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# 10 Commercial Hydrotreating and Hydrocracking

*Paul R. Robinson and Geoffrey E. Dolbear*

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## 10.1 INTRODUCTION

Hydrotreaters are the most common process units in modern petroleum refineries. As shown in Table 10.1, the world's hydrotreating capacity is nearly half as large as the world's crude distillation capacity (Stell, 2003). In more than 700 refineries around the globe, there are more than 1300 hydrotreating units. A typical Western petroleum refinery (Figure 10.1) uses at least three hydrotreaters — one for naphtha, one or two for light gas oil, and one or two for heavy gas oil or vacuum gas oil.

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.

## 10.2 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 will discuss them together. As is common in the refining industry, we use the term *hydroprocessing* when a statement applies to both hydrotreating and hydrocracking.

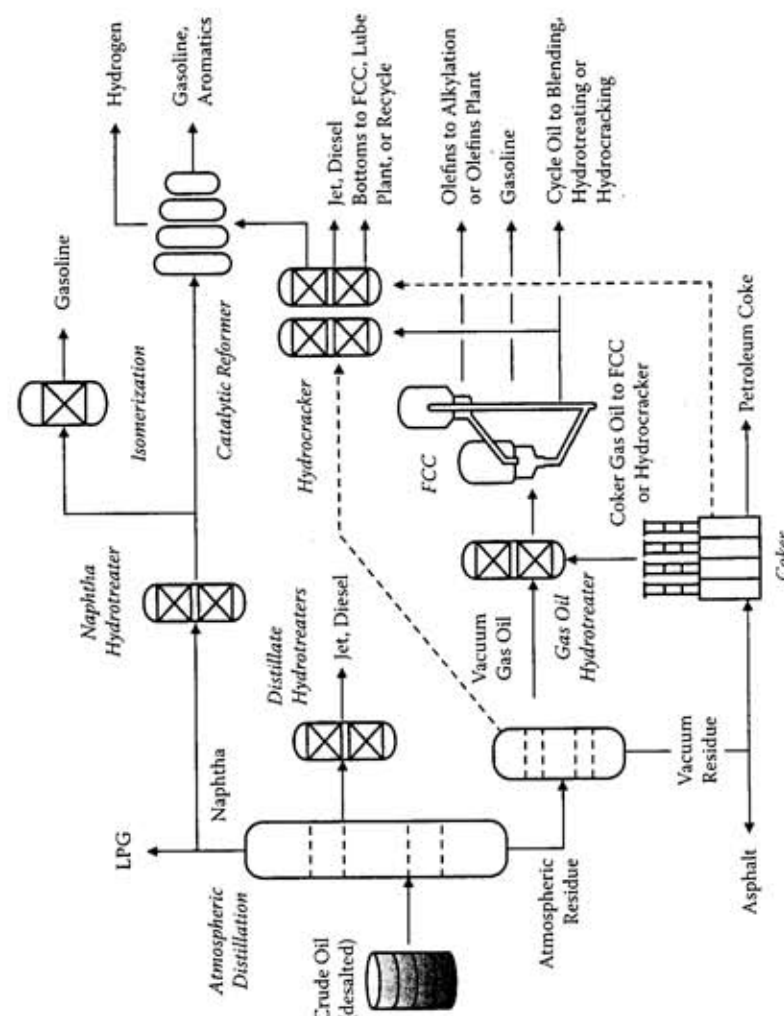
**TABLE 10.1**  
Worldwide Refining Process Units (as of January 1, 2004)

	Crude Distillation	Coking + Visbreaking	FCC	Catalytic Reforming	Hydrotreating	Hydrocracking
Number of units	>710	>330	360	550	1316	168
Total world capacity <sup>a</sup>	82.0	8.0	14.3	11.3	40.3	4.6
Average capacity <sup>b</sup>	114,000	45,700	39,700	20,500	30,600	27,400

<sup>a</sup> Million barrels per calendar day.

<sup>b</sup> Barrels per calendar day.

Source: Stell, J. *Oil & Gas J.* 101(49), December 22, 2003. (With permission.)



**FIGURE 10.1** Layout of a typical high-conversion oil refinery.

TABLE 10.2

Hydrotreating and Hydrocracking: Ranges of H<sub>2</sub> Partial Pressure and Conversion

Process, Feedstock Types	H <sub>2</sub> Partial Pressure		Conversion wt%
	psig	kPa	
<b>Hydrotreating</b>			
Naphtha	250–450	1825–3204	0.5–5
LGO (kerosene)	250–600	1825–4238	0.5–5
HGO (diesel), LCO	600–800	4238–5617	5–15
VGO, VBGO, DAO, CGO, HCO	800–2000	5617–13,891	5–15
Residual oil	2000–3000	13,891–20,786	5–15
<b>Mild Hydrocracking</b>			
VGO, VBGO, DAO, CGO, LCO, HCO	800–1200	5617–8375	20–40
<b>Once-Through Hydrocracking</b>			
VGO, VBGO, DAO, CGO, LCO, HCO	1500–2000	10,443–13,891	60–90
Residual oil	2000–3000	13,891–20,786	15–25
<b>Recycle Hydrocracking</b>			
VGO, VBGO, DAO, CGO, LCO, HCO	1500–2000	10,443–13,891	80–99
<b>Ebullated-Bed Hydrocracking</b>			
VGO, VBGO, DAO, HCO	2000	13,891	80–99
Residual oil	2000–3000	13,891–20,786	>50

Note: 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.

