

Chapter 7

HYDROTREATING AND HYDROCRACKING: FUNDAMENTALS

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1. INTRODUCTION

Hydrotreaters are the most common process units in modern petroleum refineries. As shown in Table 1, the world's hydrotreating capacity is nearly half as large as the world's crude distillation capacity.¹ In more than 700 refineries around the globe, there are more than 1300 hydrotreating units. A typical Western petroleum refinery (*Figure 1*) uses at least three hydrotreaters – one for naphtha, one or two for light gas oil, and one or two for heavy gas oil and/or vacuum gas oil.

Table 1. Worldwide Refining Process Units (as of January 1, 2004)¹

	Crude Distillation	Coking + Visbreaking	FCC	Catalytic Reforming	Hydro- treating	Hydro- cracking
Number of Units	>710	>330	360	550	1316	168
Total World Capacity*	82.0	8.0	14.3	11.3	40.3	4.6
Average Capacity†	114,000	45,700	39,700	20,500	30,600	27,400

* million barrels per calendar day

† barrels per calendar day

Hydrocracking is far less common than hydrotreating, but the number of partial-conversion “mild” hydrocrackers is increasing as refiners build new units to meet clean fuel regulations.

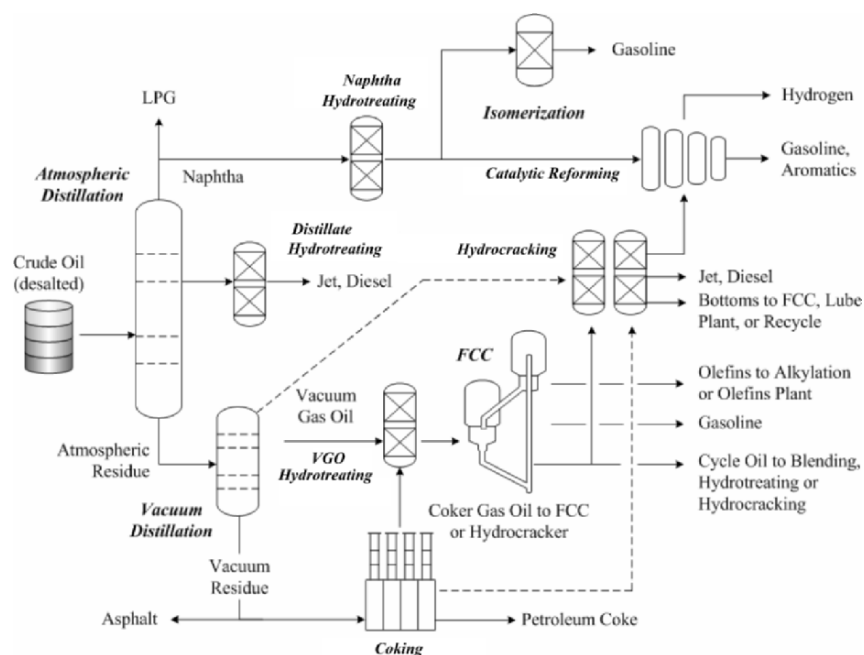


Figure 1. Layout of a Typical High-Conversion Oil Refinery

1.1 Hydroprocessing Units: Similarities and Differences

Process flow schemes for hydrotreating and hydrocracking are similar. Both use high-pressure hydrogen to catalytically remove contaminants from petroleum fractions. Both achieve at least some conversion, and they use the same kinds of hardware. Therefore, to avoid redundancy, we decided to discuss them together. As is common in the refining industry, we use the term “hydroprocessing” when a statement applies to both hydrotreating and hydrocracking.

As shown in *Table 2*, the extent of conversion is the most significant difference between hydrotreating and hydrocracking. In this context, the term “conversion” is defined as the difference in amount of unconverted oil between feed and product divided by the amount of unconverted oil in the feed. Unconverted oil is defined as material that boils above a specified temperature. For vacuum gas oil (VGO), a typical specified temperature is 650°F (343°C). Conversion in hydrotreaters is less than 15 wt%, while conversion in hydrocrackers and mild hydrocrackers exceeds 20 wt%.

In hydrotreating units, reactions that convert organic sulfur and nitrogen into H_2S and NH_3 also produce light hydrocarbons. For example, as shown in *Figure 5*, the removal of sulfur from dibenzothiophene (boiling point =

630°F, 332°C) generates biphenyl (492.6°F, 255.9°C). This reaction does not break any carbon-to-carbon bonds, but it does convert a molecule that boils above 600°F (315.5°C) into one that boils below 600°F (315.5°C).

In hydrotreaters, conversion due to the removal of sulfur, nitrogen and oxygen usually is less than 15 wt%.

Table 2. Hydrotreating and Hydrocracking: Ranges of H₂ Partial Pressure and Conversion

Process, Feedstock Types	H ₂ Partial Pressure		Conversion wt%
	psig	kPa	
<i>Hydrotreating</i>			
Naphtha	250 to 450	1825 to 3204	0.5 to 5%
LGO (Kerosene)	250 to 600	1825 to 4238	0.5 to 5%
HGO (Diesel), LCO	600 to 800	4238 to 5617	5 to 15%
VGO, VBGO, DAO, CGO, HCO	800 to 2000	5617 to 13,891	5 to 15%
Residual Oil	2000 to 3000	13,891 to 20,786	5 to 15%
<i>Mild Hydrocracking</i>			
VGO, VBGO, DAO, CGO, LCO, HCO	800 to 1200	5617 to 8375	20 to 40%
<i>Once-Through Hydrocracking</i>			
VGO, VBGO, DAO, CGO, LCO, HCO	1500 to 2000	10,443 to 13,891	60 to 90%
Residual Oil	2000 to 3000	13,891 to 20,786	15 to 25%
<i>Recycle Hydrocracking</i>			
VGO, VBGO, DAO, CGO, LCO, HCO	1500 to 2000	10,443 to 13,891	80 to 99%
<i>Ebullated-Bed Hydrocracking</i>			
VGO, VBGO, DAO, HCO	2000	13,891	80 to 99%
Residual Oil	2000 to 3000	13,891 to 20,786	>50%
LGO = light gas oil	HGO = heavy gas oil		
LCO = FCC light cycle oil	HCO = FCC heavy cycle oil		
VGO = vacuum gas oil	VBGO = visbreaker gas oil		
DAO = deasphalted oil	CGO = coker gas oil		

Hydrotreating and hydrocracking differ in other ways. For a given amount of feed, hydrocrackers use more catalyst and operate at higher pressures. They also use different catalysts. Because they make large amounts of light products, hydrocracker fractionation sections must be more complex. In some hydrocrackers, unconverted oil from the fractionation section is recycled, either back to the front of the unit or to a separate cracking reactor.

Many mild hydrocrackers contain at least one bed of cracking catalyst, which allows them to achieve higher conversion – between 20 and 40 wt%. The unconverted bottoms can go to an FCC unit, a lube plant, or fuel-oil blender. Due to its high value in other applications, the bottoms are blended into fuel oil only when there is no other feasible option.

In hydrocrackers that process vacuum gas oils or other feeds with similar boiling ranges, the typical once-through conversion exceeds 60 wt%. If the unconverted oil is recycled, the overall conversion can exceed 95 wt%. As

with mild hydrocracking, the unconverted bottoms are high-value oils, which usually are sent to FCC units, lube plants, or olefin plants. For heavier feeds – atmospheric and vacuum residues – conversions are much lower, especially in fixed-bed units. In ebullated-bed units, the conversion of 1050°F-plus (566°C-plus) residue can exceed 60 wt%.

Catalytic isomerization and dewaxing is a special kind of hydrocracking used to make high-quality lube base stocks. This topic is well-covered elsewhere, so we won't elaborate here.

2. PROCESS OBJECTIVES

Table 3 presents a list of feeds and product objectives for different kinds of hydrotreaters and hydrocrackers. In the 1950s, the first hydrotreaters were used to remove sulfur from feeds to catalytic reformers. In the 1960s, the first hydrocrackers were built to convert gas oil into naphtha.

Table 3. Feeds and Products for Hydroprocessing Units

Feeds	Products from Hydrotreating	Products from Hydrocracking
Naphtha	Catalytic reformer feed	LPG
Straight-run light gas oil	Kerosene, jet fuel	Naphtha
Straight-run heavy gas oil	Diesel fuel	Naphtha
Atmospheric residue	Lube base stock, low-sulfur fuel oil, RFCC* feed	Naphtha, middle distillates, FCC feed
Vacuum gas oil	FCC feed, lube base stock	Naphtha, middle distillates, FCC feed, lube base stock, olefin plant feed
Vacuum residue	RFCC* feed	Naphtha, middle distillates, RFCC* feed
FCC light cycle oil	Blend stocks for diesel, fuel oil	Naphtha
FCC heavy cycle oil	Blend stock for fuel oil	Naphtha, middle distillates
Visbreaker gas oil	Blend stocks for diesel, fuel oil	Naphtha, middle distillates
Coker gas oil	FCC feed	Naphtha, middle distillates, FCC feed, lube base stock, olefin plant feed
Deasphalted oil	Lube base stock, FCC feed	Naphtha, middle distillates, FCC feed, lube base stock

*RFCC = “residue FCC unit” or “reduced crude FCC unit,” which are specially designed to process feeds that contain high concentrations carbon-forming compounds.

Today, in addition to naphtha, hydrotreaters process kerosene, gas oil, vacuum gas oil, and residue. Hydrocrackers process vacuum gas oil, coker gas oil, visbreaker gas oil, FCC heavy cycle oil, and/or other feeds that boil between 650°F and 1050°F (343°C and 566°C). Most residue hydrocrackers use fluidized bed or ebullated bed technology.

For hydroprocessing units, product specifications are set to meet plant-wide objectives. For example, the naphtha that goes to catalytic reforming and isomerization units must be (essentially) sulfur free. Before it can be sold as

jet fuel, the aromatics content of kerosene must be low enough to meet smoke-point specifications (ASTM D1655). Heavier distillates cannot be sold as diesel fuel unless they meet stringent sulfur specifications.

2.1 Clean Fuels

As mentioned in Chapter 1 (Section 8.2.4), on-road diesel in the United States must contain <15 wppm sulfur by 2006. The sulfur limit for non-road diesel will be 500 wppm in 2007. The present U.S. specification for gasoline is <30 wppm sulfur. In the European Union, the sulfur content of both gasoline and diesel must be <50 wppm by 2005 and <10 wppm by 2008.

To meet clean fuel specifications, refiners in North America and Europe are increasing their hydroprocessing capabilities and adjusting operations. Two real-world examples are described below.

Example 1. A U.S. refinery is planning to produce diesel fuel that contains <15 wppm sulfur by June 2006. At present, the hydrocracker makes 39,000 barrels/day of middle distillate that is nearly sulfur-free. The existing 60,000 barrels/day distillate hydrotreater (DHT) gives a product with 600 to 700 wppm sulfur. Mixing the two streams yields a blend containing 425 to 485 wppm sulfur, which meets existing specifications for low-sulfur diesel fuel (per ASTM D975). To make ultra-low-sulfur diesel (ULSD), the refiner is adding a reactor and a high-pressure amine absorber to the existing DHT, enabling the unit to make a stream with 12 to 18 wppm sulfur. Blending this with distillate from the hydrocracker will give a final product containing 7 to 12 wppm sulfur.

Example 2. A European refiner now runs a mild hydrocracker (MHC) to maximize conversion of VGO and to pretreat the feed to its FCC unit. The plant cannot post-treat its FCC gasoline, so the sulfur content of the MHC bottoms must be less than 500 wppm to guarantee that the sulfur content of the FCC gasoline is less than 150 wppm. Other low-sulfur streams (reformate, alkylate and hydrotreated gas oil) go into the final gasoline blend, so sulfur in the FCC gasoline can exceed the final-product limit of 50 wppm.

2.2 The Process In-Between

As shown in *Figure 1*, hydrocracking often is an “in-between” process. The required hydrogen comes from catalytic reformers, steam/methane reformers or both. Liquid feeds can come from atmospheric and/or vacuum distillation units; delayed cokers; fluid cokers; visbreakers; or FCC units. Middle distillates from a hydrocracker usually meet or exceed finished product specifications, but the heavy naphtha from a hydrocracker usually is sent to a catalytic reformer for octane improvement. The fractionator bottoms can be recycled or sent to an FCC unit, an olefins plant, or a lube plant.

3. CHEMISTRY OF HYDROPROCESSING

Chemically, the boundaries between hydrotreating, mild hydrocracking, and hydrocracking are blurry. Hydrocracking occurs in many hydrotreaters, especially at high temperatures near the end of a catalyst cycle. *Table 4* lists the chemical reactions that occur in hydroprocessing units.² Most of the reactions are exothermic, so controlling heat release is a primary consideration in the design and operation of hydrotreaters and hydrocrackers.

