

HANDBOOK OF PETROLEUM REFINING PROCESSES

THIRD EDITION



- Contains the latest technologies in the field of petroleum refining processes
- Contributors are drawn from the largest petroleum producers in the world
- Detailed description and review of process chemistry and thermodynamics, product and by-product specifications, wastes and emissions
- 50% new information over the Second Edition

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designed to remove sulfur and metals from the feed to the coker so that the coke would have less sulfur and metals and be easier to sell. Since its commissioning in 1983, the RDS unit has provided significant economic benefit to the refinery. Coke production has been reduced and the proportion of light products is higher than it would have been without the RDS. This includes converting VR (which would otherwise be fed to the coker) to VGO, diesel, and naphtha in the RDS Hydrotreater. In addition, the hydrotreated VR from the RDS produces lower weight percent coke in the coker than the straight-run VR. Both of these effects lead to lower coke production and more light products from the refinery. The RDS Hydrotreater at Pascagoula remains the largest residuum hydrotreater in the world at 96,000 BPD.

Refiners have been hydrotreating residuum for over 25 years. In that time, residuum hydrotreating has changed with the needs of refiners from its initial function of removing sulfur from fuel oil to converting residuum directly and to improving the economics of downstream conversion unit. Fixed-bed residuum hydrotreating continues to be a popular route to residuum conversion.

PROCESS DESCRIPTION

A simplified flow diagram for a CLG RDS/VRDS Hydrotreater is shown in Fig. 8.1.1.

Oil feed to the RDS/VRDS Hydrotreater (AR or VR primarily, but may also include VGO, solvent deasphalted oil, solvent deasphalter pitch, and others) is combined with makeup hydrogen and recycle hydrogen and heated to the reactor inlet temperature. Heat is provided from heat exchange with the reactor effluent and by a reactor charge heater.

The reaction of hydrogen and oil occurs in the reactors in the presence of the catalyst. Hydrotreating reactions on the catalyst remove sulfur, nitrogen, vanadium, nickel, carbon residue, and other impurities from the residuum; hydrogenate the molecules; and crack the residue to lighter products. The required catalyst average temperature (CAT) is initially low, but is gradually increased by 45°C (81°F) or more as the catalyst ages. The net hydrotreating reactions (such as sulfur and metals removal) are exothermic (see "Process Chemistry"). To prevent reactor temperatures from getting too high, quench gas—cold

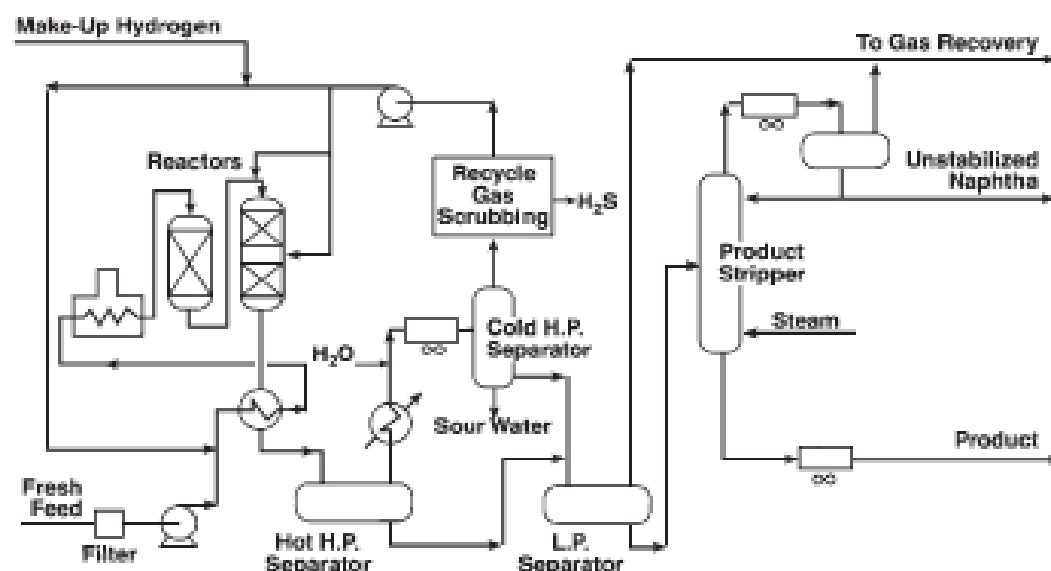


FIGURE 8.1.1 Simplified RDS/VRDS flow scheme.