As shown in Table 10.2, the extent of conversion is the most significant difference between hydrotreating and hydrocracking. In this context, the term *conversion* is defined as the amount of unconverted oil in the 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<sub>2</sub>S and NH<sub>3</sub> also produce light hydrocarbons. 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).

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 a fluid catalytic cracking (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+ (566°C+) residue can exceed 60 wt%.

Catalytic isomerization and dewaxing is a special kind of hydrocracking used to make high-quality lube base stocks.

### 10.3 PROCESS OBJECTIVES

Table 10.3 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.

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 other feeds that boil between 650 and 1050°F (343 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 (American Society for Testing and Materials [ASTM] D1655). Heavier distillates cannot be sold as diesel fuel unless they meet stringent sulfur specifications.

#### 10.3.1 CLEAN FUELS

As mentioned in Chapter 1, on-road diesel in the United States must contain <15 wppm sulfur by 2006. The sulfur limit for nonroad diesel will be 500 wppm in 2007.

**TABLE 10.3**  
**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 <sup>a</sup> 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

<sup>a</sup> RFCC = residue FCC unit or reduced crude FCC unit, both of which are specially designed to process feeds that contain high concentrations of carbon-forming compounds.

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 10.1

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 10.2

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 posttreat 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.

#### 10.3.2 THE PROCESS IN BETWEEN

As shown in Figure 10.1, 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 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.

#### 10.4 PROCESS MODELING

During the past 20 years, academic and industrial researchers have developed composition-based kinetic models with hundreds or even thousands of lumps and pure compounds. The quantitative structure-reactivity correlation (QSRC) and linear free energy relationship (LFER) lumping techniques are discussed by Klein and Hou (2006). The structure-oriented lumping (SOL) approach of Quann and Jaffe (1996) yields models rigorous enough for use in closed-loop real-time optimizers (CLRTOs), which automatically adjust setpoints for commercial process units several times each day.

In the composition-based model developed by Lapinas et al. (1991) and applied to a commercial hydrocracker by Pedersen et al. (1995) rate equations are based on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) mechanism for heterogeneous reactions. In brief, the LHHW mechanism describes (1) the adsorption of reactants to acid and metal sites on a catalyst surface; (2) reactions between the reactants, including saturation, cracking, ring opening, dealkylation, hydrodesulfurization (HDS); hydrodenitrogenation (HDN); and so forth, and (3) desorption of products. Inhibition effects are modeled, too. These include the adsorption of organic nitrogen to acid sites and the inhibition of HDS reactions by H<sub>2</sub>S.

Rigorous, flow-sheet-based models for hydrocrackers include submodels for furnaces, pumps, compressors, reactors, quench zones, flash drums, recycle gas scrubbers, fractionation towers, and — importantly — economic data. As discussed by Mudt et al. (2006) such models can comprise hundreds of reactions and hundreds of thousands of equations. The model grows when inequalities are



**TABLE 10.4**  
**Supports Used in Hydroprocessing Catalysts**

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

included to ensure a feasible solution that honors process constraints. To solve such models in real time (that is, in less than 1 h), open-equation mathematics and high-powered solvers are used.

## 10.5 HYDROPROCESSING CATALYSTS

Recent books by Magee and Dolbear (1998) and Scherzer and Gruia (1996) are superb sources of technical information on hydroprocessing catalysts. The hydroprocessing catalyst business is big, with annual sales approaching U.S.\$800 million per year. The materials most commonly used to make these catalysts are shown in Table 10.4 and Table 10.5.

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 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 75 to 85 Å for catalysts that process light and heavy gas oils. For catalysts that process residue, the average pore size ranges from 150 to 250 Å.

**TABLE 10.5**  
**Active Metals Used in Hydroprocessing Catalysts**

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

\* Pd and Pt are poisoned by sulfur and can only be used in low-H<sub>2</sub>S environments.

### 10.5.1 CATALYST PREPARATION

The following steps may be used to prepare the supported metal catalysts used in hydrotreaters and hydrocrackers (Magee and Dolbear, 1998; Scherzer and Gruia, 1996):

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

Other steps, such as kneading, mulling, grinding, and sieving, may also 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.

#### 10.5.1.1 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(NO<sub>3</sub>)<sub>3</sub>] with sodium aluminate [Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>] yields aluminum hydroxide [Al(OH)<sub>3</sub>], 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 are also prepared by precipitation. Zeolites occur naturally, but the ones used for catalysis are synthetic. Figure 10.2 outlines a common procedure for synthesizing Na-Y and H-Y zeolites.

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<sub>2</sub> superstructure. To maintain a neutral charge, every aluminum atom must be accompanied by a counter-ion such as Na<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and so forth. Counter-ions can be swapped via ion exchange. When Na-Y zeolite is exchanged with an ammonium salt, the Na<sup>+</sup> ion is replaced by NH<sub>4</sub><sup>+</sup>. When NH<sub>4</sub>-Y is heated to the right temperature, the ammonium ion decomposes, releasing NH<sub>3</sub> (gas) and leaving behind the 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 quaternary 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.