Table 4. List of Hydroprocessing Reactions

Reaction Type	Illustration	ΔH_R^*
Minimal C-C Bond Breaking		
Hydrodesulfurization (HDS) †	$R-S-R' + 2 H_2 \rightarrow RH + R'H + H_2S$	-2.5 to -3.0
Hydrodenitrogenation (HDN)	$R=N-R' + 3 H_2 \rightarrow RH + R'H + NH_3$	-2.5 to -3.0
Hydrodeoxygenation (HDO)	$R-O-R' + 2 H_2 \rightarrow RH + R'H + H_2O$	-2.5 to -3.0
Hydrodemetallation (HDM)	$R-M + \frac{1}{2} H_2 + A \rightarrow RH + M-A$	-3
Saturation of aromatics	$C_{10}H_8 + 2 H_2 \rightarrow C_{10}H_{12}$	-3
Saturation of olefins	$R=R' + H_2 \rightarrow HR-R'H$	-5.5
Isomerization	$n-RH \rightarrow i-RH$	n/a
Significant C-C Bond Breaking		
Dealkylation of aromatic rings	$\Phi-CH_2-R + H_2 \rightarrow \Phi-CH_3 + RH$	-1.3 to -1.7
Opening of naphthene rings	$Cyclo-C_6H_{12} \rightarrow C_6H_{14}$	-1.3 to -1.7
Hydrocracking of paraffins	$R-R' + H_2 \rightarrow RH + R'H$	-1.3 to -1.7
Other Reactions		
Coke formation	$2 \Phi H \rightarrow \Phi\Phi + 2 H_2$	+3
Mercaptan formation	$R=R' + H_2S \rightarrow HS-R-R'H$	-3

* Kilojoules per standard m³ of H₂ consumed. For exothermic reactions, ΔH_R is negative.

† R = alkyl; Φ = aromatic; M = Fe, Ni or V; A = metals-adsorbing material

Enthalpies for the reactions (ΔH_R) can be grouped into three categories. For HDS, HDN, HDO, HDM, and aromatics saturation, ΔH_R are about -2.5 to -3.0 kJ per standard cubic meter of consumed H₂. For reactions that break carbon-to-carbon bonds, ΔH_R are about -1.3 to -1.7 kJ per m³ of consumed H₂. And for saturation of olefins, ΔH_R are about -5.5 kJ per m³ of consumed H₂. Isomerization reactions produce a small amount of heat, but this can be neglected.

The following sections describe most of these reactions in more detail. In-depth information is provided in Chapter 20 by Michael Klein and Gang Hou, in Chapter 9 by I. Mochida and Ki-Hyouk, in Chapter 10 by Barry Cooper and Kim Knudsen, and in Chapter 11 by Chunshan Song and Xiaoliang Ma.

3.1 Saturation Reactions

Figure 2 shows examples of saturation reactions for olefins and aromatics.

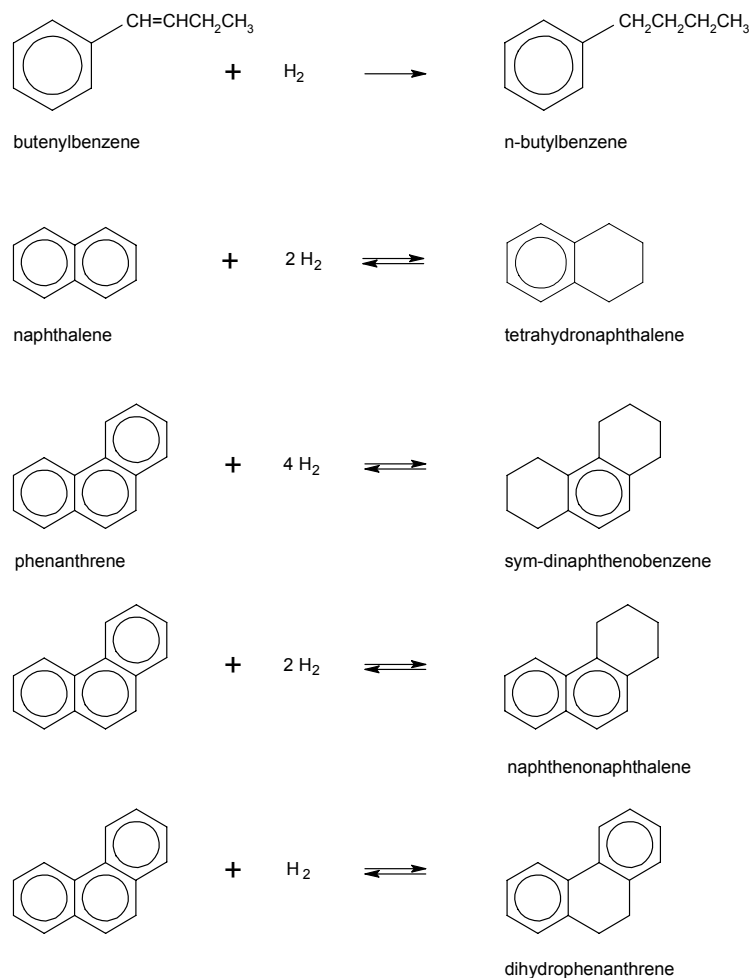


Figure 2. Saturation of butenylbenzene, naphthalene, and phenanthrene.

Practically speaking, the saturation of olefins is irreversible. The saturation of aromatics is reversible. In hydroprocessing units, at temperatures below about 700°F (370°C), forward (hydrogenation) reactions dominate and the extent of saturation goes up at higher temperatures. In the full-range product, the naphthene-to-aromatic (N/A) ratio is greater than the N/A ratio predicted by thermodynamic calculations. This indicates that the reactions are not at equilibrium and are governed by kinetics. Above about 740°F (393°C), equilibrium starts to compete with kinetics and the reverse (dehydrogenation) reactions become more important. *Figure 3* shows how LHSV affects product N/A ratio of the four saturation reactions in *Figure 2*. The product N/A ratio closest to equilibrium is for the phenanthrene/naphthenonaphthalene pair at

low space velocity (0.51). At a more typical space velocity (1.04), the N/A ratio for this pair is 1.5 times higher than the equilibrium value.

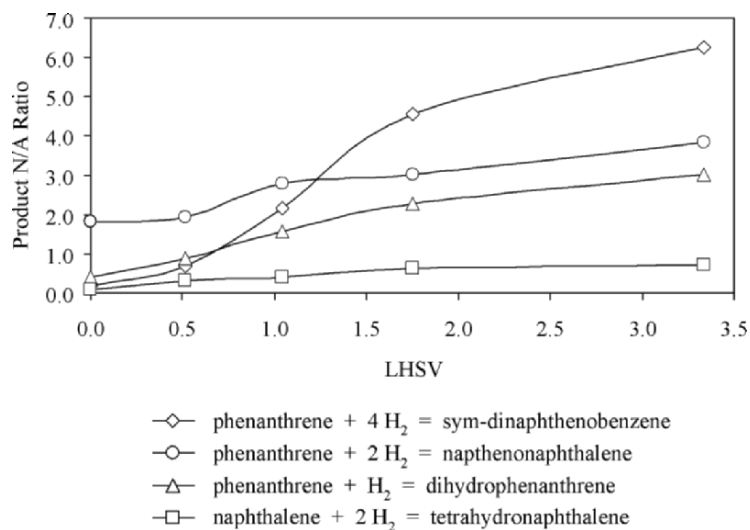


Figure 3. Product naphthene/aromatic (N/A) ratios for saturating naphthene and phenanthrene at 800°F, 2000 psig (426°C, 13,891 kPa) over a non-acidic catalyst. N/A ratios at zero LHSV (infinite reaction time) come from equilibrium calculations, not measurements.³

The saturation cross-over temperature – above which the N/A ratio of the full-range product starts to decrease – depends on feed composition, catalyst type, and reaction conditions; H₂ partial pressure is especially important. This phenomenon, illustrated by Figure 4, affects important product properties, such as kerosene smoke point and diesel cetane.

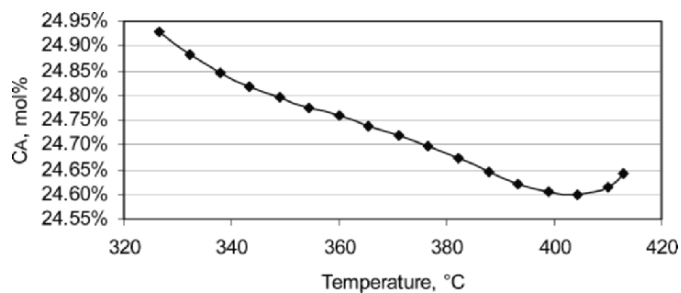


Figure 4. Aromatics cross-over in a 1500 psig (10,443 kPa) VGO hydrotreater.

3.2 HDS Reactions

Hydrodesulfurization (HDS) reactions proceed via two major pathways.⁴ “Direct” HDS (*Figure 5*) is relatively simple. However, “indirect” HDS (*Figure 6*) requires preliminary reactions, such as saturation of aromatics or ring dealkylation.

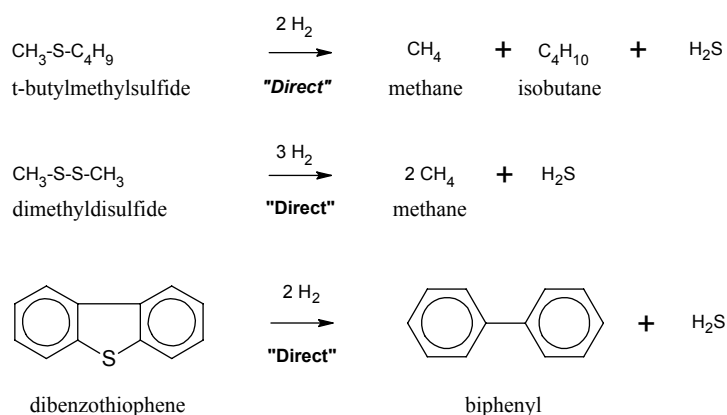


Figure 5. Hydrodesulfurization (HDS) of a sulfide, a disulfide, and dibenzothiophene

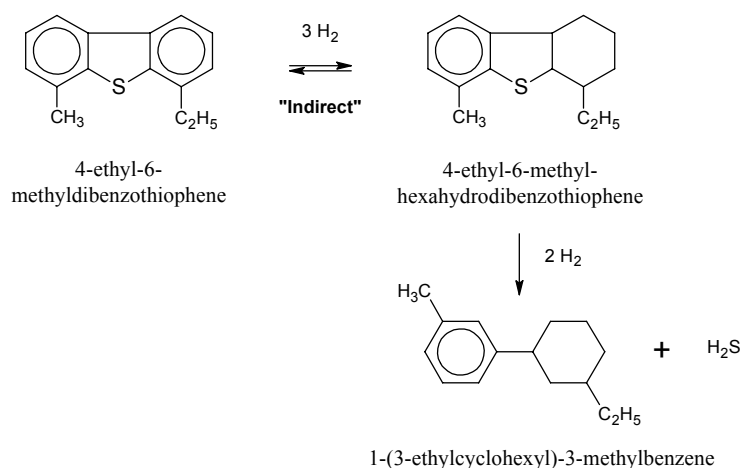


Figure 6. Mechanism for hydrodesulfurization of a hindered dibenzothiophene.

Note that the “direct” removal of a sulfur atom from dibenzothiophene requires 2 molecules of hydrogen, while the “indirect” removal of sulfur from a hindered dibenzothiophene requires 5 molecules of hydrogen per sulfur atom. This is important when estimating hydrogen requirements for deep-

desulfurization. In sterically hindered compounds, such as dibenzothiophenes with alkyl groups in the 4- and/or 6-position, HDS rates are low because the alkyl groups keep the sulfur atom away from the catalyst surface. The benzothiophene core is planar because it is aromatic. But after saturation removes aromaticity from one or both of the 6-carbon rings, the molecule can twist, allowing the sulfur atom to reach the catalyst. *Figure 7* compares HDS rates for hindered and unhindered compounds.⁵


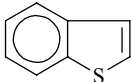
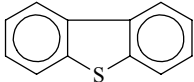
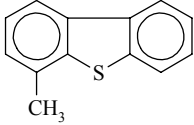
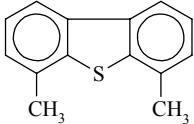
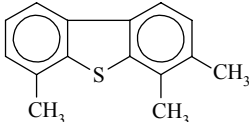
	Compound	Relative Rate
	Thiophene	100
	Benzothiophene	50
	Dibenzothiophene	30
	Methyldibenzothiophene	5
	Dimethyldibenzothiophene	1
	Trimethyldibenzothiophene	1

Figure 7. Relative rates of HDS for hindered and unhindered compounds

3.3 HDN Reactions

Almost all of the nitrogen in petroleum is found in ring compounds. These must be saturated and opened before the nitrogen can be removed. *Figure 8* shows a widely accepted mechanism for the HDN of quinoline.⁶ The fast pathway requires 7 molecules of hydrogen per nitrogen atom. The slow one

uses 4 molecules of hydrogen per nitrogen atom; however, the slow pathway is so slow that, for most practical purposes, it can be neglected.

