CHAPTER THREE

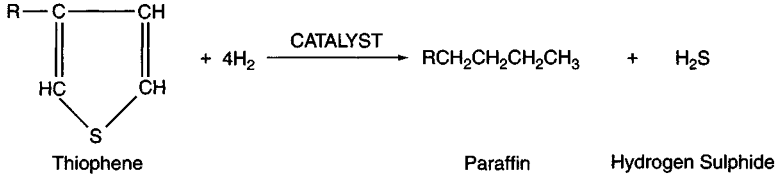
Hydrocracking Processes

Distillate hydrocracking is a refining process for conversion of heavy gas oils and heavy diesels or similar boiling-range heavy distillates into light distillates (naphtha, kerosene, diesel, etc.) or base stocks for lubricating oil manufacture. The process consists of causing feed to react with hydrogen in the presence of a catalyst under specified operating conditions: temperature, pressure, and space velocity.

HYDROCRACKING REACTIONS

DESULFURIZATION

The feedstock is desulfurized by the hydrogenation of the sulfur containing compounds to form hydrocarbon and hydrogen sulfide. The H_2S is removed from the reactor effluent leaving only the hydrocarbon product. The heat of reaction for desulfurization is about 60 Btu/scf of hydrogen consumed:



DENITRIFICATION

Nitrogen is removed from feedstock by the hydrogenation of nitrogen-containing compounds to form ammonia and hydrocarbons. Ammonia is later removed from the reactor effluent, leaving only the hydrocarbons in the product. The heat of reaction of the denitrification reactions is about

67–75 Btu/scf of hydrogen consumed, but the amount of nitrogen in the feed is generally very small, on the order of a few parts per million, and hence its contribution to overall heat of reaction is negligible:

$$R\text{-}CH_2CH_2NH_2 + H_2 \longrightarrow RCH\,CH_2CH_3 + NH_3$$

Amine Paraffin Ammonia

OLEFIN HYDROGENATION

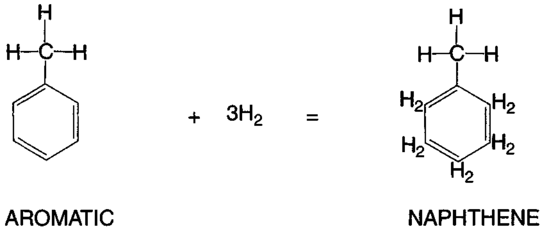
The hydrogenation of olefins is one of the most rapid reaction taking place, and therefore almost all olefins are saturated. The heat of reaction is about 140 Btu/scf of hydrogen consumed. Olefin content is generally small for straight-run products, but for stocks derived from secondary/thermal processes such as coking, visbreaking, or resid hydrocracking (H-OIL* etc.), it can contribute a considerable amount of heat liberated in the hydrocracker reactor.

$$RCH_2CH = CH_2 + H_2 = RCH_2CH_2CH_3$$

Olefin Paraffin

SATURATION OF AROMATICS

Some of the aromatics in the feed are saturated, forming naphthenes. Saturation of aromatics accounts for a significant proportion of both the hydrogen consumption and the total heat of reaction. The heat of reaction varies from 40 to 80 Btu/scf of hydrogen consumed, depending on the type of aromatics being saturated. In general, higher reactor pressure and lower temperature result in a greater degree of aromatic saturation:



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*H-OIL is a commercial processed for resid hydrocracking/resid desulfurisation, licensed by Hydrocarbon Research Inc. (USA).

HYDROCRACKING OF LARGE MOLECULES

Hydrocracking of large hydrocarbon molecules into smaller molecules occurs in nearly all processes carried out in the presence of excess hydrogen. These reactions liberate about 50 Btu/scf of hydrogen consumed. The heat released from the hydrocracking reactions contributes appreciably to the total heat liberated in the reactor. Cracking reactions involving heavy molecules contribute to lowering the specific gravity and forming light products, such as gas and light naphtha, in the hydrocracker products.

An example of a hydrocracking reaction is

$$RCH_2CH_2CH_2CH_3 + H_2 = RCH_3 + CH_3CH_2CH_3$$

The yield of light hydrocarbons is temperature dependent. Therefore, the amount of light end products produced increases significantly as the reactor temperature is increased to compensate for a decrease in catalyst activity toward the end of run conditions.

FEED SPECIFICATIONS

Hydrocracker feed is typically heavy diesel boiling above the saleable diesel range or vacuum gas oil stream originating from the crude and vacuum distillation unit, atmospheric resid desulfurizers, coker units, solvent deasphalting units, and the like. The hydrocracking catalyst is very sensitive to certain impurities, such as nitrogen and metals, and the feed must conform to the specifications laid down by the catalyst manufacturers to obtain a reasonable catalyst life.

FEED NITROGEN

Nitrogen in the feed neutralizes catalyst acidity. Higher nitrogen in the feed requires slightly more severe operating conditions, particularly the temperature, and causes more rapid catalyst deactivation.

FEED BOILING RANGE

A higher-than-designed feed distillation end point accelerates catalyst deactivation and requires higher reactor temperatures, thus decreasing catalyst life.

The feed properties have little direct effect on light product yield, but they affect the catalyst temperature required to achieve the desired conversion. The yield of light gases (C_4-) and naphtha boiling-range material is increased when the catalyst temperature is increased.

ASPHALTENES

In high cut point vacuum distillation, there is always a possibility that excessive high molecular weight, multiring aromatics (asphaltenes) can be found in vacuum gas oil distillates. In addition to causing excessive catalyst poisoning, asphaltenes may be chemically combined with the catalyst to deactivate the catalyst permanently.

METALS

Metals, particularly arsenic, and alkalies and alkaline earth deposit in the catalyst pores reduce catalyst activity. Common substances that can carry metallic catalyst contaminants include compounded lubricating oils or greases, welding fluxes, and gasketing.

Iron carried in with the feed is likely to be the most troublesome metallic catalyst contaminant. It may be chemically combined with heavy hydrocarbon molecule, or it may exist as suspended particulate matter. In either case, it not only deactivates the catalyst but also plugs the catalyst interstices such that excessive pressure drop develops. Normally, this plugging appears as a crust at the top of the first catalyst bed.

CHLORIDES

The feed may contain trace amounts of organic and inorganic chlorides, which combine with ammonia produced as a result of denitrification reactions to form very corrosive deposits in the reactor effluent exchanger and lines.

OXYGEN

Oxygenated compounds, if present in the feed, can increase deactivation of the catalyst. Also, oxygen can increase the fouling rate of the feed effluent heat exchangers.

CATALYST

Hydrocracking reactions can be divided into two groups: (1) desulfurization and denitrification—hydrogenation of polyaromatics and monoaromatics—are favored by the hydrogenating function of the catalyst (metals) and (2) hydrodealkylation, hydrodecyclization, hydrocracking, and hydroisomerization reactions are promoted by the acidic function of the catalyst (support). The support function is affected by the nitrogen content of the feed.

The catalyst employed in hydrocracking is generally of the type (Ni-Co-Fe), (Mo-W-U) on a silica/alumina support. The ratio of alumina to silica is used to control the degree of hydrocracking, hydrodealkylation, hydroisomerization, and hydrodecyclization. Cracking reactions increase with increasing silica content of the catalyst. Metals, in the form of sulfide, control the desulfurization, denitrification, and hydrogenation of olefins, aromatics, and the like.

The choice of catalyst system depends on the feedstock to be treated and the products required. Most of the time, the suitable system is obtained by the use of two or more catalysts with different acidic and hydrogenation functions. The reactor may also contain a small amount, up to 10%, of desulfurization and denitrification catalyst in the last bed of the reactor.

PROCESS CONFIGURATION

Hydrocracker units can be operated in the following possible modes: single-stage (once-through-mode) operation, single-stage operation with partial or total recycling, and two-stage operation. These operation modes are shown in Figures 3-1 and 3-2.

The choice of the process configuration is tied to the catalyst system. The main parameters to be considered are feedstock quality, the product slate and qualities required, and the investment and operating costs of the unit.

SINGLE-STAGE OPERATION

This operating mode has large effect on the product yield and quality. Single-stage operation produces about 0.3 bbl naphtha for every barrel of middle distillate. The single stage scheme is adapted for conversion of

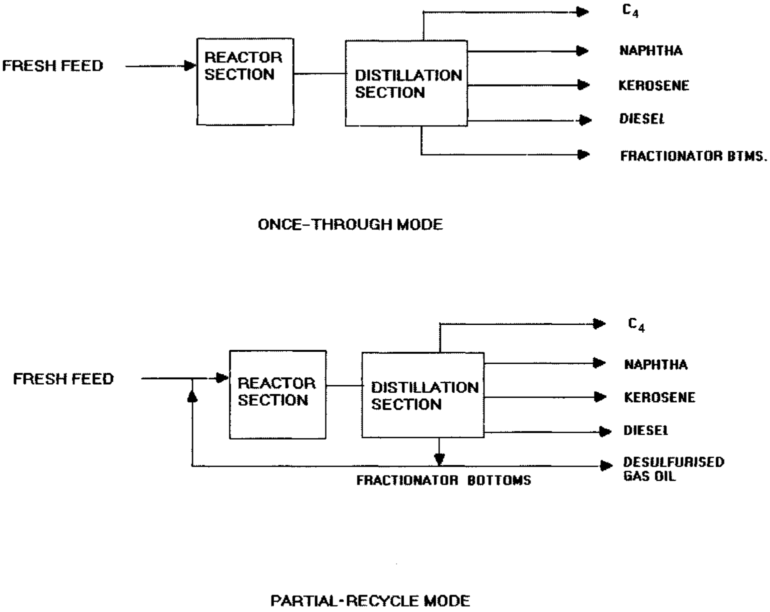

Figure 3-1. Hydrocracker operation, once-through and partial-recycle modes.

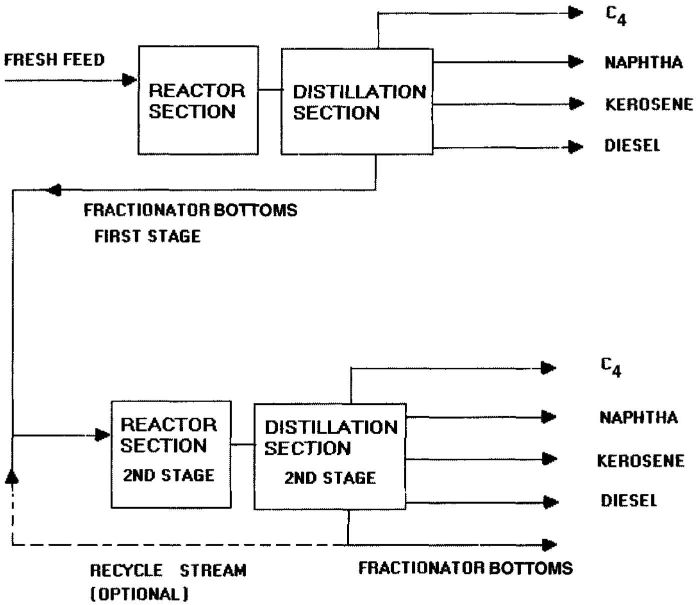

Figure 3-2. Two-stage hydrocracking process.

vacuum gas oils into middle distillate and allows for high selectivity. The conversion is typically around 50–60%. The unconverted material is low in sulfur, nitrogen, and other impurities and is used as either feed for fluid catalytic cracking units (FCCU) or a fuel oil blending component.

The single-stage process may be operated with partial or total recycling of the unconverted material. In total recycling, the yield of naphtha is approximately 0.45 bbl per barrel of middle distillate products. In these cases, the fresh feed capacity of the unit is reduced. Thus, increased conversion is achieved basically at the cost of unit's fresh feed capacity and a marginally increased utility cost. The partial recycling mode is preferable to total recycling to extinction, as the latter results in the buildup of highly refractory material in the feed to the unit, resulting in higher catalyst fouling rates.