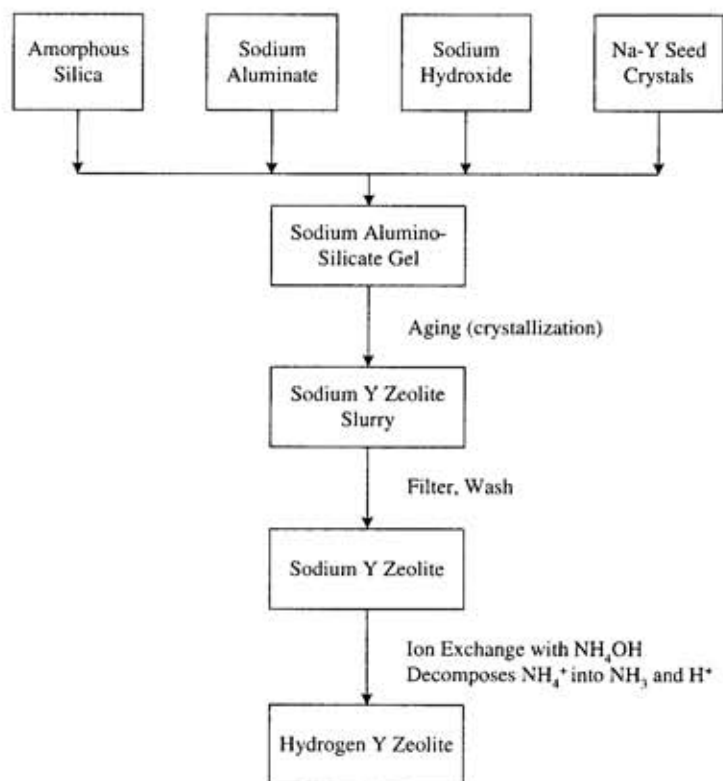


FIGURE 10.2 Synthesis procedure for H-Y zeolite.

#### 10.5.1.2 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 ( $\text{Al}_2\text{O}_3$ ).

#### 10.5.1.3 Forming

Catalyst and support precursors can be formed into extrudates, spheres, or pellets. Extrudates are generated by forcing a paste (for example, formed by mixing powdered-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 and 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  $\text{Al}_2\text{O}_3$ . The preferred alumina for catalyst supports is  $\gamma$ -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,  $\gamma$ -alumina transforms into  $\alpha$ -alumina or  $\beta$ -alumina, whose physical properties are far less desirable.

An extrudate cross section can be circular or shaped like a three- or four-leaf clover without the stem (Gruia, 2006). Compared to cylindrical extrudates, clover-leaf (multilobe) catalysts have a higher surface-to-volume ratio. In trickle-bed hydroprocessing reactors, they have less resistance to diffusion and a lower pressure drop. Spherical catalysts are made by (1) spray-drying slurries of catalyst precursors, (2) spraying liquid onto powders in a tilted rotating pan, or (c) dripping a silica-alumina slurry into hot oil (Magee and Dolbear, 1998). Pellets are made by compressing powders in a dye.

#### 10.5.1.4 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, additional solution may be added to increase loading of the same or different active metal.

#### 10.5.1.5 Activation

Prior to use, most nonnoble-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, that is, the point at which significant amounts of  $\text{H}_2\text{S}$  appear in the recycle gas.

During dry sulfiding, a mixture containing 2 to 5 vol%  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$  as the inlet gas.

Most manufacturers offer presulfided catalysts, which allow a refiner to shorten the start-up of a unit by 2 or 3 days. That may not seem like much, but for a 40,000 barrel/day FCC feed pretreater, it can generate up to U.S.\$500,000 in extra income.

### 10.5.2 NOBLE-METAL CATALYSTS

Some hydrocracking catalysts contain small amounts of highly dispersed platinum or palladium. These noble metals are expensive, but their loading is low — 0.6

to 1.0 wt% — and their high hydrogenation activity justifies the cost. They are added to hydrocracking catalysts by impregnation with tetraammine 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).

### 10.5.3 HYDROTREATING CATALYSTS

Hydrotreating catalysts comprise oxides of either Mo or W and either Co or Ni on a support comprised of  $\gamma$ -alumina. Usually, CoMo catalysts are better for HDS while NiMo catalysts are better for HDN. NiW catalysts are especially active for the saturation of aromatics. Typical physical properties are shown in Table 10.6.

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 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.

### 10.5.4 HYDROCRACKING CATALYSTS

Commercial hydrocracking catalysts comprise active metals on solid, highly acidic supports. The active metals are Pd, NiMo, and 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.

**TABLE 10.6**  
Physical Properties for Hydrotreating Catalysts

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

### 10.5.5 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 — 620 to 660°F (327 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 liquefied petroleum gas (LPG), which 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 is better to shut down for a catalyst change vs. 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 shutdown. 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 Si, or foul it with particulates, asphaltenes, 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 shutdown 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 shutdown for preventive maintenance.

Process variables that increase or decrease the rate of catalyst deactivation are shown in Table 10.7.

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.

**TABLE 10.7**  
**Factors Affecting Catalyst Cycle Life**

	Effect on Cycle Life	Comment
Higher-H <sub>2</sub> partial pressure	+	
Higher recycle gas rate	+	Increases H <sub>2</sub> partial pressure
Higher makeup gas purity	+	Increases H <sub>2</sub> partial pressure
Increased purge of recycle gas	+	Increases H <sub>2</sub> partial pressure
Higher fresh feed rate	—	
Higher conversion	—	
Higher fresh feed endpoint	—	Increases rate of catalyst coking; can increase pressure-drop buildup rate
Higher fresh feed impurities*	—	Related to feed type and feed endpoint
Process upsets <sup>b</sup>	—	

\* Deleterious feed impurities include sulfur, nitrogen, refractory carbon, asphaltenes, metals (nickel, vanadium, iron, silicon), and particulate matter (coke fines, FCC catalyst fines).