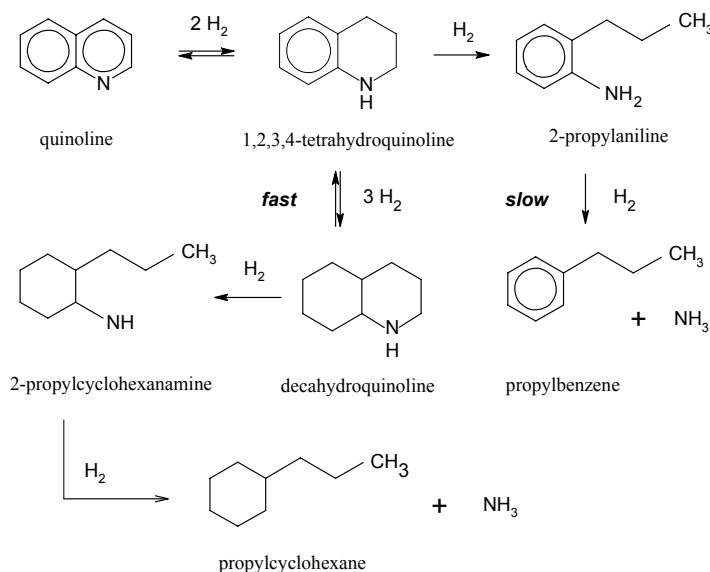


Figure 8. Hydrodenitrogenation (HDN) of quinoline.

3.4 Cracking Reactions

In hydroprocessing units, cracking reactions – those that break carbon-to-carbon bonds – can be grouped into three main categories:

- Paraffin hydrocracking
- Naphthene ring opening
- Dealkylation of aromatic and naphthenic rings

The dual mechanism for paraffin hydrocracking^{7,8} includes the steps shown in *Figure 9*. “Dual” means that catalyst has two kinds of active sites – acid-based and metal-based. Section 3.7 lists the acids and metals that are used to make these catalysts.

Step 1 of the dual mechanism involves adsorption of a paraffin molecule to a metal site, followed by reversible dehydrogenation to form an olefin. In Step 2, the olefin migrates to an acid site, where it reacts with a proton to form a carbenium ion. The carbenium ion can rearrange into a more-stable carbenium ion (Step 3), which explains why products from hydrocrackers are relatively rich in iso-paraffins. In Step 4, β -scission of the carbenium ion produces an olefin and a smaller carbenium ion. The olefin can undergo further cracking on an acid site, or it can react with hydrogen at a metal site

(Step 5) to form a saturated iso-paraffin. The carbenium ion from Step 4 can also convert to a paraffin via deprotonation (Step 6).

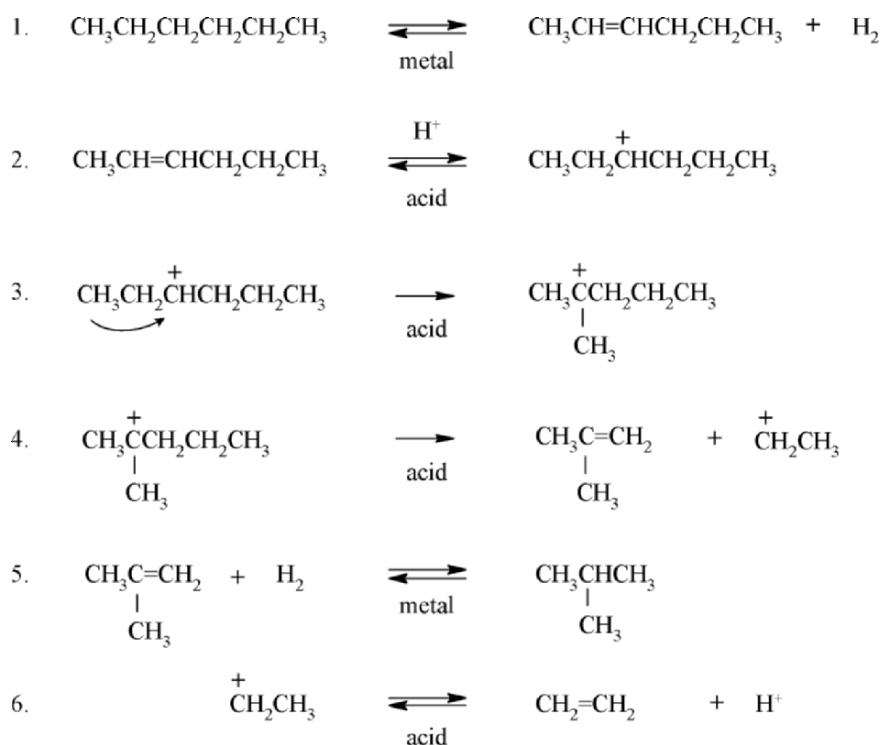


Figure 9. Metal/acid (“dual”) mechanism for paraffin hydrocracking.

Organic nitrogen compounds inhibit hydrocracking by adsorbing strongly to acid sites. Therefore, the organic nitrogen content of a feed must be greatly reduced before it can be hydrocracked. In all but a few commercial units, nitrogen is removed in one or more beds of HDN catalyst. Per Section 3.3, HDN converts organic nitrogen into ammonia, which also adsorbs to acid sites but not nearly so tightly.

Figure 10 shows the opening of a naphthene ring, and Figure 11 shows a ring dealkylation reaction. Note that both reactions leave a methyl group attached to the remaining ring. This is characteristic of β -scission cracking reactions (see Step 4 above).

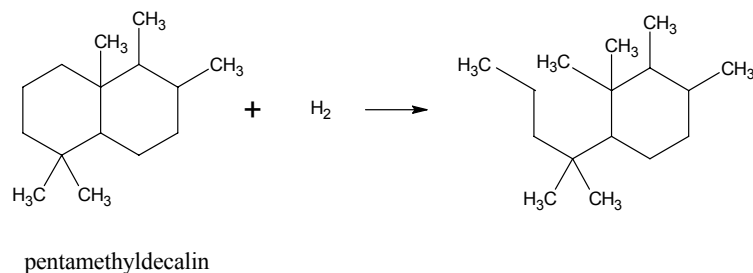


Figure 10. Naphthene ring opening.

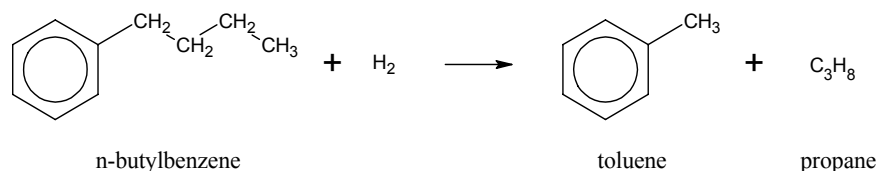


Figure 11. Ring dealkylation.

In vacuum gas oils and other 650°F-plus (343°C-plus) material, more than half of the carbon atoms may be found in ring compounds – polyaromatic hydrocarbons (PAH), partially saturated PAH (naphthene-aromatics) and fully saturated naphthenes. According to Qader and McOmber⁹ and Lapinas, et al.,¹⁰ hydrocracking converts complex ring compounds into light products by the following sequence of reactions:

- Saturation of an aromatic ring
- Opening of the resulting naphthenic ring
- Removal of paraffinic side chains (ring dealkylation)
- Isomerization of paraffins and naphthene-aromatics

Hydrocracking of paraffins, including long alkyl side chains *Figure 12* shows how these reactions might convert 2-butyl-naphthalene into propane, butane and toluene.

3.5 Coke Formation

Due to the presence of a large excess of hydrogen, coke formation in hydroprocessing units is slow – so slow that it can be neglected in material balances for commercial units. However, coke formation is one of four major causes of catalyst deactivation. The other three are poisoning, fouling, and sintering (see Section 4.1).

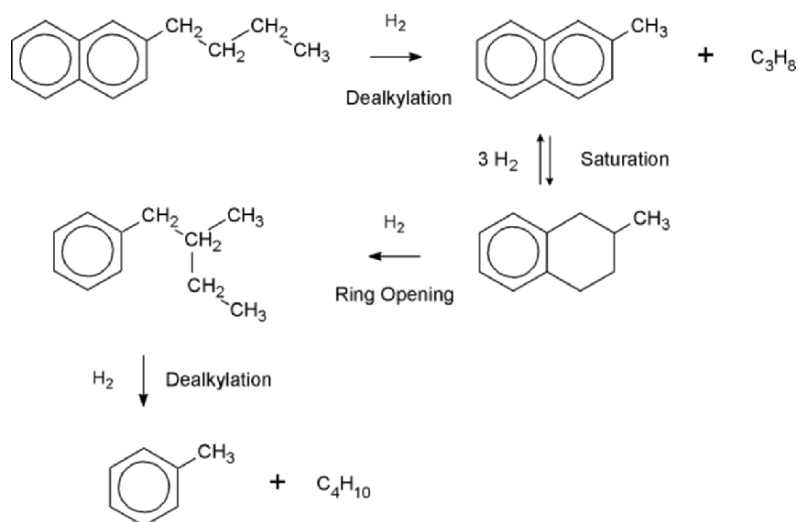


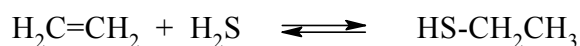
Figure 12. Reaction chain for the hydrocracking of 2-butylnaphthalene.

At the start of a catalyst cycle, a layer of coke quickly forms on the clean catalyst surface. When most of the catalyst is coated with coke, additional formation of coke is comparatively slow. A recent paper by van Speybroeck, et al.,¹¹ refers to widely cited mechanisms for coke growth. Small olefins add rings to coke nuclei with alkylation/cyclization reactions, which involve free-radical intermediates. By the same mechanism, small olefins can add rings to polyaromatic hydrocarbons (PAH). Figure 13 illustrates the addition of a ring to phenanthrene. In hydroprocessing units, coke formation and PAH growth must compete with saturation, ring-opening and hydrocracking.

The inspection of catalyst deactivation data from several commercial hydrocracking units reveals another possibility.¹² Kinetic expressions derived from these data indicate with a mechanism in which two PAH condense to form a large PAH (Figure 14). In the reactants have side chains, condensation may be accompanied by side-chain cracking.

3.6 Mercaptan Formation

In high-conversion hydrocrackers, olefins react with H_2S to form small amounts of mercaptans:



If not removed, mercaptans in hydrocracker naphtha may cause problems for downstream catalytic reforming units. Often, they are removed with a "post-treat" bed – a small layer of hydrotreating catalyst underneath the last

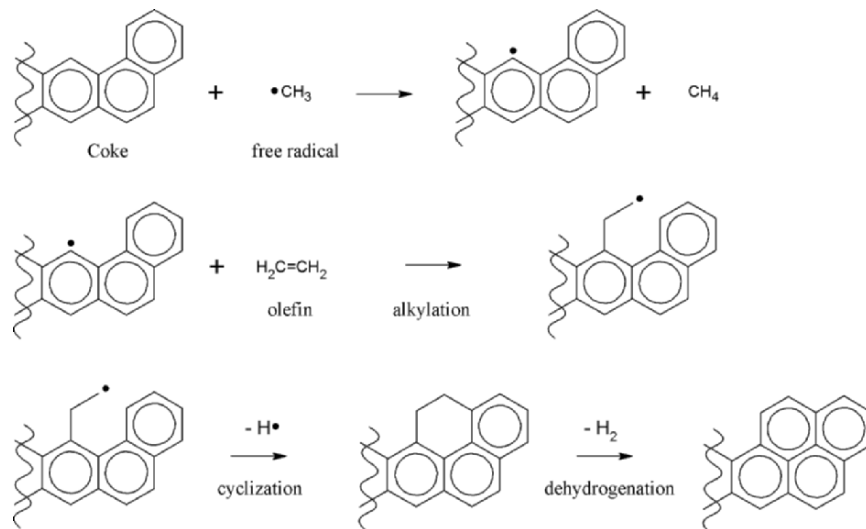


Figure 13. Free-radical mechanism for coke growth in hydroprocessing units.

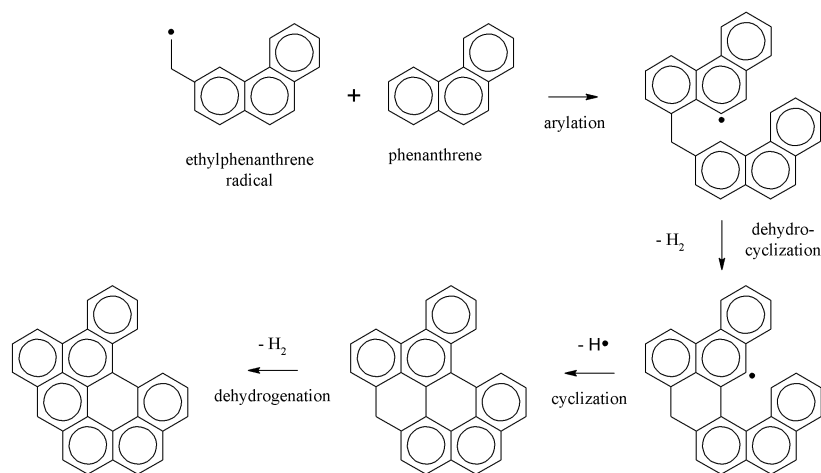


Figure 14. Proposed PAH condensation reaction.

bed of cracking catalyst. Others are removed with a hydrotreater or a guard bed loaded with a sulfur-selective sorbent.

3.7 Reaction Kinetics

Due to the tremendous complexity of heavy petroleum fractions, lumping is used to formulate reaction kinetics for conversion units. The simplest schemes treat the feed as a single entity, assume first-order kinetics and use empirical correlations to adjust for product objectives and feed properties, such as density, distillation, sulfur, nitrogen, olefins, and CCR. These models may seem austere, but they have been used for the design of commercial units since the early 1960s.