TWO-STAGE OPERATION

In the two-stage scheme, the unconverted material from the first stage becomes feed to a second hydrocracker unit. In this case, the feed is already purified by the removal of sulfur, nitrogen, and other impurities; and the second-stage can convert a larger percentage of feed with better product quality.

A heavy gas oil feed contains some very high-boiling aromatic molecules. These are difficult to crack and, in feed recycling operation, tend to concentrate in the recycle itself. High concentration of these molecules increase the catalyst fouling rate. In a two-stage operation, the first stage is a once-through operation; hence, the aromatic molecules get no chance to concentrate, since there is no recycle. The first stage also reduces the concentration of these molecules in the feed to the second stage; therefore, the second stage also sees lower concentration of these high-boiling aromatic molecules.

The two-stage operation produces less light gases and consumes less hydrogen per barrel of feed. Generally, the best product qualities (lowest mercaptans, highest smoke point, and lowest pour point) are produced from the second stage of the two-stage process. The poorest qualities are from the first stage. The combined product from the two stages is similar to that from a single stage with recycling for the same feed quality.

The two-stage scheme allows more flexible adjustment of operating conditions, and the distribution between the naphtha and middle distillate is more flexible. Compared to partial and total recycling schemes, the two-stage scheme requires a higher investment but is overall more economical.

PROCESS FLOW SCHEME

The oil feed to the reactor section consists of two or more streams (see Figure 3-3). One stream is a vacuum gas oil (VGO) feed from the storage tank and the other stream may be the VGO direct from the vacuum distillation unit. Also, there may be an optional recycling stream consisting of unconverted material from fractionator bottom. The combined feed is filtered in filters F-01 to remove most of the particulate matter that could plug the catalyst beds and cause pressure drop problems in the reactor. After the oil has passed through surge drum V-02, it is pumped to the reactor system pressure by feed pump P-01.

Hydrogen-rich recycled gas from the recycling compressor is combined with oil feed upstream of effluent/feed exchangers E-01/02. The oil gas stream than flows through the tube side of exchanger 02A and 02B, where it is heated by exchange with hot reactor effluent. Downstream of the feed effluent exchangers, the mixture is further heated in parallel passes through reactor feed heater H-01. The reactor inlet temperature is controlled by the Temperature Recorder and Controller (TRC) by controlling the burner fuel flow to the furnace.

A portion of the oil feed is by passed around the feed effluent exchanger. This bypass reduces the exchanger duty while maintaining the duty of reactor feed heater H-01 at a level high enough for good control of reactor inlet temperature. For good control, a minimum of 50–75°F temperature rise across the heater is required.

Makeup hydrogen is heated on the tube side of exchanger E-01 by the reactor effluent. This makeup hydrogen then flows to the reactor.

Hydrocracker reactor V-01 is generally a bottle-type reactor. The makeup hydrogen after preheating in exchangers E-01 flows up through the reactor in the annular space between the reactor outside shell and an inside bottle. The hydrogen acts as a purge to prevent H_2S from accumulating in the annular space between the bottle and outside shell. It also insulates the reactor shell.

After the makeup hydrogen has passed upward through the reactor, it combines with the recycled gas and the heated oil feed from the feed heater in the top head of the reactor. The hot, vaporized reaction mixture then passes down the reactor. Cold quenching gas from the recycling compressor is injected to the reactor between the catalyst beds to limit the temperature rise produced by exothermic reactions.

The reactor is divided among a number of unequal catalyst beds. This is done to give approximately the same temperature rise in each catalyst

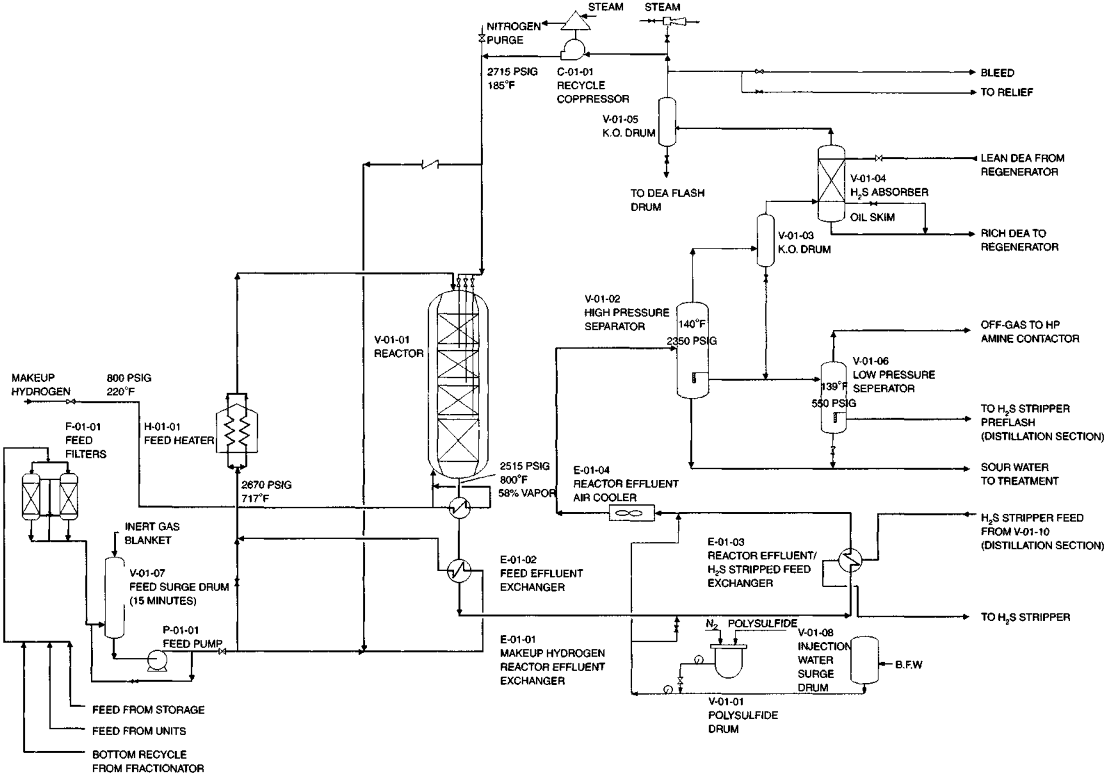

Figure 3-3. Distillate hydrocracker (reactor section). K.O. = knockout.

bed and limit the temperature rise to 50°F. Thus, the first and second beds may contain 10 and 15% of the total catalyst, while the third and fourth beds contain 30 and 45% of the total catalyst.

Reactor internals are provided between the catalyst beds to ensure thorough mixing of the reactants with quench and ensure good distribution of vapor and liquid flowing to each bed. Good distribution of reactants is of utmost importance to prevent hot spots and maximize catalyst life.

Directly under the reactor inlet nozzle is a feed distributor cone inside a screened inlet basket. These internal elements initiate feed stream distribution and catch debris entering the reactor. Below the inlet basket, the feed stream passes through a perforated plate and distributor tray for further distribution before entering the first catalyst bed.

Interbed internal equipment consists of the following:

- A catalyst support grid, which supports the catalyst in the first bed, covered with a wire screen.
- A quench ring, which disperses quenching gas into hot reactants from the bed above.
- A perforated plate for gross distribution of quenched reaction mixture.
- A distribution tray for final distribution of quenched reaction mixture before it enters the next catalyst bed.
- A catalyst drain pipe, which passes through interbed elements and connects each catalyst bed with the one below it.

To unload the catalyst charge, the catalyst from the bottom bed is drained through a catalyst drain nozzle, provided in the bottom head of the reactor. Each bed then drains into the next lower bed through the bed drain pipe, so that nearly all the catalyst charge can be removed with a minimum of effort.

Differential pressure indicators are provided to continuously measure pressure drop across top reactor beds and the entire reactor.

The reactor is provided with thermocouples located to allow observation of catalyst temperature both axially and circumferentially. Thermocouples are located at the top and bottom of each bed. The temperature measured at the same elevation but different circumferential positions in the bed indicate the location and extent of channeling through the beds.

EFFLUENT COOLING

The reactor effluent is at 800–850°F, start of run (SOR) to end of run (EOR), at reactor outlet. The reactor effluent is cooled in makeup hydrogen/reactor effluent exchanger E-01 and reactor effluent/H_2S stripper feed exchanger E-03. The reactor effluent is further cooled in reactor effluent/air cooler E-04 to about 140°F.

WATER AND POLYSULFIDE INJECTION

Condensate is injected into the reactor effluent just upstream of effluent air cooler. The function of the injection water is to remove ammonia and some H_2S from the effluent. The effluent temperature at the injection point is controlled to prevent total vaporization of the injected water and preclude deposition of solid ammonium bisulfide.

Trace amounts of cyanide ion in the reactor effluent contribute to corrosion in the effluent air cooler. A corrosion inhibitor such as sodium polysulfide is also injected to prevent cyanide corrosion.

HIGH-PRESSURE SEPARATOR

The high-pressure separator, V-02, temperature is controlled at approximately 140°F by a temperature controller, which adjusts the pitch of half the fans of the air cooler. The temperature of the separator is closely controlled to keep the downstream H_2S absorber temperature from fluctuating. The hydrogen purity is lower at higher temperatures. However, at lower temperature, poor oil/water separation occur in the separator drum.

LOW-TEMPERATURE SEPARATOR

The high-temperature separator liquid is depressurized through a HP separator level control valve to 550 psig and flashed again to low-pressure separator V-06. The low-pressure separator overhead vapors flow to high-pressure amine contractor V-04. The hydrocarbon stream leaving the separator is fed to H_2S stripper V-11 via a stripper preflash drum. The sour water drawn from the low-pressure separator is sent to sour water treating facilities.

RECYCLE GAS ABSORBER

DEA (diethanolamine) absorption is used to remove H_2S from the recycled gas in recycle gas absorber V-04. H_2S gas is absorbed by the DEA solution because of the chemical reaction of DEA with H_2S. Typical properties of DEA are shown in Table 8-19.

The amount of H_2S that can react depends on the operating conditions. The low temperature, high pressure, and high H_2S concentration in the H_2S absorber favor the reaction. In the DEA regeneration facilities, high temperature and low pressure are used to reverse the reaction and strip H_2S from the DEA solution.

About 90% of the H_2S formed by the desulfurization reactions is removed from the recycled gas in a high-pressure absorber by scrubbing the gas with aqueous diethanolamine solution. The absorber is a vertical vessel packed with stainless steel ballast rings. Recycled gas flows through a support plate and upward through the packing. A lean DEA solution from the DEA regenerator enters the top of the absorber through an inlet distributor and flows downward through the packing. Rich DEA from the bottom of the absorber is sent to the H_2S recovery unit.

RECYCLE GAS COMPRESSOR

Recycled gas is circulated by recycle gas compressor C-01, driven by a steam turbine. The largest portion of the recycled gas stream joins the oil feed stream upstream of feed effluent exchangers. A portion of the gas stream from the recycling compressor flows on temperature control to interbed quenching.

DISTILLATION SECTION

The purpose of distillation section (see Figure 3-4) is to remove H_2S and light ends from the first-stage reactor effluent and fractionate the remaining effluent into naphtha, kerosene, and diesel cuts. The bottom stream is either fed to the second stage of the hydrocracker, recycled to extinction with the fresh feed, or withdrawn as product.