<sup>b</sup> 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 depressuring.

Increasing the feed endpoint or density tends to increase the amount of coke precursors in the feed. The precursors include asphaltenes, refractory carbon, and polynuclear aromatic hydrocarbons (PAH).

#### 10.5.5.1 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 shutdown, 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 CO<sub>2</sub> and CO plus small amounts of SO<sub>2</sub> and NO<sub>x</sub>, which are formed from the sulfur and nitrogen in the coke. Typically, the temperature used for regeneration in air is 750 to 930°F (400 to 500°C).

The regenerated catalyst may also undergo rejuvenation, a wet process in which the active metals are chemically redispersed. 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 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 lower severity. Worst of all, the catalyst will not last long, which means that it will have to be regenerated or replaced sooner rather than later.

#### 10.5.5.2 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, 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 10.8.

The book by Scherzer and Gruia (1996) provides a well-written description of catalyst reclamation processes used by four major companies — CRI-MET, Eurecat, Gulf Chemical, and TNO/Metrex.



**TABLE 10.8**  
Some of the Materials Sold by Catalyst Reclamation Companies

Material	Formula
Palladium metal or chloride salt	Pd or $\text{Na}_2\text{PdCl}_4$
Platinum metal or chloride salt	Pt or $\text{Na}_2\text{PtCl}_4$
Molybdenum trisulfide	$\text{MoS}_3$
Molybdenum oxide	$\text{MoO}_3$
Ammonium molybdate	$(\text{NH}_4)_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
Sodium molybdate	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
Tungsten trioxide	$\text{WO}_3$
Ammonium para-tungstate	$(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$
Sodium tungstate	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$
Vanadium pentoxide	$\text{V}_2\text{O}_5$
Sodium (meta) vanadate	$\text{NaVO}_3$
Nickel metal or chloride	Ni or $\text{NiCl}_2$
Cobalt metal or chloride	Co or $\text{CoCl}_2$
Nickel-cobalt concentrate	$\text{Ni}_3\text{Co}_3$
Iron-molybdenum concentrate	$\text{Fe}_3\text{Mo}_3$
Alumina hydrate	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

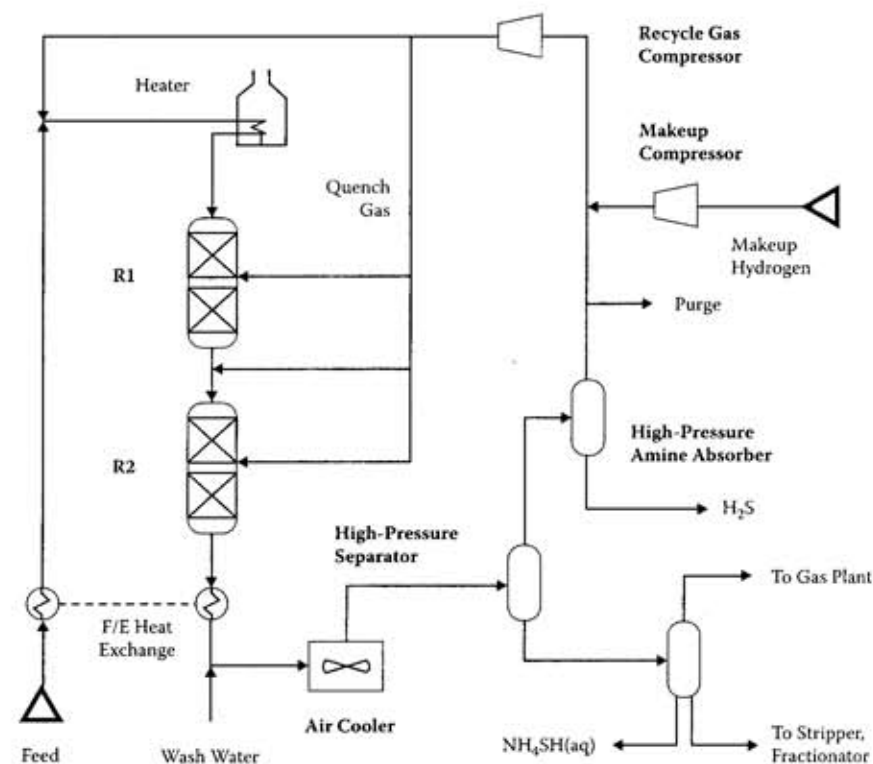
## 10.6 PROCESS FLOW

### 10.6.1 TRICKLE-BED UNITS

Most hydrotreaters and hydrocrackers are trickle-bed units. A classic article by Satterfield describes the fundamental behavior 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 10.3 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, which correspond to the bold numbers on the diagram.

1. **Heaters.** Units with gas-only heaters mix hot gas with preheated 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.
2. **Reactors, catalyst beds, and quench zones.** Addition of hydrogen typically occurs with heat release, and 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 or feeds that contain large amounts of sulfur, aromatics, or olefins, the



**FIGURE 10.3** Once-through hydroprocessing unit: two separators and recycle gas scrubber.

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 10.4 shows only 4 catalyst beds, but most hydrocrackers have more; some have as many as 30.

