CHAPTER SIX

Residuum Processing

DELAYED COKING

Delayed coking is a thermal process in which the vacuum residue from crude distillation is heated in a furnace then confined in a reaction zone or coke drum under proper operating conditions of temperature and pressure until the unvaporized portion of the furnace effluent is converted to vapor and coke.

Delayed coking is an endothermic reaction, with the furnace supplying the necessary heat for the coking reactions. The reactions in the delayed coking are complex. In the initial phase, the feed is partially vaporized and cracked as it passes through the furnace. In the next step, cracking of the vapor occurs as it passes through the drum. In the final step, successive cracking and polymerization of the liquid confined in the drum takes place at high temperatures, until the liquid is converted into vapor and coke.

The coke produced in the delayed coker is almost pure carbon containing some of the impurities of the feed, such as sulfur and metals.

THE DELAYED COKING PROCESS

The reduced crude or vacuum resid enters the coke fractionator bottom surge zone (see Figure 6-1). The feed is mixed with recycle condensed in the bottom section of the fractionator and pumped by heater charge pump P-04 through coke heater H-01, where the charge is rapidly heated to the desired temperature for coke formation in the coke drums. Steam is injected in each heater coil to maintain the required minimum velocity and residence time and suppress the formation of coke in the heater coils.

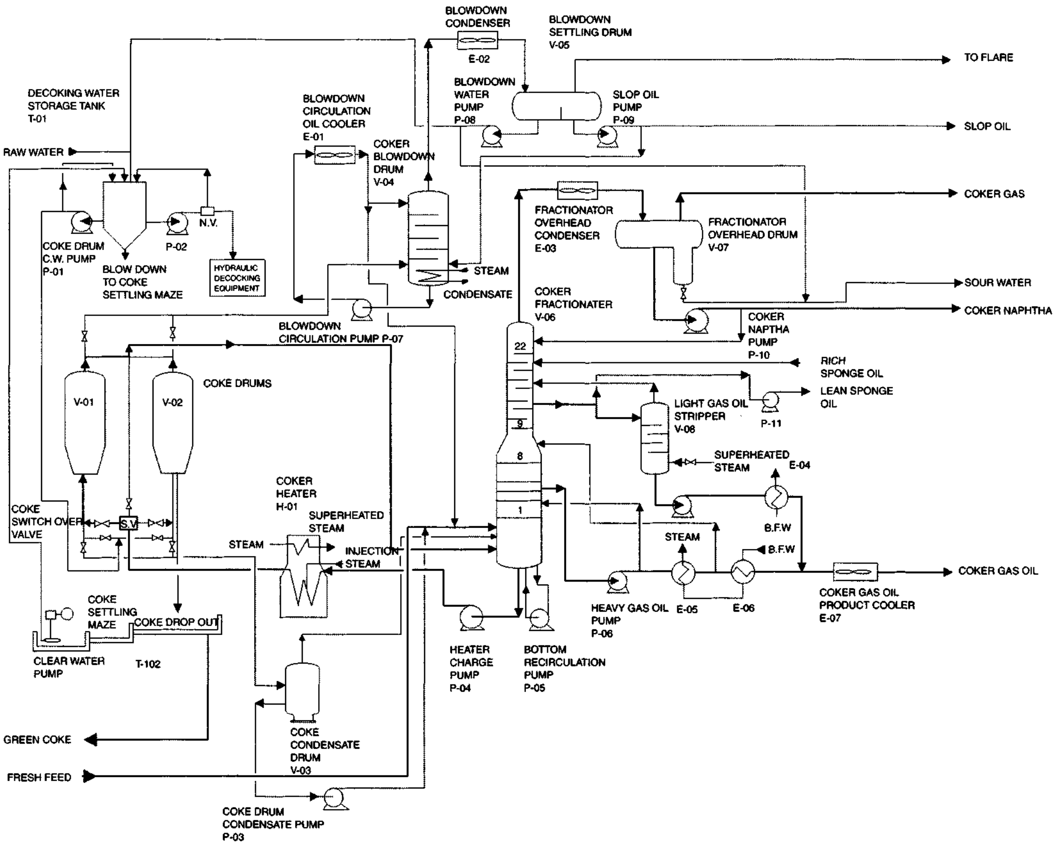

Figure 6-1. Delayed coker unit. C.W. = cooling water; SV = coker switch value; NV = by-pass value.

The vapor/liquid mixture leaving the furnace enters coke drums V-01 or V-02, where the trapped liquid is converted into coke and light hydrocarbon vapors. The vapors make their way through the drum and exit it. A minimum of two drums are required for operation. One drum receives the furnace effluent, which it converts into coke and gas, while the other drum is being decoked.

The coke overhead vapors flow to the coker fractionator and enter below the shed section. The coke drum effluent vapors are quenched with fresh feed then washed with hot gas oil pumpback in the wash section trays. These operations clean and cool the effluent product vapors and condense a recycled stream at the same time. This recycled stream, together with fresh feed, is pumped from the coker fractionator to the coker furnace. The washed vapor passes through the rectifying section of the tower. A circulating heavy gas oil pumparound stream withdrawn from the pumparound pan is used to remove heat from the tower, condensing a major portion of the heavy gas oil and cooling the ascending vapors. The hot pumparound stream of heavy gas oil withdrawn from the fractionator is used for steam generation. The heavy gas/oil product is partially cooled via exchange with steam generation then with an air cooler to storage temperature. The light gas/oil product is steam stripped for removal of light ends, partially cooled via steam generation and air cooled to storage temperature.

Lean sponge oil is withdrawn from the fractionator and cooled by heat exchange with rich sponge oil, then air cooled, before flowing to the top of the sponge absorber. Rich sponge oil is returned to the fractionator after preheat by exchange with lean sponge oil.