Hydrocarbon liquid flows to H_2S stripper V-11 from stripper preflash drum V-10. The preflash drum removes some of the light ends and H_2S from the low-pressure separator oil before it is stripped and fractionated. The stripper column contains packed sections below the feed plate and two sieve trays above the feed inlet. Stripping is achieved with steam,

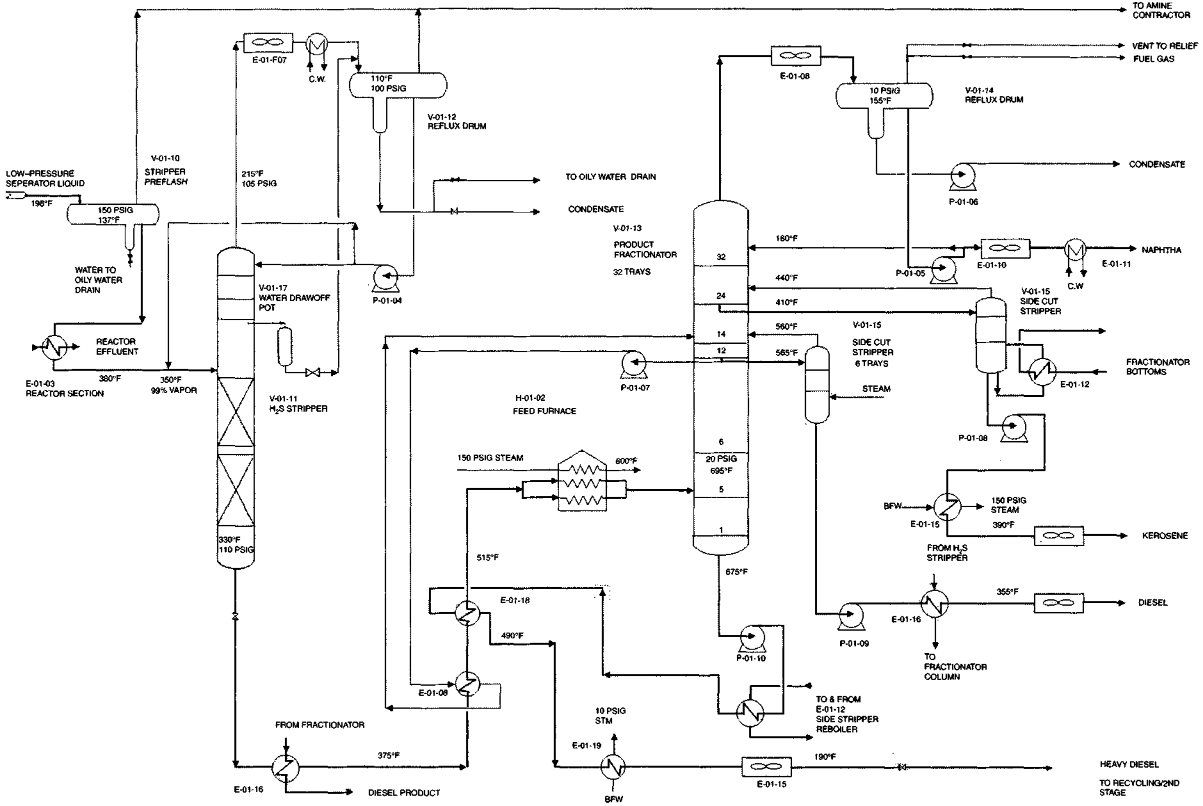

Figure 3-4. Distillate hydrocracker (distillation section).

which removes H_2S and light ends. The stripper overhead vapor is partially condensed in air cooler E-07 and a trim water cooler then flashed in reflux drum V-12. The sour gas from the reflux drum is sent to a low-pressure amine contactor. The condensed hydrocarbon liquid is refluxed back to the stripper. H_2S stripper bottoms are sent to product fractionator V-13 after heat exchange with diesel in E-16, circulating reflux in E-18, and fractionator bottoms in E-18. The fractionator feed is then brought to column temperature by heating in the feed heater H-02. After heating, the partially vaporized fractionator feed is introduced into the flash zone of product fractionator V-12. In the flash zone, the vapor and liquid separate. The vapor passes up through the rectifying section, containing approximately 27 trays.

Heat is removed from the fractionator column in the overhead condenser and in a circulating reflux heat removal system. Vapor leaving the top tray of the column is condensed in overhead condensers. The condensed overhead vapor is separated into hydrocarbon and water phases. Part of the hydrocarbon is recovered as overhead product, and the rest is sent back to the column as reflux to ensure good separation.

The portion of the column below the flash zone contains five trays. Superheated steam is injected below the bottom tray. As the steam passes up through the stripping section, it strips light components from the residual liquid from the flash zone.

OPERATING CONDITIONS

The operating conditions for single-stage hydrocracking are shown in Table 3-1. The yields and qualities for once-through operation, two-stage hydrocracking, and one-stage operation with partial recycling of unconverted material are shown in Tables 3-2 to 3-5. It must be stressed that the yields depend on the catalyst composition and process configuration employed, and these can vary significantly.

TEMPERATURE

The typical hydrocracker reactor operates between 775–825°F and 2600 psig reactor inlet pressure. The high temperatures are necessary for the catalyst to hydrocrack the feed. The high reactor pressure is

Table 3-1
Single-Stage Hydrocracker Operating Conditions

OPERATING PARAMETERS	UNITS	
CATALYST AVERAGE TEMPERATURE	°F	775
SPACE VELOCITY, LHSV	hr^{-1}	1.72
REACTOR INLET PRESSURE	psig	2600
REACTOR PRESSURE DROP	psi	50
HYDROGEN PARTIAL PRESSURE, INLET	psi	2000
HYDROGEN CHEMICAL CONSUMPTION	scf/bbl	1150
MAKEUP + RECYCLE AT REACTOR INLET, SOR	scf/bbl	5000
MAKEUP H_2 PURITY	VOL%	95
HP SEPARATOR TEMPERATURE	°F	140
HP SEPARATOR PRESSURE, SOR	psig	2415
BLEED RATE, SOR (100% H_2)	scf/bbl	200
RECYCLE COMPRESSOR SUCTION PRESSURE	psig	2390
RECYCLE COMPRESSOR DISCHARGE PRESSURE	psig	2715

necessary for catalyst life. Higher hydrogen partial pressure increases catalyst life. To keep the hydrogen partial pressure at a high level, high reactor pressure and high hydrogen content of the reactor feed are necessary. To accomplish this, an excess of hydrogen gas is recycled through the reactor. A makeup hydrogen stream provides hydrogen to replace the hydrogen consumed chemically in hydrocracking, olefin, aromatics saturation, and the hydrogen lost to atmosphere through purge or dissolved in oil. A cold hydrogen-rich gas is injected between the catalyst beds in the reactor to limit the temperature rise caused by exothermic hydrocracking reactions.

In the hydrocracking process, the feed rate, operating pressure, and recycle gas rate are normally held constant. The reactor temperature is the only remaining variable requiring close control to achieve the required liquid feed conversion.

As the catalyst activity declines with time on stream due to catalyst fouling, it becomes necessary to increase the reactor temperature to maintain the original liquid feed conversion rate. This rate of increase of reaction temperature with time is called the *fouling rate*. Additional temperature variation may be required to compensate for changes in reactor feed rate or feed properties, gas/oil ratio, hydrogen partial pressure, and the like (see Figure 3-5).

Table 3-2
Hydrocracker Feed and Product Qualities

PROPERTY	FEED	LIGHT NAPHTHA	HEAVY NAPHTHA	KEROSENE	DIESEL
SINGLE-STAGE OPERATION					
API	22.6	80	53	38	34
ANILINE POINT °F	174		106	124	176
ASTM	D-1160	D-86	D-86	D-86	D-86
IBP/5	590/-	110/-	215/-	350/-	440/-
10/30	715/790	115/125	225/245	375/410	545/590
50	840	135	260	445	610
70/90	885/940	150/170	270/290	475/515	640/685
95/FBP	960/1010	-/195	-/325	-/550	-/725
COMPOSITION, LV%					
PARAFFINS	16	76	30	20	26
NAPHTHENES	22	20	54	55	49
AROMATICS	62	4	16	25	25
SULFUR, ppmw	25000		<10	<10	10
MERCAPTANS, ppm			<5	<5	
NITROGEN, ppmw	970		1	1	5
SMOKE POINT mm				15	
FREEZE POINT °F				−50	
POUR POINT °F	75			−80	20
CLOUD POINT °F				−55	25
DIESEL INDEX				47	60
OCTANE CLEAR		76	61		
VISCOSITY, CST, 100°F	59			2	9

Table 3-2
Continued

PROPERTY	FEED	LIGHT NAPHTHA	HEAVY NAPHTHA	KEROSENE	DIESEL
SINGLE-STAGE WITH RECYCLE					
API	20.9	80	56	42.2	38
ANILINE POINT °F	175		124	148	193
ASTM	D-1160	D-86	D-86	D-86	D-86
IBP/5	740/760	110/-	195/-	330/-	485/-
10/30	775/835	115/125	215/230	350/390	560/585
50	875	135	250	420	600
70/90	915/975	150/170	265/290	460/520	620/655
95/FBP	975/1035	-/195	-/320	-/550	/705
COMPOSITION, LV%					
PARAFFINS		77	45	38	48
NAPHTHENES		21	47	45	43
AROMATICS		2	8	17	9
SULFUR, ppmw	31000	<5	10	6	8
MERCAPTANS, ppm					
NITROGEN, ppmw	1050		1	2	1.5
SMOKE POINT, mm				22	
CETANE NUMBER					68
FREEZE POINT °F				−50	
POUR POINT °F	90			−65	5
CLOUD POINT °F					
DIESEL INDEX					73.2
OCTANE CLEAR		80	54		

TWO-STAGE OPERATION

API	81	56	43	40	37
ANILINE POINT °F		126	147	169	190
ASTM D-86					
IBP/5	110/-	210/-	345/365	375/400	460/520
10/30	115/125	225/240	375/410	415/475	545/590
50	135	255	446	540	610
70/90	150/170	270/295	475/515	595/655	635/675
95/FBP	-/195	305/325	530/550	675/700	695/720
COMPOSITION, LV%					
PARAFFINS	83	43	35	39	42
NAPHTHENES	15	49	50	46	42
AROMATICS	2	8	15	15	16
SULFUR, ppmw	<5	<5	<5	<5	6
MERCAPTANS, ppm	<5	<5	<5	<5	
NITROGEN, ppmw			<1	2	3
SMOKE POINT, mm			20		
FREEZE POINT °F			−54		
POUR POINT °F			−70	−15	10
CLOUD POINT °F			−65	−10	15
DIESEL INDEX			63	68	70
OCTANE CLEAR	75	54			
VISCOSITY, CST, 100°F			2	4	8

Table 3-3
Distillate Hydrocracker Yields

STREAM	ONCE THROUGH	PARTIAL RECYCLE	TWO-STAGE OVERALL
VGO FEED	1.0000	1.0000	1.0000
HYDROGEN	0.0225	0.0293	0.0345
TOTAL FEED	1.0225	1.0293	0.0345
GASES	0.0166	0.0257	0.0391
HP GAS	0.0070	0.0069	0.0127
ACID GAS	0.0216	0.0243	0.0221
CRACKED NAPHTHA	0.0969	0.1637	0.2132
KEROSENE	0.1372	0.1861	0.2636
DIESEL	0.2961	0.3955	0.4365
HEAVY DIESEL (ONCE-THROUGH MODE)	0.4471		
HEAVY DIESEL (PARTIAL-RECYCLE MODE)		0.2271	
BLEED FROM SECOND STAGE			0.0473
TOTAL PRODUCTS	1.0225	1.0293	1.0345

NOTE: ALL FIGURES ON W/W BASIS. W/W = WEIGHT/WEIGHT BASIS.

Table 3-4
Utility Consumption *(per Ton Feed)*

UTILITY	UNITS	SINGLE STAGE	PARTIAL RECYCLE MODE
FUEL GAS	mmBtu	0.6	0.76
POWER	kWhr	18	23
STEAM	mmBtu	0.12	0.15
DISTILLED WATER	MIG*	0.016	0.02
COOLING WATER	MIG*	0.33	0.42

*MIG = 1000 IMPERIAL GALLONS.