Desulfurization

Desulfurization is by far the most common of the hydrotreating reactions. Sulfur-containing hydrocarbons come in a number of forms, and the ability to remove sulfur from the different types of hydrocarbons varies from one type to the next. The degree to which sulfur can be removed from the hydrocarbon varies from near-complete desulfurization for light straight-run naphthas to 50 to 70 percent for heavier residual materials. Figure 8.3.1 lists several sulfur-containing compounds in order of the difficulty in removing the sulfur.

The reaction of thiophenol, which is at the top of the list in Fig. 8.3.1, proceeds quite rapidly; the reaction is shown schematically in Fig. 8.3.2. Multiring thiophene-type sulfurs are more difficult to treat because the ring structure, which is attached to the sulfur on two sides, must be broken. Figure 8.3.3 is a schematic representation of the reaction for the desulfurization of dibenzothiophene.

In each case, the desulfurization reaction results in the production of hydrogen sulfide (H_2S) in the reactor section of the plant. To complete the desulfurization reaction, the H_2S must be removed in downstream fractionation.

Denitrification

The nitrogen compounds that occur naturally in crude oils and that would normally be found in the feed to a hydrotreater can be classified into two categories: *basic* nitrogen,

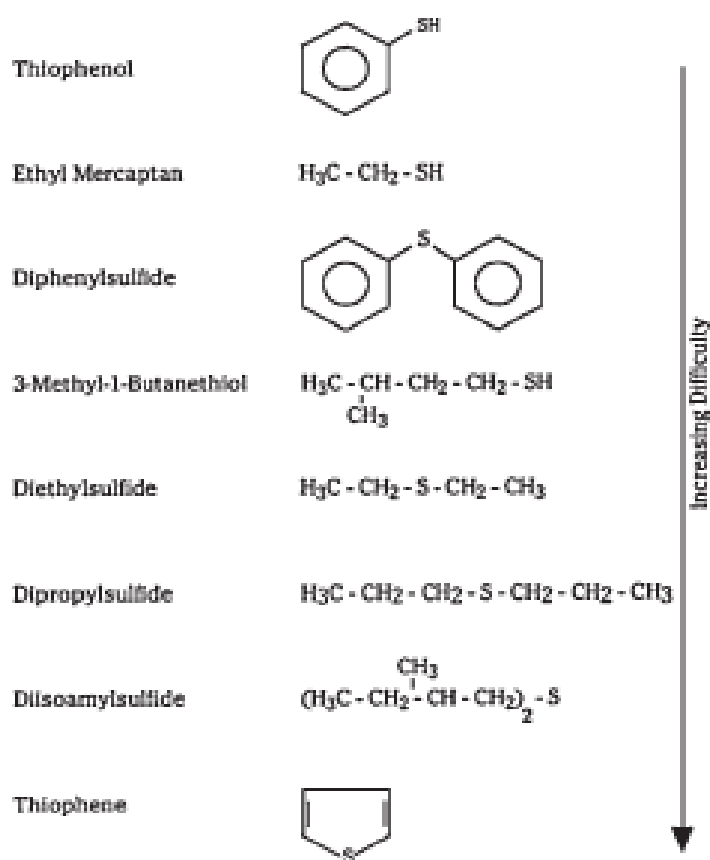


FIGURE 8.3.1 Relative desulfurization reactivities.

as silicon and lead-containing materials that are added elsewhere in the refinery. These metals are poisons to downstream processing unit and can pose environmental problems if they are contained in a fuel product that will eventually combust. In the past, refiners would operate their hydrotreating unit until the hydrotreating catalyst had no more capacity to absorb metals. In a hydrotreating unit, the reactor is loaded with a catalyst that is designed specifically to have a high capacity for metals removal if the feed metals are anticipated to be high.

CATALYST

The primary function of the catalyst used in the hydrotreating reaction is to change the rate of reactions. The suitability of a catalyst depends on a variety of factors related to the feed quality and processing objectives. The catalyst used in the UOP Unionfining processes are typically a high-surface-area base loaded with highly dispersed active metals.

For hydrodesulfurization operations, the preferred catalyst has been a cobalt molybdenum (Co/Mo) catalyst as it has a higher activity for desulfurization than nickel molybdenum (Ni/Mo) catalysts when the product sulfur level is high, that is, ~ 200 wt ppm S, meeting present-day environmental regulations. With much more stringent regulations slated to take effect within the next few years, a nickel molybdenum catalyst may be the optimal choice (see discussion of distillate unionfining for ULSD). Typical compositions of Co/Mo and Ni/Mo catalysts are shown in Table 8.3.1.