The overhead vapors are partially condensed in fractionator overhead condenser before flowing to the fractionator overhead drum. The vapor is separated from the liquid in this drum. The vapor flows under pressure control to the suction of the gas compressor in the gas recovery section. The top of the fractionator is refluxed with part of the condensed hydrocarbon liquid collected in the overhead drum. The balance of this liquid is sent with the vapors to the gas recovery plant. Sour water is withdrawn from the overhead drum and pumped to off-site treating facilities.

VAPOR RECOVERY SECTION

The vapors from the fractionator overhead drum flow to the compressor suction drum and then to two-stage coker gas compressor C-151 (see Figure 6-2). The first stage discharge flows through the compressor

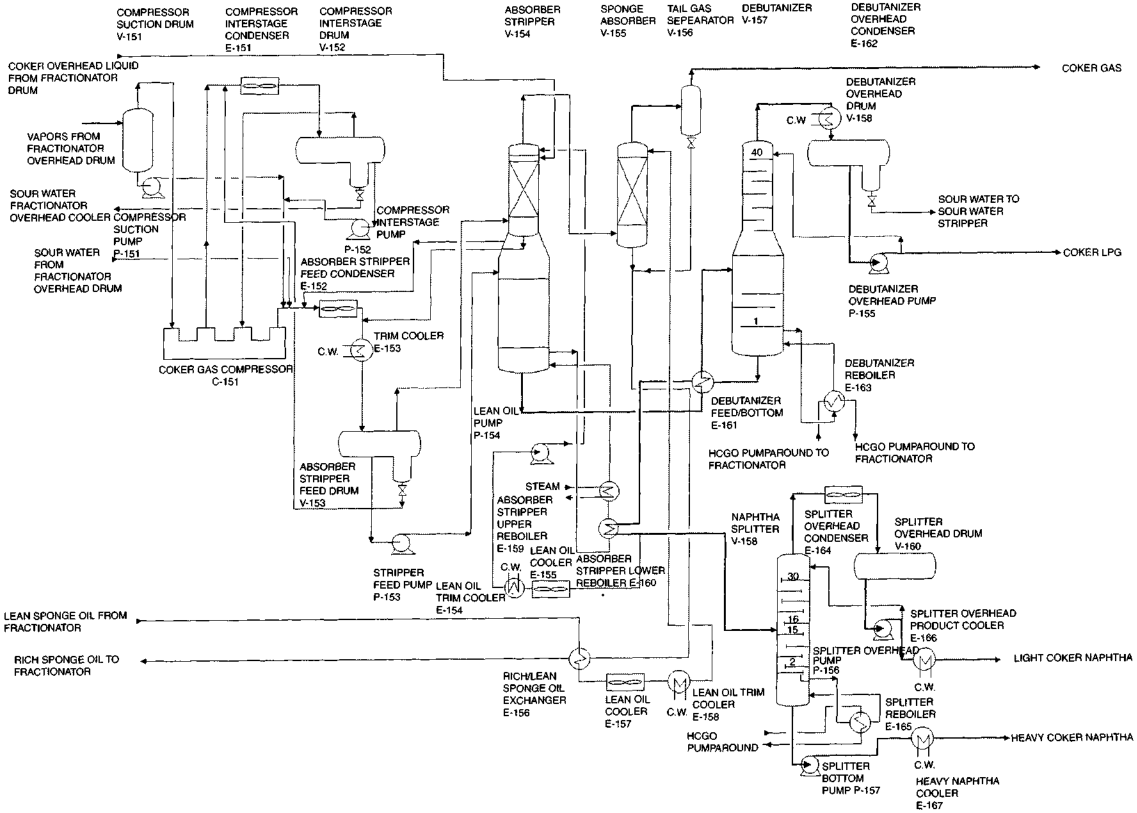

Figure 6-2. Delayed coker (vapor recovery section). C.W. = cooling water.

interstage condenser to the compressor interstage drum. Sour water from absorber stripper feed drum V-153 is injected into the compressor first-stage discharge to prevent cyanide-induced corrosion in the downstream equipment. Vapors from the compressor interstage drum enter the second stage of the compressor.

Liquid hydrocarbon from the interstage drum is pumped to absorber stripper feed condenser E-152, and sour water flows to the coker fractionator overhead cooler. Vapor from the second stage of the compressor is combined with the following: overhead vapor from the stripper, sour water from fractionator overhead drum, and hydrocarbon liquid from compressor interstage drum.

The combined flow is cooled in absorber stripper feed trim condenser E-152. The cooled vapor/liquid mixture from trim cooler E-153 flows to absorber stripper feed drum V-153. The hydrocarbon liquid from the feed drum is pumped by stripper feed pump to the absorber stripper. Sour water from the absorber stripper feed drum flows to the compressor inter stage condenser.

In the stripper, light hydrocarbons are stripped out. The liquid from the bottom of the absorber stripper flows through debutanizer feed bottom exchanger E-161 to debutanizer V-157. Stripper overhead vapors return to absorber stripper feed condenser E-152. The stripper is reboiled with a steam reboiler. Sour water withdrawn from the stripper enters a water separator (not shown in Figure 6-2) then to the battery limit.

Vapor from the absorber stripper feed drum flows to the bottom of the absorber. This vapor is contacted in countercurrent flow with the lean oil. This lean oil consists of unstabilized gasoline from the fractionator overhead drum and a stream of cooled naphtha from the bottom of the debutanizer V-157. Rich oil from the bottom of the absorber flows to absorber stripper feed trim condenser E-153.

The vapor from the top of the absorber flows to the bottom of sponge absorber V-155, where it is contacted in counercurrent flow with cool lean sponge oil. The sponge absorber minimizes the loss of naphtha to the fuel gas. The tail gas from the top of the sponge absorber flows to tail gas separator V-156, where entrained liquids are removed before flowing to battery limits. Rich sponge oil from the bottom of the sponge absorber is sent to the coke fractionator.

Debutanizer V-157 splits the liquid from the stripper into two streams, a C_3/C_4 overhead and a naphtha bottom stream. The debutanizer is reboiled using heavy coker gas oil (HCGO) pumparound from the fractionator.

