CHAPTER TWO

Distillate Hydrotreating

Hydrotreating processes aim at the removal of impurities such as sulfur and nitrogen from distillate fuels—naphtha, kerosene, and diesel—by treating the feed with hydrogen at elevated temperature and pressure in the presence of a catalyst. Hydrotreating has been extended in recent years to atmospheric resids to reduce the sulfur and metal content of resids for producing low-sulfur fuel oils. The operating conditions of treatment are a function of type of feed and the desulfurization levels desired in the treated product. The feed types considered here are

Naphtha.
Kerosene.
Gas oils.
Atmospheric resids or reduced crudes.

The principal impurities to be removed are

Sulfur.
Nitrogen.
Oxygen.
Olefins.
Metals.

The basic reactions involved are outlined in Figure 2-1.

Sulfur

The sulfur-containing compounds are mainly mercaptans, sulfides, disulfides, polysulfides, and thiophenes. The thiophenes are more difficult to eliminate than most other types of sulfur.

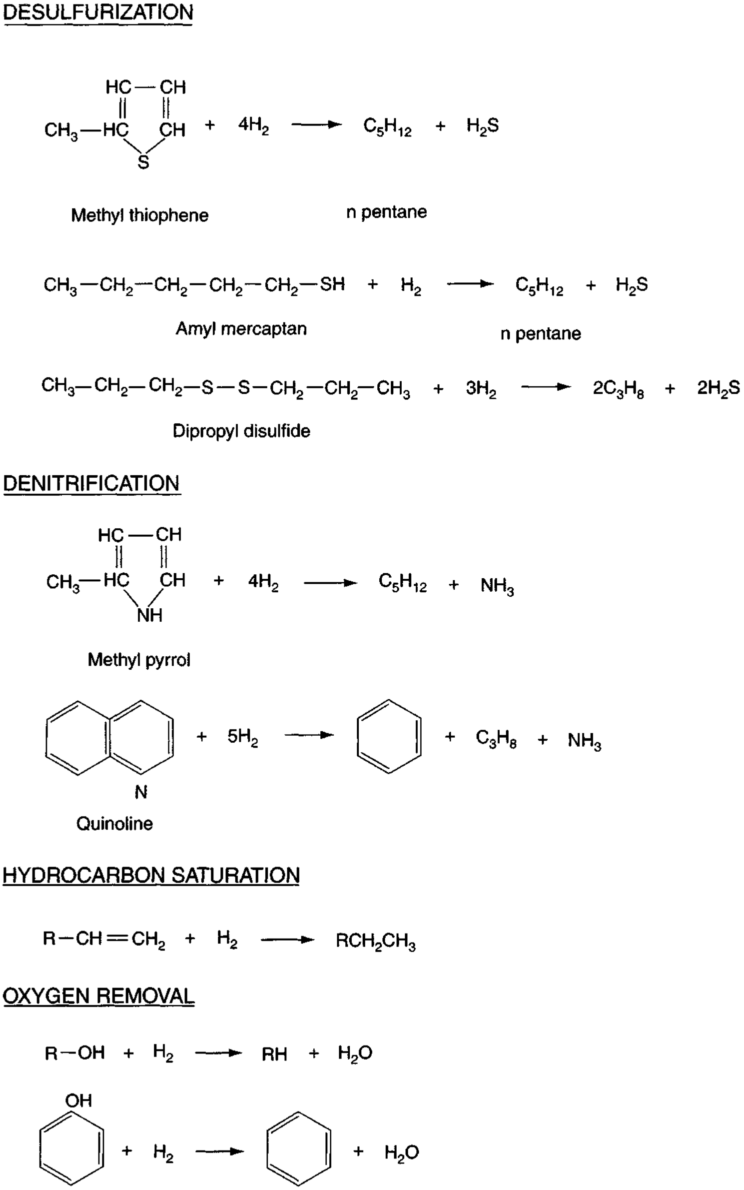

Figure 2-1. Basic reactions.

Nitrogen

The nitrogen compounds inhibit the acidic function of the catalyst considerably. These are transformed into ammonia by reaction with hydrogen.

Oxygen

The oxygen dissolved or present in the form of compounds such as phenols or peroxides are eliminated in the form of water after reacting with hydrogen.

Olefins

The olefinic hydrocarbons at high temperature can cause formation of coke deposits on the catalyst or in the furnaces. These are easily transformed into stable paraffinic hydrocarbons. Such reactions are highly exothermic. Straight run feeds from the crude unit usually contain no olefins. If, however, the feed contains a significant amount of olefins, a liquid quench stream is used in the reactor to control the reactor outlet temperature within the design operating range.

Metals

The metals contained in the naphtha feed are arsenic, lead, and to a lesser degree copper and nickel, which damage the reforming catalyst permanently. Vacuum gas oils and resid feeds can contain a significant amount of vanadium and nickel. During the hydrotreating process, the compounds that contain these metals are destroyed and the metals get deposited on the hydrotreating catalyst.

OPERATING VARIABLES

The principal variables for hydrodesulfurization (HDS) reactions are temperature, the total reactor pressure and partial pressure (PPH_2) of hydrogen, the hydrogen recycle rate, and the space velocity (VVH).

Temperature

The HDS reactions are favored by an increase in temperature, but at the same time, high temperature causes coking reactions, diminishing the activity of the catalyst. The desulfurization reactions are exothermic and the heat of reaction is approximately 22–30 Btu/mole hydrogen. It is necessary to find a compromise between the reaction rate and the overall catalyst life. The operating temperature (start of run/end of run) is approximately 625–698°F according to the nature of the charge. During the course of a run, the temperature of the catalyst is gradually raised to compensate for the fall in activity due to coke deposits until the maximum permissible temperature limit (EOR) for the HDS catalyst is reached. At this stage, the catalyst must be regenerated or discarded.

Pressure

The increase in partial pressure of hydrogen increases the HDS rate and diminishes the coke deposits on the catalyst, thereby reducing the catalyst fouling rate and increasing the catalyst life. Also, many unstable compounds are converted to stable compounds. Operation at higher pressure increases the hydrodesulfurization rate because of higher hydrogen partial pressure in the reactor, requiring a smaller quantity of catalyst for a given desulfurization service. In an operating unit, higher-pressure operation can increase the feed throughput of the unit while maintaining the given desulfurization rate.

Space Velocity

The liquid hourly space velocity (LHSV) is defined as

$$\text{LHSV} = \frac{\text{per hour feed rate of the charge } (\text{ft}^3/\text{hr})}{\text{volume of the catalyst bed (in ft}^3)}$$

Hydrodesulfurization reactions are favored by a reduction in VVH. The rate of desulfurization is a function of (PPH_2/VVH) or the ratio of partial pressure of hydrogen in the reactor to liquid hourly space velocity. For a given desulfurization rate (at constant temperature), the ratio PPH_2/VVH is fixed. Fixing the total reactor pressure automatically fixes the partial pressure and the required hydrogen recycle rate. In general, the total reactor pressure is fixed from the available hydrogen pressure, the hydrogen partial pressure, and other variables such as VVH are adjusted until these fall within the acceptable limits.

Recycle Rate

In an HDS process, the hydrogen separated in a high-pressure (HP) separator drum is recycled to the reactor via a recycle compressor and furnace. This stream joins the incoming fresh feed, which has been heated in the feed furnace. The recycle rate is the ratio of volume of hydrogen at 1 atm and 15°C to the volume of fresh liquid feed at 15°C.

MAKEUP HYDROGEN

While the hydrogen recycling assures the requisite partial pressure of hydrogen in the reactor, makeup hydrogen is required to replace the hydrogen consumed in HDS reactions. The hydrogen is lost through solution losses in the liquid phase and purges for regulating unit pressure and maintaining recycle gas purity.

PURGE RATIO

A purge ratio is the ratio of the volume of hydrogen in the purged gas to the volume of hydrogen in the makeup gas. Purging is required to prevent the buildup of inert gases and light hydrocarbons in the recycle gas. The quantity of purge directly influences the purity of the hydrogen in the recycle gas. For low-sulfur feeds such as naphtha, the purge ratio required is small. For heavy, high-sulfur feeds the purge ratio required to maintain the purity of recycled hydrogen is quite high. Typical purge values used are shown in Table 2-1.