TABLE 8.3.1 Typical Composition of Unionfining Catalysts

Species	Range, wt %
CoO or NiO	1-6
MoO ₃	6-23
Al ₂ O ₃	Balance

In denitritication operations, a catalyst with a different hydrogen function is required to allow operation at normal temperatures. In these instances, the *nickel molybdenum* catalyst is more common. These catalyst are also good desulfurization catalysts; however, their hydrogen consumption could be higher because of their better denitritication activity.

Either of these catalyst provides adequate activity for the saturation of olefins. As previously mentioned, these reactions are fast and occur at temperatures lower than those required for desulfurization or denitritication.

For the saturation of aromatics, the selection of the proper catalyst is quite dependent on the processing objectives. In many cases, a nickel molybdenum catalyst provides the required level of aromatic saturation. In cases where the feed aromatics content is high or the product aromatics specification is low, UOP might suggest a catalyst that has some level of noble metal (such as platinum or palladium) to be used after the nickel molybdenum catalyst.

The metals-removal catalysts are designed specifically for the purpose of removing metals from the feed so that they do not affect the hydrotreating capability of the hydroprocessing catalyst. These catalyst typically have a different shape or pore structure or both.

than the normal hydrotreating catalyst and are often designed to have some reduced level of desulfurization or denitrification activity.

PROCESS FLOW

The actual flow scheme of the UOP Unionfining process varies, depending on the application. Figure 8.3.9 provides a generic look at the flow scheme of a UOP Unionfining unit. The feed is exchanged with the reactor effluent, mixed with recycle hydrogen, and then heated to reaction temperature in a fired heater. The combined feed then flows through the reactor, which contains the catalyst that will accelerate the reaction. The reactor effluent is cooled in exchange with the feed and then in a series of coolers before being separated in a vapor-liquid separator. The vapor portion is recompressed, combined with fresh hydrogen, and returned to the reactor feed. The liquid portion is fed to a fractionator, where it is stripped of light ends, H_2S , and NH_3 .

UNIONFINING APPLICATIONS

Generally speaking, the most common way to categorize hydrotreating applications is by feed type. This section provides general information on a limited number of Unionfining applications.

Naphtha Unionfining

The main use of the hydrotreating process in naphtha applications is in the preparation of feedstocks for the naphtha reforming unit. The reforming process requires low levels of sul-

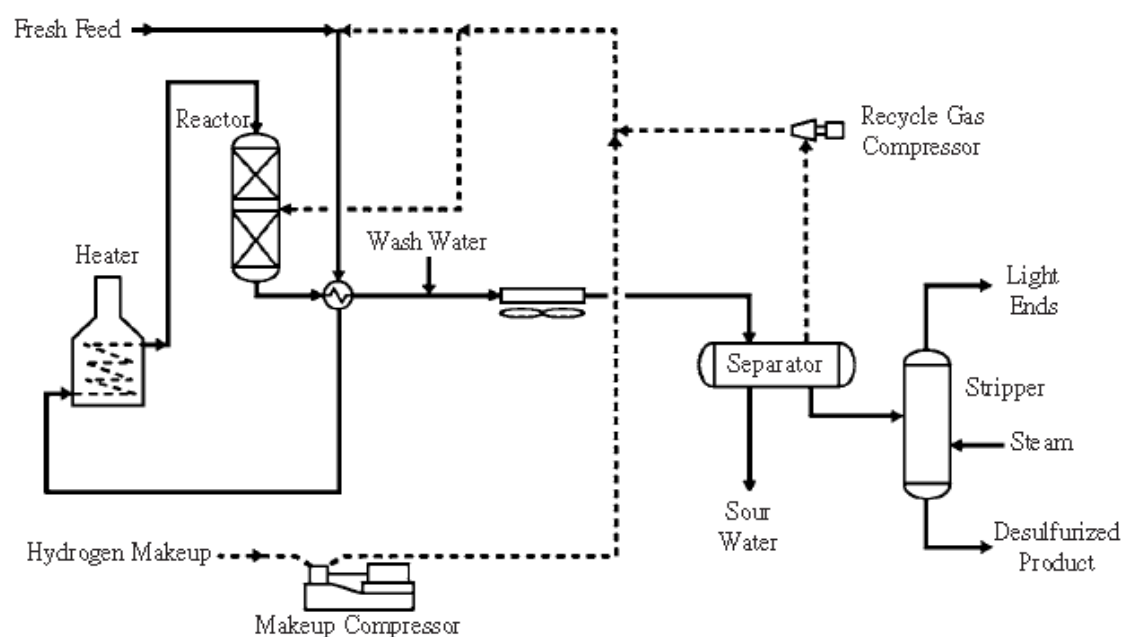


FIGURE 8.3.9 Typical Unionfining process flow.