Naphtha from the bottom of the debutanizer is cooled as it passes through the debutanizer feed/bottom exchanger and absorber stripper reboiler. The net naphtha product flows under level control to splitter V-159. A stream of cooled naphtha is recycled by the lean oil pump to the absorber for use as lean oil. The overhead vapor from debutanizer is condensed in debutanizer overhead condenser E-162 and enters debutanizer overhead drum V-158. Any uncondensable vapor from the overhead drum is vented to the compressor suction drum. Hydrocarbon liquid from the debutanizer overhead drum flows to the debutanizer overhead pump, which handles both the debutanizer reflux and the C_3/C_4 product stream.

Naphtha splitter V-159 separates the net naphtha product from the debutanizer into a light coker naphtha and heavy coker naphtha product. The naphtha splitter is reboiled with HCGO pumparound. The naphtha splitter overhead vapor is condensed in the splitter overhead condenser and collected in the splitter overhead drum. The splitter overhead pump pumps both the splitter reflux and the light coker naphtha stream. The heavy coker naphtha from the bottom of the naphtha splitter is pumped through the splitter bottom product cooler to the battery limits by the splitter bottom product pump.

The light hydrocarbon vapor from the blowdown settling drum are sent to the fuel gas recovery system.

STEAM GENERATION

The net heat removed from the fractionator by the heavy gas oil pumparound stream is used to reboil towers in the vapor recovery section. Additional heat may be removed from the pumparounds by steam generation and preheating boiler feed water.

DECOKING

The decoking operation consists of the following steps:

1. *Steaming*. The full coke drum is steamed to remove any residual oil liquid. This mixture of steam and hydrocarbon is sent first to the fractionator and second to coker blowdown system, where the hydrocarbons are recovered.
2. *Cooling*. The coke drum is filled with water, allowing it to cool below 200°F. The steam generated during cooling is condensed in the blowdown system and may be recovered outside battery limits.

3. *Draining.* The cooling water is drained from the drum and recovered for reuse.
4. *Unheading.* The top and bottom heads are removed in preparation for coke removal.
5. *Decoking.* Hydraulic decoking is the most common cutting method. High-pressure water jets are used to cut coke from the coke drum. Water is separated from the coke fines and reused.
6. *Heading and testing.* After the heads are replaced, the drum is tightened, purged, and pressure tested.
7. *Heating.* Steam and vapors from hot coke drum are used to heat the cold coke drum. The condensed water is sent to the blow down drum. Condensed hydrocarbons are sent to either the coke fractionator or the blowdown drum.
8. *Coking.* The heated coke drum is placed on stream and the cycle is repeated for the other drum.

OPERATING CONDITIONS

Operating conditions for a delayed coker unit processing a vacuum resid from a light Arabian/Kuwait mix are shown in Table 6-1. The basic variables contributing to yield and product quality are temperature, pressure, and recycle ratio. The effect of temperature, pressure, and recycle ratio and their correlation with coker yields have been discussed in detail by Castiglioni[1] and Deblane and Elliot.[2]

Temperature

The temperature is used to control the volatile combustible material (VCM) of the coke product. Coke is generally produced with a VCM

Table 6-1
Delayed Coker Operating Conditions

OPERATING PARAMETER	UNIT	
HEATER COIL OUTLET TEMPERATURE	°F	927
DRUM OUTLET TEMPERATURE	°F	802
DRUM PRESSURE	psig	24.5
FLASH ZONE TEMPERATURE	°F	749
COMBINED FEED RATIO (CFR)		1.24
TOWER TOP TEMPERATURE	°F	204
ACCUMULATOR PRESSURE	psig	10.7

ranging between 6 and 8%. This produces harder and, if the impurities level is acceptable, more desirable anode-grade coke. At constant drum pressure and recycle ratio, the coke yield decreases as drum temperature is increased. If the coking temperature is too low, the coking reactions do not proceed far enough and produce pitch or soft coke. When the temperature is too high, the coke formed is generally too hard and difficult to remove from the coke drum with hydraulic decoking equipment.

As the furnace supplies all the necessary heat to sustain endothermic coking reactions, higher temperature increases the potential of coking furnace tubes and transfer lines. Therefore, in actual practice, the furnace outlet temperature and corresponding coke drum vapor temperature must be maintained within a narrow limit.

Pressure

Pressure increases at constant temperature cause more heavy hydrocarbons to be retained in the coke drum. This increases the coke yield and slightly increases the gas yield. Therefore, delayed cokers are designed with the lowest possible operating pressure to minimize coke and increase distillate yields. Lower pressure results in increased expense for the vapor handling system. The range of pressure used is between 15 and 35 psig.

Recycle Ratio

The recycle ratio has the same general effect as pressure on product distribution. As recycling is increased, the coke and gas yields increase while the liquid yield decreases. Recycling is used primarily to control the end point of the coker gas oil. In general, the refinery operates at as low a recycle ratio as product quality and unit operation permit.

COKER RUN LENGTH

The run length between decoking while processing heavier, high Conradson carbon feed stocks is an important variable. Run length is affected by feedstock quality and operating conditions. Although it is not possible to predict a run length, values generally encountered are between 9 and 12 months for a maximum radiant heat flux of 10,000 to 12,000 Btu/(hr)(ft^2) and feed cold velocities in the tube of around 6 ft/sec. Multiple injections of steam are used to adjust coil residence time and velocity.

COKER YIELDS AND QUALITY

The yield and quality from a typical coker unit processing Middle Eastern crude are shown in Tables 6-2 to 6-7.

COKE PROPERTIES AND END USES

The properties of the coke produced and its end uses can vary widely, depending on the properties of the feedstock to the delayed coker unit and

Table 6-2
Delayed Coker Utility Consumption *(per Ton Feed)*

UTILITY	UNIT	CONSUMPTION
FUEL	mmBtu	0.8571
STEAM	mmBtu	−0.07
POWER	kWhr	7.35
COOLING WATER	MIG*	1.63

*MIG = 1000 IMPERIAL GALLONS.