Table 3-5
Mild Hydrocracker Operating Conditions

OPERATING PARAMETERS	UNITS	
CATALYST AVERAGE TEMPERATURE	°F	775
SPACE VELOCITY, LHSV	hr^{-1}	1.4
REACTOR INLET PRESSURE	psig	1051
REACTOR PRESSURE DROP	psi	38
HYDROGEN PARTIAL PRESSURE, INLET	psi	749
HYDROGEN CHEMICAL CONSUMPTION	scf/bbl	358
MAKEUP + RECYCLE AT REACTOR INLET, SOR	scf/bbl	2766
MAKEUP H_2 PURITY	VOL%	92
HP SEPARATOR TEMPERATURE	°F	140
HP SEPARATOR PRESSURE, SOR	psig	850
BLEED RATE, SOR (100% H_2)	scf/bbl	10.5
RECYCLE COMPRESSOR SUCTION PRESSURE	psig	820
RECYCLE COMPRESSOR DISCHARGE PRESSURE	psig	1070
LEAN DEA TEMPERATURE	°F	150

CATALYST AVERAGE TEMPERATURE

The catalyst average temperature (CAT) is determined by the following equation:

$$\mathrm{CAT} = \left[A_1 \times \left[\frac{(T_I + T_O)}{2}\right] \text{top bed} + A_2 \times \left[\frac{(T_I + T_O)}{2}\right] \text{second bed}\right.$$

$$\left. + A_3 \times \left[\frac{(T_I + T_O)}{2}\right] \text{third bed} + A_4 \times \left[\frac{(T_I + T_O)}{2}\right] \text{fourth bed} + \cdots\right]$$

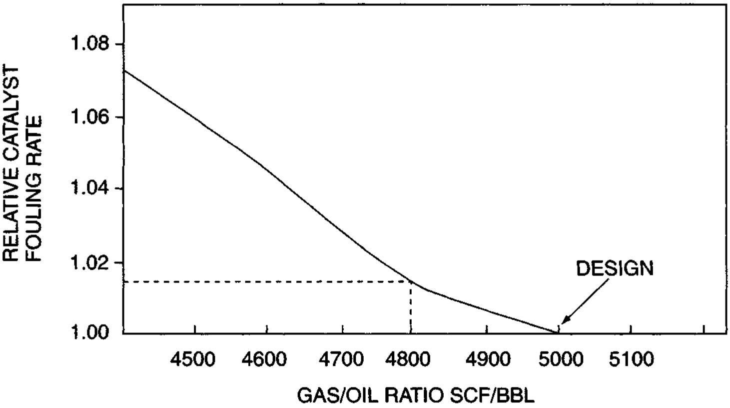

Figure 3-5. The effect of the gas/oil ratio on the catalyst fouling rate.

where T_1 is the bed inlet temperature; T_0 is the bed outlet temperature; and A_1, A_2, A_3, and A_4 are the volume fractions of the total reactor catalyst in the individual bed. A typical hydrocracker reactor temperature profile is shown in Figure 3-6.

CATALYST FOULING RATE

The design of a hydrocracker unit is based on a specified conversion rate of the feed and a specified catalyst life, usually 2–3 years between catalyst regeneration. During the course of the run, the activity of the catalyst declines due to coke and metal deposits, and to maintain the design conversion rate, the temperature of the catalyst has to be increased. The catalyst manufacturers specify a maximum temperature, called the *end of run* temperature, which signifies the EOR condition. When this temperature is reached, the catalyst must be regenerated or discarded.

The rate of increase in average reactor catalyst temperature (to maintain the design conversion rate) with time is called the *catalyst fouling rate*. It is an important parameter, used to make an estimate of time when the EOR conditions are likely to be reached. The refinery keeps a record of the reactor average temperature with time, starting from the day the feed is introduced into the reactor after the new catalyst has been loaded. A graph is drawn between the time on stream vs. the average reactor temperature (Figure 3-7). The data may show scatter, so a straight line is drawn through the data. From this curve, an estimate of the catalyst fouling rate and remaining life of the catalyst can be estimated.

BED 1

IN	TI-151	778	AVG. 776	REACTOR AVG. BED ΔT 18°F
	TI-152	770		
	TI-153	781		
OUT	TI-154	793	AVG. 794	
	TI-155	794		
	TI-156	795		

QUENCH BED 2 = MMSCFD

BED 2

IN	TI-157	770	AVG. 774	REACTOR AVG. BED ΔT 24°F
	TI-158	780		
	TI-159	771		
OUT	TI-160	799	AVG. 798	
	TI-161	796		
	TI-162	799		

QUENCH BED 3 = 18.7 MMSCFD

BED 3

IN	TI-163	770	AVG. 774	REACTOR AVG. BED ΔT 20°F
	TI-164	776		
	TI-165	775		
OUT	TI-166	797	AVG. 794	
	TI-167	799		
	TI-168	801		

QUENCH BED 4 = 18.7 MMSCFD

BED 4

IN	TI-169	774	AVG. 775	REACTOR AVG. BED ΔT 20°F
	TI-170	771		
	TI-171	779		
UPPER MID	TI-172	795	AVG. 796	
	TI-173	786		
	TI-174	787		
LOWER MID	TI-175	795	AVG. 795	
	TI-176	792		
	TI-177	798		

DESULFURAZATION BED

OUT	TI-178	799	AVG. 803	BED ΔT 20°F
	TI-179	802		
	TI-180	805		

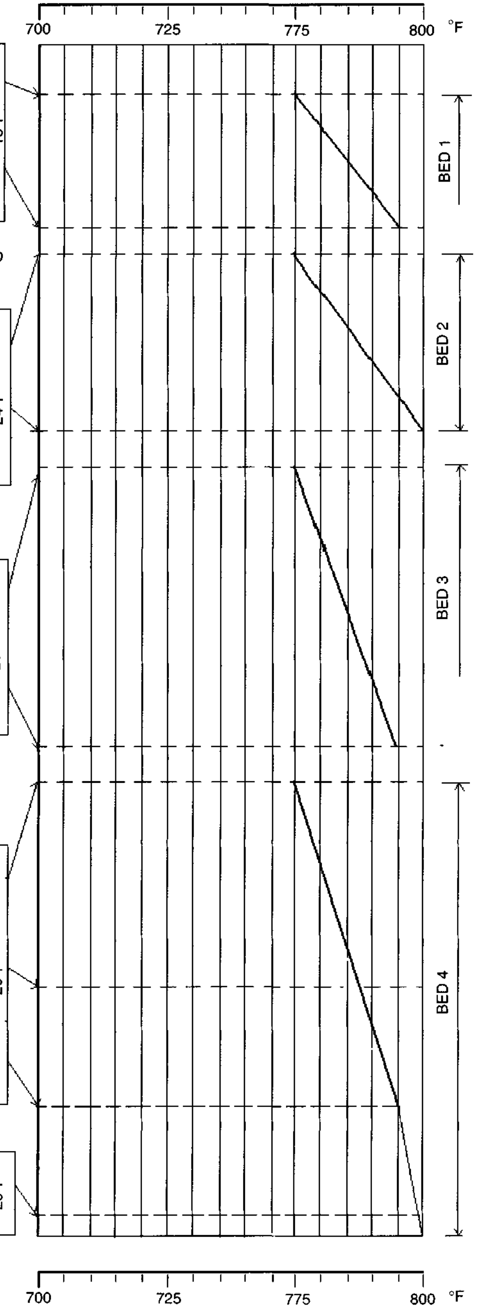

Figure 3-6. Hydrocracker reactor temperature profile.

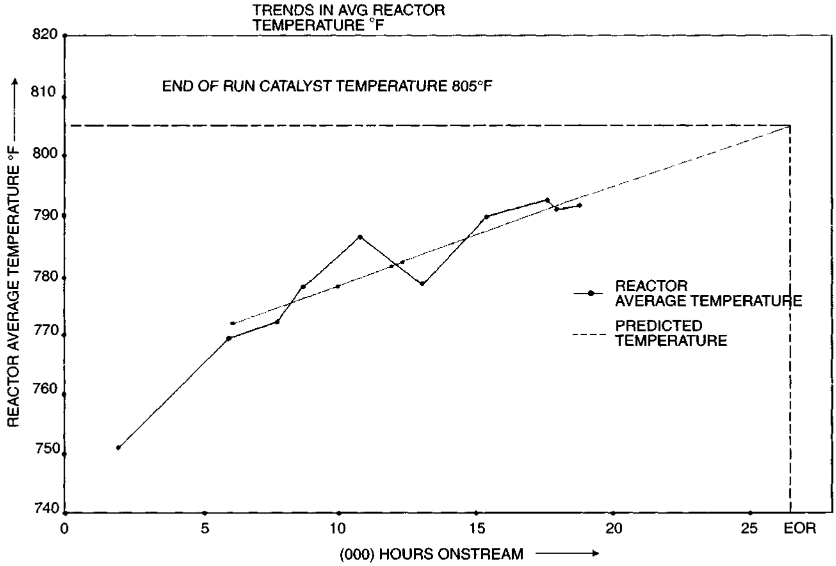

Figure 3-7. Estimating the remaining catalyst life.

EXAMPLE 3-1

The design start of run (SOR) temperature of a hydrocracker reactor is 775°F. After the unit is onstream for 12,000 hours, the CAT (weighted average bed temperature) is 800°F. Estimate the remaining life of the catalyst if the design EOR temperature of the catalyst is 805°F:

$$\text{Catalyst fouling rate} = \frac{(800 - 775)}{12{,}000}$$

$$= 0.00208°\text{F/hr}$$

$$\text{Remaining life} = \frac{(805 - 800)}{0.00208}$$

$$= 2404 \text{ hr or } 3.33 \text{ months}$$

HYDROGEN PARTIAL PRESSURE

The factors affecting hydrogen partial pressure in the hydrocracker reactor are

1. Total system pressure.
2. Makeup hydrogen purity.
3. Recycle gas rate.
4. HP gas bleed rate.
5. HP separator temperature.

Hydrogen partial pressure in the hydrocracker reactor is a basic operating parameter that provides the driving force for hydrocracking reactions. Also, the hydrogen partial pressure has an important effect on the catalyst fouling rate (Figure 3-8). An increase in the hydrogen partial pressure serve to suppress the catalyst fouling rate. In an operating unit, the hydrogen partial pressure is maximized to operate the unit at the lowest possible temperature. This increases the run length and minimize light ends production.

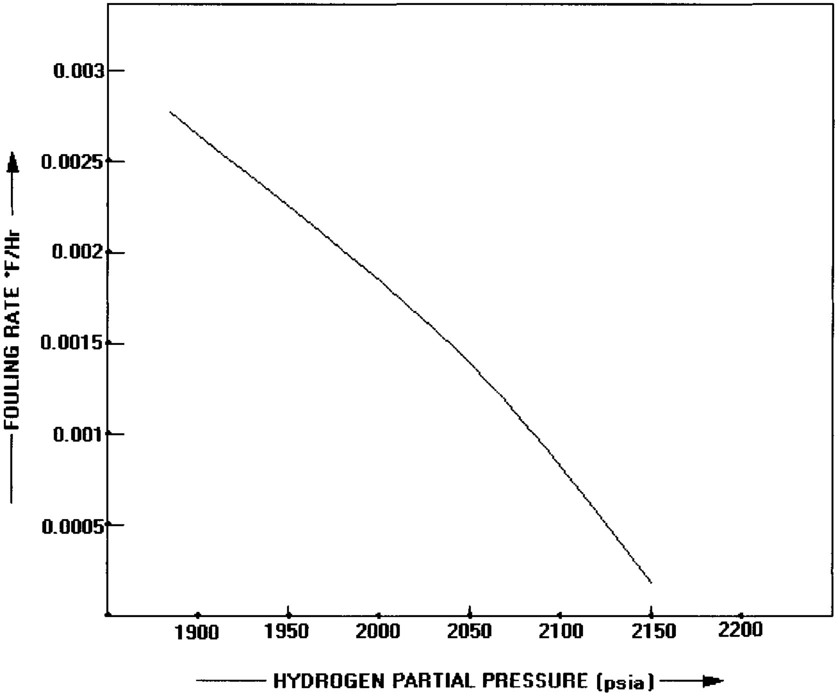

Figure 3-8. Effect of H_2 partial pressure on catalyst fouling rate (schematic).