Table 2-1
Purge Requirements of HDS Processes

PROCESS	HYDROGEN IN PURGE/ HYDROGEN IN MAKEUP GAS
NAPHTHA HDS	10%
KEROSENE HDS	15%
DIESEL HDS	20%
VGO HDS	30%

CATALYSTS

The catalyst consists of two parts, the catalyst support and the active elements. The support consists of solid substances with high porosity and able to withstand the temperature, pressure, and the environment encountered in HDS reactors. The support utilized by the HDS catalyst is alumina in the form of balls or extrudates. The active elements are the metals deposited on the support in form of oxides. Before operation, the catalyst is sulfided in order to moderate activity.

The principal types of catalyst used in the HDS service are

1. Cobalt (molybdenum on alumina support). This is the general catalyst for HDS service.
2. Nickel (molybdenum on alumina support). This is used especially for denitrification.
3. Cobalt (molybdenum and other metals on neutral support). The neutral support prevents the polymerization of the olefins. This catalyst is employed in conjunction with other catalysts for olefinic feeds.

NAPHTHA HYDRODESULFURIZATION PROCESS

Naphtha is hydrodesulfurized to make the feed suitable for subsequent treatment; catalytic reforming to improve octane or steam reforming for hydrogen production. In the first case, this takes the name *pretreatment.* The process consists of treating the feed with hydrogen in the presence of a catalyst under suitable operating conditions to remove feed contaminants (see Figure 2-2).

The naphtha feed enters the unit through charge pump P-101. It is mixed with hydrogen gas coming from a cat reforming unit or hydrogen plant. The feed/hydrogen mix is next heated in succession through heat exchange with reactor effluent in E-101 and fired heater H-101. The heated feed/hydrogen mix next enters the desulfurization reactor V-101 at the top. The desulfurization reactions take place over a Co-Mo on alumina catalyst contained in the reactor. The reactor effluent contains the desulfurized naphtha, excess hydrogen, H_2S, and light end elements formed as a result of reaction of sulfur in the feed with hydrogen in the presence of the catalyst.

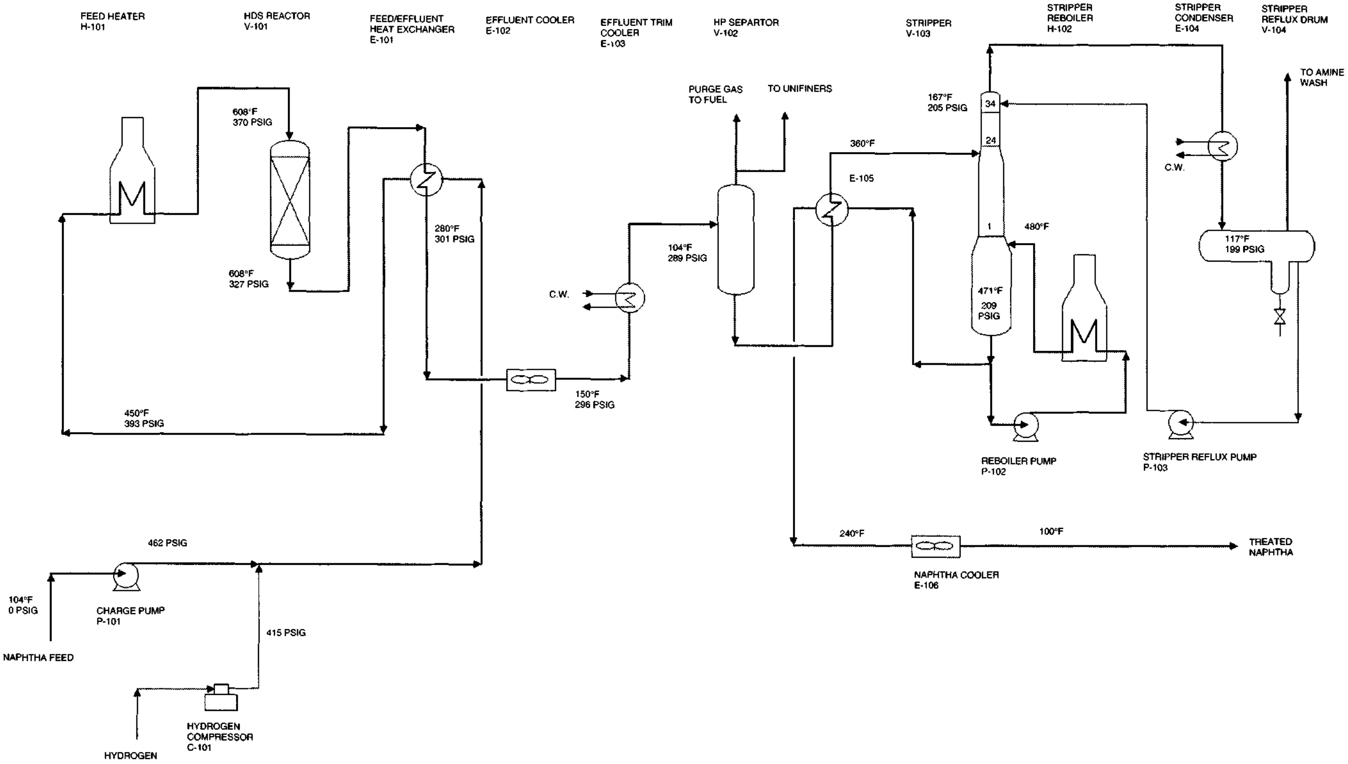

Figure 2-2. Naphtha HDS unit.

The reactor effluent is cooled and partially condensed through feed/effluent heat exchanger E-101, an air cooler E-102, and a trim cooler E-103, before flowing into high-pressure separator V-102. The separation between the vapor and liquid phases occurs in this separator drum. The vapor from this drum containing H_2S, light hydrocarbons formed as a result of desulfurization reactions, and excess hydrogen are purged and sent out of unit's battery limit.

The liquid from V-102 is preheated through a heat exchange with the stripper bottom in heat exchanger E-105 before charging to the stripper column V-103, where the dissolved hydrogen and H_2S contained in the HP separator liquid is removed as overhead product. The gross overhead product from V-103 is partially condensed through heat exchanger E-104. The uncondensed vapor, containing most of the separated H_2S, is sent to an amine unit for H_2S recovery. The liquid is refluxed back to the column through pump P-103.

The column is reboiled with a fired heater H-102. The bottom recirculation is provided by P-102. The stripper bottom product is cooled by heat exchange with incoming feed in E-105 and next in E-106 to 100°F before going out of unit's battery limits.

Operating conditions of a naphtha HDS unit for preparing cat reformer feed are shown in Table 2-2. Corresponding feed and product properties, unit yields, and utility consumption are shown in Tables 2-3 to 2-5.

Table 2-2
Naphtha HDS Operating Conditions

OPERATING PARAMETERS	UNITS	
REACTOR INLET TEMPERATURE		
SOR	°F	608
EOR	°F	698
TOTAL PRESSURE AT SEPARATOR DRUM	psia	303
HYDROGEN PARTIAL PRESSURE AT REACTOR OUTLET	psia	160
LIQUID HOURLY SPACE VELOCITY (LHSV)	hr^{-1}	4.00
HYDROGEN CONSUMPTION	scf/bbl	45

CATALYST: CO-MO ON ALUMINA SUPPORT
TYPICAL COMPOSITION AND PROPERTIES:
CO = 2.2%, MO = 12.0%
SURFACE AREA = 225 m^2/gm
PORE VOLUME = 0.45 cm^3/gm
CRUSH STRENGTH = 30 kg

Table 2-3
Naphtha HDS Feed (Sulfur-Run) and Product Properties

QUALITY	UNITS	
SULFUR GRAVITY		0.734
TBP DISTILLATION		
IBP	°F	194
10%	°F	203
30%	°F	221
50%	°F	239
70%	°F	257
90%	°F	275
FBP	°F	284
HYDROCARBON TYPE		
PARAFFINS	VOL%	69
NAPHTHENES	VOL%	20
AROMATICS	VOL%	11
TOTAL SULFUR	Wt%	0.015
MERCAPTAN		
SULFUR	Wt%	0.008
TOTAL NITROGEN	ppmw	1
MOLECULAR WEIGHT		111
PRODUCT SULFUR	ppmw	0.5

IBP = INITIAL BOILING POINT; FBP = FINAL BOILING POINT.