Table 6-3
Delayed Coker Yield, Vacuum Resids

COMPONENT	FEED 1 WT%	FEED 2 WT%
FEED		
UNDESULFURIZED VACUUM RESID	1.0000	
DESULFURIZED VACUUM RESID		1.0000
TOTAL FEED	1.0000	1.0000
PRODUCTS		
ACID GAS	0.0141	0.0050
COKER OFF GAS	0.0809	0.0830
COKER LIGHT NAPHTHA	0.0430	0.0200
COKER HEAVY NAPHTHA	0.0850	0.0695
COKER KEROSENE		0.1750
COKER DIESEL	0.2220	0.2550
COKER GAS OIL	0.2360	0.1690
COKE	0.3190	0.2135
LOSS		0.0100
TOTAL PRODUCT	1.0000	1.0000

FEED 1: FROM LIGHT ARABIAN/KUWAIT MIX.
FEED 2: DESULFURIZED VACUUM RESID FEED FROM KUWAIT CRUDE.

Table 6-4
Delayed Coker Gas Yield, Undesulfurized Vacuum Resid Feed

COMPONENT	WT% FEED
H_2	0.03
H_2S	1.41
C_1	1.94
$C_2 =$	0.27
C_2	1.85
$C_3 =$	0.62
C_3	1.58
IC_4	0.24
$C_4 =$	0.73
NC_4	0.83
TOTAL (INCLUDING ACID GAS)	9.50

Table 6-5
Feed and Product Qualities, Undesulfurized Feed

PROPERTY	UNITS	FEED	C5-175°F	175–355°F	350°F+	COKE
GRAVITY	°API	7.3	74	56.6	26.8	
SULFUR	Wt%	4.7	0.4	0.9	2.9	6.2
NITROGEN	ppmw		100	200	1500	
PONA	vol%		50/46/3/1	30/40/20/10		
BROMINE NUMBER			100	70	25	
RON			81			
VISCOSITY	122, cst				4	
VANADIUM	ppmw				0.2	229
NICKEL	ppmw				0.3	50
CON. CARBON	Wt%	21.2			0.1	
VOLATILES	Wt%					10

processing conditions employed. Coke product from coker units is known as *green coke*. Green coke is composed mainly of carbon but also contains 10–15% volatile hydrocarbons, together with other impurities, such as sulfur, vanadium, nickel, or nitrogen. If green coke has sufficiently low levels of impurities, such as sulfur and metals, it may be suitable for calcining. The higher-quality green coke is often said to be of "anode quality." Calcining involves heating the green coke to drive off volatile

Table 6-6
Feed and Product Qualities, Desulfurised Feed

PROPERTY	UNITS	FEED	LIGHT NAPHTHA	HEAVY NAPHTHA	KEROSENE	DIESEL	GAS OIL	COKE
GRAVITY	°API	14	82.5	63.6	44.2	29.8	19.2	
REAL DENSITY	gm/cc							2.105
ASTM D86								
	10%, F	1015	118	192	331	548	717	
	50%		126	213	390	609	831	
	90%		147	255	476	697	932	
SULFUR	Wt%	1.51	0.1	0.1	0.27	0.79	1.2	2.67
NITROGEN	ppmw		100			2300		
PONA	vol%							
BROMINE NUMBER								
FREEZE POINT	°F				−54.6			
POUR POINT	°F					38.1		
RON			81.8	73.7				
VISCOSITY	122, cst					25.6		
VANADIUM	ppmw							150
NICKEL	ppmw							80
SODIUM	ppmw							90
CON. CARBON	Wt%	12.3						
VOLATILES	Wt%							9.5

Table 6-7
Typical Coke Specifications

TYPE	UNITS	SPONGE COKE	NEEDLE COKE
USE		ANODES	ELECTRODES
GREEN COKE			
SULFUR	Wt%	<3	<1.5
METALS			
V	ppmw	<350	
Ni	ppmw	<300	
Si	ppmw	<150	
Fe	ppmw	<270	
VOLATILE MATTER	Wt%	<12	<6
CALCINED COKE			
MOISTURE	Wt%	<0.5	<0.5
VOLATILE MATTER	Wt%	<0.5	
ASH	Wt%	0.5	0.5
SULFUR	Wt%	<3.0	<1.50
METALS			
V	ppmw	<350	
Ni	ppmw	<300	
Si	ppmw	<150	
Fe	ppmw	<270	
DENSITY	gm/cc		
200 MESH, R.D.		2.04–2.08	>2.12
VIBRATED BULK DENSITY		>0.80	
CTE*	1/°C × 10^{-7}	<40	<4

*CTE = COEFFICIENT OF THERMAL EXPANSION.

components and improve its electrical conductivity. Calcined coke produced is used in aluminum smelting, titanium dioxide production, and to increase the carbon content in iron and steel production. Petroleum coke not suitable for calcining is used as fuel in various applications and said to be of "fuel grade." Its high sulfur content frequently limits its scope for use in power generation. A major consumer is the cement industry, where impurities present in fuel are absorbed in the cement product and not released to atmosphere.

Petroleum coke can be broadly classified into two categories, sponge coke and needle coke, depending on its physical properties, such as its texture, density, porosity, electric resistivity, and coefficient of thermal conductivity. Typical properties of sponge and needle coke are shown in Table 6-7.

