

PROCESS DESCRIPTIONS:

Hydrocracking Process Description and CRITERION / ZEOLYST Hydrocracking Catalyst Applications

OBJECTIVE

The objective of hydrocracking is to convert heavy oil feedstocks into high quality, lighter fuel products such as gasoline, naphtha, jet or kerosene, and diesel, and hydrowax (unconverted bottoms) which can be used as petrochemical plant feedstock or lube basestock. A two-step process is typically employed. In the first (pretreat) step, polyaromatic compounds are saturated and organic nitrogen and sulfur are converted to ammonia and hydrogen sulfide. The organic nitrogen contained in the feedstock would otherwise inhibit the activity of the cracking catalyst. In the second (cracking) step, higher molecular weight hydrocarbon molecules are preferentially cracked over an acidic metal-containing hydrocracking catalyst. The product yields and product properties are determined by the feedstock, the cracking catalyst selectivity and the process conditions.

FEEDS AND UNIT OPERATION

A wide variety of feedstocks are processed in hydrocrackers, including atmospheric gas oils, catalytically cracked light and heavy cycle oils, vacuum gas oils, coker or thermally cracked gas oils and deasphalted oil.

Hydrocrackers are typically classified as single-stage, series-flow or two-stage units (some hybrid configurations also exist). In single-stage hydrocrackers, all catalysts are contained in a single stage (in one or more series or parallel reactors). A single catalyst type might be employed or a stacked-bed arrangement of two different catalysts might be used. In single-stage or series-flow hydrocracking, all catalysts are exposed to the high levels of H₂S and NH₃ that are generated during removal of organic sulfur and nitrogen from the feed.

Ammonia inhibits the hydrocracking catalyst activity, requiring higher operating temperatures to achieve target conversion, but this generally results in somewhat better liquid yields than would be the case if no ammonia were present. There is no interstage product separation in single-stage or series-flow operation. Two-stage hydrocrackers employ interstage product separation that removes H₂S and NH₃, so the second-stage hydrocracking catalyst is exposed to lower levels of these gases, especially NH₃. Some two-stage hydrocracker designs do result in very high H₂S levels in the second stage.

Frequently, unconverted product is separated and recycled back to either the pretreat or the cracking reactors. Typical operating conditions applied in hydrocracking are:

H ₂ partial pressure, psig (bar)	1100 - 2300 (75 – 160)
LHSV, v/v/hr	0.7 – 2.5
H ₂ /Oil ratio, SCF/bbl (Nm ³ /m ³)	4000 - 10000 (700 – 800)
Nitrogen slip, ppmw	0.1 – 50+
Conversion per pass	35 – 80%

CRITERION / ZEOLYST CATALYSTS

In some applications, hydrocracker unit run length is limited by catalyst life. In these instances, changing to a higher activity pre-treat and zeolitic cracking catalyst, such as CRITERION / ZEOLYST Hydrocracking Catalysts, can result in significant increases in unit run length. This is due to the superior start-of-run activity and stability characteristics of these high performance catalysts. The broad range of activity and selectivity of CRITERION / ZEOLYST catalysts allows selection of optimized catalyst systems which will meet run length requirements, maximize the production of desired products for a specific unit, and meet product quality specifications.

PRETREAT CATALYSTS:

The main objectives for the pretreat catalyst are: (i) the removal of organic nitrogen and sulphur from the HCU feed to levels which allow the second-stage catalysts to better perform the hydrocracking function, and (ii) the initiation of the sequence of hydrocracking reactions by saturation of the aromatic compounds in the HCU feed. Pretreat catalysts must have adequate activity to achieve both objectives within the operating limits of the HCU (hydrogen partial pressure, temperature, and LHSV).

CRITERION offers an impressive line of widely used and proven catalysts such as TRILOBE* 424, 411, DN-120, and the newly-developed CENTURY DN-190 and CENTINEL DN-3100. The TRILOBE* shape of the CRITERION pretreat catalysts significantly reduces diffusional limitations and provide reduced pressure drop compared with the same size cylindrical catalysts.

The CRITERION 424 pore-size distribution was optimized for heavier feedstocks to provide easy access for large molecules and to make the catalyst more tolerant to metals and contaminants present in hydrocracker feeds. The good metal dispersion throughout this catalyst improves hydrogenation and helps reduce catalyst coking, thus extending catalyst life. The 411 catalyst offers even higher denitrogenation and hydrogenation activities for cracked feedstocks (e.g cat cracker and coker products). These feedstock components contain not only more concentrated organic nitrogen, but also more refractory nitrogen compounds. 411 provides the additional activity necessary to give low start-of-run temperatures and longer cycle life for the processing of these feedstocks. The DN-120 catalyst was developed to further improve on 411 denitrogenation activity.