Table 2-4
Naphtha HDS Unit Yields

	YIELD WEIGHT FRACTION
FEED	
NAPHTHA FEED	1.0000
HYDROGEN	0.0080
TOTAL FEED	1.0080
PRODUCTS	
ACID GAS	0.0012
H_2 RICH GAS	0.0110
LPG RICH GAS	0.0058
HYDROTREATED NAPHTHA	0.9900
TOTAL PRODUCT	1.0080

Table 2-5
Naphtha HDS Unit Utility Consumption per Ton Feed

UTILITY	UNITS	VALUE
FUEL GAS	mmBtu	0.4330
STEAM	mmBtu	0.3680
POWER	kWhr	10.0000
COOLING WATER	mig	1.0600
DISTILLED WATER	mig	0.0025

KEROSENE HYDROTREATING

The objective of kerosene hydrotreating is to upgrade raw kerosene distillate to produce specification products suitable for marketing as kerosene and jet fuel. Sulfur and mercaptans in the raw kerosene cuts coming from the crude distillation unit can cause corrosion problems in aircraft engines and fuel handling and storage facilities. Nitrogen in the raw kerosene feed from some crude oils can cause color stability problems in the product. For aviation turbine fuels (ATF), the ASTM distillation, flash point, and freeze point of the hydrotreated kerosene cut has to be rigorously controlled to meet the stringent requirements. This is done by distillation in a series of columns to remove gases, light ends, and heavy kerosene fractions. The upgrading is achieved by treating hydrogen in the presence of a catalyst, where sulfur and nitrogen compounds are converted into hydrogen sulfide and ammonia.

Because of the very stringent product specifications, the ATF product can have only straight run kerosene or hydrotreated blend components. Another important property of aviation turbine fuel is its smoke point, which in turn is a function of the aromatic type hydrocarbons in the cut. Higher aromatic content yields lower smoke point kerosene cuts, which may not meet the aviation turbine fuel specification. Depending on the severity of hydrotreating, the smoke point of the kerosene may be improved by saturation of aromatics to corresponding naphthenes (see Figure 2-3).

Kerosene feed from storage is pumped via charge pump P-101 and preheated in effluent/feed exchanger E-103, followed by final heating in fired heater H-101. The effluent from H-101 next joins the recycle

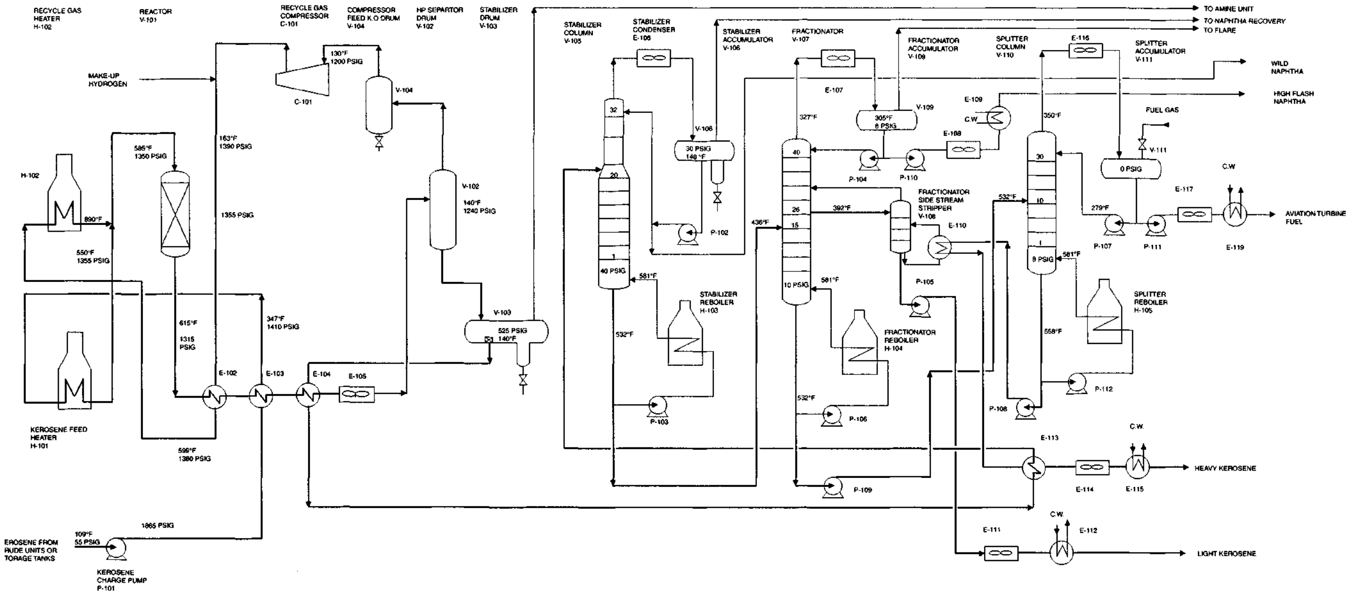

Figure 2-3. Kerosene HDS unit. C.W. = cooling water.

hydrogen coming from compressor C-101 and is heated successively in feed/effluent exchanger E-102 and fired heater H-102. The heated kerosene feed and hydrogen mix stream next flow through reactor V-101, loaded with a Co-Mo or Mo-Ni catalyst. Hydrodesulfurization and hydrodenitrification reactions take place in the reactor. These reactions are exothermic. The reactor effluent is cooled in the effluent/feed exchangers E-102, E-103, and E-104 by exchanging heat with incoming kerosene feed and hydrogen. The effluent is next cooled in air cooler E-105 before being flashed in high pressure separator drum V-102 at 140°F.

The hydrogen-rich gas from the separator is compressed and recycled to the reactor section by centrifugal compressor C-101. Recycled hydrogen gas is preheated in effluent/hydrogen exchanger E-102. It is further heated in fired heater H-102 and joins the hydrocarbon feed to reactor V-101.

The hydrocarbon liquid from the separator drum is depressurized into flash drum V-104. The flash gas is sent to the amine unit for H_2S removal before being sent to refinery fuel system. The liquid from the flash drum is sent to a stabilizer column V-105. The stabilizer overhead vapor is partially condensed in air cooler E-106 and flows into accumulator V-106. A part of the accumulator liquid naphtha is returned to the column as reflux, the rest is withdrawn as wild naphtha.

The stabilizer bottom product is sent to fractionator column V-107, where a high flash naphtha cut is taken as overhead product. Light kerosene base stock is withdrawn from the fractionator as a sidestream. It passes through kerosene side stripper V-108 to adjust its flash point and cooled in E-111 and E-112 before sending to storage. The stabilizer column is reboiled by fired heater H-103.

Fractionator bottoms flow to splitter column V-110, where aviation turbine kerosene is withdrawn as an overhead product. Antioxidant is injected into the ATK product before it is finally sent to storage. The splitter column is heated in a forced recirculation-type reboiler, the heat provided by the H-106 fired heater.

The bottom product is pumped through air cooler E-114 and water trim cooler E-115 to storage as heavy kerosene. This product is used as a blend stock for diesel or as a cutter for various fuel oil grades.

The operating conditions of a kerosene hydrotreating unit are shown in Table 2-6. The corresponding feed and product properties, unit yields, and utility consumption are shown in Tables 2-7 to 2-10.