Sponge Coke

Sponge coke is average-quality petroleum coke produced from mainly nonaromatic feedstocks. The aluminum industry is the largest single user for this coke, where it is used for anode making. Roughly 0.4–0.5 ton anode is consumed per ton of aluminum produced. Anodes are manufactured by blending petroleum coke aggregates with coal tar pitch. The characteristics of calcined coke follow:

- *Sulfur.* Anode-grade calcined petroleum coke varies in sulfur content between 0.5 and 3%. Although sulfur in calcined petroleum coke improves anode performance because it inhibits the negative side reactions of air and carbon dioxide, the allowable sulfur level in most cases is determined by environmental regulations in areas where the smelting plants are located.
- *Metals.* Metals are contaminants with a negative impact on the purity of aluminum and other products produced. Vanadium promotes air reactivity and inhibits conductivity of the aluminum produced. Calcium and sodium have a significant negative impact on CO_2 and air reactivity.
- *Density.* The apparent and bulk density are variables that determine the density of the resulting anode constructed from the material. They are also important parameters for the amount of pitch (coal tar) used as a coke binder during anode construction. Higher density values are desirable.
- *Air and CO_2 reactivity.* At an anode operating temperature of approximately 1800°F, the carbon reacts and is consumed by the hot air around the anode and CO_2 being generated as a part of the process. Values of 10% and 0.1% per minute of air and CO_2 reactivity are typical.
- *Particle size.* In general, calcined coke needs to have 30–35% of the particles larger than ¼ in. to produce a suitable aggregate required for the production of anodes.

Needle Coke

Needle coke is used in the manufacture of large diameter (24–28 in.) graphite rods for ultra high-power furnace electrodes. The material used must be of high density, low resistivity, high strength, and very low coefficient of thermal expansion (CTE).

This material is produced from aromatic feedstocks to the coker unit. Also, the feed must be very low in sulfur, metals, and asphaltenes. Refinery-derived feedstocks such as thermal tars, decant or slurry oil from catalytic cracking, and extracts from the lube solvent extraction unit are most suitable.

The operating conditions for needle coke require higher drum temperatures, which decrease the CTE of the coke produced. This, however, increases furnace fouling rate and coke cutting time, as the coke produced is harder. A 15°F increase in drum temperature is known to decrease the CTE by 30% but triples the coke cutting time.[3]

VISBREAKING

Visbreaking is a mild thermal cracking process.[4] The function of a visbreaking unit is to produce lower viscosity and low-pour resid for blending to fuel oil. In this cracking process, cracked gas, gasoline/naphtha, gas oil, and thermal tar are produced. The gas oil is blended back into the thermal tar to yield fuel oil. Thermal cracking reduces the viscosity and pour point of the resid and hence the cutter stock requirement for blending this resid to fuel oil. Thus, the overall production of fuel oil is reduced. A second consideration is the removal of some feed sulfur. Although visbreaking is an inefficient process in this respect, sulfur removal does occur to some extent.

THE VISBREAKING PROCESS

The feed to the unit is vacuum resid at 670°F coming from the vacuum distillation unit (see Figure 6-3). The charge stream is pumped by a charge pump P-101 to visbreaker heater H-101A and 101B, where it is heated to 920°F. The visbreaker heater is a single-pass, controlled-gradiant, box-type heater with a preheater and two soaking coils. The temperature profile of a visbreaker heater is shown in Figure 6-4. Water injection connections are provided at the inlet of the soaking coils, although during normal operation, no water is injected. Normally, one heater is in operation while the other one is on standby.

During the course of the run, coke forms in the tube. Therefore, permanent steam/air decoking facilities are provided. The tube metal temperature is assumed to reach a maximum of 1400°F during decoking. The coil is designed for approximately 133% of the clean tube pressure drop.

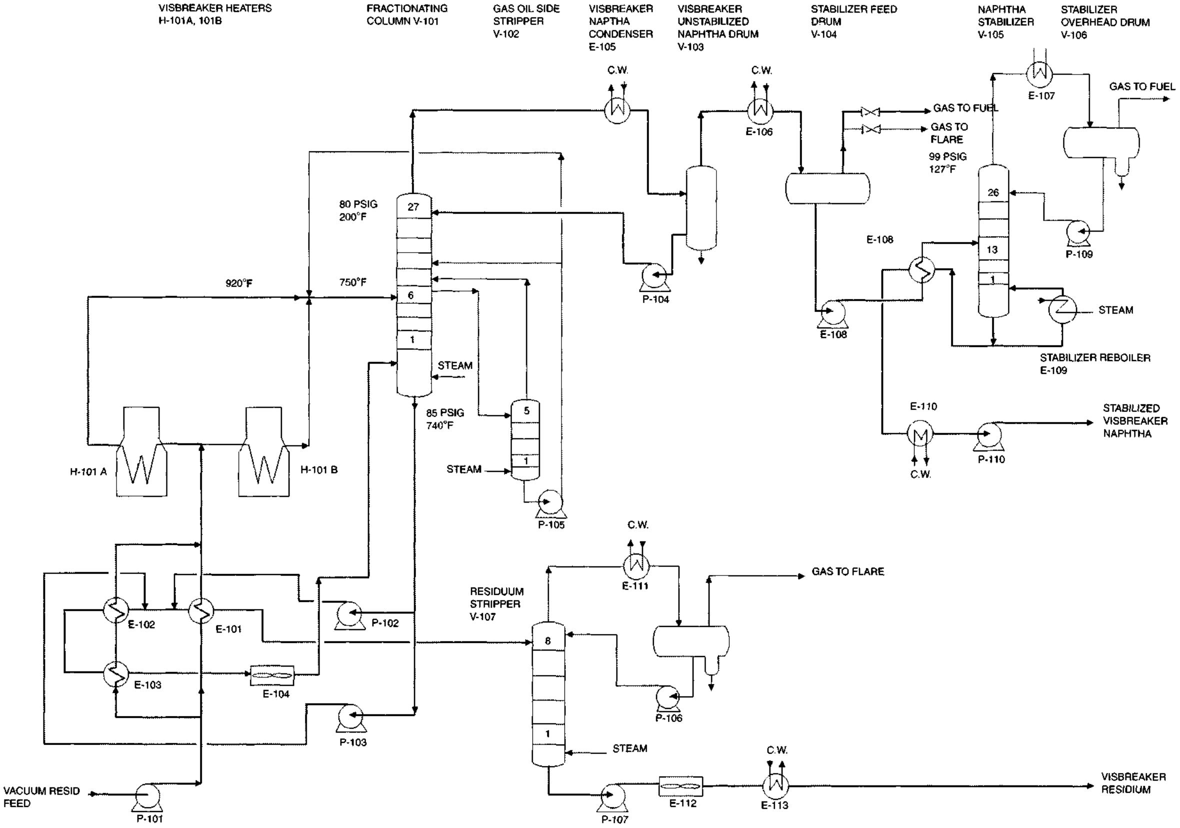

Figure 6-3. Visbreaker unit.

