment catalysts provide a very high yield of middle distillates, while giving a low content of normal paraffins in the product and thus good cold flow properties.

**High VI of unconverted oil for lubes**

When the unconverted oil (UCO) is used as a lube oil base stock, its viscosity, viscosity index (VI), volatility and pour point are all crucial product parameters for the lube plant. Using catalysts from our **RED** series such as TK-931 and TK-941 in combination with the pretreatment catalyst TK-607 BRIM™ ensures not only a high yield of middle distillates but also a very high yield of VI barrels and an excellent quality of the UCO. This is achieved through the very high HDN, aromatic saturation and ring opening activities of the catalyst system.

<table>
<thead>
<tr>
<th>Type of molecules</th>
<th>Influence on VI</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="Molecules" /></td>
<td><img src="image2.png" alt="Influence" /></td>
</tr>
</tbody>
</table>

Figure 2: The composition of unconverted oils has a significant impact on the viscosity index with normal paraffins being the most favourable and aromatics and poly-naphthenics being the least favourable.
**HPNA management**

Heavy Polynuclear Aromatics (HPNA) are formed in the reactor due to condensation of aromatics and dehydrogenation of poly-naphthenes. These compounds cause fouling on the exchangers and coking of the catalyst. In general, high endpoint feed, low pressure, high operating temperature and high catalyst acidity are the factors that promote formation of HPNA. Topsøe’s hydrocracking catalysts are developed with an emphasis on balancing the catalyst hydrogenation function with the cracking function. Together with our high-performance pretreatment catalysts, Topsøe’s hydrocracking catalyst system has shown that the HPNA in the unconverted oil fraction is low compared to competitor catalyst systems. The HPNA compounds in the UCO have a significant impact on the colour as shown in figure 3.

![Figure 3: Display of the structure of typical heavy polynuclear aromatics. These species are found in concentrations varying from 25 to 2000 wt ppm.](image)

**Role of nitrogen compounds**

Organic nitrogen compounds have a significantly negative effect on hydrotreating reactions such as HDS and HDN as well as on hydrogenation reactions. Nitrogen poisoning of the acidic catalysts employed in a hydrocracker is even more severe. An increase in nitrogen slip into the cracking catalyst from for instance 20 wt ppm to 80 wt ppm has a very negative impact on the conversion as well as on the product properties as seen in table 1.

![Figure 4: The most refractive nitrogen compounds found in VGO are a family of carbazole derived compounds called 4, 8, 9, 10-Tetrahydrocyclohepta[def]carbazole. They have been isolated and characterised](image)

<table>
<thead>
<tr>
<th></th>
<th>Low N-slip</th>
<th>High N-slip</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-slip</td>
<td>20 wt ppm</td>
<td>80 wt ppm</td>
</tr>
<tr>
<td>Pressure, barg (psig)</td>
<td>150 (2133)</td>
<td>150 (2133)</td>
</tr>
<tr>
<td>HC temperature, °C (ºF)</td>
<td>395 (743)</td>
<td>395 (743)</td>
</tr>
<tr>
<td>H₂ consumption, wt % FF</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Conversion, wt % Base</td>
<td>-17%</td>
<td>-17%</td>
</tr>
<tr>
<td>C₃ + C₄ yields, wt % Base</td>
<td>-2%</td>
<td>-2%</td>
</tr>
<tr>
<td>C₅ yields, wt % Base</td>
<td>-9%</td>
<td>-9%</td>
</tr>
<tr>
<td>Jet yields, wt % Base</td>
<td>-7.6%</td>
<td>-7.6%</td>
</tr>
<tr>
<td>Diesel yields, wt % Base</td>
<td>+0.5%</td>
<td>+0.5%</td>
</tr>
</tbody>
</table>

Table 1: Due to the poisoning of acidic sites, the negative impact of N-slip on performance of the hydrocracker is very large. Not only conversion and yield structure, but also cycle length and product properties are impacted.
Topsøe's technical service programme

An expert and dedicated technical service support is an important element in the success of operating a hydrocracking unit. Topsøe is not only a catalyst but also a technology provider. With our expertise, we can provide you with technical service both from a catalyst standpoint as well as from a technology (hardware) standpoint.

Among the potential Topsøe support activities are:

- detailed technical consultancy by our hydrocracking experts to optimise current and future operation of our clients’ hydrocracking units
- pilot plant performance data based on the refiner’s feed and operating conditions – Topsøe has several hydrocracking pilot plant units in operation in Lyngby, Denmark that are capable of simulating the client’s process conditions
- review and recommendation of the existing hydrocracker catalyst loading and catalyst activation procedures
- start-up assistance during the catalyst activation phase
- plant visits, on-site periodic reviews of unit operations, analysis of the operating data, feed analysis, catalyst analysis and ad-hoc troubleshooting
- spent catalyst analysis and estimate of catalyst regenerability
- assistance in the optimum operation of the hydrocracking unit

Know-how and commercial experiences have placed Topsøe among the leaders in providing hydrocracking catalyst solutions. Let Topsøe offer you the proper catalysts to enhance the performance of your hydrocracker unit.
The information and recommendations have been prepared by Topsøe specialists having a thorough knowledge of the catalysts. However, any operation instructions should be considered to be of a general nature and we cannot assume any liability for upsets or damage of the customer’s plants or personnel. Nothing herein is to be construed as recommending any practice or any product in violation of any patent, law or regulation.