Impact of Feedstock Quality and Processing Objectives

The ease of processing a feedstock depends on the nature of the asphaltenic molecule and the distribution of contaminants throughout the resin and asphaltene fractions. Relative processing severity is dependent on feedstock type and processing objectives (Fig. 8.4.5). Consequently, the process operates over a large range of operating conditions: 1500 to 3000 lb/in² and 0.10 to 1.0 LHSV. Feedstocks with high contaminants, such as vacuum residues, typically have higher pressures and lower space velocities.

Process Flow

A simplified flow diagram of the UOP RCD Unionfining process is presented in Fig. 8.4.6. The filtered liquid feed is combined with makeup hydrogen and recycled separator offgas and sent first to a feed-effluent exchanger and then to a direct-fired heater. In this flow scheme, the direct-fired heater is shown as a two-phase heater, but the alternative of separate feed and gas heaters is also an option. The mixed-phase heater effluent is charged to a guard bed and then to the reactor or reactors. As indicated earlier, the guard bed is loaded with a *graded bed* of catalyst to guard against unacceptable pressure drop, but this catalyst also performs some impurities removal. Removal of the remaining impurity occurs in the reactor.

The RCD Unionfining reactors use a simple downflow design, which precludes problems of catalyst carryover and consequent plugging and erosion of downstream equipment. Because this reactor system has three phases, uniform flow distribution is crucial. UOP provides special reactor internals to ensure proper flow distribution. The reactor-effluent stream flows to a hot separator to allow a rough separation of heavy liquid products, recycle gas, and lighter liquid products. The hot separator overhead is cooled and separated again to produce cold separator liquid and recycle gas, which is scrubbed to remove H₂S before being recycled. A portion of the scrubbed recycle gas is sent to membrane separation to reject light components, mainly methane, that are formed in the reactor. If these components are not removed, they could adversely affect the hydrogen partial pressure in the reactor. Hot separator liquid is fed to a hot flash drum, where the overhead is cooled and mixed with cold separator liquid, and the mixture is charged to the cold flash drum. Bottoms from both the hot and cold flash drums are charged to the unit's fractionation system, which can be set up to either yield low-sulfur fuel oil or match feed specifications for downstream processing.

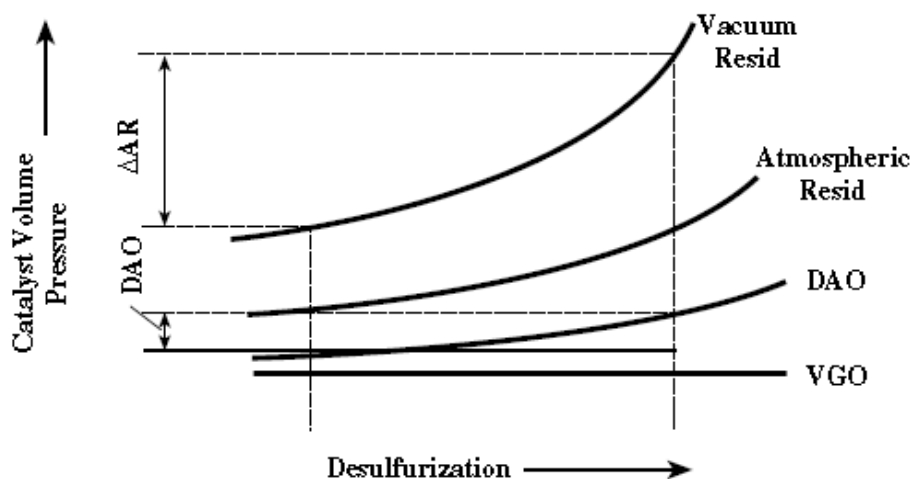


FIGURE 8.4.5 Required processing severity versus feedstock type.