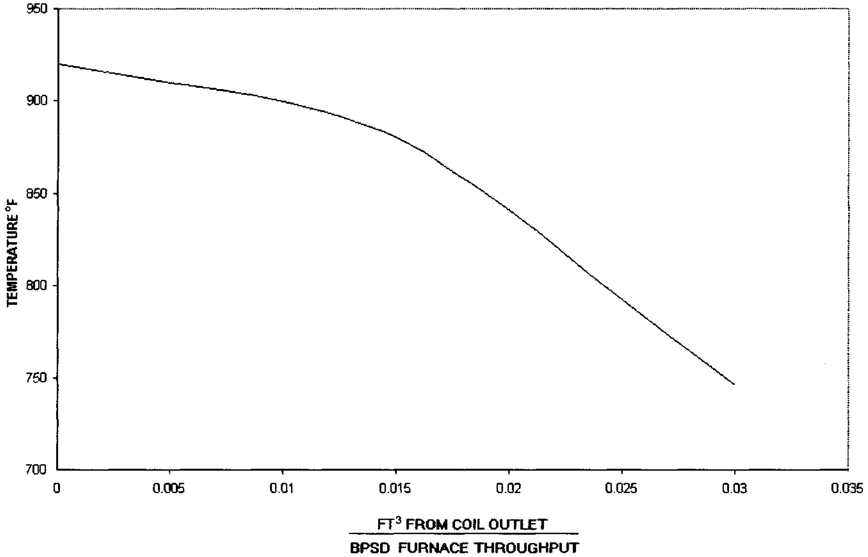

Figure 6-4. Visbreaker temperature gradient.

The effluent from the heater is quenched to 750°F, with cracked gas oil coming from gas oil side-stripper. The quenched visbreaker effluent flows to main fractionator column V-101, with about 27 plates. The vapor is flashed off and separated into gas, gasoline, cracked naphtha, and a gas oil cut. The overhead vapor condensed in condenser E-105 accumulates in unstabilized naphtha drum V-103, which provides reflux to the main fractionator column. The uncondensed vapor is further cooled in E-103 and accumulates in stabilizer feed drum V-104. The unstabilized naphtha from V-104 flows to a stabilizer or debutanizer column V-105, with 26 plates, which removes any C_4 gases as the top stream and a stabilized naphtha stream as the bottom product.

A gas oil sidestream is withdrawn from the main fractionator column and steam stripped in V-102, the gas oil stripper. This stream is pumped by P-105 and quenches the visbreaker heater effluent at the heater outlet.

To minimize coke formation in the bottom sump section, the fractionator column is maintained at 650°F by removing a slipstream of thermal tar and cooling it by heat exchange with incoming fresh feed and an air cooler before returning it to the column.

The bulk of visbroken thermal tar is transferred by P-102 to residuum stripper column V-107, where it is steam stripped with medium-pressure steam to remove light ends and gas. The visbroken tar is withdrawn from the stripper column and cooled in exchangers E-112 and E-113 before being sent to storage.

The operating conditions of a visbreaker unit are shown in Table 6-8. The yield from a visbreaker unit, the unit's utility consumption, and the properties of feed and product are shown in Tables 6-9 to 6-12.

The important process variables are charge stock quality, cracking temperature, and residence time of oil in the coil. Feed to visbreaker units is either reduced crude or vacuum resids. Resids from paraffinic crudes are the most suitable because of the larger reduction in pour point achieved. The coil temperature profile and residence time are very closely controlled (Figure 6-4) to monitor the severity of operation, usually measured by the amount of gasoline produced. Higher than optimum temperatures can produce unstable tar and more frequent coking of visbreaker coil or shorter run lengths.

Table 6-8
Visbreaker Operating Conditions, *Basis 7634 BPSD Vacuum Resid from Darius (Iranian) Crude*

OPERATING PARAMETER	UNITS	
PREHEATER SECTION (CONVECTION + ONE RADIANT COIL)		
FEED INLET TEMPERATURE	°F	670
OUTLET TEMPERATURE	°F	800
DUTY	mmBtu/hr	10.73
HEAT FLUX	Btu/hr °F	10000
FIRST SOAKING SECTION		
INLET TEMPERATURE	°F	800
OUTLET TEMPERATURE	°F	883
DUTY	mmBtu/hr	9.00
COIL VOLUME	ft^3	93
SECOND SOAKING SECTION		
INLET TEMPERATURE	°F	883
OUTLET TEMPERATURE	°F	920
DUTY	mmBtu/hr	12.9
COIL VOLUME	ft^3	93
STEAM SUPERHEATER SECTION (*CONVECTION COIL*)		
INLET PRESSURE	psia	170
INLET TEMPERATURE	°F	370
OUTLET PRESSURE	psia	160
OUTLET TEMP	°F	600

Table 6-9
Visbreaker Unit Yields

COMPONENT	VACUUM RESID FEED, W/W	ATMOSPHERIC RESID, W/W
FEED		
ATM RESID FEED		1.0000
VACUUM RESID FEED	1.0000	
TOTAL FEED	1.0000	1.0000
PRODUCTS		
H_2	0.0001	
H_2S	0.0053	
C_1	0.0047	
$C_2 =$	0.0006	
C_2	0.0047	
$C_3 =$	0.0026	
C_3	0.0051	
IC_4	0.0015	
$C_4 =$	0.0063	
NC_4	0.0069	
IC_5	0.0061	
$C_5 =$	0.0061	
NC_5	0.0023	
GASES, TOTAL		0.0250
LIGHT GASOLINE	0.0198	
NAPHTHA	0.0437	0.0750
GAS OIL	0.1455	0.2400
700°F + TAR	0.7387	0.6600
TOTAL	1.0000	1.0000

Table 6-10
Visbreaker Utility Consumption *per Ton Vacuum Resid Feed*

UTILITY	UNITS	CONSUMPTION
FUEL	mmBtu	1.8010
STEAM	mmBtu	−0.6520
POWER	kWhr	6.1840
DISTILLED WATER	MIG*	0.0257
COOLING WATER	MIG*	1.3011

*MIG = 1000 IMPERIAL GALLONS.