Recently, Hu, et al.¹³ used a steady-state hydrotreater model (HTR-SIM) in combination with typical single-lump kinetics to monitor the performance of a commercial HDS unit in Japan. The equations used to model the conversion of feed sulfur into product sulfur are:

1. $k_{\text{HDS}} = (\text{LHSV}) \ln (S_{\text{F}}/S_{\text{P}})$
2. $k_{\text{HDS}} = [(\text{LHSV})/(n-1)](S_{\text{P}}^{(1-n)} - S_{\text{F}}^{(1-n)})$
3. $k_{\text{T}} = (k_0) \exp[-E_a/RT]$

where k_{HDS} , K_{T} , and K_0 are rate constants, LHSV is the liquid hourly space velocity, n is the reaction order, S_{P} is the product sulfur concentration, S_{F} is the feed sulfur concentration, E_a is the activation energy, R is the gas-law constant, and T is temperature. Equation 1 is used for any 1st order process in which one material is transformed into another. Equation 2 applies to any n^{th} order process in which $n \neq 1$. Equation 3 is the well-known Arrhenius expression for calculating the effect of temperature on reaction rate. For single-lump HDS kinetics, E_a ranges between 100 and 140 kJ/mol. E_a varies with feed composition, catalyst type, and reaction conditions.

Sue and Sugiyama,¹⁴ Steinberg et al.,¹⁵ and Mohanty et al.¹⁶ have written reviews of kinetic studies on hydrocracking reactions. In most of the cited literature, pure compounds or simple mixtures were processed in small isothermal reactors. For example, a publication by Rappaport¹⁷ reported that the rate of hydrocracking for pure normal paraffins increases as shown in Table 5.

Table 5. Relative Rates of Hydrocracking for Pure n-Paraffins

Carbon Number	Relative Rate
C ₅	1
C ₁₀	32
C ₁₅	72
C ₂₀	120

Figure 15 and Table 6 show data from an especially informative study by Filimonov, et al.,¹⁸ which determined relative reaction rates for different

classes of compounds at temperatures between 716°F and 482°F (380°C and 450°C). In the table, negative relative rates indicate that a reverse reaction is faster than its corresponding forward reaction. In agreement with Section 3.1, the rates of aromatics saturation reactions decrease at higher temperature.

Table 6. Relative Rates for Groups of Hydrocracking Reactions (as Shown in Figure 15)

Rxn No.	Reactants / Products	Reaction Type	Relative Reaction Rate at:			
			380°C	400°C	425°C	450°C
1	Pyrenes, chrysenes / Polybenzonaphthenes	Saturation	–	–	–	–
2	Phenanthrenes / Dinaphthenobenzenes, acenaphthenes, fluorenes	Saturation	–	–	–	–
3	Naphthalenes / Indanes	Saturation	0.6	0.5	0.5	0.5
4	Polybenzonaphthenes / Dinaphthenobenzenes, acenaphthenes, fluorenes	Saturation	–	–	–	–
5	Benzonaphthenes / Dinaphthenobenzenes, acenaphthenes, fluorenes	Saturation	3.7	3.0	2.6	2.4
6	Indanes / Alkylbenzenes	Ring opening	4.2	3.5	3.4	3.2
7	Alkylbenzenes / Single-ring naphthenes	Saturation	4.5	2.4	0.3	-0.8
8	Polycyclic naphthenes / Three-ring naphthenes	Ring opening	1.0	1.0	1.0	1.0
9	Three-ring naphthenes / Two-ring naphthenes	Ring opening	1.1	1.6	1.9	2.1
10	Two-ring naphthenes / Single-ring naphthenes	Ring opening	1.3	1.7	2.7	3.1
11	Single-ring naphthenes / Paraffins	Ring opening	0.9	-1.8	-2.8	-3.2
12	Long paraffins / Short paraffins	Cracking	0.3	2.1	3.3	3.8
13	Alkylbenzenes / Methyl benzenes, paraffins	Cracking	2.2	2.9	3.4	4.1

In 1974, Stangeland¹⁹ developed a pseudo-component approach to the modelling of conversion kinetics in hydrocrackers. Conceptually, he divided the feed and products into a set of 50°F-wide slices – 100°F to 150°F, 150°F to 200°F, etc. He then built a set of rate expressions for converting higher-boiling slices into lower-boiling slices and linked them with an expression that reflects the fact that heavy hydrocarbons react faster than light ones:

$$k_{(T)} = k_0[T + A(T^3 - T)]$$

In this equation, $T = \text{TBP}/1000$ (TBP = true boiling point) and A is a tuning parameter that usually falls between 0 and 1.

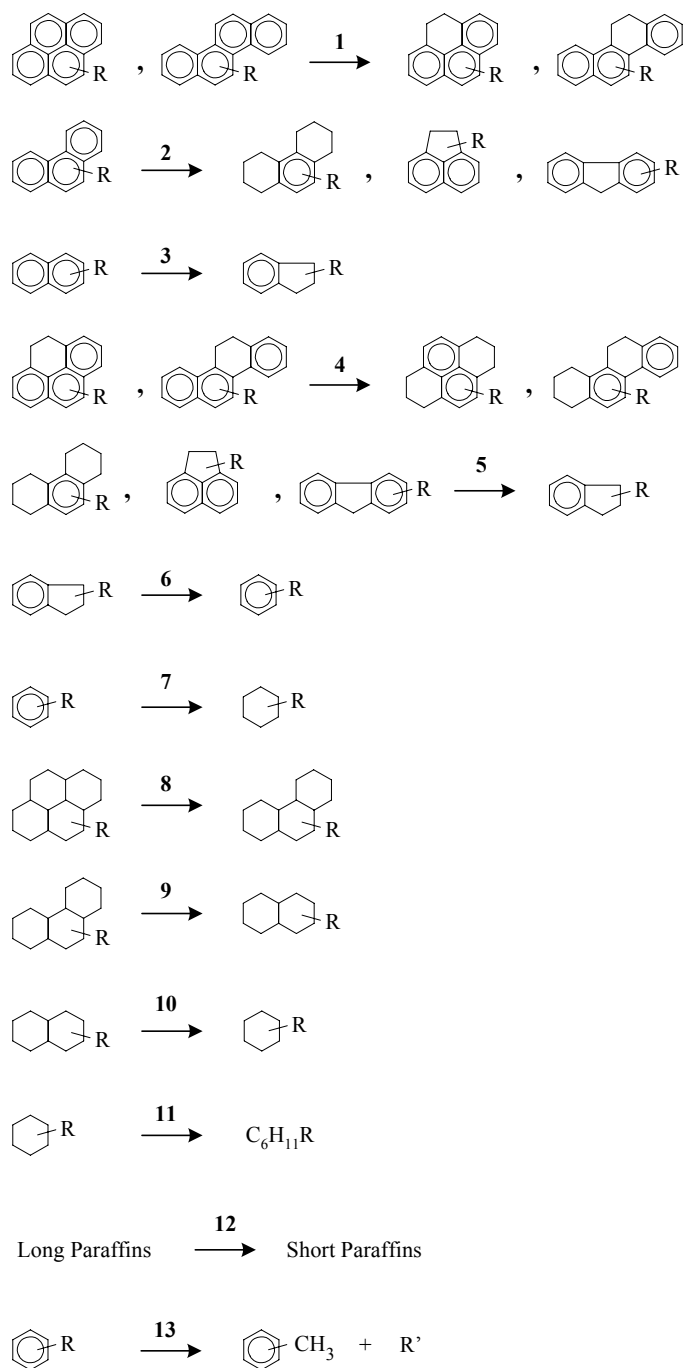


Figure 15. Hydrocracking reaction chain for polyaromatic and naphtheno-aromatic compounds, per Filimonov, et al.¹⁸ The relative rates of Reactions 1 to 12 are shown in Table 6.

During the past 20 years, academic and industrial researchers developed composition-based kinetic models with hundreds or even thousands of lumps and pure compounds. The QSRC (quantitative structure-reactivity correlation) and LFER (linear free energy relationship) lumping techniques are discussed in Chapter 20 by Professor Klein and Chapter 9 by Professor Mochida. The structure-oriented lumping (SOL) approach of Quann and Jaffe^{20,21} yields models rigorous enough for use in closed-loop real-time optimizers (CLRTO), which automatically adjust setpoints for commercial process units several times each day.²²

In the composition-based model developed by Lapinas, et al.,¹⁰ and applied to a commercial hydrocracker by Pedersen, et al.,²² rate equations are based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism for heterogeneous reactions. In brief, the LHHW mechanism describes (a) the adsorption of reactants to acid and metal sites on a catalyst surface, (b) reactions between the reactants, including saturation, cracking, ring opening, dealkylation, HDS, HDN, etc., and (c) desorption of products. Inhibition effects are modelled, too. These include the adsorption of organic nitrogen to acid sites and the inhibition of HDS reactions by H₂S.

Rigorous, flow-sheet-based models for hydrocrackers include sub-models for furnaces, pumps, compressors, reactors, quench zones, flash drums, recycle gas scrubbers, fractionation towers, and – importantly – economic data. As discussed in Chapter 23 by Mudt, et al., such models can comprise hundreds of reactions and hundreds of thousands of equations. The model grows when inequalities are included to ensure a feasible solution that honors process constraints. To solve such models in real time (i.e., in less than an hour), open-equation mathematics and high-powered solvers are used.

4. HYDROPROCESSING CATALYSTS

Recent books by Magee and Dolbear²³ and by Scherzer and Gruia² are superb sources of technical information on hydroprocessing catalysts, which are also discussed in Chapters 9-12. The hydroprocessing catalyst business is big, with annual sales approaching US\$800 million per year. The materials most commonly used to make these catalysts are shown in *Table 7* and *Table 8*.

Table 7. Supports Used in Hydroprocessing Catalysts

Support	Major Use	Acidity
γ -Alumina	Hydrotreating catalysts	Low
Amorphous aluminosilicates	Distillate-selective hydrocracking catalysts	High
Zeolites (X, Y or mordenite)	High-stability hydrocracking catalysts	Very high

Table 8. Active Metals Used in Hydroprocessing Catalysts

Metals	Major Use	Activation Method	Hydrogenation Acitivity
CoMo	HDS	Sulfiding	Moderate
NiMo	HDN, hydrocracking	Sulfiding	High
NiW	HDN, hydrocracking	Sulfiding	Very high
Pd, Pt*	Hydrocracking	Reduction by H ₂	Highest

*Pd and Pt are poisoned by sulfur and can only be used in low-H₂S environments

In fixed-bed hydroprocessing units, the catalysts must be able to drive the desired reactions, but they also must possess a high surface area and great physical strength, enough to resist crushing under the forces imposed by rapidly flowing high-pressure fluids and the weight of the catalyst itself. A single bed can contain several hundred of tons of catalyst.

Chemical reactions take place inside small pores, which account for most of the catalyst surface area. The diameters of these pores range from 75Å to 85Å for catalysts that process light and heavy gas oils. For catalysts that process residue, the average pore size ranges from 150Å to 250Å.

4.1 Catalyst Preparation

The following steps may be used to prepare the supported metal catalysts used in hydrotreaters and hydrocrackers.^{2,23}

- Precipitation
- Filtration (or centrifugation), washing and drying
- Forming
- Calcining
- Impregnation
- Activation

Other steps, such as kneading, mulling, grinding, and/or sieving also may be used. For some catalysts, some of the above-listed steps are eliminated or additional steps are added. For example, if mulling is used to mix active metals with a support, precipitation and impregnation may not be needed.

4.1.1 Precipitation

In the catalyst world, precipitation involves combining two solutions to form a desired solid. For example, mixing an aqueous solution of aluminum nitrate [Al(NO₃)₃] with sodium aluminate [Na₂Al₂O₄] yields aluminum hydroxide [Al(OH)₃], which forms a gelatinous solid. As the gel ages, tiny crystals grow larger and a pore structure starts to develop.

The zeolites used in hydrocracking catalysts also are prepared by precipitation. Zeolites occur naturally, but the ones used for catalysis are synthetic. *Figure 16* outlines a common procedure for synthesizing Na-Y and H-Y zeolites.