In a quench section (Figure 10.4), 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).

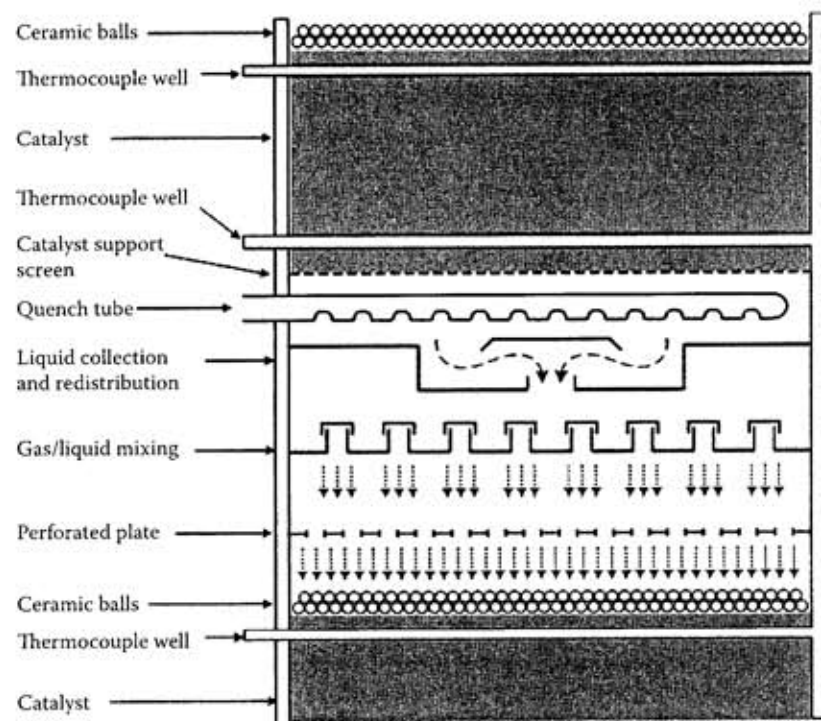


FIGURE 10.4 Hydroprocessing reactor: quench zone.

The truth is, we never know the actual highest and lowest temperatures, because we cannot place thermocouples everywhere. But if the measured RTD is small — less than 5°F (3°C) — we can assume that the actual RTD is also 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 maldistribution.

Modern quench sections are designed to do three things: (1) lower the overall temperature of the reacting fluids, (2) reduce radial maldistribution with radial mixing, and (3) 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 redistributor, 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 redistributor, 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.

In residue hydroprocessing units, heat release is high, but some licensors avoid using intrareactor quench because residue feeds often form lumps of coke-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 one-bed reactors in series with quench in between. In many cases, the first reactor is a guard bed filled with one or more catalysts designed to remove metals.

3. **Catalysts.** Hydrotreaters are loaded with either a CoMo HDS or 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 catalyst 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.

The last bed in a hydrocracker often contains a final layer of posttreat 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 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 CLPS is used to drive a power recovery turbine. As shown in Figure 10.5, 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.

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,  $NH_4HS(aq)$ . The  $NH_4HS(aq)$  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  $C_3+$  compounds from the CLPS overhead.

Conversion units may employ a full-fledged fractionation train, with a preflash 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

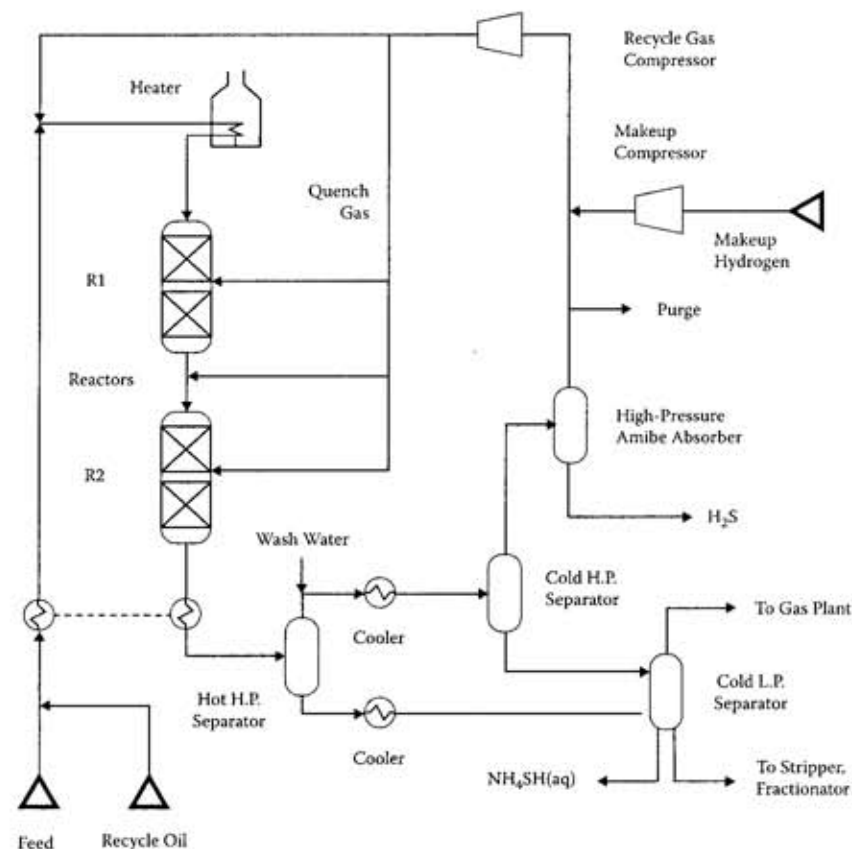


FIGURE 10.5 Single-stage hydrocracker: HHPS, recycle to R1.

with multiple reactors (Figure 10.5) 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 10.6 shows a two-stage hydrocracker. In these units, unconverted oil goes to a separate cracking reactor (R3) with its own high-pressure separator.