Table 2-6
Kerosene HDS Operating Conditions

OPERATING PARAMETERS	UNITS	
TEMPERATURE (W.A.B.T.)		
SOR	°F	600
EOR	°F	698
REACTOR ΔT	°F	30
REACTOR ΔP	psi	35
TOTAL REACTOR PRESSURE	psig	1350
HYDROGEN PARTIAL PRESSURE	psia	1105
RECYCLE RATIO	scf/bbl	3072
HYDROGEN CONSUMPTION	scf/bbl	555
% DESULFURIZATION	Wt%	99.6
% DENITRIFICATION	Wt%	98.0
SEPARATOR DRUM		
PRESSURE	psig	1240
TEMPERATURE	°F	140
RECYCLE GAS COMPRESSOR		
SUCTION PRESSURE	psig	1200
DISCHARGE PRESSURE	psig	1390
DISCHARGE TEMPERATURE	°F	161

W.A.B.T. = WEIGHTED AVERAGE BED TEMPERATURE.

GAS OIL HYDRODESULFURIZATION

Gas oil hydrodesulfurization is designed to reduce the sulfur and other impurities (e.g., nitrogen) present in the raw gas oil cuts. The feed to the unit may be a straight run diesel cut from the crude distillation unit or secondary units such as FCCU (light cycle gas oil) or delayed coker. The feed from these secondary units may contain significant amount of olefinic hydrocarbons, which must be converted to saturates in the diesel hydrotreating unit to improve the storage stability of these products.

The primary improvement in product quality is with respect to sulfur and conradson carbon. The raw diesel cut from most Middle Eastern crudes, for example, may contain as much as 1–2% sulfur. Because of atmospheric pollution concerns, the sulfur content of saleable diesel grades allowable in most countries has fallen very rapidly. Until a few years ago 1.0% sulfur was acceptable. But, because of very rapid increase in the number of vehicles using diesel worldwide, the pollution level has

Table 2-7
Kerosene HDS Unit Feed and Product Properties

PROPERTY	FEED	NAPHTHA	STABILIZER BOTTOMS	HIGH FLASH NAPHTHA	LIGHT KERO	ATK	HEAVY KERO
ANILINE POINT, °F	143		151.5				156.5
API GRAVITY	46.44	58.89	45.40	56.02	47.93	44.82	41.17
DENSITY	0.7952	0.7432	0.7999	0.7546	0.7886	0.8025	0.8195
AROMATICS VOL%	22	10.3		12.3	18.2	19.1	19.9
CLOUD POINT, °F							2
CORROSION, Ag STRIP					ZERO	ZERO	
ASTM DISTILLATION °F							
(IBP)	192	124	318	256	322	384	452
5 VOL%	306	178	344	264	338	396	464
10	324	202	354	268	342	400	472
20	346	232	368	272	346	404	478
30	362	256	386	276	350	406	484
50	396	292	424	280	362	412	500
70	440	316	468	286	382	422	518
90	504	348	520	296	418	440	544
95	526	360	536	302	436	448	556
(FBP)	556	394	562	326	470	470	576
FLASH POINT °F			138		140	184	226
FREEZE POINT °C					−59	−54	
POUR POINT °F							ZERO
SMOKE POINT mm	24		25		27	26	25
SULFUR PPMW	4500	1900	17	6.4	3	3.6	41.1
VIS KIN. @ 122°F	1.1		1.31	0.66	0.99	1.32	2.2

IBP = INITIAL BOILING POINT; FBP = FINAL BOILING POINT.

Table 2-8
Kerosene HDS Unit Overall Yields

STREAM	WEIGHT FRACTION
FEED	
KEROSENE FEED	1.0000
H_2 GAS	0.0137
TOTAL FEED	1.0137
PRODUCTS	
GAS FROM UNIFINER	0.0109
HP GAS	0.0060
ACID GAS	0.0018
NAPHTHA	0.1568
ATK	0.7582
HEAVY KEROSENE	0.0800
TOTAL PRODUCT	1.0137

Table 2-9
Kerosene HDS Unit Utility Consumption per Ton Feed

UTILITY	UNITS	CONSUMPTION
FUEL	mmBtu	1.7
POWER	kWhr	15
STEAM	mmBtu	0.03
COOLING WATER	MIG	0.48
DISTILLED WATER	MIG	0.0034

risen exponentially. To curb this increasing atmospheric pollution, sulfur specifications in most developed countries have fallen to 0.005 wt% or lower. The average sulfur decline is often pushed by vehicle and engine manufacturers aiming at lower particulate emissions.

In Figure 2-4, the diesel feed is pumped by charge pump P-101 to effluent/feed heat exchangers E-103 and E-101, then it joins the hot recycle hydrogen stream before entering reactor V-101 loaded with the desulfurization catalyst (Co-Mo or Ni-Mo on alumina type). The recycled gas from compressor discharge C-101 is heated in effluent/feed heat exchanger E-102, next in fired heater H-101 then mixed with the hydrocarbon feed before going to HDS reactor V-101.

In the reactor, hydrodesulfurization reactions take place, in which sulfur and nitrogen attached to hydrocarbon molecules are separated

Table 2-10
Typical Specifications of Dual-Purpose Kerosene

ACIDITY, TOTAL	mg KOH/gm	MAX	0.015	ASTM D 3242
ANILINE GRAVITY PRODUCT		MIN	4800	ASTM D611
OR				
NET SPECIFIC ENERGY	J/gm	MIN	42800	ASTM D 240
AROMATICS	VOL%	MAX	22	ASTM D 1319
COLOR SAYBOLT		MIN	+25	ASTM D156
CORROSION Cu STRIP				ASTM D130
2 HOURS, 100°C		MAX	NO. 1	
CORROSION SILVER STRIP				IP 227
4 HOURS, 50°C		MAX	NO. 1	
DENSITY, 15°C	kg/litre	MIN	0.775	
		MAX	0.83	
DISTILLATION				ASTM D 86
IBP	°C	MIN	145	
10% RECOVERED	°C	MAX	205	
95% RECOVERED	°C	MAX	275	
EP	°C	MAX	300	
FLASH POINT, ABEL	°C	MIN	40	IP 170
FREEZING POINT	°C	MAX	−47	ASTM D 2386
HYDROGEN CONTENT	Wt%	MIN	13.8	ASTM D 3701
MERCAPTAN SULFUR	Wt%	MAX	0.003	ASTM 3227
NAPHTHLENES	VOL%	MAX	3	ASTM D 1840
OLEFINS	VOL%	MAX	5	ASTM 1319
SMOKE POINT	mm	MIN	23	IP 27
SULFUR	Wt%	MAX	0.04	ASTM 1266
THERMAL STABILITY				ASTM D 3241
FILTER PRESSURE DIFFERENTIAL	mmHg	MAX	25	
TUBE DEPOSIT RATING, VISUAL		MAX	<3	
VISCOSITY KINEMATIC @ −20°C	Cst	MAX	8	ASTM D 445
WATER REACTION				ASTM 1094
INTERFACE RATING		MAX	1b	
SEPARATION RATING		MAX	2	

IBP = INITIAL BOILING POINT; EP = END POINT.

and converted into hydrogen sulfide and ammonia. Hydrodesulfurization reactions are exothermic and a cool hydrogen quench is added to the interbed areas to limit the temperature rise in the reactor. The reactor effluent is cooled in effluent/feed heat exchangers E-101 to E-104, next in