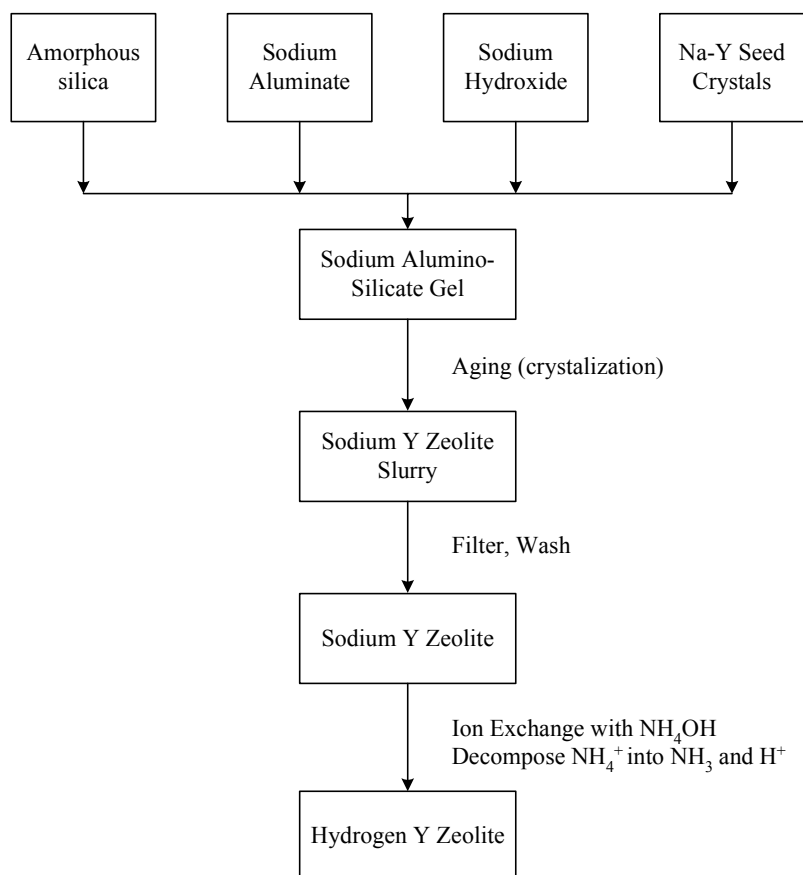


Figure 16. Synthesis procedure for H-Y zeolite.

These remarkable aluminosilicates can be used as drying agents, ion-exchangers, and molecular sieves for gas separation. Their microporosity provides them with high surface area, and they can be converted into solid acids with superb catalytic activity.

The Al(III) atoms in zeolites replace Si(IV) atoms in a SiO_2 superstructure. To maintain a neutral charge, every aluminum atom must be accompanied by a counter-ion such as Na^+ , K^+ , H^+ , NH_4^+ , etc. Counter ions can be swapped via ion exchange. When Na-Y zeolite is exchanged with an ammonium salt, the Na^+ ion is replaced by NH_4^+ . When $\text{NH}_4\text{-Y}$ is heated to the right temperature, the ammonium ion decomposes, releasing NH_3 (gas) and leaving behind highly acidic H-Y zeolite.

The synthetic zeolites used in catalysts for hydrocracking include X, Y, mordenite and ZSM-5. The latter is made by including a soluble organic

template, such as a quarternary ammonium salt, in the mix of raw materials. ZSM-5 is used for catalytic dewaxing. Due to its unique pore structure, it selectively cracks waxy n-paraffins into lighter molecules. It is also used in FCC catalysts to increase propylene yields.

4.1.2 Filtration, Washing and Drying

Filtration, washing and drying remove undesired impurities. In our $\text{Al}(\text{OH})_3$ example, sodium nitrate is washed away with water. Sometimes, ammonium hydroxide is added to expedite sodium removal. Subsequent air- and oven-drying removes most of the excess water and initiates the transformation of $\text{Al}(\text{OH})_3$ into alumina [Al_2O_3].

4.1.3 Forming

Catalyst and support precursors can be formed into extrudates, spheres or pellets. Extrudates are generated by forcing a paste (e.g., a mixture of powdered γ -alumina with water) through a die. Adding peptizing agents such as nitric acid increases the average pore size of the product. Raising the extrusion pressure tends to decrease the average pore size.

The resulting spaghetti-like strands are dried and broken into short pieces with a length/diameter ratio of 3 to 4. The particles are dried then calcined. In our alumina example, calcination decomposes residual ammonium nitrate. It also hardens the particles and completes the conversion of $\text{Al}(\text{OH})_3$ into Al_2O_3 . The preferred alumina for catalyst supports is γ -alumina, also known as bohemite. This material has a high surface area, great physical strength, and a well-defined network of pores. If the calcination temperature gets too high, γ -alumina transforms into α -alumina or β -alumina, whose physical properties are far less desirable.

An extrudate cross-section can be circular or shaped like 3-leaf or 4-leaf clover without the stem (see Chapter 8 by Adrian Gruia). Compared to cylindrical extrudates, clover-leaf (“multi-lobe”) catalysts have a higher surface-to-volume ratio. In trickle-bed hydroprocessing reactors, they have less resistance to diffusion and lower pressure drop. Spherical catalysts are made (a) by spray-drying slurries of catalyst precursors, (b) by spraying liquid onto powders in a tilted rotating pan, or (c) by dripping a silica-alumina slurry into hot oil.² Pellets are made by compressing powders in a die.

4.1.4 Impregnation

Impregnation is a common technique for distributing active metals within the pores of a catalyst support. Calcined supports are especially porous. Like sponges, they use capillary action to suck up aqueous solutions containing

active metals. For some catalysts, the support is soaked in excess metal-containing solution, which saturates the pores fully.

In the “incipient wetness” method, precise amounts of solution are added – just enough to leave the support dry to the touch. After a drying step, addition solution may be added to increase loading of the same or different active metal.

4.1.5 Activation

Prior to use, most non-noble-metal catalysts are activated (“sulfided”) by circulating hydrogen and a light, sulfur-containing start-up oil through the catalyst. Often, the start-up oil is spiked with dimethyl sulfide ($\text{CH}_3\text{-S-CH}_3$) or dimethyl disulfide ($\text{CH}_3\text{-S-S-CH}_3$). The temperature is raised slowly to the decomposition temperature of the sulfiding agent. The process continues until breakthrough, i.e., the point at which significant amounts of H_2S appear in the recycle gas. After breakthrough, sulfiding continues until the catalyst is completely saturated with sulfur.

During “dry sulfiding,” a mixture containing 2 to 5 vol% H_2S in hydrogen is circulated through the catalyst. The temperature is increased slowly to the temperature at which the unit is expected to operate. The process continues until the exit gas contains the same amount of H_2S as the inlet gas.

Most manufacturers offer pre-sulfided catalysts, which allow a refiner to shorten the start-up of a unit by two or three days. That may not seem like much, but for a 40,000 barrel/day FCC feed pretreater, it can generate up to US\$500,000 in extra income.

4.1.6 Noble-Metal Catalysts

Some hydrocracking catalysts contain highly dispersed platinum or palladium. These noble metals are expensive, but their loading is low – 0.6 to 1.0 wt% – and their high activity justifies the cost. They are added by impregnation with tetraamine complexes – $\text{Pt}(\text{NH}_3)_4^{2+}$ or $\text{Pd}(\text{NH}_3)_4^{2+}$. When the catalysts are heated in air to about 840°F (450°C), the complexes decompose, giving off ammonia and leaving behind divalent metal oxides. In commercial hydrocrackers, catalysts containing noble-metal oxides are activated by direct reduction with high-pressure hydrogen at 700°F (350°C).

4.2 Hydrotreating Catalysts

Hydrotreating catalysts comprise oxides of either Mo or W and either Co or Ni on a support comprised of γ -alumina. Usually, CoMo catalysts are used for HDS. NiMo catalysts are used for HDS and HDN. NiW catalysts are especially active for the saturation of aromatics. Typical physical properties are shown in Table 9.

Hydrotreating catalyst particles are surprisingly small, with diameters of 1.5 to 3.0 mm and length/diameter ratios of 3 to 4. In many units, ceramic balls and/or successively larger catalyst particles are loaded on top of the first catalyst bed. This “graded bed” protects the bulk of the catalyst by filtering particulate matter out of the feed.

Table 9. Physical Properties for Hydrotreating Catalysts

Property	Low	High
Surface area, m ² /gram	150	250
Pore volume, ml/gram	0.5	1.0
Pore diameter (average), Ångströms	75	250
Bulk density, lbs/ft ³	30	60
Bulk density, kg/m ³	490	980
Co or Ni (as CoO or NiO), wt%	3	8
Mo or W (as MoO ₃ or WO ₃), wt%	10	30

4.3 Hydrocracking Catalysts

Commercial hydrocracking catalysts comprise active metals on solid, highly acidic supports. The active metals are Pd, NiMo or NiW, all of which catalyze both hydrogenation and dehydrogenation reactions. The most common supports are synthetic crystalline zeolites and amorphous silica-aluminas.

Hydrocracking catalyst shapes can be spherical or cylindrical, with gross dimensions similar to those for hydrotreating catalysts.

As already mentioned, in most hydrocrackers, the first few catalyst beds contain a high-activity HDN catalyst, which also is active for HDS, saturation of olefins, and saturation of aromatics. Other hydrocrackers use a bifunction catalyst – one that is active for both hydrotreating and hydrocracking – in all catalyst beds.

4.4 Catalyst Cycle Life

Catalyst cycle life has a major impact on the economics of fixed-bed refinery units, including hydrotreaters and hydrocrackers. Cycles can be as short as 12 months and as long as 60 months. Two-year cycles are typical. At the start of a cycle, average reactor temperatures are low – 580°F to 660°F (304°C to 349°C). As the cycle proceeds, the catalyst deactivates and refiners must raise temperatures to maintain conversion. A catalyst cycle is terminated for one of the following reasons, whichever occurs first. Note that only one of the listed events relates directly to catalyst activity.

1. **The temperature required to achieve the unit’s main process objective hits a metallurgical limit.** Or alternatively, the main process objective can be met only at reduced feed rate. To ensure safe operation, the maximum

average reactor temperature is about 760°F (404°C) and the maximum peak temperature is about 800°F (427°C).

2. **Side reactions are starting to cause process or economic problems.** If the production of light gases exceeds the capacity of one or more towers in the downstream gas plant, operators must decrease feed rate or reduce conversion. Both options are expensive. Excess gas production consumes expensive hydrogen and converts it into low-value LPG. This also is expensive. Running at high temperature decreases selectivity to middle distillates and increases aromatics in middle distillates. At some point, due to one or more of these factors, refinery-wide economics show that it's better to shut down for a catalyst change versus trying to keep limping along – even though metallurgical limits have not yet been reached.
3. **The recycle compressor cannot overcome pressure drop across the unit.** The overall pressure drop is the difference in pressure between the recycle compressor suction and the recycle compressor discharge. At start-of-run, the pressure drop across the catalyst is low – 3 to 10 psi (0.2 to 0.7 bar) for each bed – but it increases as the run proceeds. Usually, the increase is largest in the first catalyst bed, which is most susceptible to fouling. Attempts to continue running a unit despite very high pressure drop can deform the quench-deck support beams inside a reactor.
4. **A related unit has to shut down for more than a few weeks.** Related units might include an upstream vacuum distillation unit, an upstream hydrogen source, or a downstream FCC unit. In refineries with enough intermediate tankage, hydroprocessing units can continue to run for a few days despite an interruption in the supply of liquid feed, but a loss of hydrogen supply can cause an immediate shut-down. At best, if the unit gets hydrogen from multiple sources, the feed rate must be reduced.
5. **Major process upsets.** Most process upsets are caused by sudden changes in feed quality. For a fixed-bed VGO hydrotreater, a slug of residue can poison part of the catalyst with trace metals such as Fe, Ni, V, and/or Si; or foul it with particulates, asphaltenes and/or refractory carbon. In fixed-bed units, poisoning and fouling usually are confined to the top few feet of the first catalyst bed. If so, the ruined catalyst can be skimmed off the top and replaced during a brief, scheduled shutdown. A brief, scheduled shut-down does not require a cycle-ending catalyst change-out.
6. **Equipment failure.** Hardware problems occur most frequently in rotating equipment – pumps and compressors. Fortunately, many problems can be detected in advance, allowing operators to schedule a brief shut-down for preventive maintenance.

Process variables that increase or decrease the rate of catalyst deactivation are shown in Table 10.

Table 10. Factors Affecting Catalyst Cycle Life

	Effect on Cycle Life	Comment
Higher H ₂ partial pressure	+	
Higher recycle gas rate	+	Increases H ₂ partial pressure
Higher makeup gas purity	+	Increases H ₂ partial pressure
Increased purge of recycle gas	+	Increases H ₂ partial pressure
Higher fresh feed rate	-	
Higher conversion	-	
Higher fresh feed endpoint	-	Increases rate of catalyst coking. Also can increase pressure-drop buildup rate.
Higher fresh feed impurities ¹	-	Related to feed type and feed endpoint
Process upsets ²	-	

1. Deleterious feed impurities include sulfur, nitrogen, refractory carbon, asphaltenes, metals (nickel, vanadium, iron, silicon) and particulate matter (coke fines, FCC catalyst fines).
2. Process upsets include "burps" in upstream units that feed the hydrocracker, equipment failures (typically, loss of a feed pump or compressor) or temperature excursions requiring de-pressuring.

Hydrogen keeps the catalyst clean by inhibiting coke formation. This explains why increasing the hydrogen partial pressure decreases the rate of catalyst deactivation.

Raising the temperature increases the rates of most hydrocracking reactions, including coke formation. Raising the hydrogen/oil ratio increases heat removal, which limits temperature rise.

If the feed rate goes up and targets for HDS, HDN or conversion remain the same, the temperature must go up. If the feed rate goes up and the temperature does not, then HDS, HDN or conversion will decrease.

Increasing the feed endpoint and/or density tends to increase the amount of coke precursors in the feed. The precursors include asphaltenes, refractory carbon, and PAH.