Table 6-11
Feed and Product Properties from Visbreaker, *Vacuum Resid Feed from an Iranian Crude*

PROPERTY	UNITS	FEED	LIGHT CRACKED GAS	CRACKED NAPHTHA	CRACKED GAS OIL	VISBREAKER TAR
GRAVITY	°API	4.8	73.9	52.3	34	4.4
SPECIFIC GRAVITY		1.0382	0.6889	0.7699	0.8550	1.0412
TBP RANGE	°F		C_5–180	180–330	330–670	
SULFUR	Wt%	6.28	0.34	0.57	1.35	6.32
VISCOSITY	Cst, 122°F	450000			2	300000
	Cst, 210°F	2300				1200
	Cst, 300°F	130				72
	Cst, 500°F	7.2				
MOL WT		690	77	106.7	193	480
UOP "K"		11.6				
POUR POINT	°F	135			30	60

Table 6-12
Feed and Product Properties from Visbreaker, *Atmospheric Resid Feed*

PROPERTY	UNITS	FEED	VISBREAKER TAR
GRAVITY	°API	17.7	21.5
SPECIFIC GRAVITY		0.9484	0.9248
VISCOSITY	Cst, 122°F	175	
	Cst, 210°F	22	10
POUR POINT	°F	50	40
DRY SEDIMENT	Wt%		0.15

HEATER DECOKING

Decoking is done by first introducing 450 psig steam, shutting off the burners and charge pump, then allowing several minutes to elapse while the heater tubes are blown to the column. The 450 psig steam is shut off and the heater blocked with blinds.

The decoking pipes are next connected to both the inlet and outlet of the heater and 150 psig steam is introduced at the inlet. One or more burners are lit in the preheat section to bring the steam temperature to 800°F. Water is introduced in the effluent line to limit the temperature to 250°F. After an hour has elapsed, to allow any volatile matter in the coke to be stripped off, air (105 psia) is very gradually introduced to burn off carbon. The progress of the burn off can be observed through heater peepholes as a relatively narrow band of red hot tubing. This band gradually progresses down the heater coil as the coke is burned off. The air rate is adjusted as necessary to maintain the dark red appearance of the tube.

The piping is arranged to permit reversing the direction of flow of air and steam, should a localized burning section becomes too hot (>1300°F). When the decoking step is complete, the tubes are cooled with steam, followed by air cooling, and finally water is very gradually introduced then increased in rate to wash out any residual fly ash. Afterward, the water is drained from the heater.

REGENERATION TIME

Regeneration or decoking time of visbreaker heater coil can be calculated by simple calculations.

EXAMPLE 6-1

The particulars of an actual visbreaker coil follow. We are to estimate the time required for decoking this coil. Assume that coking takes place in tubes operating above 800°F. Neglect heat losses and hydrogen content of coke.

Visbreaker coil nominal diameter = 4 in.

Visbreaker coil pipe schedule = 80

Visbreaker coil internal diameter = 3.826 in.

Total length of visbreaker pipe = 5080 ft

Length of pipe operating above 800°F = 2300 ft

SOLUTION

$$\text{Volume of coke deposited assuming } {}^{3}/_{16}\text{-in. coke layer (ft}^3\text{)} = \frac{3.14 \times 3.826 \times 2300 \times 3}{(12 \times 12 \times 16)}$$

$$= 35.97$$

$$\text{Density of coke (assume)} = 75\ \text{lb/ft}^3$$

$$\text{Weight of coke deposited} = 35.97 \times 75$$

$$= 2700\ \text{lb}$$

Heat of Combustion

Assume coke deposits in the coil consist of 92% carbon and 8% sulfur.

$$\text{Heat from carbon} = 2700 \times 0.92 \times 14{,}100$$

$$= 35.02\ \text{million Btu}$$

$$\text{Heat from sulfur} = 2700 \times 0.08 \times 4000$$

$$= 0.864\ \text{million Btu}$$

$$\text{Total hat} = 35.884\ \text{million Btu}$$

Time of Regeneration

Assume superheated steam at 800°F is used for decoking and the available steam supply is 2500 lb/hr. In the operation, steam leaving the combustion zone is at 1250°F. The specific heat of steam is assumed at 0.51. The time of coil decoking can be calculated as follows:

$$\text{Time required} = \frac{35.884 \times 1{,}000{,}000}{(450 \times 0.51 \times 2500)}$$
$$= 62.54\,\text{hr}$$

Heater Duty

$$\text{For steam superheating from 340 to } 800^\circ\text{F} = 2500\ (1432 - 1194)$$
$$= 535{,}000\,\text{Btu/hr}$$

Quench Water Requirements

The amount of water (90°F) required to quench 2500 lbs/hr steam from 1250 to 250°F is estimated as follows:

$$\text{Quench water} = \frac{2500 \times (1250 - 250) \times 0.5}{(1164 - 58)}$$
$$= 1130\,\text{lb/hr}$$
$$= 2.25\,\text{GPM}$$

SOLVENT DEASPHALTING

Historically, solvent deasphalting of vacuum residues has been used in the manufacture of lubricating oil to separate out the heavy fraction of crude oil beyond the range of economical commercial distillation, using propane as solvent. The feed to the deasphalting unit is usually a vacuum resid with a 950°F TBP cut point. Over time, this process has come to be used to prepare catalytic cracking feeds, hydrocracking feeds, hydrodesulfurizer feeds, and asphalts.