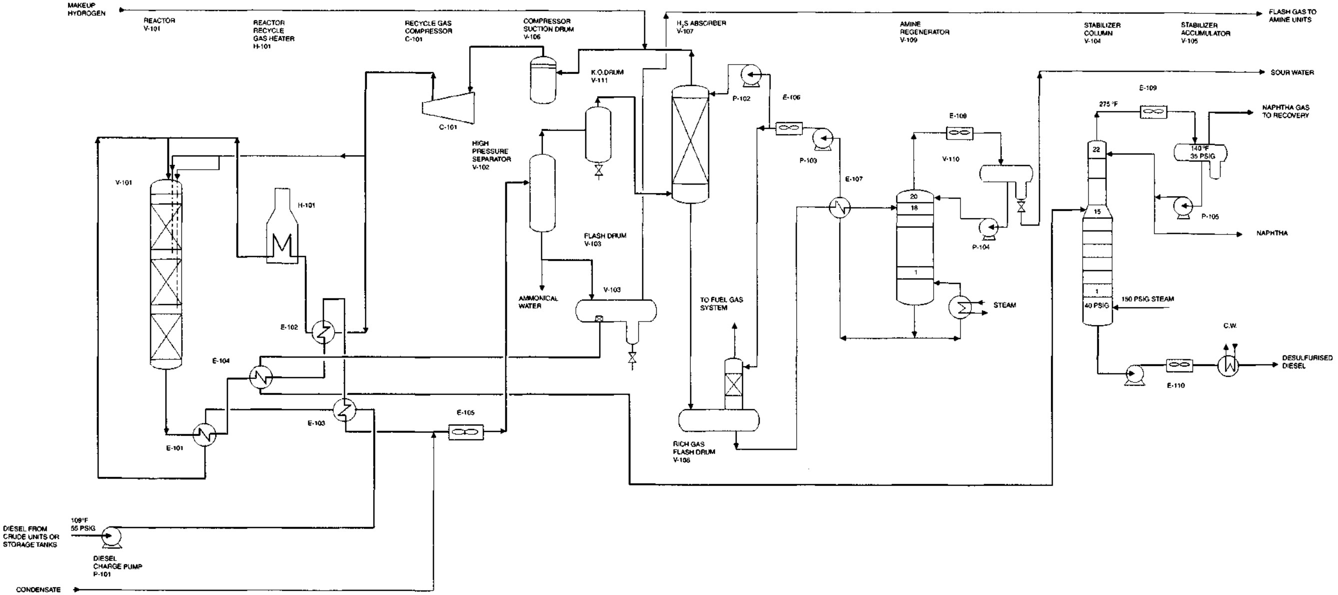

Figure 2-4. Gas oil HDS unit. K.O. = knockout.

air cooler E-105, and then is flashed into high-pressure separator drum V-102. Condensate is injected into the reactor effluent just before air cooler E-105 to dissolve and remove ammonium salts, formed as a result of nitrogen in the feed and the reaction of ammonia with H_2S, which can cause pipe blockages. The ammonium salt solution is removed from high-pressure separator drum V-102 and sent to the refinery wastewater system.

The hydrogen-rich gas from the HP separator, which is mainly hydrogen and some hydrogen sulfide, enters H_2S absorber V-107, where the H_2S is removed by a circulating diethanolamine (DEA) solution. The H_2S-free gas is mixed with makeup hydrogen coming from the hydrogen plant. The makeup and recycled hydrogen are compressed by centrifugal compressor C-101 to the reactor pressure and recycled to the HDS reactor. Part of the recycled gas is used as an interbed quench in the reactor, while the remaining hydrogen, after being heated in effluent/H_2 gas heat exchanger E-102 and fired heater H-101, joins the hydrocarbon feed before entering the reactor V-101.

The liquid hydrocarbon stream from separator V-102 is depressurized into flash drum V-103. The flash gas is sent for H_2S removal before going to refinery fuel system. The bottoms liquid stream from V-103 is preheated in the reactor effluent heat exchanger E-104 stream before flowing into the stabilizer column V-104.

Stabilizer column V-104 separates the gases, light ends, and naphtha formed as a result of HDS reactions in the reactor. The stabilizer overhead vapors are condensed in air-cooled exchanger E-109 into the overhead accumulator drum V-105. This liquid (unstabilized naphtha) is used as a reflux to the stabilizer column, and the excess is pumped out as naphtha product.

Heat is supplied to the stabilizer through medium-pressure steam. The stabilizer bottoms is the desulfurized diesel product. This stream is cooled in heat exchangers E-110 and E-111 before being sent to storage.

ULTRA-LOW SULFUR DIESELS

The production of diesel with ultra-low sulfur (<500 ppm) requires a high-severity operation. Small fluctuations in feedstock properties, unit operating parameters, and catalyst activity significantly affect the required operating conditions, catalyst deactivation, and cycle length.

Essential to deep HDS is good contacting efficiency between the catalyst and the liquid. Homogeneous gas and liquid distribution over the entire cross section of the top of the catalyst bed is essential.[1] Dense loading of catalyst is essential to ensure more homogenous catalyst loading, minimizing the risk of preferential flow through regions with lower catalyst loading density. The pressure drop at the start of the run is higher than that for sock loading but more stable during the cycle.

Hydrogen sulfide in the recycle gas inhibits the desulfurization activity of the catalyst. At 5 vol% H_2S, about 25–30% catalyst activity is lost. For deep HDS operations, H_2S scrubbing of the recycled gas is justified.[2]

Feedstock properties greatly affect the degree of desulfurization. Most of the sulfur in the middle distillates is present only as few types of alkyl-substituted benzothiophenes (BT) and dibenzothiophenes (DBT). These compounds differ greatly in their refractivity toward HDS. In the straight run gas oils, the sulfur concentration increases gradually over the boiling range, peaking at 662°F, followed by a decline. The Light Cycle Gas oil (LCO) containing feed shows a double peak structure consistent with sulfur existing predominently as benzothiophene and dibenzothiophenes.[3]

The effect of feed distillation on color is significant. The color bodies are concentrated in the tail end of the boiling range. A significant improvement in color can be obtained if the end point of the feedstock is reduced slightly. Also, the color of product increase with time, due to higher reactor temperatures.

Operating conditions of a gas oil HDS unit are shown in Table 2-11. The corresponding feed and product properties, unit yield, utility consumption, and diesel specifications are shown in Tables 2-12 to 2-15.

Table 2-11
Gas Oil HDS Operating Conditions

OPERATING PARAMETER	UNITS	
REACTOR INLET TEMPERATURE	°F	645
REACTOR ΔT	°F	55
REACTOR INLET PRESSURE	psig	2280
H_2 PARTIAL PRESSURE	psig	1728
REACTOR PRESSURE DROP	psi	34.5
LHSV*	hr^{-1}	1.42
H_2/OIL RATIO	scf/bbl	4575
RECYCLED GAS/FEED RATIO	scf/bbl	5065
QUENCH GAS/FEED RATIO	scf/bbl	971
H_2 CHEMICAL CONSUMPTION	scf/bbl	422.3
% DESULFURIZATION		98.9
% DENITRIFICATION		73.9

* NI-MO ON ALUMINA BASE CATALYST.

Table 2-12
Gas Oil HDS Feed and Product Properties

PROPERTY	UNITS	FEED	NAPHTHA	LIGHT DSL	HEAVY DSL
DENSITY	60°F	0.8967	0.7716	0.8597	0.8702
ANILINE POINT	°F	156		150	196
ASTM D-86, °F					
IBP	°F	450	98	444	615
10%	°F	575	172	520	660
30%	°F	645	234	566	690
50%	°F	685	284	594	725
90%	°F	795	386	652	805
95%	°F	810	410	666	815
EP	°F	825	456	692	835
SULFUR	ppmw	22900	3000	93	1158
NITROGEN	ppmw	800		196	450

IBP = INITIAL BOILING POINT; EP = END POINT.