The unit shown in Figure 10.6 uses a single makeup and recycle gas system to supply all reactors. In other units, the second 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 second stage can operate at lower pressure, which can reduce both investment and operating costs. Also, the second stage can use sweet gas (no  $H_2S$ ) rather than sour, allowing the refiner to employ a wider range of catalysts.

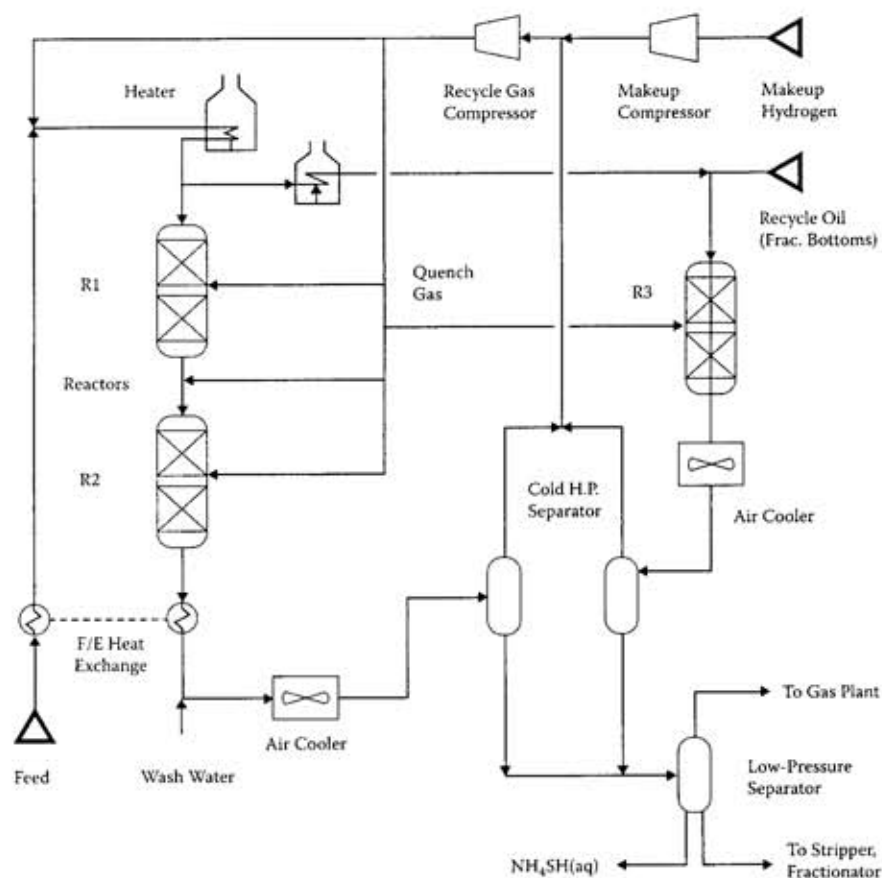


FIGURE 10.6 Two-stage hydrocracker: common recycle gas system.

Early fixed-bed hydrocrackers used a separate hydrotreat flow scheme, which resembles a two-stage design with nothing but hydrotreating catalyst in the first stage. This flow scheme is discussed in further detail by Gruia (2006).

### 10.6.2 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 cannot 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 5000 barrels/day CANMET demonstration plant in Canada, the pitch is sent to a cement kiln for use as a clinker. Other slurry-phase processes include COMBIcracking (developed by Veba Oel), Aurabon (UOP), and HDH Cracking (Intevip). Although several slurry-phase demonstration plants have been built, the pitch-disposal problem has kept it from gaining industry-wide acceptance.

### 10.6.3 EBULLATING-BED UNITS

In contrast to fixed-bed VGO hydrocrackers, ebullating-bed units can (and do) process residual oils. In ebullating-bed units (Figure 10.7), hydrogen-rich recycle