FEED RATE

Increasing the feed rate requires an increase in average catalyst temperature to maintain the required feed rate conversion. The increased feed rate also causes an increase in the catalyst fouling rate and the hydrogen consumed chemically and dissolved in the high-pressure separator liquid. The effect of the feed rate on the catalyst fouling rate is shown in Figure 3-9.

FEED CHARACTERIZATION

A heavier feed, as characterized by the ASTM D1160 weighted boiling point, requires an increase in average catalyst temperature to maintain the desired level of feed conversion. An increase in the catalyst fouling rate also occurs. Further, a feed having a higher end point for a given weighted boiling point requires an increased temperature for desired conversion over that required by a lower-end point feed.

LIQUID FEED CONVERSION

The following equation shows how to determine liquid feed conversion:

$$\text{Conversion rate} = \frac{(\text{reactor liquid feed rate} - \text{fractionator bottom rate})}{\text{reactor liquid feed rate}}$$

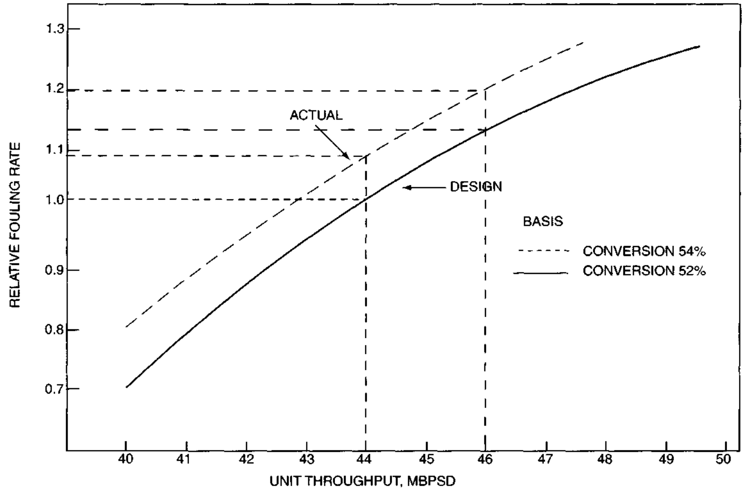

Figure 3-9. The effect of the feed rate on the catalyst fouling rate (schematic).

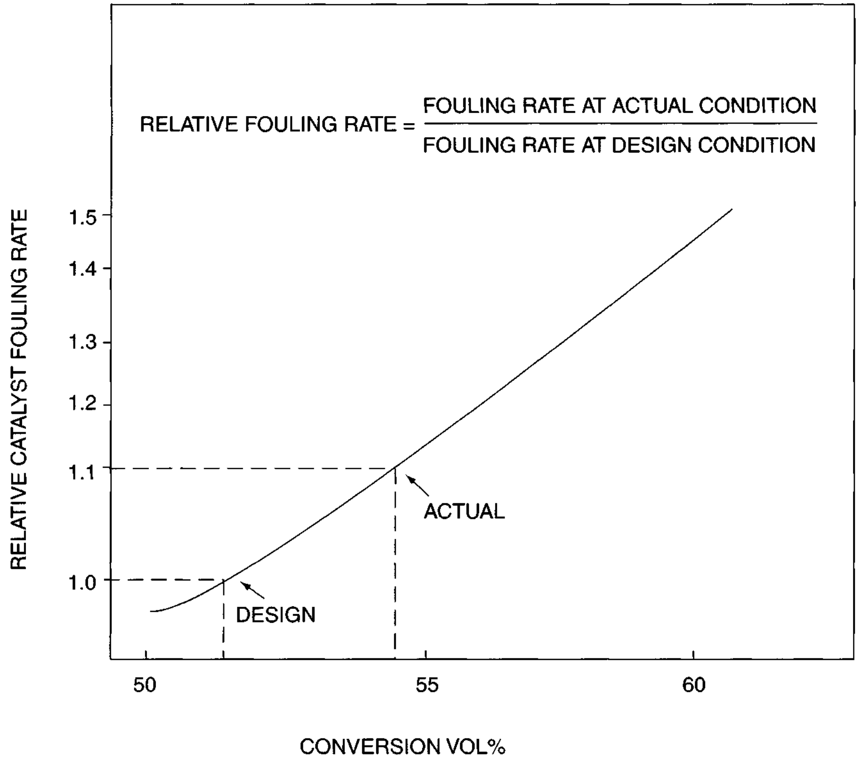

Figure 3-10. The effect of conversion on the catalyst fouling rate (schematic).

The liquid feed conversion depends strongly on temperature dependent and, as such, has a direct effect on the catalyst fouling rate (Figure 3-10).

GAS BLEED RATE

Bleeding minimizes the buildup of light hydrocarbons in the recycling gas, which lowers hydrogen partial pressure. Increasing the gas bleed rate lowers the light hydrocarbon concentration in the recycling gas and increases the hydrogen partial pressure. Decreasing the bleed rate allows light hydrocarbons in the recycle gas to build up to higher concentrations and thus lower hydrogen concentration. The bleed rate is typically kept at about 20% of the hydrogen chemical consumption.

CATALYST SULFIDING AND UNIT STARTUP

The catalyst is sulfided during startup. Before initiating the sulfiding, the distillation and the amine absorber are put into operation.

Sulfiding is the injection of a sulfur-containing chemical such as dimethyl sulfide into the hot circulating gas stream prior to the introduction of liquid feed. The chemical injection is performed with a chemical injection pump from a storage drum under an inert gas blanket. The reactor is first evacuated to 24–26 in. mercury to remove all air, tested for leaks, and purged with nitrogen a number of times.

The furnace is next purged and fired, and the reactor is heated to 450°F. When the reactor is ready for sulfiding, the reactor inlet temperature is increased to 500–525°F. When the catalyst temperature reaches 500–525° at the top bed, this temperature is held until the temperature is at least 500° at the inlet and about 450° at reactor outlet.

The feed heater fire is reduced. With recycle compressor operating, the reactor pressure is adjusted to about 300 psi. At 300 psig, the hydrogen is introduced slowly, through the makeup compressor and pressure increased to 700 psig at reactor inlet.

Sulfiding chemical or sour gas injection is then added into gas stream at the reactor inlet, at a rate equivalent to 0.5 mol% but no more than 1.0 mol% H_2S.

Addition of a sulfiding agent causes two temperature rises in the reactor, first due to reaction of hydrogen with the sulfiding chemical to form H_2S, which occurs at the reactor inlet, and second due to reaction of the sulfiding chemical with the catalyst, and this moves down through the catalyst bed. The catalyst temperature is closely monitored during sulfiding, and it is not allowed to exceed 600°F.

After the sulfiding temperature rise has passed through the reactor, the H_2S concentration of gases out of the reactor begin to rise rapidly. When 0.1% H_2S is detected in the effluent gas, the recycle gas bleed is stopped and sulfiding continued at a low injection rate until the concentration of H_2S in the circulating gas is 1–2 mol%. At the same time, the reactor inlet temperature is increased to 560° and the reactor outlet temperature to at least 535°F.

When no significant reaction is apparent in the reactor, the system pressure is increased by adding makeup hydrogen until a normal operating pressure is reached at the suction of the recycling compressor. The sulfiding medium is added batchwise to maintain the H_2S concentration of 1–2 mol% in the recycle gas.

When the reactor system has remained steady at the design pressure, at reactor inlet/outlet temperature of 560/530° and H_2S concentration of 1–2 mol%, for 2 hours, sulfiding is complete. The reactor is slowly cooled by reducing inlet temperature and adding quench between the catalyst beds until reactor temperature reaches about 425°F. No point in the reactor is allowed to cool below 425°F.

The startup temperature is next approached from the lower side by increasing the reactor inlet temperature to 450–475° and outlet temperature to 425–450°, the quench temperature controller is set at 450°F. The recycle gas rate is set at the design rate. Also the HP separator pressure is set at the design value. Condensate and polysulfide injection at the design rate is started.

The reactor is now ready for introduction of the feed. The feed pump starts pumping only 20% of the design feed rate to the reactor, shunting the rest of the feed back to the feed tank.

Heat is released due to adsorption of hydrocarbon when the feed passes over the catalyst for the first time. This shows up as a temperature wave that passes down through the catalyst. When the temperature wave due to hydrocarbon adsorption has passed through the reactor and a liquid level is established in the high pressure separator, the liquid is sent to a low-pressure separator and the distillation section.

As the reactor temperature and feed rate is increased in the steps that follow, amine circulation is established through the recycling gas absorber.

The reactor feed rate is increased by 10–15% of the design at a time, allowing the system to line out for at least 1 hour after each feed rate increase. The process is repeated until the feed is at 50% of the design rate.

Next, the temperature is increased in about 20°F increments or less at the inlet to each reactor bed. When increasing reactor temperature, the top bed should be adjusted first then each succeeding lower bed. The system is allowed to line out for at least 1 hour after each reactor temperature increase until all reactor temperatures are steady. Then, the reactor temperature is increased again until the desired conversion is reached.

When the desired operation (conversion and feed rate) has been reached and the unit is fully lined out, it is monitored so that recycle gas rate is steady and at the design rate. The H_2S absorber bypass is slowly closed, forcing all the recycling gas through the absorber. While closing this bypass, close attention is given to knockout drum level, absorber-packed bed ΔP, and absorber level to avoid compressor shutdown due to a sudden carryover of amine solution.

NORMAL SHUTDOWN

The following procedures are typical when a run is ended to replace spent catalyst or perform general maintenance. The same procedure is followed when a run is ended for catalyst regeneration, except that the reactor is not opened.

Care must be taken to avoid furnace and catalyst coking during shutdown and the formation of highly toxic nickel carbonyl when the reactor is cooled, the possibility of fires due to explosive hydrogen oxygen mixtures or exposure of pyrophoric material to air when the reactor is opened, and exposure of personnel to toxic or noxious conditions when the catalyst is drained or equipment is entered.

SHUTDOWN PROCEDURE

The following presents a general procedure to be followed for a normal shutdown.

1. Gradually reduce the liquid feed and adjust the catalyst temperature downward, so that feed conversion remains at the desired level. When a very low feed rate is reached, stop all liquid feed to the reactor but continue to circulate recycle gas rate at the normal rate. As the liquid feed rate is cut, the reactor feed and effluent rates will be out of balance for short periods. The feed must be gradually reduced to prevent temperatures greater than the maximum design temperature occurring in the effluent/feed heat exchangers.
2. To strip off as much of adsorbed hydrocarbon as possible from the catalyst, raise the reactor temperature to the normal operating temperature after the feed is stopped. Circulate hot hydrogen until no more liquid hydrocarbon appears in the high-pressure separator. If the shutdown is for only brief maintenance, which does not require stopping the recycle compressor, continue circulation at the normal operating temperature and pressure. After the maintenance work is complete and unit is ready for feed, lower the reactor temperature and introduce the feed following the normal startup procedure.
3. If the shutdown is for catalyst regeneration, catalyst replacement, or maintenance that requires stopping the recycle compressor or depressurizing the reactor system, continue circulation at the normal operating pressure for 2 hours. Reduce the furnace firing

rate and start gradually reducing the reactor temperature to 400°F. Any cooldown design restrictions for the reactor must be adhered to, to avoid thermal shock.