Table 2-13
Gas Oil HDS Unit Yields

STREAM	WT FRACTION
FEED	
DIESEL FEED	1.0000
HYDROGEN	0.0071
TOTAL FEED	1.0071
PRODUCT	
OFF GAS	0.0030
ACID GASES	0.0236
CRACKED NAPHTHA	0.0109
LIGHT DIESEL	0.4372
HEAVY DIESEL	0.5324
TOTAL PRODUCT	1.0071

Table 2-14
Utility Consumption per Tons Feed

UTILITY	UNITS	CONSUMPTION
FUEL GAS	mmBtu	0.24
STEAM	mmBtu	0.11
POWER	kWhr	6.25
COOLING WATER	mig	0.35

Table 2-15
Typical Automotive Diesel Specifications

SPECIFICATION	UNITS			TEST METHOD
ACID NUMBER, STRONG	mg KOH/g	MAX	NIL	ASTM D 974
ACID NUMBER, TOTAL		MAX	0.1	
CARBON RESIDUE, RAMESBOTTOM ON 10% DISTILLATION	Wt%	MAX	0.2	ASTM D 482
CETANE INDEX		MIN	50	ASTM D 976
COLD FLOW PROPERTIES				
CLOUD POINT	°C	MAX	−5	ASTM D 2500
CFPP	°C	MAX	−15	IP 309
COLOR ASTM		MAX	1.5	ASTM D 1500
CORROSION COPPER STRIP @ 3 HOURS, 100°C		MAX	NO 1	ASTM D 130
DENSITY AT 15°C	kg/L	MIN	0.836	ASTM D 1298
		MAX	0.865	
DISTILLATION				
10%	°C	MAX	240	ASTM D 86
50%		MIN	240	
85%		MAX	350	
97%		MAX	370	
RECOVERY	VOL%	MIN	96	
FLASH POINT, PMcc	°C	MIN	66	ASTM D 93
SULFUR	Wt%	MAX	0.05	ASTM D 1552
VISCOSITY, KINEMATIC @ 37.8°C	Cst	MIN	2.5	ASTM D 445
		MAX	5	
WATER AND SEDIMENT	VOL%	MAX	0.01	ASTM D 2709

ATMOSPHERIC RESIDUUM DESULFURIZATION

The residuum produced from the crude unit has a high sulfur and metal (Ni, V, etc.) content. The atmospheric resids from most Middle Eastern crudes have a sulfur content of 4–5%. The purpose of the atmospheric residuum desulfurization (ARDS) unit (see Figure 2-5) is to reduce the sulfur content to less than 0.5 wt% sulfur to meet the quality criteria of products from downstream units. Also, a significant percentage of feed metals are removed during the process. The desulfurized atmospheric resid is used as a blend component for blending low-sulfur fuel oils or as feed for another processing unit; for example, a delayed coker unit.

THE PROCESS

In the crude unit, upstream of the ARDS unit, crude oil is treated in a two-stage desalting unit to reduce salt and sediment in the ARDS feed to a very low levels (>3 ppmw as sodium). This treatment is necessary to reduce catalyst bed fouling and catalyst deactivation in the ARDS reactors.

The cold resid feed is heated by heat exchange with ARDS distillate products to 450°F and the feed is next filtered in continuous backwashing feed filters. The filters remove all particles larger than 25 microns from the feed. The filtered resid flows to a surge drum with about 10 minutes hold up and is blanketed with fuel gas to prevent contamination of feed with air.

The feed is preheated first by exchange of heat with HP hot separator vapor then in feed heater H-101. Condensate-quality water is added to the feed at the heater inlet to increase the activity and stability of the catalyst. Water also prevents the deposit of solid ammonium salts in the effluent heat exchangers, downstream of the reactors. The heater outlet temperature is about 650°F. The temperature is kept below 700°F to prevent coking of heater tubes. Recycled gas plus makeup hydrogen are heated by exchange with the HP warm separator, HP hot separator, and in recycle gas heater H-102.

The hot recycled gas is mixed with heated resid upstream of guard reactor R-102. The guard reactor is the first reaction vessel and contains about 8% of the total catalyst in the unit. The function of the guard reactor is to remove sodium and other fouling material from the feed to minimize

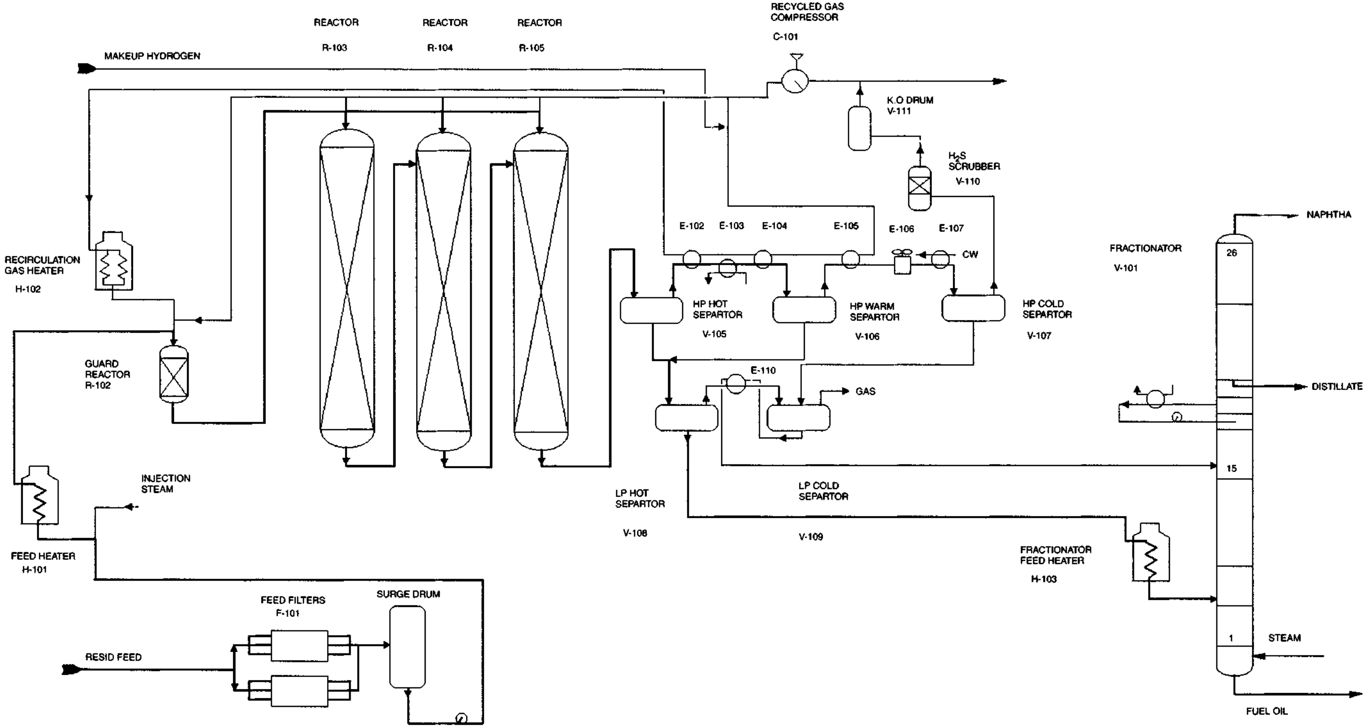

Figure 2-5. Atmospheric resid desulfuriser unit. LP = low pressure; K.O. = knockout.

plugging in the main reactors. The reactants leaving the guard chamber are quenched with cold recycled gas. The quenched mixture then flows into the first main reactor. The guard chamber catalyst is the same as in the main reactors. There are three main reactors in series. All reactors are the same size and contain only one bed of catalyst. The flow through the reactors is downward. Because desulfurization is an exothermic reaction, cold recycled gas is injected between reactors to control inlet temperatures to each succeeding reactor. Scale baskets and liquid distribution trays are provided in each reactor. In addition, layers of size-graded catalyst are installed in the top of each reactor. The upper 2 ft layer is of $\frac{1}{4}$-in. catalyst, the next 2 ft of $\frac{1}{8}$-in., and the main catalyst bed is of $\frac{1}{20}$-in. catalyst. The graded catalyst allows buildup in the top part of the bed without building up excessive pressure drop.

HIGH-PRESSURE SEPARATOR

The effluent from the last reactor flows to high-pressure hot separator V-105, which makes the necessary separation between the desulfurized liquid product and recycled gas. Vapor from HP hot separator is cooled to 500°F by heat exchange with recycled gas. The cooled, partially condensed HP hot separator vapors are fed to HP warm separator V-106. The function of the HP warm separator is to remove asphaltenes that may be entrained in the vapor leaving the HP hot separator. If the asphaltenes are not removed, an oil/water emulsion may form when water and oil condense in the high pressure loop. The HP warm separator operates at 500°F, which is well above the dew point of water, 330°F.

Liquid from the HP warm separator is combined with liquid from the HP hot separator and let down in pressure through a power recovery turbine. Vapor from the HP warm separator is cooled to 105°F by heat exchange with recycled gas, by air cooler E-106, and finally by water cooler E-107. The partially condensed HP warm separator vapor at 105°F feeds HP cold separator V-107. The final separation between the liquid and recycled gas is made in this vessel. The condensed water is also removed in this vessel. Water and oil are separated here, although both the streams are sent to the low-pressure (LP) cold separator. The separation of oil and water in the HP cold separator is necessary to avoid emulsification of an oil/water mixture across the pressure let-down valve in the line to the low-pressure cold separator.