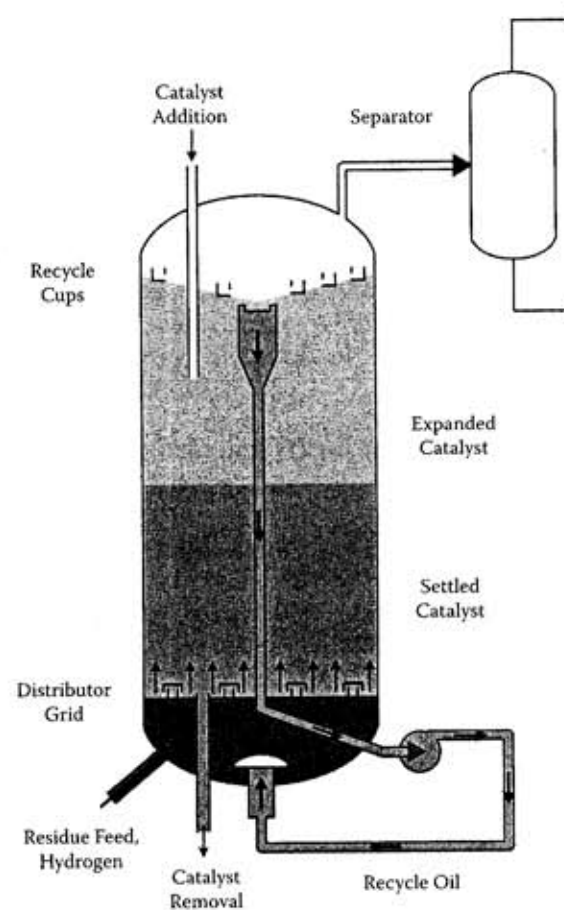


FIGURE 10.7 Ebullating-bed hydrocracking reactor.



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.

## 10.7 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 10.9 shows typical process conditions for the hydrotreating of different feeds in fixed-bed hydrotreating units. The values shown are approximate.

**TABLE 10.9**  
Typical Process Conditions for Hydrotreating Different Petroleum Fractions

	Naphtha	Kerosene	Diesel	VGO	Residue
WART <sup>a</sup>					
°F	530	550	575–600	680–700	700–725
°C	277	288	300–315	360–370	370–385
H <sub>2</sub> pressure <sup>b</sup>					
psig	250–450	250–600	600–800	800–2000	>2000
kPa	1825–3204	1825–4238	4238–5617	5617–13,891	>13,891
LHSV	5	4	2–3	0.8–1.5	0.5
H <sub>2</sub> /oil ratio <sup>c</sup>					
scf/bbl	350	450	800	1200	>3000
M <sup>3</sup> /m <sup>3</sup>	60	80	140	210	>525

<sup>a</sup> Approximate weighted average reactor temperature at start of run.

<sup>b</sup> Approximate hydrogen partial pressure at the high-pressure separator.

<sup>c</sup> Approximate hydrogen-to-oil ratio at the first reactor inlet.

The H<sub>2</sub>/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<sub>2</sub>/oil ratio can be much higher than 350 scf/bbl (60 m<sup>3</sup>/m<sup>3</sup>). For units that treat olefinic cracked stocks from FCC or coking units, H<sub>2</sub>/oil ratios are higher to control the extra heat released by olefin saturation.

## 10.8 YIELDS AND PRODUCT PROPERTIES

Table 10.10 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 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.

## 10.9 OVERVIEW OF ECONOMICS

### 10.9.1 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/day hydrocracker can cost between U.S.\$40 million and U.S.\$100 million. These estimates do not include costs for a hydrogen plant and off-site utilities.

For hydrotreaters, operating costs are roughly U.S.\$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 U.S.\$4.0 to U.S.\$4.5 per barrel, of which 75 to 80% is due to hydrogen.

### 10.9.2 BENEFITS

Many hydrotreaters are stay-in-business investments, so it is difficult to quantify their upgrade value, which is the value of products minus costs — labor, materials

**TABLE 10.10**  
**Feed and Product Properties for a Flexible Single-Stage Hydrocracker**

Feedstock Type	Straight-Run Vacuum Gas Oil		
Boiling range, °C	340–550		
Boiling range, °F	644–1022		
API gravity	22.0		
Specific gravity	0.9218		
Nitrogen, wppm	950		
Sulfur, wt%	2.5		
Product Objective	Naphtha	Jet	Diesel
Weighted average reactor temperature, °C	Base	–6	–12
Weighted average reactor temperature, °F	Base	–11	–22
<b>Yields, vol% Fresh Feed</b>			
C <sub>4</sub>	11	8	7
C <sub>5</sub> , 82°C (C <sub>5</sub> , 180°F)	25	18	16
82°C+ (180°F+) Naphtha	90	29	21
Jet A-1 or diesel	—	69	77
Total C <sub>4</sub> +	126	124	121
Chemical H <sub>2</sub> Consumption			
Nm <sup>3</sup> /m <sup>3</sup>	345	315	292
Scf/bbl	2050	1870	1730
<b>Product Qualities</b>			
C <sub>5</sub> , 82°C			
RONC	79	79	80
<b>Heavy Naphtha</b>			
P/N/A	45/50/5	44/52/4	—
RONC	41	63	67
Endpoint, °C (°F)	216 (421)	121 (250)	118 (244)
<b>Jet A-1</b>			
Flash point, °C (°F)	—	38 (100)	—
Freeze point, °C (°F)	—	–48 (–54)	—
Smoke point, mm	—	34	—
FIA aromatics, vol%	—	7	—
Endpoint, °C (°F)	—	282 (540)	—
<b>Diesel</b>			
Cloud point, °C (°F)	—	—	–15 (5)
API gravity	—	—	44
Cetane number	—	—	55
Flash point, °C (°F)	—	—	52 (126)
Endpoint, °C (°F)	—	—	349 (660)

(liquid feed, hydrogen, catalysts, and chemicals), utilities, maintenance, and investment amortization. In some plants, the refinery planning linear program (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, that is, the upgrade value is zero. In other LPs, the naphtha hydrotreater (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 a reduced rate, but that can be said of most units.

For an FCC feed pretreater, the upgrade value can be more than U.S.\$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 U.S.\$3 to U.S.\$4 per barrel.