4.4.1 Catalyst Regeneration and Rejuvenation

After working 24/7 for a year or two (or in some cases five) in a fixed-bed hydroprocessing unit, the catalyst is spent. The entire unit is shut down and catalyst is removed. During the shut-down, which typically lasts 3 to 4 weeks, refiners inspect and repair equipment. Meanwhile, the catalyst is shipped to an off-site facility, where it is regenerated by controlled combustion in air, air plus oxygen, or air plus steam. During combustion, accumulated coke is converted to CO₂ and CO plus small amounts of SO₂ and NO_x, which are formed from the sulfur and nitrogen in the coke. Typically, the temperature used for regeneration in air is (750°F to 930°F) 400°C to 500°C.

The regenerated catalyst may also undergo rejuvenation, a wet process in which the active metals are chemically re-dispersed. A combination of regeneration and rejuvenation can restore a catalyst to more than 95% of its original activity.

Inevitably, some particles break apart during the unloading, transportation, regeneration, and rejuvenation of spent catalysts. If part of the catalyst is

contaminated with excessive amounts of Fe, Ni, V, or Si, that part cannot be regenerated. Typically, losses due to fragmentation and fouling amount to 10 to 15%.

In the bad old days, regeneration meant burning coke off the catalyst while it was still inside the reactor. Today, “in situ” regeneration is rare because it is hard to control and often gives poor results. A poor regeneration is costly, because afterwards the unit’s performance will be poor. With a crippled catalyst, the unit may have to limp along for several months at lower feed rates and/or lower severity. Worst of all, the catalyst won’t last long, which means that it will have to be regenerated or replaced sooner rather than later.

4.4.2 Catalyst Reclamation

Even though noble-metal hydrocracking catalysts contain only small amounts of Pd or Pt, these metals are so expensive that recovering the metals is more cost-effective than throwing them away. Other hydroprocessing catalysts contain Mo or W, Ni, and/or Co. Spent hydrotreating catalysts – especially those used to hydrotreat residue – can be very rich in vanadium, richer than many ores.

Reclamation companies convert these materials into salable products using different combinations of oxidation, pyrolysis, dissolution in acid or alkali, precipitation, extraction or ion exchange. Depending on the process used, the salable products may include several of the materials shown in Table 11.

The book by Scherzer and Gruia² provides a well-written description of catalyst reclamation processes used by four major companies – CRI-MET, Eurecat, Gulf Chemical, and TNO/Metrex.

Table 11. Some of the Materials Sold by Catalyst Reclamation Companies

Material	Formula
Palladium metal or chloride salt	Pd or Na ₂ PdCl ₄
Platinum metal or chloride salt	Pt or Na ₂ PtCl ₄
Molybdenum trisulfide	MoS ₃
Molybdenum oxide	MoO ₃
Ammonium molybdate	(NH ₄) ₂ Mo ₄ O ₁₃ •2H ₂ O
Sodium molybdate	Na ₂ MoO ₄ •2H ₂ O
Tungsten trioxide	WO ₃
Ammonium para-tungstate	(NH ₄) ₁₀ W ₁₂ O ₄₁ •5 H ₂ O
Sodium tungstate	Na ₂ WO ₄ •2H ₂ O
Vanadium pentoxide	V ₂ O ₅
Sodium (meta) vanadate	NaVO ₃
Nickel metal or chloride	Ni or NiCl ₂
Cobalt metal or chloride	Co or CoCl ₂
Nickel-cobalt concentrate	Ni _x Co _y
Iron-molybdenum concentrate	Fe _x Mo _y
Alumina hydrate	Al ₂ O ₃ •3H ₂ O

5. PROCESS FLOW

5.1 Trickle-Bed Units

Most hydrotreaters and hydrocrackers are trickle-bed units. A classic article by Satterfield²⁴ describes the fundamental behaviour of such units, in which mixtures of liquid and gaseous reactants pass down over fixed beds of catalyst. In hydroprocessing units, the liquid reactants are petroleum fractions, and the gaseous reactant is hydrogen.

Figure 17 shows a flow scheme for a once-through unit designed to process heavy gas oil feeds. Designs offered by major process licensors can differ in several areas.

(1) **Heaters.** Units with gas-only heaters mix hot gas with pre-heated liquid feed just before the reactants enter the first reactor. Other designs use a gas-plus-oil heater to bring the mixed fluids up to reaction temperature.

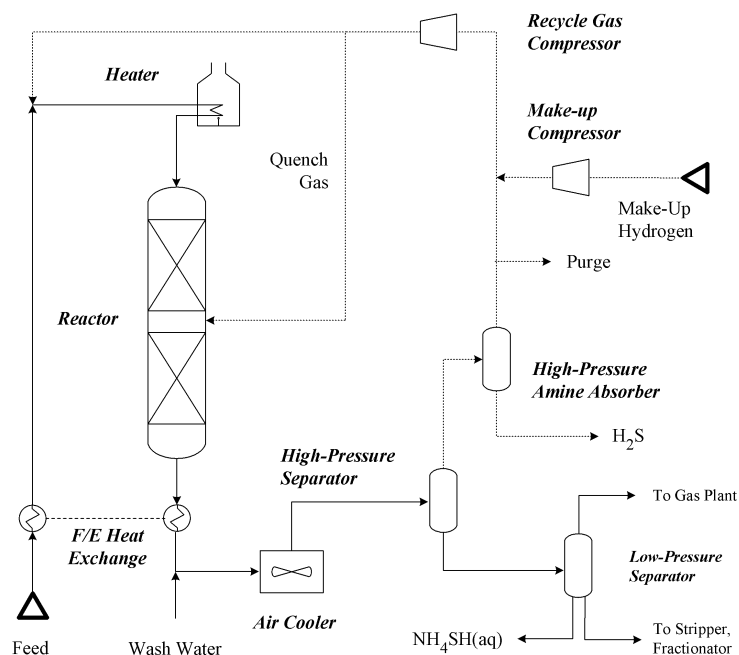


Figure 17. Once-through hydroprocessing unit: two separators, recycle gas scrubber.

(2) **Reactors, Catalyst Beds and Quench Zones.** As shown in Table 4, most hydroprocessing reactions are exothermic. The heat released in naphtha and kerosene hydrotreaters is relatively low, so units designed for these feeds may use just one reactor that contains a single catalyst bed. However, for heavier feeds and/or feeds that contain large amounts of sulfur, aromatics or

olefins, the total increase in temperature can exceed 180°F (100°C). It is unsafe to allow that much temperature rise in a single bed of catalyst. To divide the heat release into smaller, safer portions, commercial units use multiple catalyst beds with cooling in between. A unit can have one bed per reactor, or multiple beds in each reactor with quench zones in between. For simplicity, Figure 18 shows only 2 catalyst beds, but most hydrocrackers have more; some have as many as 30!

In a quench section (*Figure 18*), hot process fluids from the preceding bed are combined with relatively cold hydrogen-rich quench gas before the mixture passes into the next bed. We can think of a catalyst bed as a stack of thin, horizontal discs. Ideally, the top disc is the coolest, the bottom disc is the hottest, and at every point in each given disc, temperatures are identical. But in real units, the downward flow of reactants is never perfectly uniform, so the temperatures within the discs are different, especially near the bottom.

The difference between the highest and lowest temperature at the bottom of a catalyst bed is called the “radial temperature difference” (RTD). The truth is, we never know the actual highest and lowest temperature, because we can’t place thermocouples everywhere. But if the measured RTD is small – less than 5°F (3°C) – we can assume that the actual RTD also is small, and that flow through the bed is nearly uniform. If the measured RTD is large, the actual RTD is almost certainly larger, and we have to be concerned about hot spots, flow blockages, and other potentially dangerous symptoms of mal-distribution.

Modern quench sections are designed to do three things: (a) to lower the overall temperature of the reacting fluids, (b) to reduce radial mal-distribution with radial mixing, and (c) to redistribute the reactants and deliver them to the next bed. The major parts of a quench deck are the quench tube, the liquid collector and re-distributor, the gas/liquid mixing zone, and the final distributor.

Quench tubes bring quench gas into the reactor. Some are very simple – just a tube with a series of holes in it. Others, such as the ExxonMobil “spider vortex” design, are more complex, distributing gas horizontally through several “spokes” to different parts of the quench deck.

In the liquid collector and re-distributor, liquids are forced to flow down two angled slides into a raceway. The slides give the liquids some angular momentum, and the raceway gives them time to mix. More than anything else, this part of the quench deck reduces RTD.

In the gas/liquid mixing zone, a bubble-cap tray or similar device provides intimate contact between gases and liquids from the redistribution zone. The final distributor sends a fine spray of fluids down to the catalyst bed below.

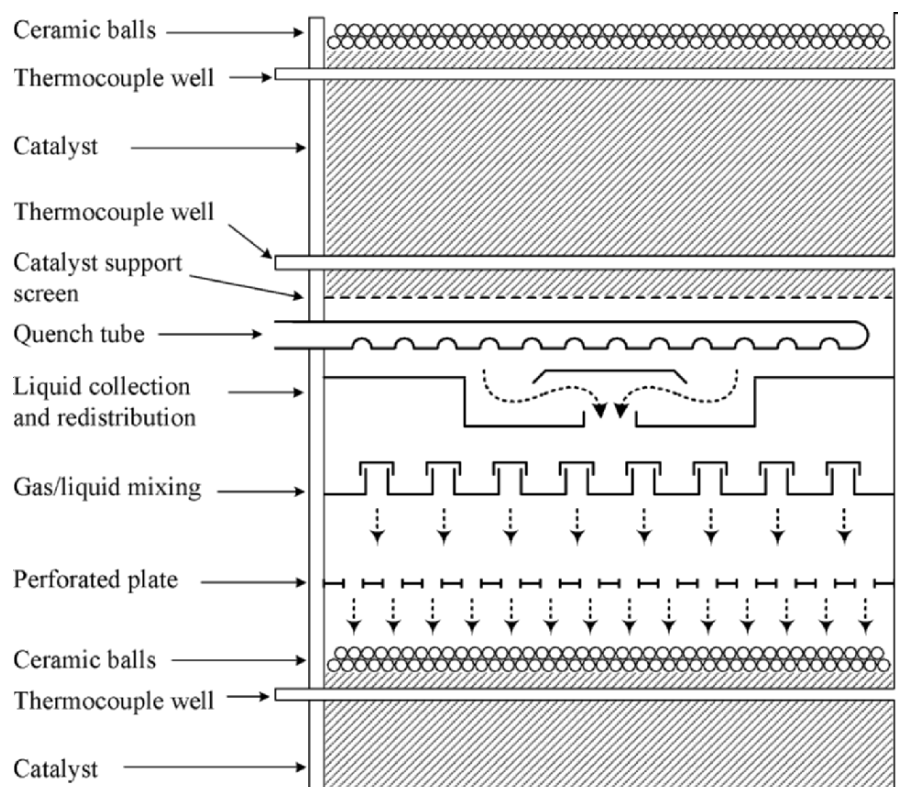


Figure 18. Hydroprocessing reactor: quench zone

In residue hydroprocessing units, heat release is high, but some licensors avoid using intra-reactor quench because residue feeds often form lumps of coked-bonded catalyst in fixed-bed units. In reactors with complex internals, such lumps are very hard to remove during a catalyst change-out. Therefore, fixed-bed residue units often comprise three or more 1-bed reactors in series with quench in between. In many cases, the first reactor is “guard bed” filled with one or catalysts designed to remove metals.

(3) Catalysts. Hydrotreaters are loaded either with a CoMo HDS catalyst, a NiMo HDN catalyst, or both. NiMo catalysts are better for the saturation of aromatics, which is required for the removal of hindered sulfur compounds during deep desulfurization. Therefore, some refiners load a layer of NiMo catalyst on top of a CoMo catalysts in diesel desulfurization units. Recently, catalyst manufacturers have been offering trimetallic (CoNiMo) hydrotreating catalysts.

Most of the cracking in hydrocracking units is driven by catalysts with high acidity. The acidic sites are inhibited by organic nitrogen, so the first several catalyst beds in a hydrocracking unit typically contain a high activity HDN catalyst. In a few units, all beds in a hydrocracker are filled with an

amorphous “dual function” catalyst, which catalyzes both HDN and cracking. This type of catalyst has a high selectivity for producing middle distillates from VGO.

As mentioned in Section 3.6, the last bed in a hydrocracker often contains a final layer of “post-treat” catalyst to remove mercaptans.

(4) Makeup and Recycle Hydrogen. Compressors for makeup hydrogen are reciprocating machines, most of which are driven by electric motors. Recycle gas compressors can be reciprocating or centrifugal; the latter are often driven by steam. In naphtha hydrotreaters, the high-pressure off-gas can be purer than the makeup gas, because (a) conversion is nil, and (b) liquids in the makeup gas are absorbed by the naphtha. In most other units, the makeup gas is purer than the recycle gas.

Makeup hydrogen can enter the unit at the cold high-pressure separator (CHPS), at the suction of the recycle gas compressor, or at the discharge of the recycle gas compressor. If the makeup comes in at the CHPS, the makeup compressor discharge pressure is lower, which can reduce electricity costs. However, if part of the recycle gas is purged after leaving the CHPS, part of the incoming makeup gas goes right back out again. If the makeup comes in at the discharge of the recycle gas compressor, the discharge pressure of the makeup compressor is higher, but none of the high-purity makeup is lost with purge gas.