LOW-PRESSURE SEPARATOR AND EXCHANGERS

Liquids from high-pressure hot and warm separators after let-down in pressure are fed to low-pressure hot separator V-108. The flashed mixture is separated in this drum. The liquid from the LP hot separator flows directly to fractionator feed heater H-103. Flashed vapor from the LP hot separator is partially condensed by heat exchange in E-110 and flow to LP cold separator V-109. The feeds to LP cold separator V-109 consist of separated oil and water streams from HP cold separator V-107. LP cold separator off-gas is sent to the hydrocarbon recovery system. Water from the LP cold separator is sent to sour water stripping unit. Hydrocarbon liquid from the LP cold separator is heated in low pressure hot separator (LPHS) vapor condenser E-110 and then flows to the fractionation section of the column.

HYDROGEN SULFIDE REMOVAL

The vapor from the high-pressure cold separator flows through the recycle gas filter, where the entrained oil and scale are removed to prevent foaming in the amine system. The vapor next flows to H_2S scrubber V-110, where it is in contact with a lean amine solution. The rich amine solution goes to amine regeneration unit.

RECYCLE GAS COMPRESSOR

The scrubbed recycled gas is sent to recycle gas compressor C-101, driven by a steam turbine. The compressed recycled gas is combined with makeup hydrogen and split into two streams. One stream is heated in the recycled gas preheater by heat exchange with HP warm separator and hot separator off-gases and finally in recycled gas heater H-102. The other stream of recycled gas from the compressor is utilized to quench the effluent from each reactor before entering the next reactor.

PROCESS WATER

Three uses are made of process water in the ARDS unit. Water is used to increase the activity of the catalyst and prevent the deposit of solids in the reactor effluent cooler. Water is also used to wash recycled gas before and after the amine wash. Water used to increase catalyst activity is added to the resid charge upstream of the charge heater and called *injection water.*

Deaerated condensate, stored under an inert gas blanket, is used for this purpose.

FRACTIONATION SECTION

The function of the fractionation section is to separate the desulfurized liquid stream from hot and cold low-pressure separators into the following products:

1. An overhead hydrogen-rich vapor to be processed in the gas handling plant.
2. A stabilized naphtha stream for processing in naphtha hydrotreater.
3. A distillate side cut product with an ASTM end point of 735°F.
4. A 680 plus bottom product.

The fractionator has 26 trays. The heated resid feed enters the column on tray 6. A small amount of the distillate from the low-pressure cold separator enters the column on tray 10. A stripping steam is introduced below the bottom tray to strip the material boiling below 680°F from the fractionator bottom.

CATALYST

The catalyst used in resid desulfurizers is cobalt, molybdenum, and nickel oxides on a high-purity alumina support. The catalyst for demetallization (HDM) and reduction of Conradson carbon have higher pore

Table 2-16
Properties of ARDS Catalyst

PROPERTY	HDM SERVICE	HDS SERVICE
COMPOSITION		
CoO, Wt%		3
MoO_3	12	14
NiO_3	2.5	0.2
BASE	Al_2O_3	Al_2O_3
SURFACE AREA, m^2/gram	115	200
PORE VOLUME, cm^3/gram	0.9	0.5
BULK DENSITY, gm/cc	0.51	0.67

volume that those used in the desulfurization (HDS) service. Properties of catalysts used in the resid service are shown in Table 2-16.

Catalyst is produced in $\frac{1}{4}$-, $\frac{1}{8}$-, $\frac{1}{20}$-in. diameter extrudates. Larger sizes are loaded in the top portion of the reactors to trap metal scales and other contaminants, while the lower portion of the reactor has a smaller-sized catalyst.

In the ARDS process, the high deactivation rate of the catalyst is due to the deposit of metals and carbon. A number of different catalysts are used, each playing a specific, complementary role. The catalyst in the guard reactor has the main job of retaining most of the metals contained in the feed. A demetallization catalyst with larger pore volume is used, which preferentially converts the resins and asphaltenes to which most metals are attached. In operation, these catalysts can retain metals of up to 50% of their body weight before they are completely deactivated.

The catalysts in the main reactors have hydrodesulfurization and hydrodenitrification as their main functions. At the end of run conditions, these may have adsorbed metals of up to 8–9% of their weight.

The operating conditions of an ARDS unit are shown in Table 2-17. The corresponding feed and product properties, unit yields, and utility consumption are shown in Tables 2-18 to 2-20.

ONSTREAM CATALYST REPLACEMENT

Resid desulfurizer units are expensive to build and operate because of severe operating conditions and high catalyst consumption compared to distillate desulfurization units. Thus, there is always an economic incentive to increase the onstream operating factors and run length, maximize throughput of an operating unit, and increase the conversion of resid to distillate and so minimize fuel oil production.

A major impediment in these objectives is the high metal content (mainly nickel and vanadium) of the feed, which rapidly deactivates the catalyst in the guard reactor, resulting in short run lengths, and limits the severity of operation of the unit. To appreciate the impact of high metal feeds, consider an ARDS unit processing 40 MBPSD of 680°F plus Middle Eastern atmospheric resid feed with the following characteristics:

API gravity = 13.5°
Sulfur = 4.2 wt%

Table 2-17
Operating Conditions for the Atmospheric Resid Desulfurizer Unit

OPERATING PARAMETER	UNITS	
REACTORS INLET TEMPERATURE	°F	681
REACTORS OUTLET TEMPERATURE	°F	716
CATALYST BED WABT	°F	700
FIRST REACTOR INLET PRESSURE	psig	1880
H_2 PARTIAL PRESSURE, INLET	psig	1475
HP HOT SEPARATOR PRESSURE	psig	1812
HP HOT SEPARATOR TEMPERATURE	°F	716
HP WARM SEPARATOR PRESSURE	psig	1785
HP WARM SEPARATOR TEMPERATURE	°F	500
HP COLD SEPARATOR PRESSURE	psig	1735
HP COLD SEPARATOR TEMPERATURE	°F	105
LP HOT SEPARATOR PRESSURE	psig	340
LP HOT SEPARATOR TEMPERATURE	°F	701
LP COLD SEPARATOR PRESSURE	psig	325
LP COLD SEPARATOR TEMPERATURE	°F	105
RECYCLED GAS RATE	scf/bbl	5060
H_2 CHEMICAL CONSUMPTION	scf/bbl	460
MAKEUP H_2	scf/bbl	771
PURGE RATIO, PURGE TO MAKEUP	Wt%	45
FRACTIONATOR		
FLASH ZONE TEMPERATURE	°F	694
OVERFLASH	VOL%	0.6
COLUMN TOP PRESSURE	psig	21.0
GAS OIL/RESID CUT POINT	°F	695

WABT = WEIGHTED AVERAGE BED TEMPERATURE.

Metals:

$$\text{Ni} = 58\,\text{ppmw}$$
$$\text{V} = 18\,\text{ppmw}$$

Assuming a run length of 12 months, a unit onstream factor of 0.98%, and a desulfurized resid metal content of 15 ppmw, it can be seen that, during the course of the run, feed will contain approximately 170 tons metals, out of which approximately 140 tons would be deposited on the catalyst. This may represent almost 30–35% of the fresh overall catalyst weight, assuming a liquid hourly space velocity (LHSV) of 0.29.