The newer CENTURY DN-190 pre-treat catalyst is a significant step-out in high-activity catalyst technology. It is the result of significant advancements in catalyst formulation and manufacturing technologies. It offers 30-45% higher denitrogenation activity than the most active conventional Ni/Mo catalysts available on the market. DN-190 has been selected for use in over 50 hydrocrackers processing a large number of feedstocks including straight-run atmospheric and vacuum gasoils, cat cracker and coker gasoils. The commercial results have shown that DN-190 activity benefits increase with increasing severity. Refiners who choose to use DN-190 can look forward to significant economic benefits resulting from:

- Processing more heavy/difficult/high-margin feedstocks and/or
- Increased unit throughput and/or
- Longer catalyst life.

The newest Criterion HDN catalyst for hydrocracker pretreat use is CENTINEL DN-3100 which offers significantly higher activity than DN-190. Introduced in late 2000, this catalyst has already been selected for use in 7 hydrocrackers.

Early generation catalysts for hydrocracking were generally based on amorphous silica aluminas (ASA). Later, zeolitic hydrocracking catalysts were developed which have the advantages of higher activity, organic nitrogen tolerance, and robustness. However, zeolitic hydrocracking catalysts require tighter control of reactor bed temperatures, because their greater activity causes a greater temperature response to bed inlet temperature changes.

ZEOLYST™ Z-503 is specifically designed to maximize production of heavier distillates, especially diesel, from heavy feedstocks. It has also gained widespread use in stack-bed use in combinations with HDN catalysts in hydrocracker pretreaters to convert the most difficult nitrogen compounds more easily and increase the pretreater cycle length.

ZEOLYST™ Z-603 is specifically designed to convert heavy oil feedstocks to maximum yields of middle-distillates. Its unique formulation produces middle-distillate yields comparable to the yields derived from amorphous silica alumina hydrocracking catalysts, and provides better activity and stability than ASA catalysts are able to achieve. This combination of properties makes the Z-603 catalyst especially suited for converting high boiling range feedstocks into diesel and jet fuel products.

ZEOLYST™ Z-623 combines intermediate activity with high selectivity to middle distillates. It is specifically designed to provide a constant high yield of kerosene and gasoil with excellent product properties. This catalyst is also tolerant of the relatively unreactive molecules in a recycle unconverted oil stream, requiring only small bleed rates to prevent longer term deactivation and/or poly-aromatics deposition. Z-623 is well suited to a variety of heavy feeds and will give increased life for units that process lighter feeds.

ZEOLYST™ Z-673 has demonstrated high selectivity to middle distillates with an enhanced hydrogenation and denitrogenation activity. Its high hydrogenation and denitrogenation activity allows a much less severe pretreatment than required for other catalysts. Consequently, Z-673 can be employed to extend unit run length in pretreat-limited operations, and/or can allow the processing of heavier feeds.

ZEOLYST™ Z-723 is specifically designed to hydrocrack heavy oil feedstocks to produce high yields of high quality middle-distillates with reduced gas byproducts. Its advanced formulation enhances aromatics saturation and thus improves middle-distillate yields, product quality, and catalyst stability. This combination of properties makes the Z-723 catalyst especially suitable for converting high boiling range feedstocks into high quality diesel and jet fuel products either in recycle or once through operations.

ZEOLYST™ Z-733 is specifically designed for maximum naphtha/kerosene production in two-stage or series-flow, with or without recycle. Z-733 is applied in the cracking beds, following high activity pretreat catalysts such as Criterion's DN-190 or DN-3100, or optionally stacked-bed systems of these catalysts with Z-663 or Z-673. The unconverted part of the product stream from the cracking stage can be recycled to the pretreater catalyst or optionally to Z-733. This catalyst has been designed to produce middle distillate range products with improved properties like density, smoke point and cetane number.

ZEOLYST™ Z-753 is designed for applications involving any of the feedstocks listed previously, for which higher activity or naphtha selectivity is desired. Z-753 produces a high quality naphtha with reduced hydrogen consumption. Gas make is lower and liquid yields are higher than competitive catalysts. Throughout the course of the operating cycle, Z-753 product yields are more stable than available competitive catalysts. ZEOLYST Z-753 operation can swing on demand into a naphtha plus middle-distillate mode of production if desired.

ZEOLYST™ Z-773 is specifically designed for maximum naphtha production. Alternatively, hydrocracker operation is shifted on demand between maximum naphtha and jet modes. ZEOLYST Z-773 is designed for use in the second cracking reactor of two-stage hydrocrackers. Organic nitrogen is typically very low (less than 1 ppmw) in this application. Z-773 can also be applied in series-flow first-stage applications in a high ammonia environment. Z-773 can operate in low or high levels of hydrogen sulfide, the presence of which depends on the configuration of the hydrocracker hydrogen system. The liquid yields and activity/selectivity stability of noble metal Z-773 is superior to that of other commercially available noble metal naphtha catalysts.