4. Add quench gas as required to evenly cool the reactor.
5. To maintain heater duty high enough for good control and speed up cooling after heater fires are put out, bypass reactor feed gas around the feed/effluent exchanger, as required.
6. While cooling, remove the bulk of hydrocarbon oil from the high-pressure separator by raising the water level and pressure to the low-pressure separator. Also, increase the pressure of any low-pressure liquid remaining in the H_2S absorber to the amine section. Purge and block the liquid hydrocarbon line from the high-pressure separator. Block in the H_2S absorber and drain the amine lines. Drain all vessels and the low points of all lines to remove hydrocarbon inventory.
7. If the shutdown is for catalyst regeneration, hold the reactor at 400°F.
8. If the shutdown is for catalyst replacement or maintenance that requires opening the reactor, determine the CO content of the recycle gas. If the CO content is below 30 ppm CO, continue the cooling procedure; if more than 30 ppm, proceed as follows:

    a. If more than 30 ppm CO has been detected in the recycle gas and the reactor is to be opened, the CO must be purged before cooling can continue to eliminate possible formation of metal carbonyls. Stop recycling gas circulation while the catalyst temperature is still above 400°F. Do not cool any portion of the bed below 400°F. Before depressurizing the system, check that all these valves are closed:

        - Suction and discharge valves on charge pump and spares.
        - Block lines on liquid feed lines.
        - Block valves on the high-pressure separator, liquid product and water lines.
        - Recycle and makeup compressor suction and discharge lines.
        - Chemical injection and water lines.
        - Makeup hydrogen line.
        - H_2S absorber.

    b. Depressure the system. Do not evacuate below atmospheric pressure, as there is the danger of explosion if air is drawn into

   the system. For effective purging of the reactor system, the nitrogen gas is injected at the recycle compressor discharge and follows the normal flow path through the catalyst beds.
   c. Pressurize the system with dry nitrogen to 150 psig. Purge the compressor with nitrogen.
   d. Depressurize the system to 5 psig and purge with nitrogen for 5 minutes.
   e. Repressurize the system to 150 psig and purge all blocked lines as mentioned previously.
   f. Pressurize the system with nitrogen from nitrogen header and recycle compressor.

9. Relight the furnace fires and maintain the reactor at a temperature of 400°F for at least 2 hours. Then analyze the recycling gas for CO content. If the CO content is still above 30 ppm, repeat the preceding procedure.
10. If the CO content is below 30 ppm, the reactor can be cooled below 400°F following the cooling rates restrictions for the hydrocracker vessel metallurgy. Stop the furnace fires and continue cooling by circulating nitrogen until the temperature has fallen to 120°F.
11. Stop nitrogen circulation and ensure that the system is blocked in preparation to depressurizing. Depressurize and purge the system again with nitrogen. Maintain the system under slight nitrogen pressure, so that no oxygen is admitted.

CATALYST REGENERATION

The activity of the catalyst declines with time on stream. To recover the lost activity, the catalyst is regenerated in place at infrequent intervals.

In the regeneration process, the coke and sulfur deposits on the catalyst are burned off in a controlled manner with a dilute stream of oxygen. The burning or oxidation consists of three burns at successively higher temperatures. This is followed by a controlled reduction of some of the compounds formed during the oxidation step, in a dilute hydrogen stream. The catalyst is next stabilized by sulfiding. During the combustion phase, sulfur oxides are liberated and some metal sulfates are formed as the sulfided catalyst is converted to the oxide form. During the reduction phase, the residual metal sulfates are reduced to the metal sulfides with liberation of sulfur dioxide.

During both the combustion and the reduction phases, a dilute caustic quenching solution is mixed with reactor effluent to cool the gases through the H_2O-SO_3 dew point and to neutralize the SO_2/SO_3 present. Cooling the gases in this manner prevents corrosion of heat exchangers and other downstream equipment. Also, sulfur oxides must be neutralized to prevent damage to the catalyst.

During regeneration, maximum use is made of equipment used in the normal operation. The recycle compressor is used to recirculate the inert gas. Compressed diluted makeup air is mixed with recycled inert gas flowing to the reactor inlet to provide oxygen to sustain a burn wave in the top catalyst beds. The reactor inert gas is preheated in the feed effluent exchanger then combined with diluted makeup air and heated in the feed furnace before flowing to the reactor inlet.

The reactor/effluent gases are cooled in the feed effluent exchanger and mixed with recirculating dilute caustic quench solution before being cooled in the effluent/air cooler. The cooled mixture then flows to the high-pressure separator to separate out the vapor and liquid phases. A portion of the inert gas from the separator is bled to the atmosphere and the reminder recirculated. The dilute caustic quench solution then flows to the low-pressure separator. This allows the use of a lean DEA pump for quencher solution circulation. Some of the dilute caustic quench solution is bled to limit the concentration of dissolved solids. Fresh caustic and process water are added to maintain the quench solution at a proper pH.

The regeneration is carried out at the pressure that allows the maximum flow rate as limited by the maximum power of the recycle compressor or the discharge temperature of the makeup compressor (1150 psig). The makeup air is diluted with the recycling inert gas to avoid forming a combustible mixture in the lubricated makeup compressor. With hydrogen present the maximum O_2 concentration is 4 mol% maximum at a compressor outlet temperature of 265°F.

After the regeneration burn has started and the recycling gas stream is free of hydrogen, the O_2 concentration through the makeup compressor is raised to 7%.

The concentration of O_2 in the first burn is kept at 0.5%. The initial burn is started at an inlet temperature of 650°F or less. This produces a temperature rise of 100°F. The burn is concluded when the last bed temperature starts to drop off and oxygen appears in the recycle gas.

After the first burn is completed, the reactor inlet temperature is increased to 750°F and air is introduced to obtain 0.5 vol% oxygen at the reactor inlet. The oxygen may not be totally consumed as it passes through the reactor during this burn and the oxygen content of recycling gas at the reactor outlet may remain at fairly constant level, even though oxygen is being consumed in the reactor. This burn normally produces only a small temperature rise and sometimes no temperature rise is apparent.

For the third or final burn, the temperature at reactor inlet is raised to 850°F ± 25°F and the oxygen content of the inlet gas is slowly increased to 2% by volume. This condition is maintained at least for 6 hours or until the oxygen consumption is essentially nil, as indicated by a drop in inlet oxygen content of less than 1% for 2 hours with makeup air stopped. No point in the reactor should be allowed to exceed 875°F. The reactor temperature should never be allowed to exceed 900°F. Throughout the regeneration, a circulating dilute caustic solution is injected into reactor effluent gases.

REDUCTION PHASE

After the hydrocarbon, coke, and sulfur have been burned from the catalyst, a reduction step is necessary before introducing the sulfiding and feed. During oxidation, a portion of sulfur on the catalyst is converted into sulfates. These sulfates may be reduced when exposed to high-pressure hydrogen, and the reduction can occur at temperatures below those required for sulfiding. A large heat release accompanies these reactions, which can result in loss of catalyst activity or structural damage to the catalyst and reactor.

The oxidized catalyst is reduced in a very dilute hydrogen atmosphere so that the heat of reduction is released gradually under controlled conditions.

The reactor is pressurized with nitrogen while heating to 650°F. Hydrogen is then introduced to obtain a concentration of 1–2 mol% at the reactor inlet. This causes a controlled reduction reaction to move through the reactor, as indicated by a temperature rise of 25–40°F per percent hydrogen.

If, after 1 or 2 hours, the reduction is proceeding smoothly, slowly increase concentration of hydrogen to 2–3 mol% at the reactor inlet. If the temperature rise exceeds 100°F or the reactor temperature at the reduction wave exceeds 750°F, stop increasing the hydrogen content. Do not exceed 3% hydrogen at the reactor inlet or allow the temperature to exceed 750°F at any point in the reactor during this procedure.

The reduction reaction is controlled by limiting the quantity of hydrogen available. The catalyst temperature is held below 750°F during the reduction step to avoid damage to the catalyst.

When hydrogen breaks through the bottom of the reactor, reduce or stop hydrogen addition. Hold the reactor temperature at 650° and 2–3% hydrogen at the reactor inlet for at least 8 hours and until hydrogen consumption has dropped to a low rate. When the wave has passed through the reactor and no more hydrogen is consumed, the reactor is cooled to about 400°F.

Some sulfur oxides are generated by the reduction reactions and consequently a dilute quench is circulated as during the oxidation phase to neutralize the quenched effluent gases. However, since the quantity of sulfur oxides is relatively small compared to that liberated during the carbon/sulfur burn, an ammonia quench may be used instead of a caustic one. This arrangement uses equipment used during normal operation rather than the quench circulation, piping, and mixing header. It is important to note that a catalytic reformer hydrogen is unsuitable for reduction and the first phase of subsequent sulfiding. Accordingly, the procedure requires manufactured or electrolytic hydrogen.

MILD HYDROCRACKING

Mild hydrocracking, as the name suggests, operates at much lower pressure and much milder other operating conditions than the normal hydrocracking process. The objective of the process is basically to desulfurize the VGO to make it suitable for FCCU feed. Other impurities, like nitrogen, are also removed and about 30% of the feed is converted into saleable diesel. Compared to normal hydrocracker units, mild hydrocrackers require much less initial investment. The operating conditions and yield from a mild hydrocracker unit are shown in Tables 3-5 and 3-6, respectively.

RESIDUUM HYDROCRACKING

Resid hydrocracking is designed to convert straight-run residual stocks and atmospheric or vacuum resids into distillates by reacting them with hydrogen in the presence of a catalyst. The process operates under severe operating conditions of high temperature and pressure, comparable to

Table 3-6
Mild Hydrocracker Yields

VGO FEED	1.0000
HYDROGEN	0.0061
TOTAL FEED	1.0061
GASES	0.0191
CRACKED NAPHTHA	0.0134
KEROSENE	0.0110
DIESEL	0.3117
HEAVY DIESEL	0.6509
TOTAL PRODUCTS	1.0061

NOTES: ALL FIGURES ON A W/W BASIS.
FEED SG = 0.9169, 2.7% SULFUR
PRODUCT.
DIESEL: 0.07% S, 43 DI.
HEAVY DIESEL: 0.12% S.

Table 3-7
Resid Hydrocracking Catalyst Characteristics

PROPERTY	UNITS	
CATALYST COMPOSITION		NI-MO ON ALUMINA BASE
SHAPE		EXTRUDATES 0.963 mm × 3.93 mm
BULK DENSITY	lb/ft^3	45
CATALYST DENSITY, WITH PORES	lb/ft^3	105
CATALYST DENSITY, EXCLUDING PORES	lb/ft^3	186

distillate hydrocracker units. A part of the resid is converted into distillates. Also, the resid is partially desulfurized and demetallized. The distillates produced are separated in a distillation column into naphtha, kerosene, and light diesel. The heavy products from the reaction section and fractionation tower are separated in a vacuum distillation section into heavy diesel, heavy vacuum gas oil, and vacuum resid (see Tables 3-7 and 3-8). The major reactions that occur are shown in Figure 3-11.

RESID HYDROCRACKER REACTOR

The resid hydrocracking reactions are conducted in an ebullated or fluidized bed reactor to overcome the problems associated with a fixed

Table 3-8
Resid Hydrocracking Spent Catalyst Composition

COMPONENT	UNITS	WT%
NICKEL	Wt%	2.1
MOLYBDENUM	Wt%	3.73
COBALT	Wt%	0.006
CARBON	Wt%	12.18
SULFUR	Wt%	11.9
VANADIUM	Wt%	7.1

bed (see Figure 3-12). A liquid phase passes upward through a bed of catalyst at a velocity sufficient to maintain the catalyst particles in continuous random motion. This liquid velocity is achieved by circulating a liquid recycling stream by means of an ebullating pump external to the reactor.