(5) High-Pressure Amine Absorption. Prior to the advent of ultra-low-sulfur fuels, it was rare to find hydroprocessing units with a high-pressure amine absorber to remove H_2S from the recycle gas. H_2S inhibits HDS reactions and lowers the purity of the recycle gas. For both of these reasons, high-pressure amine absorbers are now included in most new and revamped diesel hydrotreaters and mild hydrocrackers.

(6) Product Cooling and Separation. Commercial units comprise a number of different product cooling and flash drum configurations. The simplest comprises a feed/effluent heat exchanger train, a large air- or water-cooled heat exchanger, and one or two flash drums.

Heavy-feed units have at least a cold high-pressure separator (CHPS) and a low-pressure separator (LPS). The CHPS overhead stream can go directly to the recycle gas system or through a high-pressure amine absorber for removal of H_2S . The CHPS bottoms go to the CLPS. Sometimes the pressure differential between the CHPS and the CLPS is used to drive a power recovery turbine. As shown in *Figure 19*, some units include a hot high-pressure separator (HHPS) upstream from the CHPS. The HHPS overhead goes through a cooler to the CHPS, and HHPS bottoms go through a cooler to the LPS. This arrangement provides better heat recovery. In single-stage hydrocrackers with recycle of unconverted oil, hot separation minimizes fouling caused by the accumulation of PAH in the recycle oil.

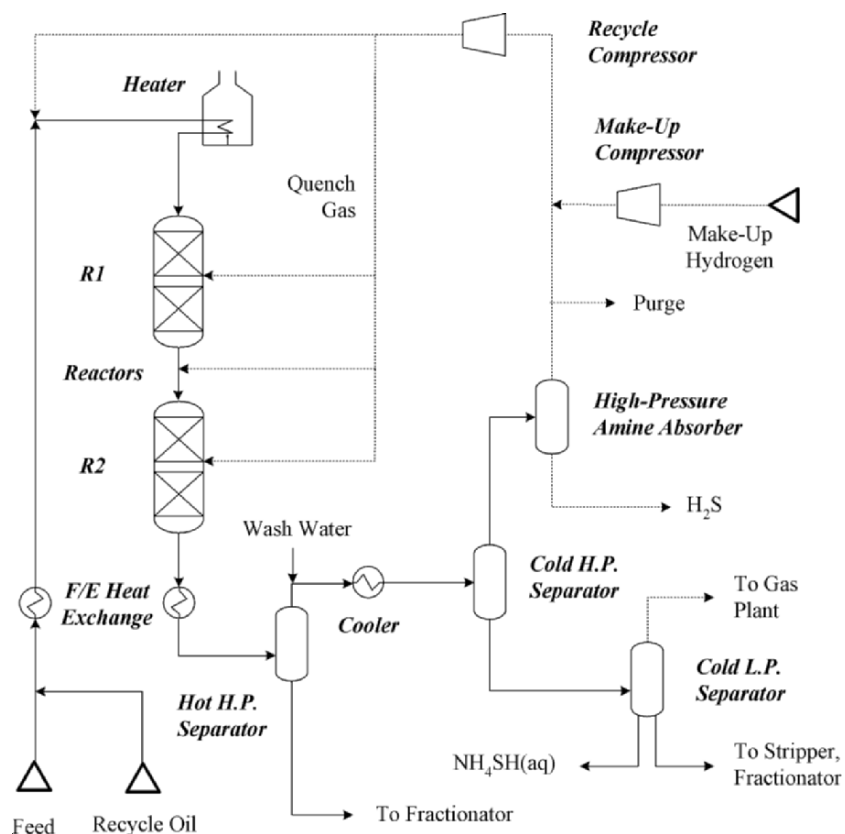


Figure 19. Single-stage hydrocracker: hot H.P. separator, recycle to R1

(7) **Wash Water Addition.** As mentioned above, HDS and HDN reactions produce H_2S and NH_3 , respectively. Wash water is injected into the effluent from the last reactor to convert almost all of the NH_3 and some of the H_2S into aqueous ammonium bisulfide, $\text{NH}_4\text{HS}(\text{aq})$. The $\text{NH}_4\text{HS}(\text{aq})$ is rejected from the unit as sour water in the low-pressure flash drum.

(8) **Fractionation.** For product fractionation, HDS units that treat naphtha or light gas oil may use a simple steam stripper to remove H_2S and traces of light hydrocarbons from the liquid product (CLPS bottoms). An absorber may be used to recover C_3 -plus compounds from the CLPS overhead.

Conversion units may employ a full-fledged fractionation train, with a pre-flash tower to remove light ends; an atmospheric fractionator to separate light naphtha, heavy naphtha, middle distillates, and unconverted oil; and a vacuum tower to maximize the recovery of diesel. Some hydrocrackers use the atmospheric tower to produce full-range naphtha, which is then separated into light and heavy fractions in a naphtha splitter.

(9) Recycle of Fractionator Bottoms. In full-conversion hydrocrackers, unconverted oil from the fractionator is recycled. Single-stage units with multiple reactors (*Figure 19*) send the recycled oil either to the hydrotreating reactor (R1) via the feed surge drum or to the hydrocracking reactor (R2). Recycle to R1 means that R1 must be larger, but recycle to R2 eliminates an expensive and troublesome high-pressure pump.

Figure 20 shows a two-stage hydrocracker. In these units, unconverted oil goes to a separate cracking reactor (R3) with its own high-pressure separator.

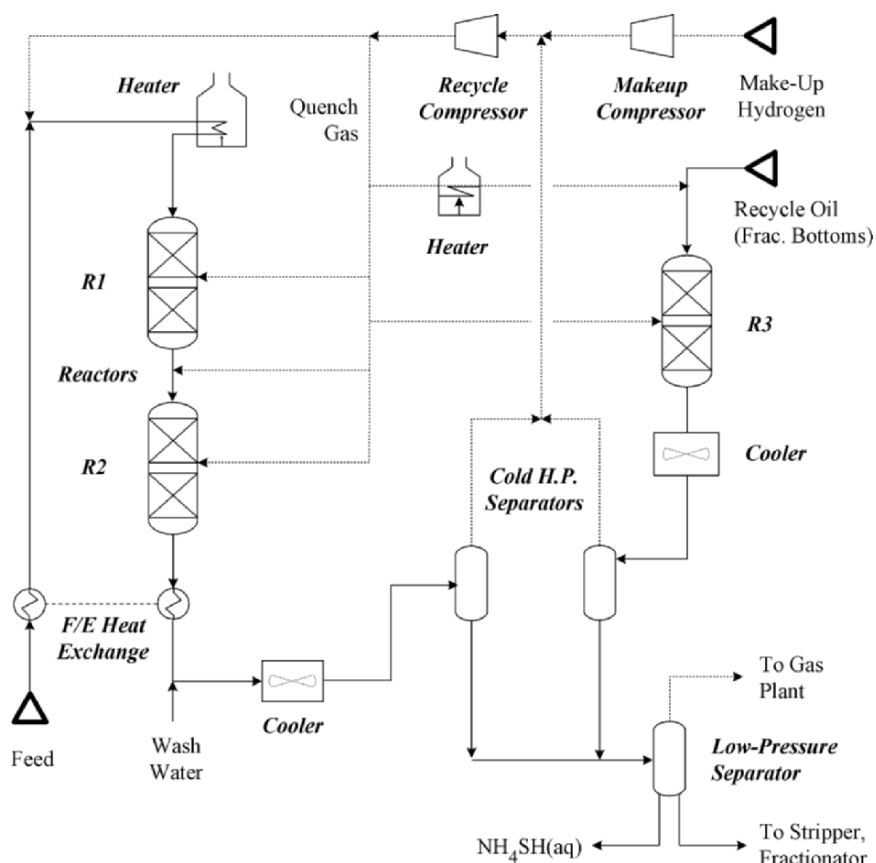


Figure 20. Two-stage hydrocracker: common recycle gas system.

The unit shown in *Figure 20* uses a single makeup and recycle gas system to supply all reactors. In other units, the 2nd stage has a separate gas system. Units with a common recycle gas system need only one recycle compressor, but in units with two gas systems, the 2nd stage can operate at lower pressure, which can reduce both investment and operating costs. Also, the 2nd stage can use sweet gas (no H₂S) rather than sour, allowing the refiner to employ a wider range of catalysts.

Early fixed-bed hydrocrackers used a “separate hydrotreat” flow scheme, which resembles a 2-stage design with nothing but hydrotreating catalyst in the 1st stage. This flow scheme is discussed in further detail in Chapter 8 by Adrian Gruia.

5.2 Slurry-Phase Hydrocracking

Slurry-phase hydrocracking converts residue in the presence of hydrogen under severe process conditions – more than 840°F (450°C) and 2000 to 3000 psig (13,891 to 20,786 kPa). To prevent excessive coking, finely powdered additives made from carbon or iron salts are added to the liquid feed. Inside the reactor, the liquid/powder mixture behaves as a single phase due to the small size of the additive particles. Residue conversion can exceed 90%, and the quality of converted products is fairly good.

Unfortunately, the quality of the unconverted pitch is poor, so poor that it can't be used as a fuel unless it is blended with something else – coal or heavy fuel oil. Even then, its high metals and sulfur content can create problems.

At the 5,000 b/d CANMET demonstration plant in Canada, the pitch is sent to a cement kiln for use as clinker. Other slurry-phase processes include COMBIcracking (developed by Veba Oel), Aurabon (UOP), and HDH Cracking (Intevap). Although several slurry-phase demonstration plants have been built, the pitch-disposal problem has kept it from gaining industry-wide acceptance.

5.3 Ebullating Bed Units

In contrast to fixed-bed VGO hydrocrackers, ebullating bed units can (and do) process residual oils. In ebullating bed units (*Figure 21*), hydrogen-rich recycle gas is bubbled up through a mixture of oil and catalyst particles. This provides three-phase turbulent mixing, which is needed to ensure a uniform temperature distribution. At the top of the reactor, catalyst is disengaged from the process fluids, which are separated in downstream flash drums. Most of the catalyst is returned to the reactor. Some is withdrawn and replaced with fresh catalyst. The two major ebullating-bed processes are H-Oil, which is offered for license by Axens (IFP), and LC-Fining, which is offered by Chevron Lummus Global. Their main advantages are:

- High conversion of atmospheric residue, up to 90 vol%.
- Better product quality than many other residue conversion processes, especially delayed coking.
- Long run length. Catalyst life does not limit these units. Fresh catalyst is added and spent catalyst is removed continuously. Therefore, barring any mechanical problems, the units can run for a much longer time than fixed-bed residue units.

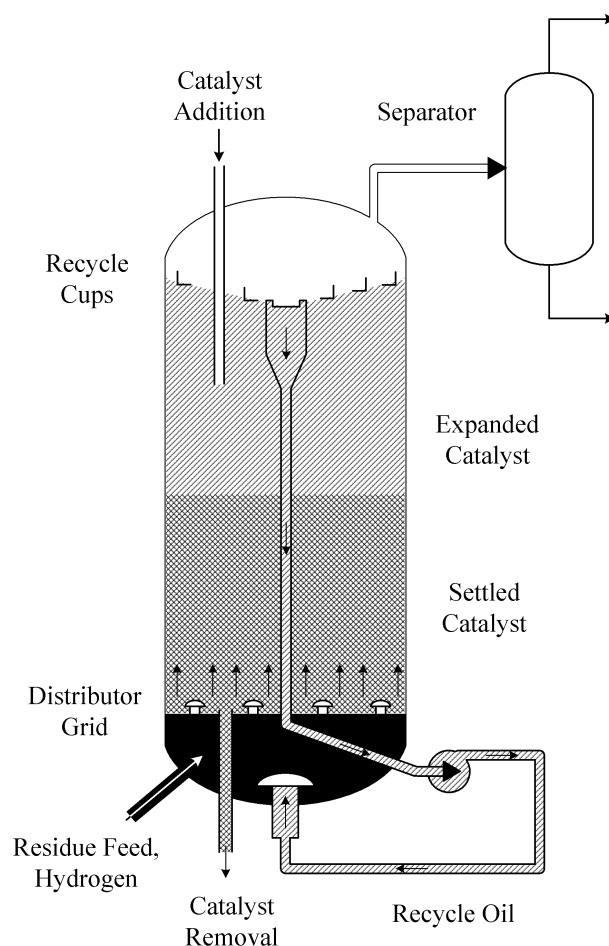


Figure 21. Ebullating bed hydrocracking reactor.

6. PROCESS CONDITIONS

For fixed-bed hydroprocessing units, the process conditions – pressure, temperature, space velocity, and catalyst – are determined by feed quality and process objectives. Table 12 shows typical process conditions for the hydrotreating of different feeds in fixed-bed hydrotreating units. The values shown are approximate.

The H_2/Oil ratios are for units in which off-gas from the high-pressure separator is recycled. For once-through naphtha hydrotreaters associated with catalytic reformers, the H_2/Oil ratio can be much higher than 350 scf/bbl ($60 \text{ m}^3/\text{m}^3$). For units that treat olefinic cracked stocks from FCC or coking units, H_2/Oil ratios are higher to control the extra heat released by olefin saturation.