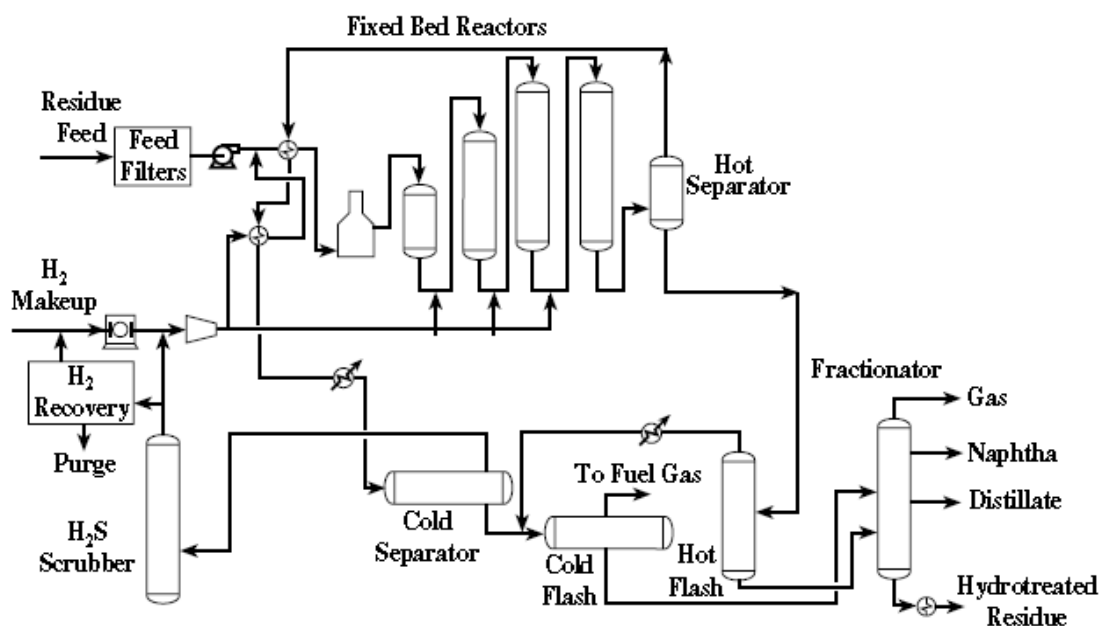


FIGURE 8.4.6 RCD Unionfining process.

Process Applications

As trends toward heavier crudes and lower fuel oil demand have become evident, UOP has devoted increased attention to bottom-of-the-barrel processing. As a result, several flow schemes that offer a variety of advantages have been developed. The most common of these flow schemes is shown in Fig. 8.4.7. Atmospheric residual oil is directly hydrotreated to provide FCC feed. Hydrotreating allows a high percentage of the crude to be catalytically cracked to gasoline while maintaining reasonable FCC catalyst consumption rates and regenerator SO_x emissions. Hydrotreating can also help refiners meet some of the newly emerging gasoline sulfur specifications in most parts of the world.

For upgrading residual oils high in metals, the best processing route may be a combination of solvent extraction (UOP/FWUSA solvent deasphalting process) and the RCD Unionfining process. The SDA process separates vacuum residual oil with a high metal content into a deasphalted oil (DAO) of relatively low metal content and a pitch of high metal content. The pitch has several uses, including fuel oil blending, solid-fuel production, and feed to a partial-oxidation unit for hydrogen production. If the metal and Conradson carbon content of the DAO are sufficiently low, it may be used directly as an FCC or hydrocracker feed component. In some cases, however, hydrotreating the DAO prior to cracking is desirable, as shown in Fig. 8.4.8. This combination of processes shows better economics than either process alone. The arrangement provides an extremely flexible processing route, because a change in feedstock can be compensated for by adjusting the ratio of DAO to pitch in the SDA unit to maintain DAO quality. In some cases, the treated material can be blended with virgin vacuum gas oil (VGO) and fed directly to the conversion unit.

When the RCD Unionfining process is used to pretreat coker feed (Fig 8.4.9), it reduces the yield of coke and increases its quality and produces a higher-quality cracking feedstock.

Of course, these examples are just a few of the bottom-of-the-barrel upgrading flow schemes involving the RCD Unionfining process. The correct selection of flow scheme is typically specific to a given refiner's needs and crude type.