An ebullating bed system offers the following advantages over the conventional fixed-bed system:

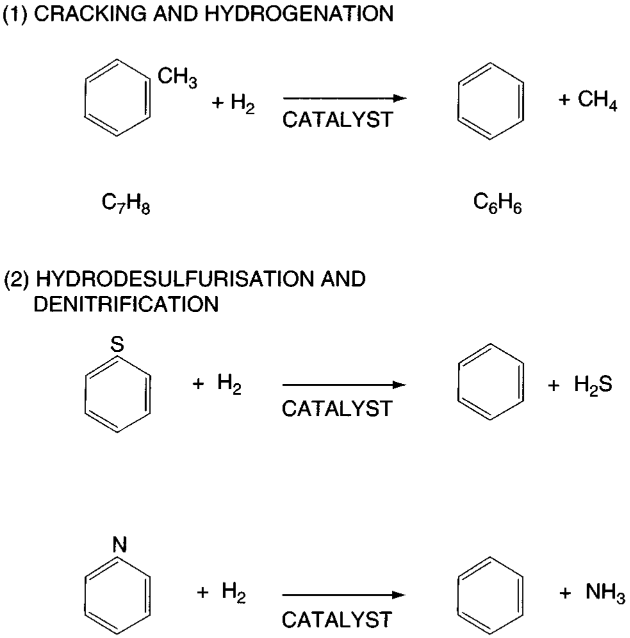

Figure 3-11. Resid hydrocracking reactions.

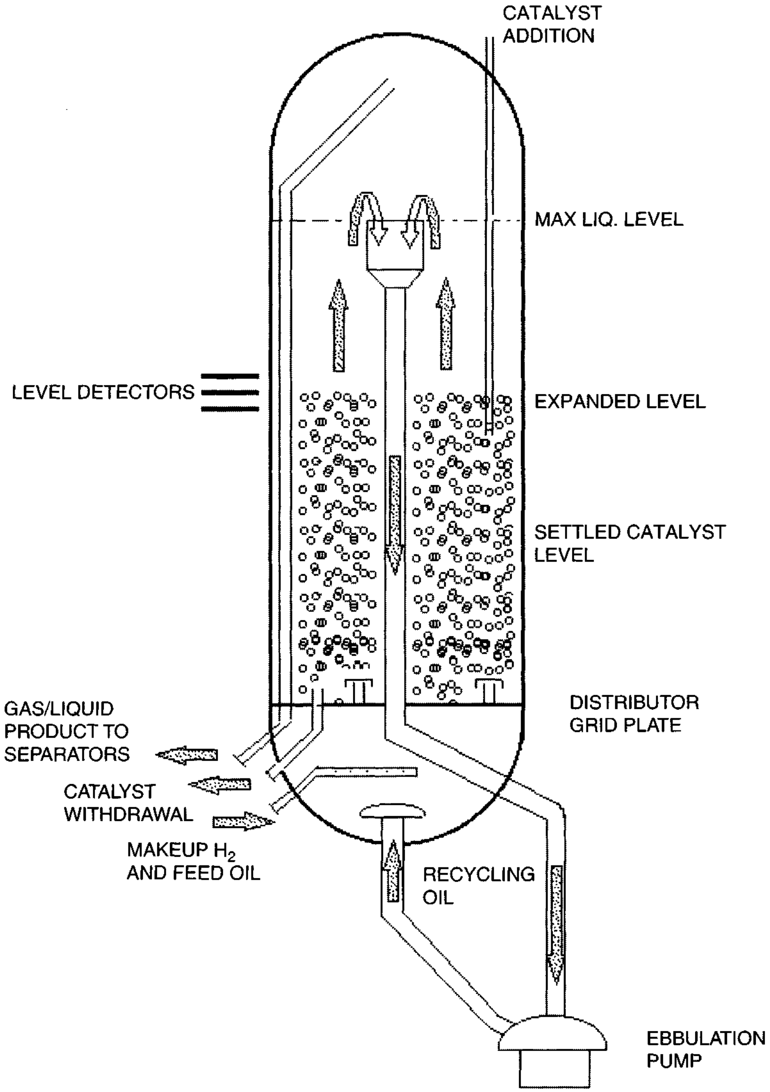

Figure 3-12. Resid hydrocracker reactor.

1. *Isothermal reactor conditions.* The mixed conditions of this reactor provide excellent temperature control of the highly exothermic reactions without the need for any quench system. Undesirable temperature sensitive reactions are controlled.

2. *Constant pressure drop.* Since the catalyst is in a state of constant random motion, there is no tendency for pressure drop to build up as a result of foreign material accumulation.
3. *Catalyst addition and withdrawal.* The catalyst can be added or withdrawn from an ebullating bed on either a continuously or intermittent basis. This feature permits operation at an equilibrium activity level, thereby avoiding change in yield and product quality with time encountered in fixed-bed reactors due to aging of the catalyst.

Within the reactor, the feed enters the lower head of the reactor through a sparger to provide adequate distribution of the reactant stream. The ebullating stream is distributed through the lower portion of the reactor by an individual sparger. These spargers effect a primary distribution of the feed stream across the reactor cross-sectional area. The feed then passes through a specially designed distributor plate, which further ensures uniform distribution as the vapor and liquid flow upward through the catalyst bed.

The oil and hydrogen dissolved in liquid phase under relatively high hydrogen partial pressure react with each other when brought in intimate contact with active catalyst above the distribution plate. The primary reactions taking place are hydrocracking, hydrogenation, hydrodesulfurization, and denitrification. In addition, the organometallic compounds in the feed are broken down under high temperature and high hydrogen partial pressure and are, in part, adsorbed on the catalyst, the remainder passing through the catalyst bed, ultimately ending up in fuel oil. The metal buildup on the catalyst would result in complete deactivation of the catalyst. Therefore, the activity level of the catalyst is maintained by addition of fresh catalyst and withdrawal of spent catalyst in a programmed manner.

The temperature and the catalyst activity level control the conversion level. The other variables such as hydrogen partial pressure, circulating gas rate, reactor space velocity, and ebullating rate are unchanged in an operating unit.

The reactor average temperature is varied by the amount of preheating performed on the total oil and gas streams that pass through separate fired heaters. Normally, the oil heater outlet is maintained at a moderate temperature to minimize skin cracking of the oil, and the adjustment of the reactor temperature is done primarily by increasing the preheating of the hydrogen feed gas to the maximum temperature possible within the heater design limitation.

The ebullating oil flow is controlled by varying the speed of the ebullating pump. Within the reactor, the ebullating liquid is drawn into a conical collecting pan, located several feet above the catalyst bed interface to ensure catalyst-free liquid circulation down the internal stand pipe and into external ebullating pump. The ebullating liquid is distributed through the reactor bottom by its individual sparger.

The height of the fluidized bed of the catalyst in the reactor is related to the gas flow rate, the liquid flow rate, and the physical properties of the fluid, which in turn are affected by the operating temperature and pressure, conversion, size, density, and shape of the catalyst particles. All these parameters are maintained within the constraints imposed by these correlations.

RESID HYDROCRACKER UNITS

The feed to resid hydrocracker is crude unit vacuum bottoms. Fresh feed is mixed with a heavy vacuum gas oil diluent. The combined feed enters surge drum V-33, is pumped to feed heater H-01 then mixed with high-pressure recycled hydrogen gas, is preheated in H-02 in mixers, then fed to the reactor V-01 at about 750°F and 2450 psig (see Figure 3-13).

Ebullation pump P-02 maintains circulation to keep catalyst particles in suspension. The catalyst bed level is monitored by a radioactive source. Fresh catalyst is added to the reactor and spent catalyst is withdrawn from the reactor periodically to maintain the catalyst level.

The reactor effluent flows as a vapor/liquid mixture into vapor/liquid separator V-02. The vapor from separator drum is a hydrogen-rich stream containing equilibrium quantities of hydrocarbon reaction products. The liquid is composed essentially of heavier hydrocarbon products from resid hydrocracking reactions and unconverted feed. The hot flash liquid contains an appreciable amount of dissolved hydrogen and light ends. The flash vapor leaving V-02 is cooled with light distillate in exchanger E-02. The cooled vapor effluent is then fed to primary distillate knockout drum V-03 for removal of condensed liquid. Vapor from V-03 is further cooled to about 140°F in air cooler E-03 and then enters distillate separator drum V-04. On leaving separator V-04, the hydrogen-rich gas is split into two streams. The larger stream is compressed to approximately 2700 psig in a recycle gas compressor and returned to the reactor V-01 as recycled gas. The smaller purge gas stream is withdrawn as purge to maintain the purity of the recycled gas.

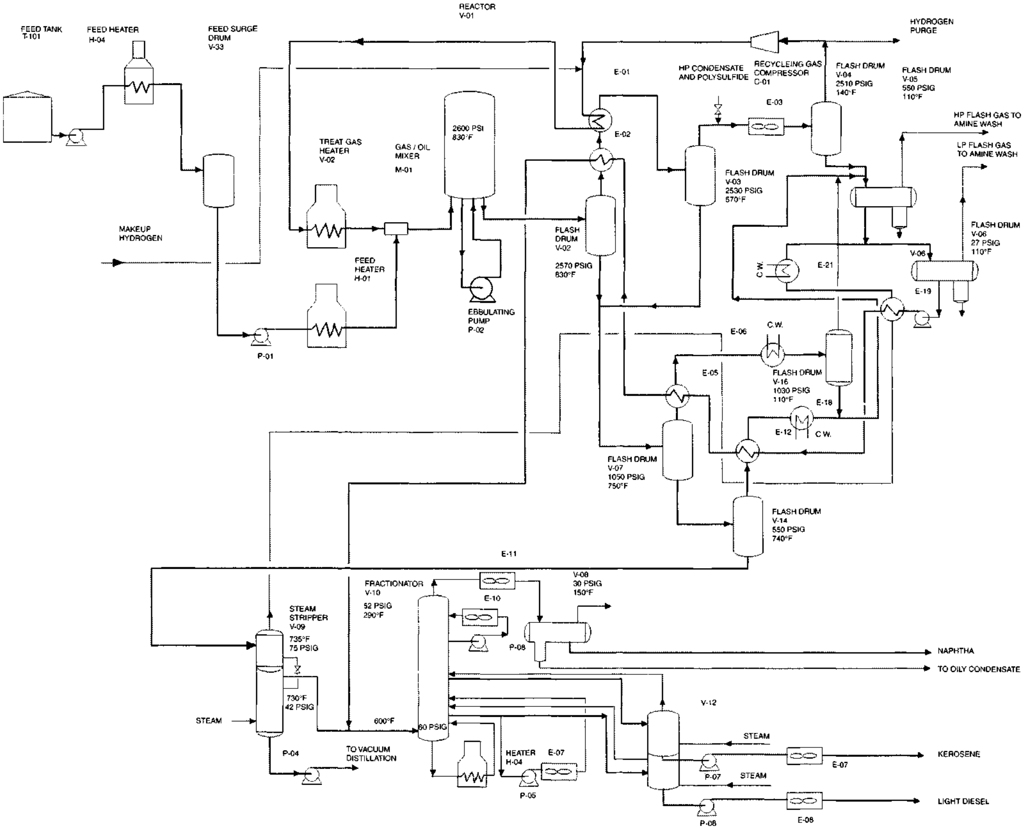

Figure 3-13. Resid hydrocracking (reactor section).

Condensed liquid from V-03 joins with reactor effluent liquid from V-02, then the combined stream is flashed to remove hydrogen in three successive stages.

The first stage let down occurs at 1050 psig in V-07. The resulting hydrogen-rich vapor is cooled in exchanger E-05 then cooled with cooling water to approximately 110°F in E-06. This cooled stream is flashed again in flash gas drum V-16. The vapor from V-16 is let down to a pressure of about 550 psig and joins the high-pressure flash gas from V-05. The liquid from V-16 is further let down to a pressure of 550 psig in high-pressure flash drum V-05.

Ammonical condensate is injected upstream of E-03 and E-06 to dissolve ammonium bisulfide deposits. The ammonical water from V-04 and V-05 are returned to the ammonical water treatment plant to strip away H_2S and NH_3.