Table 12. Typical Process Conditions for Hydrotreating Different Petroleum Fractions

	Naphtha	Kerosene	Diesel	VGO	Residue
WART*					
°F	530	550	575 to 600	680 to 700	700 to 725
°C	277	288	300 to 315	360 to 370	370 to 385
H ₂ Pressure†					
psig	250 to 450	250 to 600	600 to 800	800 to 2000	>2000
kPa	1825 to 3204	1825 to 4238	4238 to 5617	5617 to 13,891	>13,891
LHSV	5	4	2 to 3	0.8 to 1.5	0.5
H ₂ /Oil Ratio‡					
scf/bbl	350	450	800	1200	>3000
M ³ /m ³	60	80	140	210	>525

*Approximate weighted average reactor temperature at start of run

†Approximate hydrogen partial pressure at the high-pressure separator

‡Approximate hydrogen-to-oil ratio at the first reactor inlet

7. YIELDS AND PRODUCT PROPERTIES

Table 13 illustrates the yield flexibility of recycle hydrocracking. The ability to swing in just a day or two from 90 vol% full-range naphtha to >75 vol% full-range diesel provides unparalleled capability to respond to short-term changes in market conditions – if the refinery has sufficient blending, storage and distribution capacity. To shift the product slate, operators adjust reactor temperatures and change cut points in the fractionation section.

For all process units, product specifications are set to meet refinery-wide objectives. For example, if a refinery wants to produce diesel fuel containing <15 wppm sulfur, and if its hydrocracker makes 40,000 barrels/day of sulfur-free middle distillate, the product sulfur specification for its 20,000 barrels/day distillate hydrotreater (DHT) could be as high as 45 wppm – if a blend of the two streams satisfies the requirements of ASTM D975, which is the standard specification for heavy-duty diesel fuel in the United States. In practice, the DHT sulfur target would be lower than 45 wppm to cushion the refinery against upsets and measurement error. For a diesel fuel containing 10 wppm sulfur, the analytical reproducibility for ASTM Method D5453 is ± 1.8 wppm. For a diesel containing 50 wppm sulfur, the reproducibility is ± 8.1 wppm. ASTM D5453 is an x-ray fluorescence method for measuring sulfur in distillate fuels, including ultra-low-sulfur diesel.

8. OVERVIEW OF ECONOMICS

8.1 Costs

Throughput, operating pressure and process configuration – once-through or recycle of unconverted oil – are the major factors affecting construction costs for hydroprocessing units, which range from \$1000 to \$4000 per daily

barrel. On this basis, a fully-installed 25,000 barrels-per-day hydrocracker can cost between US\$40 million and US\$100 million. These estimates do not include costs for a hydrogen plant and off-site utilities.

Table 13. Feed and Product Properties for a flexible Single-Stage Hydrocracker

<u>Feedstock Type</u>	<u>Straight-run Vacuum Gas Oil</u>		
Boiling Range, °C	340 to 550		
Boiling Range, °F	644 to 1022		
API Gravity	22.0		
Specific Gravity	0.9218		
Nitrogen, wppm	950		
Sulfur, wt%	2.5		
<u>Product Objective</u>	<u>Naphtha</u>	<u>Jet</u>	<u>Diesel</u>
Weighted Average Reactor Temp, °C	"base"	-6	-12
Weighted Average Reactor Temp, °F	"base"	-11	-22
<u>Yields, vol% Fresh Feed</u>			
C ₄	11	8	7
C ₅ -82°C (C ₅ -180°F)	25	18	16
82°C-plus (180°F-plus) Naphtha	90	29	21
Jet A-1 or Diesel	---	69	77
Total C ₄ -plus	126	124	121
Chemical H ₂ Consumption			
Nm ³ /m ³	345	315	292
Scf/bbl	2050	1870	1730
<u>Product Qualities</u>			
<i>C₅-82°C</i>			
RONC	79	79	80
<i>Heavy Naphtha</i>			
P/N/A	45/50/5	44/52/4	---
RONC	41	63	67
End Point, °C (°F)	216 (421)	121 (250)	118 (244)
<i>Jet A-1</i>			
Flash Point, °C (°F)	---	38 (100)	---
Freeze Point, °C (°F)	---	-48 (-54)	---
Smoke Point, mm	---	34	---
FIA Aromatics, vol%	---	7	---
End Point, °C (°F)	---	282 (540)	---
<i>Diesel</i>			
Cloud Point, °C (°F)	---	---	-15 (5)
API Gravity	---	---	44
Cetane Number	---	---	55
Flash Point, °C (°F)	---	---	52 (126)
End Point, °C (°F)	---	---	349 (660)

For hydrotreaters, operating costs are roughly US\$1.7 per barrel. The cost of producing and compressing hydrogen accounts for 60% to 70% of this. For high-conversion hydrocrackers, operating costs are roughly US\$4.0 to US\$4.5 per barrel, of which 75% to 80% is due to hydrogen.

8.2 Benefits

Many hydrotreaters are stay-in-business investments, so it's difficult to quantify their upgrade value, which is the value of products minus costs – labor, materials (liquid feed, hydrogen, catalysts and chemicals), utilities, maintenance, and investment amortization. In some plants, the refinery planning LP assigns equal value to treated and untreated naphtha, and even to treated and untreated distillates. This reflects the underlying assumption that the increase in value across a hydrotreater is equal to the cost of running the unit, i.e., the upgrade value is zero. In other LPs, the NHT that pretreats catalytic reformer feed is lumped in with the reformer. Certainly, if a key naphtha or distillate hydrotreater shuts down, the refinery may have to run at reduced rate, but that can be said of most units.

For an FCC feed pretreater, the upgrade value can be more than US\$3 per barrel if the calculation includes its positive impact on FCC yields. Usually, benefits to the FCC are greater than the value of conversion and volume swell in the hydrotreater itself. Typically, the upgrade value for a high-conversion VGO hydrocracker is US\$3 to US\$4 per barrel.

With hydroprocessing units, most refiners try to maximize feed rate while (a) meeting other process objectives and (b) maintaining a high on-stream factor. Some try to maximize conversion, while others just want to hit a key process target at minimum cost.

8.3 Catalyst Cycle Life

For fixed-bed units, catalyst cycle life dominates economics. Catalysts can't be changed if the units are operating, so shorter catalyst cycles mean decreased production. For a typical 25,000 b/d unit, one day of lost production can cost US\$100,000.

Here are some of the many economic tradeoffs that must be considered when setting hydrocracker process targets:

- Higher feed rates and higher conversion are desirable economically, but they increase consumption of hydrogen and decrease catalyst cycle life.
- In units that can recycle fractionator bottoms, higher recycle oil rates can increase selectivity, but they may impose limits on fresh feed rate.

For many recycle units, switching to once-through (zero recycle) operation is attractive economically if the unconverted oil (i.e., the fractionator bottoms) goes to an FCC, olefins plant or lube plant for further upgrading. Conversion goes down in the hydrocracker, but it may be possible to increase fresh feed rates without decreasing catalyst cycle life, and operating costs may go down due to decreased hydrogen consumption.

9. HYDROCRACKER-FCC COMPARISON

In a petroleum refinery, heavy molecules with low hydrogen-to-carbon ratios (H/C) are converted into light molecules with higher H/C. The FCC process increases H/C by rejecting carbon, while hydrocracking increases H/C by adding hydrogen. Consequently, FCC and hydrocracking have marked differences in operating conditions, volume swell, product yields and product properties. *Table 14* summarizes some of these differences.

Table 14. Comparison of Hydrocracking with FCC

	<i>FCC</i>	<i>Hydrocracking</i>
Operating pressure	Low	High 1500 – 2800 psi
Operating temperature	High 900 – 1000°F	Moderate 600 – 780°F
Construction costs	Moderate	High
Volume swell	112 – 118 vol% Incl. fuel gas FOEB ¹	115 – 140 vol% Fresh feed basis
Product olefins	High	Nil
Light naphtha octane (RONC) ²	>100	78-81
Heavy naphtha octane (RONC) ²	95 – 100	40-64
Distillate cetane index	Low	56 – 60
Distillate sulfur content	Moderate to High	Very low
Bottoms sulfur content	Moderate to High	Very low

1. FOEB = fuel oil equivalent barrels

2. RONC = research octane number clear (without tetraethyl lead)

10. OPERATIONAL ISSUES

Hydroprocessing – especially hydrocracking – is exothermic. Effective control of produced heat is the primary concern of designers, owners and operators of hydrocracking units. In modern units, a high flux of recycle gas provides a sink for process heat. It also promotes plug flow and the transport of heat through the reactors. Most licensors recommend that the ratio of recycle gas to makeup gas should exceed 4:1.

During design, limits on temperature rise ($T_{\text{rise}} = T_{\text{out}} - T_{\text{in}}$) set the size of catalyst beds and determine the number and location of quench zones. During operation, when feeds (and maybe catalysts) are different, the T_{rise} is also different – sometimes dangerously different. A sudden spike in T_{rise} can lead to a “temperature runaway” or “temperature excursion.” These are dangerous. The rates of cracking reactions increase exponentially with temperature – the hotter they get, the faster they get hot. In a few cases, temperature runaways have melted holes in the stainless steel walls of hydrocracking reactors. This is remarkable, because the walls were more than 8 inches (20 cm) thick.

The best way to stop a temperature excursion is to de-pressure the unit by venting recycle gas through a special valve at the CHPS. This decelerates all hydrocracking reactions by rapidly reducing H_2 partial pressure in the reactors. De-pressuring can also lead to catalyst mal-distribution, decreased

catalyst activity, and/or increased pressure drop. For these reasons, operators are extremely careful when re-starting a unit after a temperature excursion.

Due to the presence of hydrogen, leaks in hydroprocessing units often cause fires. Such fires can be devastating, if not deadly. The replacement of a reactor and the reconstruction of other equipment damaged by the accident can take 12 months. The cost of lost production can exceed US\$50 million.

Safety concerns are responsible for several operating constraints, such as:

- An upper limit on temperature in the reactors. This and other temperature constraints prevent damage to the reactor.
- Upper limits on the T_{rise} in each bed and each reactor, and upper limits on the rate at which T_{rise} changes. These are designed to decrease the likelihood of temperature excursions.
- An upper limit on the velocity of fluid flow through elbows in high-pressure piping. This constraint emerged after erosion-corrosion cut a hole in a high-pressure pipe in a hydrocracker, causing a major accident.
- A lower limit on reserve quench gas – usually 15% of the total flow of recycle gas. Reserve quench provides a way to react quickly to non-emergency changes in T_{rise} .
- A lower limit on wash water injection. This ensures the near-total removal of ammonia from the system.

11. LICENSORS

Leading licensors of hydroprocessing technology are listed in Table 15.

Table 15. Leading Licensors of Hydroprocessing Technology

Company	Process Name	Description
Axens (IFP)	Prime-G	Gasoline desulfurization
	IFP Hydrotreating	Naphtha, Distillate, VGO hydrotreating
	IFP Hydrocracking	High-conversion fixed-bed hydrocracking
	T-Star	Ebullating bed hydrotreating
	H-Oil	Ebullating bed hydrocracking
CDTECH	CDHydro, CDHDS	Hydrotreating with catalytic distillation
Chevron Lummus	ISOCRACKING	High-conversion hydrocracking
	RDS	Atmospheric residue hydrotreating
	VRDS	Vacuum residue hydrotreating
	OCR	Onstream catalyst replacement
	ISODEWAXING	Catalytic dewaxing
	LC-Fining	Ebullating bed hydrocracking
Criterion/ABB /	SynSat	Distillate hydrotreating, aromatics saturation
Shell Global	Deep Gasoil HDS	Hydrotreating to make ultra-low-sulfur diesel
ExxonMobil	SCANfining	Hydrotreating to make low-sulfur gasoline
	OCTGAIN	Hydrotreating to make low-sulfur gasoline
	ULSD-fining	Hydrotreating to make ultra-low-sulfur diesel
	MAXSAT	Saturation of aromatics in distillate streams

Table 15. (Continued)

Company	Process Name	Description
	LCO-finishing	LCO hydrotreating
	GO-finishing	FCC feed pretreating
	RESIDfinishing	Residue hydrotreating
	MIDW	Lube isomerization/dewaxing
Haldor Topsøe		Naphtha, distillate, VGO hydrotreating
KBR	MAK Hydrotreating	Distillate and VGO hydrotreating
	MAK Hydrocracking	Mild hydrocracking, FCC feed pre-treatment
UOP	ISAL	Gasoline desulfurization
	Unifinishing	Naphtha hydrotreating
	Unionfinishing	Distillate, VGO, residue hydrotreating
	Unicracking	High-conversion VGO hydrocracking

Many engineering contractors gladly will build un-licensed hydrotreaters. However, for hydrocrackers and special-application hydrotreaters, especially those designed to meet clean-fuel specifications, refiners almost always select licensed technology from an experienced vendor willing to offer guarantees.

12. CONCLUSION

Advances in hydroprocessing are driven by competitive forces and clean-fuel regulations. These advances include improved catalysts (Chapters 9-11), better reactor design (Chapters 7-8), advanced process control (Chapter 22), and online optimization (Chapter 23). As clean-fuel regulations migrate from North America and the EU into the rest of the world, and as globalization of the oil industry continues apace, the need will continue for new (and better) hydroprocessing units. Hopefully, within a few years, this chapter will be obsolete and we'll have to write an update.

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