With hydroprocessing units, most refiners try to maximize feed rate while (1) meeting other process objectives and (2) maintaining a high on-stream factor. Some try to maximize conversion, while others just want to hit a key process target at minimum cost.

### 10.9.3 CATALYST CYCLE LIFE

For fixed-bed units, catalyst cycle life dominates economics. Catalysts can not be changed if the units are operating, so shorter catalyst cycles mean decreased production. For a typical 25,000 barrels/day unit, 1 day of lost production can cost U.S.\$100,000.

Here are some of the many economic trade-offs 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 (that is, 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.

### 10.10 HYDROCRACKER-FLUID CATALYTIC CRACKER (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 ratios. The FCC process

**TABLE 10.11**  
**Comparison of Hydrocracking with FCC**

	FCC	Hydrocracking
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%	115–140 vol%
	Includes fuel gas FOEB	Fresh feed basis
Product olefins	High	Nil
Light naphtha octane (RONC)	>100	78–81
Heavy naphtha octane (RONC)	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

Note: FOEB = fuel oil equivalent barrels; RONC = research octane number clear (without tetraethyl lead).

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 10.11 summarizes some of these differences.

## 10.11 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 ( $T_{rise} = T_{out} - T_{in}$ ) 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 so. 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 in. (20 cm) thick.

The best way to stop a temperature excursion is to depressure 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. Depressuring can also lead to catalyst maldistribution, decreased catalyst activity, or increased pressure drop. For these reasons, operators are extremely careful when restarting 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 U.S.\$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 nonemergency changes in  $T_{rise}$ .
- A lower limit on wash water injection. This ensures the near-total removal of ammonia from the system.

## 10.12 LICENSORS

Leading licensors of hydroprocessing technology are listed in Table 10.12.

Many engineering contractors will gladly build unlicensed 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.

## 10.13 CONCLUSION

Advances in hydroprocessing are driven by competitive forces and clean-fuel regulations. These advances include improved catalysts, better reactor design, advanced process control, and online optimization. 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 will have to write an update.

**TABLE 10.12**  
**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	Hydrotreating with catalytic distillation
	CDHDS	
Chevron Lummus	Isocracking	High-conversion hydrocracking
	RDS	Atmospheric residue hydrotreating
	VRDS	Vacuum residue hydrotreating
	OCR	On-stream catalyst replacement
	Isodewaxing	Catalytic dewaxing
	LC-Fining	Ebullating-bed hydrocracking
Criterion/ABB/Shell Global	SynSat	Distillate hydrotreating; aromatics saturation
	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
	LCO-fining	LCO hydrotreating
	GO-fining	FCC feed pretreating
	RESIDfining	Residue hydrotreating
Haldor Topsøe	MIDW	Lube isomerization/dewaxing
		Naphtha, distillate, VGO hydrotreating
	MAK hydrotreating	Distillate and VGO hydrotreating
	MAK hydrocracking	Mild hydrocracking; FCC feed pretreatment
UOP	ISAL	Gasoline desulfurization
	Unifining	Naphtha hydrotreating
	Unionfining	Distillate, VGO, residue hydrotreating
	Unicracking	High-conversion VGO hydrocracking

## REFERENCES

1. Gruia, A. 2006. Recent Advances in Hydrocracking. In *Practical Advances in Petroleum Processing*, Hsu, C.S. and Robinson, P.R. (Eds.). Springer, New York, chap. 8.
2. Klein, M.T. and Hou, G. 2006. Mechanistic Kinetic Modeling of Heavy Paraffin Hydrocracking. In *Practical Advances in Petroleum Processing*, Hsu, C.S. and Robinson, P.R. (Eds.). Springer, New York, chap. 20.
3. Lapinas, A.T., Klein, M.T., Gates, B.C., Macris, A., and Lyons, J.E. 1991. Catalytic hydrogenation and cracking of fluorene: Reaction pathways, kinetics, and mechanisms. *Ind. Eng. Chem. Res.* 30(42).
4. Magee, J.S. and Dolbear, G.E. 1998. *Petroleum Catalysis in Nontechnical Language*. PennWell, Tulsa, OK.
5. Mudt, D.R., Pederson, C.C., Jett, M.D., Marur, S., McIntyre, B., and Robinson, P.R. 2006. Refinery-Wide Optimization with Rigorous Models. In *Practical Advances in Petroleum Processing*, Hsu, C.S., and Robinson, P.R. (Eds.). Springer, New York, chap. 23.
6. Pedersen, C.C., Mudt, D.R., Bailey, J.K., and Ayala, J.S. 1995. Closed Loop Real Time Optimization of a Hydrocracker Complex, 1995 NPRA Computer Conference, CC-95-121, November 6-8.
7. Quann, R.J. and Jaffe, S.B. 1996. Building useful models of complex reaction systems in petroleum refining. *Chem. Eng. Sci.* 51:1615.
8. Quann, R.J. and Jaffe, S.B. 1992. Structure oriented lumping: Describing the chemistry of complex hydrocarbon mixtures, *I & EC Res.* 31:2483.
9. Satterfield, C.N. 1975. Trickle-bed reactors. *AIChE J.* 21(2):20.
10. Scherzer, J. and Gruia, A.J. 1996. *Hydrocracking Science and Technology*, Marcel Dekker, New York.
11. Stell, J. 2003. Worldwide refineries, capacities as of January 1, 2004. *Oil & Gas J.* 101(49), December 22.