The second stage of let down of the combined liquid stream to about 550 psig occurs in high-pressure, high-temperature flash drum V-14. Vapor from this flash drum is cooled with light distillate in exchanger E-12 and cooling water in E-18. It is then fed to flash drum V-05, in addition to high-pressure condensate from V-04 and V-16. High-pressure flash gas from V-05 and gas let down from V-16 are sent to an amine wash.

The final let down of the combined reactor liquid stream occurs at 75 psig in steam stripper V-09. The resulting vapor is cooled through light distillate exchanger E-19 to 300°F and then through a water cooler to the ambient temperature before it is fed to low-pressure flash drum V-06 at about 30 psig, along with condensate from V-05. The low-pressure flash gas from V-06 is sent to the amine wash unit.

The light distillate from V-06 is pumped by P-03 through exchangers E-19 and E-12, E-05, and E-02, preheated to approximately 600°F, and fed to the fractionator V-10.

The hot flashed reactor liquid from V-14 flows into stripper V-09, where it is steam stripped to remove middle distillates. The stripped overhead vapors are fed to fractionator tower V-10 along with preheated light distillate from V-06.

The fractionator tower feed consists of light and middle distillates from V-06 and stripped gases from V-09. The fractionator produces two sidestreams and overhead vapor and liquid streams. A light diesel cut is fed to diesel side stripper V-13 for removal of light ends by steam stripping. The raw light diesel stream is pumped by P-06 and cooled in air cooler E-07/8 before sending it to storage.

A kerosene cut is withdrawn to stripper V-12 for removal of light components by steam stripping. The raw kerosene stream is sent by P-07, cooled in air cooler E-07, and sent to storage.

A pumparound sidestream is circulated near the top of the fractionator to provide internal reflux to upper section with P-08 and air cooler E-10.

A lower pumparound is taken at light diesel drawoff by pump P-05, passing through air cooler E-07 to the fractionator to provide internal reflux in the lower section of the tower.

The fractionator overhead vapor is cooled and partially condensed in air cooler E-11 before going to naphtha accumulator drum V-08. Vapor from this drum is sent to an amine wash. The unstabilized liquid naphtha from V-08 is sent to storage by pump P-07.

The separated water withdrawn from V-08 is sent to the oily water condensate system.

PRODUCT FRACTIONATION

The fractionator bottom product is pumped by P-16 to a vacuum feed surge drum, then the charge is heated to a temperature of about 780°F before it enters the vacuum tower (see Figure 3-14). The flash zone is at 700°F and 26 inch vacuum maintained by steam ejectors.

The feed is fractionated into heavy diesel, heavy vacuum gas oil, and vacuum bottoms.

The heavy diesel is withdrawn as side cut, cooled in air cooler E-52, and sent to storage. The heavy vacuum gas oil (HVGO) side cut is cooled by raising 150 psig steam then in air cooler E-54. A part of HVGO is used as diluent in the resid hydrocracker feed, and the rest is used in fuel oil blending.

The vacuum bottoms from the unit are pumped by P-53 to off-site storage tanks and used in fuel oil blending.

The typical operating conditions of resid hydrocracker units are shown in Table 3-9, and yields and product qualities are shown in Tables 3-10 to 3-12.

The liquid hourly space velocity is calculated based on the flow volume of the liquid feed at the reactor operating conditions divided by the volume of the catalyst up to the fluidized bed height. Only the fresh feed flow is considered, since the net recycle flow is zero. Also, the volume of the makeup and recycled hydrogen is neglected.

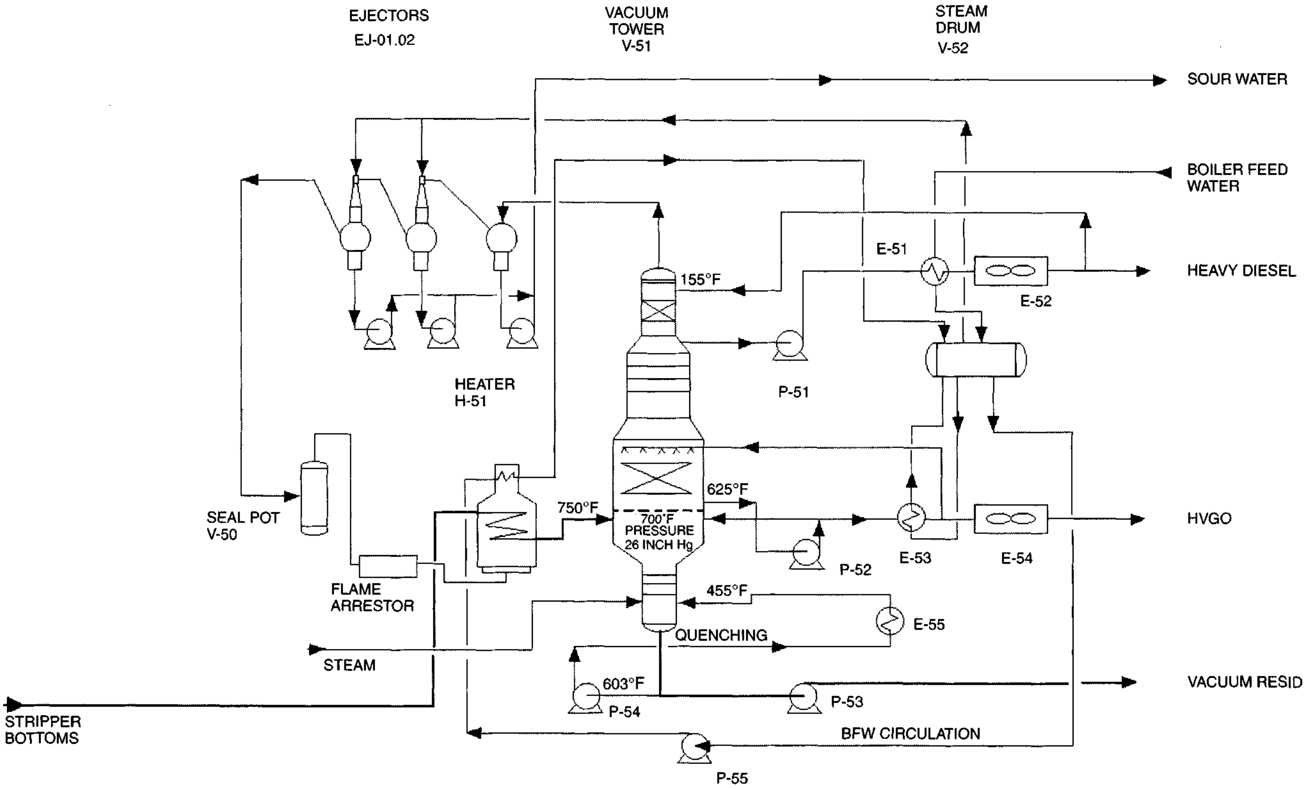

Figure 3-14. Residuum hydrocracking (distillation section). BFW = boiler feedwater.

Table 3-9
Resid Hydrocracker Operating Conditions

OPERATING VARIABLE	UNIT	
REACTOR AVERAGE TEMP	°F	827
REACTOR SYSTEM PRESSURE	psig	2400
HYDROGEN PARTIAL PRESSURE	psig	1895
MAKEUP HYDROGEN	scf/bbl	1400
RECYCLING GAS FLOW	scf/bbl	4300
BLEED GAS FLOW	scf/bbl	700
HYDROGEN CONSUMPTION	scf/bbl	660
LIQUID HOURLY SPACE VELOCITY	(hr^{-1})	0.906
HP FLASH GAS PRESSURE	psig	500
LP FLASH GAS PRESSURE	psig	43
FEED/H_2 MIX TEMPERATURE	°F	748
PLENUM CHAMBER TEMPERATURE	°F	811
CATALYST ADDITION RATE	lb/bbl	0.106

EXAMPLE 3-2

Calculate the LHSV for a resid hydrocracker reactor with the following operating conditions:

$$\begin{aligned}
\text{Resid feed rate} &= 24{,}150\,\text{bpsd} \\
\text{Diluent in feed} &= 3000\,\text{bpsd} \\
\text{Total reactor feed} &= 27{,}150\,\text{bpsd}, 60^\circ\text{F} \\
\text{Reactor cross section} &= 133\,\text{ft}^2 \\
\text{Reactor temperature} &= 850^\circ\text{F} \\
\text{Fluidized bed height} &= 47\,\text{ft} \\
\text{Specific gravity of oil at } 60^\circ\text{F} &= 0.900 \\
\text{Specific gravity at } 850^\circ\text{F} &= 0.553 \\
\text{Makeup H}_2\text{ flow} &= 33.7\,\text{mmscf} \\
\text{Recycled H}_2\text{ flow} &= 69.5\,\text{mmscf}
\end{aligned}$$

Neglecting the volume of the makeup and recycled hydrogen gas, the superficial liquid linear velocity in the reactor is due to total temperature

Table 3-10
Resid Hydrocracker Feed and Product Qualities

PROPERTY	UNITS	FEED	NAPHTHA	KEROSENE	LIGHT DIESEL	HEAVY DIESEL	VGO	VACUUM BOTTOM
API GRAVITY		7.5	64.5	40.9	30.9	24.8	18.9	6.6
DENSITY		1.018	0.7219	0.8208	0.8713	0.9065	0.9408	1.0245
ASPHALTENES	Wt%	6.85						7.3
CON CARBON	Wt%	17.2						20.8
BROMINE NUMBER			30	22	20			
DISTILLATION, ASTM	°F							
IBP		725	102	318	365	440	615	800
5%		870	144	360	468	540		880
10%		930	158	372	520	575	740	925
20%		975	184	380	548	600	760	—
50%			244	422	592	710	815	
70%			278	452	622	765	850	
90%			310	490	688	785	905	
95%			322	504	720	800	945	
EP			344	522	744	820	970	
METALS	ppmw							
Ni		32						30
Na		19						11
V		89						70
NITROGEN	ppmw	2575	155	729	1295	1875	2000	4120
SULFUR	Wt%	4.82	0.19	0.43	0.97	1.6	2	3.59
VISCOSITY	Cst, 210°F	775						363

Table 3-11
Resid Hydrocracker Yields

STREAM	YIELD WT FRACTION
FEED	0.8840
DILUENT	0.1160
HYDROGEN	0.0360
TOTAL	1.0360
PRODUCTS	
GASES	0.0626
H_2S	0.0200
NAPHTHA	0.0600
KEROSENE	0.0913
LIGHT DIESEL	0.0655
HEAVY DIESEL	0.0797
HEAVY GAS OIL	0.1833
RESIDUE	0.4647
LOSSES	0.0089
TOTAL	1.0360

corrected volume of fresh oil plus that of recycled oil. Since the net recycle flow is zero, this can be neglected.

$$\begin{aligned}\text{Flow rate in the reactor} &= 27{,}150 \times 0.90 \times 5.6146/(24 \times 0.553)\\ &= 10{,}337\ \text{ft}^3/\text{hr}\\ \text{Reactor velocity} &= 10{,}337/(133 \times 3600)\\ &= 0.0215\ \text{ft/sec}\end{aligned}$$

$$\begin{aligned}\text{Catalyst volume up to fluidization level} &= 47 \times 133\\ &= 6251\ \text{ft}^3\\ \text{Liquid hourly space velocity} &= 6251/10{,}337\\ &= 0.6047\end{aligned}$$

From the data in Table 3-10, we see that virtually all products from the unit require some further treatment before blending. Naphtha, kerosene, and diesels have high bromine numbers and high nitrogen content, requiring further hydrofinishing treatment to make them suitable for blending. Similarly, the heavy diesel cut requires further hydrotreating to reduce its nitrogen content and make it suitable for FCCU or hydrocracker feed.

Table 3-12
Utilities Consumption *(per Ton Feed)*

UTILITY	UNITS	CONSUMPTION
ELECTRICITY	kWh	5.70
FUEL	mmBtu	1.06
STEAM	mmBtu	0.20
COOLED WATER	MIG*	1.56
CATALYST	LBS	0.71

*MIG = 1000 IMPERIAL GALLONS.