Table 2-18
ARDS Unit Feed and Product Properties

PROPERTY	UNITS	ATM RESID FEED	NAPHTHA	DIESEL	RESIDUUM
TBP CUT POINT	°F	680	C5-320	320–680	680+
END POINT	°F		345		
BROMINE NUMBER	MAX		2		
OCTANE, RON			62		
OCTANE, MON			60		
COLOR, MAX.	ASTM			1	
API GRAVITY		13.2		32.5	
S. GRAVITY		0.978			0.937
CON CARBON	% Wt	12			6.5
ASPHALTENE	% Wt	3.9			
NICKEL	ppmw	20.1			8
VANADIUM	ppmw	67			20
SODIUM	ppmw				
SULFUR	% Wt	4.2	0.01	0.05	0.5
NITROGEN	% Wt	0.245		0.02	0.13
VISCOSITY, 210	Cst	60			
VISCOSITY, 122	Cst	770			275
CETANE INDEX				45	
POUR POINT	°F			0	

Table 2-19
ARDS Unit Yields

FEED	
ATMOSPHERIC RESID	1.0000
HYDROGEN	0.0160
TOTAL INPUT	1.0160
PRODUCTS	
ACID GAS	0.0380
OFF-GASES	0.0200
NAPHTHA	0.0170
DIESEL	0.1860
FUEL OIL 680+	0.7550
TOTAL OUTPUT	1.0160

NOTE: ALL YIELDS ARE IN MASS FRACTION.

Table 2-20
ARDS Unit Utility Consumption per Ton Feed

UTILITY	UNITS	
FUEL	mmBtu	0.3000
ELECTRICITY	kWhr	17.0000
STEAM	mmBtu	0.2200
DISTILLED WATER	MIG*	0.0240
COOLING WATER	MIG*	0.6500

*MIG = THOUSAND IMPERIAL GALLONS.

To achieve a higher onstream factor and longer run lengths even while treating heavy resids with high metal content, many innovative reactor designs have been developed, such as the Shell "moving bed bunker technology" for processing vacuum resids and similar feeds. In these, the guard reactor is operated at high temperature and its catalyst deactivates at the fastest rate due to metal deposits. This is replaced either more frequently or continuously. Reactors downstream of guard reactor receive feed with much lower metal content and can therefore operate at much lower severity or increased conversion levels.

In practice, the on-line catalyst in the guard reactor is replaced using a variety of designs: two fixed-bed guard reactors in series (permutable reactors), continuous addition of fresh catalyst and withdrawal of spent catalyst in an ebullated type (OCR, or onstream catalyst replacement) guard reactor, or other, similar configurations. A reduction up to 50% in vanadium content is typical. A spherical catalyst with demetallization-promoting metals on an inert carrier with large pores (typically, nickel and molybdenum on macroporous alumina, pore volume 0.9 cm^3/gm) is used.

PERMUTABLE REACTOR SYSTEM

An permutable reactor system (IFP process) has two fixed-bed guard reactors in a swing arrangement and permutable operation (Figure 2-6). In the lead position, the deactivation rate is very high due to large amounts of metals, sodium, and sediment deposits on the catalyst. The catalyst deactivation rate in the reactor in second position is much smaller. The permutable reactors with high pore demetallization catalyst are designed

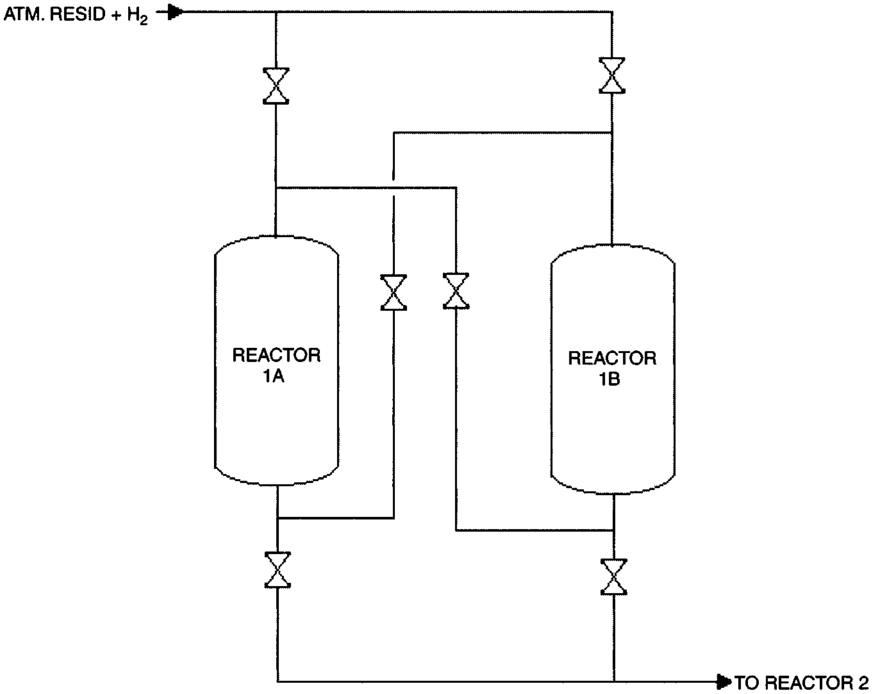

Figure 2-6. Permutable guard reactors for ARDS the unit.

for higher-temperature operation to counter the effect of metal deactivation and reach the end of run condition in shorter time.

Consider two reactors, 1A and 1B in the permutable arrangement, with reactor 1A in the first position and 1B in the second position. When the catalyst contained in the lead reactor (1A) is deactivated or the pressure drop exceeds the permissible limit, this reactor is bypassed without shutting down the unit, thereby avoiding a drop in unit throughput.

The deactivated catalyst in reactor (1A) is stripped and cooled, the catalyst is unloaded, and fresh catalyst is loaded. The catalyst is sulfided and activated and the reactor is heated before returning it to service.

The reactor (1A) with fresh catalyst is brought back on-line in the second or lag position in less than 15 days and this combination (1B and 1A) continues operation until the lead reactor (1B) reaches its EOR condition.

PERMUTATION CYCLE

The frequency of permutation is determined depending on the feed and unit design. If, for example, the overall run length of the ARDS unit is 64 weeks, the first permutation may be done after 20 weeks, when catalyst activity decrease or pressure drop increase in the lead reactor. For example,

- During weeks 1–20, both reactors (1A and 1B), with reactor 1A in the lead position, are in operation.
- During weeks 21 and 22, 1A is under regeneration and only reactor (1B) is in operation. The feed rate may be decreased to maintain performance.
- During weeks 23–32, reactor 1A is back in operation in second position. The reactor operation during this period is 1B and 1A. At the end of week 32, the catalyst in reactor 1B is completely deactivated.
- During weeks 33 and 34, reactor 1B is under regeneration and only reactor (1A) is in operation. The feed rate is decreased to maintain performance.
- During weeks 35–46, reactor 1B is back in service and put in the first position. The reactor operation is 1A and 1B. At the end of week 46, the catalyst in reactor 1A is completely deactivated.
- During weeks 47 and 48, the catalyst in reactor 1A is regenerated and the unit operation is based on only one guard reactor (1B).
- During weeks 49–64, reactor 1A is back in service, with reactor 1A again in the lead position instead of the lag or second position. The reactor operation is 1A and 1B.

At the end of week 64 (end of cycle), all the catalyst is fully deactivated and disposed of.

ONSTREAM CATALYST REPLACEMENT REACTOR

In OCR configuration (Chevron process technology), the guard reactor is an ebullated bed reactor. The feed is introduced at the bottom of the reactor and flows upward through the catalyst, slightly ($<3\%$) expanding the catalyst bed. Fresh catalyst is added at the top of the bed and spent catalyst is withdrawn at the bottom. Both catalyst addition and withdrawal are batch operations, usually done once a week, and this creates a plug flow of catalyst. Thus, the least active catalyst is in contact with most reactive feed at the bottom of the reactor. The upward flow of feed in reactor results in liquid as the continuous phase. Hydrogen is needed only for reaction and not for ebullating the bed. Pressure drop in the bed is low and constant. The catalyst used is spherical with high HDM activity, which allows for downstream fixed-bed reactors to operate at lower temperature.

A charge heater controls the feed temperature. The temperature inside the reactor is controlled by liquid quenching through a quench distributor located at different elevations in the reactor.

The advantages of a permutable or OCR reactor system for guard reactor are

1. Greater run length.
2. Higher space velocities or increased unit throughput.
3. Higher conversion of resid.
4. Increased stream factor.

NOTES

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