ZEOLYST™ Z-803 is specifically designed to hydrocrack heavy oil feedstocks to produce high yields of high quality middle-distillates and lower yields of light-end products and gas. Its advanced formulation provides high activity and enhanced aromatics saturation, resulting in improved middle-distillate yields, product quality and stability. This combination of properties makes Z-803 especially suited for converting high boiling range feedstocks into high quality diesel and jet fuel in either recycle or once-through operations. Additionally, Z-803 can be utilized in hydrocracking units which swing between maximum distillate and naphtha modes of operation.

ZEOLYST™ Z-863 is designed for applications in which maximum catalyst activity and cycle length are paramount. Product yields are similar to Z-753. Although all ZEOLYST catalysts are robust and recover well from process upsets, Z-863 is particularly robust. It withstands severe process upsets, and will recover faster and more completely than competitive catalysts. ZEOLYST™ Z-863 is the only hydrocracking catalyst in the world, specifically designed to be highly nitrogen tolerant. For this reason, it is the catalyst of choice for use in the leading one or two cracking beds in series-flow hydrocrackers.

In some hydrocracking applications, overall hydrocracking catalyst activity is generally good but the activity of catalyst in the top beds is less than desired. Due to relatively high “nitrogen slip” to the leading cracking bed(s), it is sometimes impossible to achieve the desired conversion over these hydrocracking beds, and overall unit performance suffers as a result. In these instances, replacing the existing catalyst in the leading beds with Z-863 can completely correct the problem. ZEOLYST™ Z-863 is often employed in a stacked-bed arrangement over other hydrocracking catalysts such as Z-753. The high activity of Z-863 allows balancing of the cracking reactor bed delta-T's, resulting in reduced overcracking, improved product quality and yields, and improved catalyst stability. Even if “top-bed” activity is not limiting, Z-863 provides the opportunity/ability to increase N-slip, thus extending pretreater catalyst life and/or to process more difficult feedstocks.

POST-TREAT CATALYSTS:

A post-treat catalyst is often loaded in the bottom portion of the cracking reactor to prevent mercaptans formation due to recombination of H₂S and trace levels of olefins. The use of CRITERION pretreat catalysts (such as DN-120 and DN-190) in post-treat services has been proven effective. CRITERION / ZEOLYST will work together with the client to tailor post-treat catalyst recommendations to the client's specific unit constraints and conditions.

At the end of an operating cycle, spent hydrocracking catalyst is usually regenerated. CRITERION / ZEOLYST hydrocracking catalysts lose very little activity upon regeneration, so reuse for multiple operating cycles is a feasible and commonly utilized option. Additional information on the CRITERION / ZEOLYST catalysts is contained in specific CRITERION /ZEOLYST product bulletins which are available through your CRITERION sales representative.

Choosing the best hydrocracking catalyst for a specific application is a complex undertaking, involving a detailed examination of customer feedstocks, unit operation, desired performance, and constraints. Your CRITERION sales representative and the ZEOLYST INTERNATIONAL technical service engineers stand ready to work with you to determine the optimal hydrocracking catalyst for your application, including detailed performance estimates and pilot plant testing as required.

SUPPLY AND TECHNICAL SUPPORT

Criterion Catalysts & Technologies L.P. is the exclusive world-wide sales agent for ZEOLYST catalysts, and will be pleased to provide hydrocracking unit performance estimates prepared by CRITERION / ZEOLYST INTERNATIONAL. CRITERION / ZEOLYST INTERNATIONAL provide full technical support for your use of CRITERION / ZEOLYST hydrocracking catalysts, including start-up and operating guidelines, on-site start-up support, troubleshooting and technical advice, performance monitoring, quality assurance testing, analytical testing in state-of-the-art laboratories and more.

ADDITIONAL INFORMATION

All catalyst information supplied by CRITERION/ZEOLYST is considered accurate but is furnished with the express understanding that the customer receiving such information shall make its own assessments to determine suitability of such information for customer's particular purpose. All purchases of CRITERION/ZEOLYST catalysts are subject to CRITERION/ZEOLYST's standard terms and conditions of sale set forth in a sales proposal, sales contract, order acknowledgement, and/or bill of lading.

HOUSTON:

16825 Northchase Drive, Suite 1000
Houston, Texas 77060-6029
Telephone: (1) 281- 874-2600
Telefax: (1) 281- 874-2641

ENGLAND:

1650 Parkway
The Solent Business Park,
Whiteley, Fareham
Hampshire, PO15 7AH England
Telephone: (44) 1 489-881881
Telefax: (44) 1 489-881882

CANADA:

5241 Calgary Trail Southbound
Centre 104, Suite # 810
Edmonton, Alberta T6H 5G8
Telephone: (1) 780-438-4188
Telefax: (1) 780-438-3473

SINGAPORE:

298 Tiong Bahru Road
#07-03 Central Plaza
Singapore 168730
Telephone: (65) 6276-3627
Telefax: (65) 6276-7455

DUBAI:

10th Floor, Dubai Convention Tower
Zabeel Area
Dubai, UAE
Telephone: +971 4 4405 4640
Telefax: +971 4 4405 4656

EMAIL: CriterionPublicAffairs@cri-criterion.com