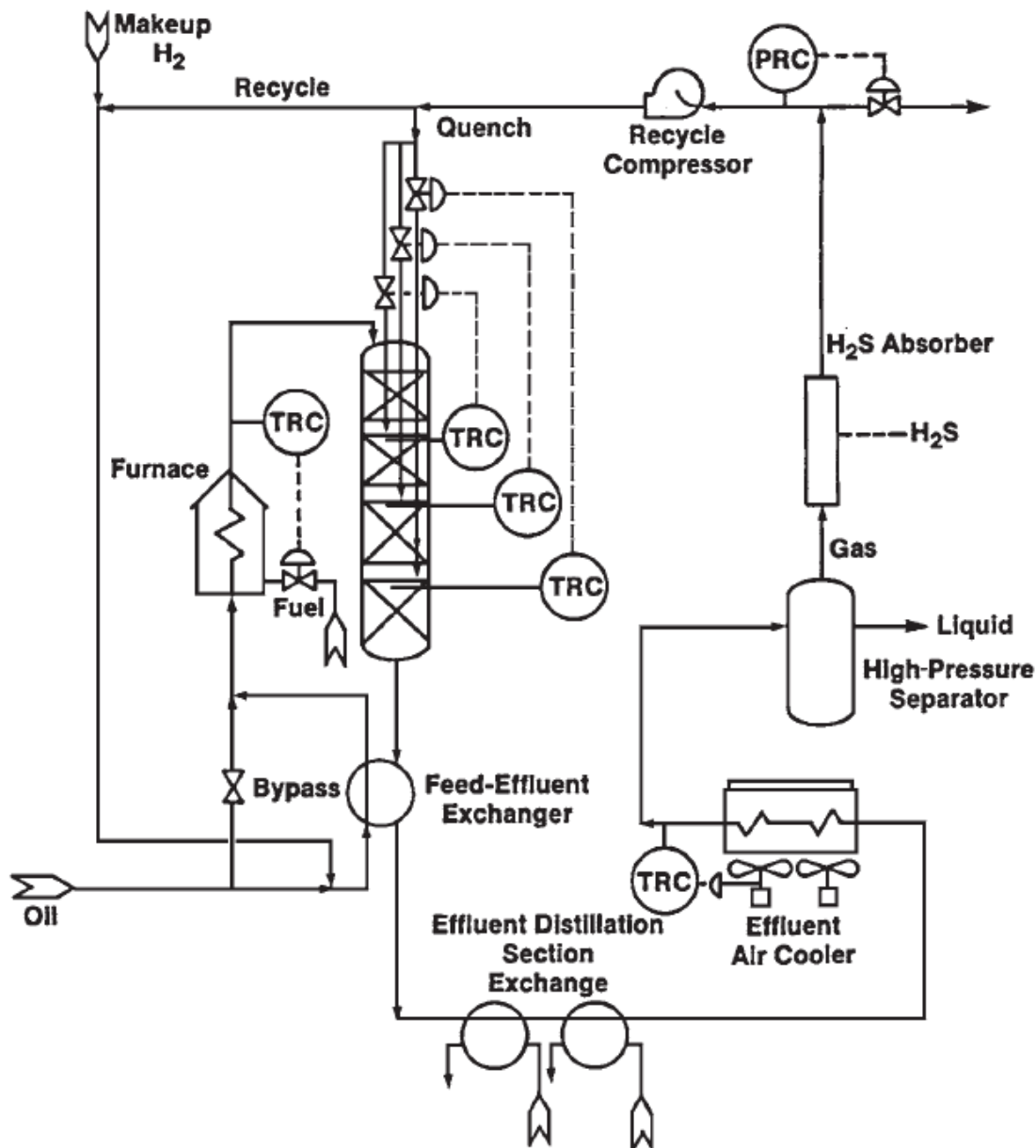


FIGURE 14.129 Control of a hydrocracker.³³

on this same feed can consume 1200 SCFB of hydrogen and make 108 volumes of C₅+ product out of 100 volumes of VGO feed. The maximum volume expansion is achieved in a recycle mode operating at an RCP of 700 to 735°F (which maximizes diesel fuel yield). More hydrogen can be consumed in a recycle hydrocracker if the RCP is dropped so that lighter products are made. An RCP of 550°F maximizes the production of jet fuel while consuming about 2000 SCFB of hydrogen. Motor gasoline yield is maximized at 380°F RCP and aromatics (via catalytic reforming) at somewhat lower RCP.

With more aromatic feedstocks, the amount of hydrogen consumed and the amount of expansion will be higher than shown. Scott, Mayer, and Meyer⁸⁹ have taken this representation even further by assuming the heavy naphtha produced by hydrocracking will usually be catalytically reformed, so that some hydrogen will be recovered. Also, the light gases produced in the hydrocracker can be used as feedstock to a hydrogen plant. Therefore they