Studies have shown that high yield of oil can be obtained, while limiting asphaltenes and metals, by using the proper heavier solvent. Thus, extraction rates from 65 to 85% of deasphalted oil (DAO) have been obtained. Whereas vacuum residue is a very difficult feed stock for catalytic processes, DAO can be easily processed, like other heavy distillates. The asphalt produced can be blended with straight-run asphalts or blended back with fuel oil.

Modern solvent deasphalting units usually use a blend of light hydrocarbon solvents (C_5-C_6 paraffinic cut) to allow maximum operating flexibility. The solubility of oil in solvent at a fixed temperature increases as the concentration of heavier components in the solvent increase.

Selectivity is the ability of the solvent to separate paraffinic and sometimes resinous oils from the asphalt or vacuum resid feed. As the metals, sulfur, and nitrogen are generally concentrated in the larger molecules, the metal, sulfur, and nitrogen content of deasphalted oil is considerably reduced, as shown in Figure 6-5. Maximum selectivity subject to economic constraints is always the processing objective. Selec-

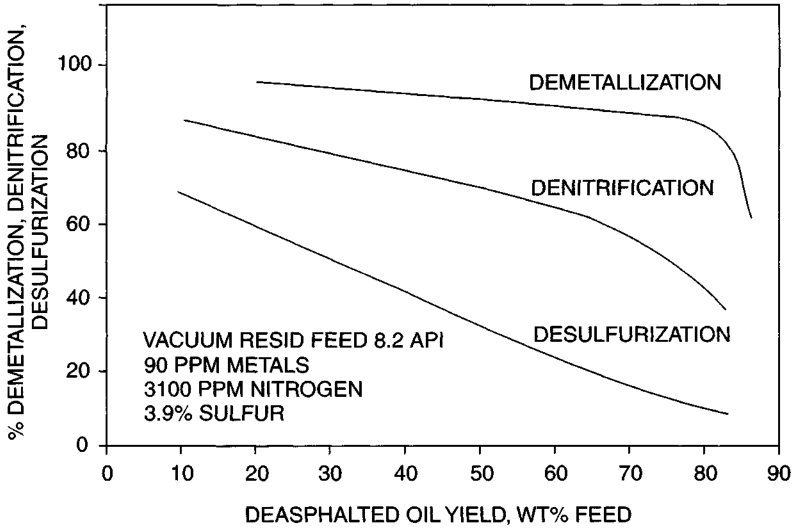

Figure 6-5. Percent of demetallization and desulfurization as a function of a desasphalted oil yield.

tivity can be improved by increasing the solvent/oil ratio at a constant DAO yield. Since considerable energy is required to recover the solvent, there is always an optimum solvent/oil ratio for each operation. The yield of DAO and asphalt from vacuum resid feed is shown in Table 6-13. Table 6-14 shows the deasphalting unit's utility consumption.

The solubility of oil in the solvent decreases with increasing temperature and this variable provides the major method of day-to-day operational control of the process.

Table 6-13
Solvent Deasphalting Yields and Product Qualities

PROPERTY	UNITS	FEED 1	FEED 2
FEED			
GRAVITY	API	8.2	13.8
SULFUR	Wt%	3.9	0.6
NITROGEN	wppm	3100	2100
NICKEL	wppm	19	2
VANADIUM	wppm	61	11
CON CARBON	Wt%	19	13
VISCOSITY	Cst, 210°F	500	375
DEASPHALTED OIL			
YIELD LV%		83	75
GRAVITY	API	14.4	19.5
SULFUR	Wt%	3.55	0.47
NITROGEN	wppm	2000	1200
NICKEL	wppm	3	0.3
VANADIUM	wppm	11	1.3
CON CARBON	Wt%	8.4	4.7
VISCOSITY	Cst, 210°F	92	79
ASPHALT			
YIELD	LV%	17	25
SPECIFIC GRAVITY		1.125	1.0839
SULFUR	Wt%	5.6	0.94
SOFTENING POINT	R. & B, °F	302	200
VISCOSITY	Cst, 400°F		100

NOTE:
FEED 1, START RUN VACUUM RESID FROM MIDDLE EASTERN CRUDE.
FEED 2, VACUUM RESID EX ARDS UNIT, MIDDLE EASTERN CRUDE.

Table 6-14
Solvent Deasphalting Unit Utility Consumption

UTILITY	UNITS	CONSUMPTION
FUEL	mmBtu	0.533
LP STEAM	mmBtu	0.632
ELECTRIC POWER	kWhr	18.1

THE DEASPHALTING PROCESS

Extraction Section

Fresh feed (vacuum residue) is pumped into the solvent deasphalting unit and combined with a small quantity of predilution solvent to reduce its viscosity (see Figure 6-6). The combined vacuum residue and predilution solvent at the desired extraction temperature flow into the middle of rotating disk contactor (RDC) V-101. Solvent streams from HP and LP solvent receivers V-106 and V-107 are combined, and a portion of the combined stream is used as predilution solvent. The major portion of the solvent is regulated to the desired temperature by solvent heater E-101A and cooler E-101B then flows into the bottom section of the RDC. The desired temperature gradient across the RDC is maintained by steam coils located at the top of the tower. The highest temperature is at the top of the RDC, and the lowest temperature is at solvent inlet. In the top section of the RDC, relatively insoluble, heavier material separates from the solution of DAO. The material flowing back down the RDC provides internal reflux and improves the separation between DAO and asphalt.

DAO RECOVERY SECTION

DAO plus the bulk of the solvent (DAO mix) leaves the top of the RDC tower and flows to the DAO recovery system. The pressure at the top of the RDC is controlled by a back-pressure control valve. The DAO mix flows to fired heater H-101, to vaporize a portion of the solvent. The DAO mix then flows into HP flash tower V-104, where the solvent vapor is taken overhead. The DAO mix is held under level control in the bottom of this tower. The liquid mix then flows to pressure vapor heat exchanger (PVHE) E-102, where it is heated by condensing solvent from high-pressure flash. The solvent, totally condensed, flows to HP solvent

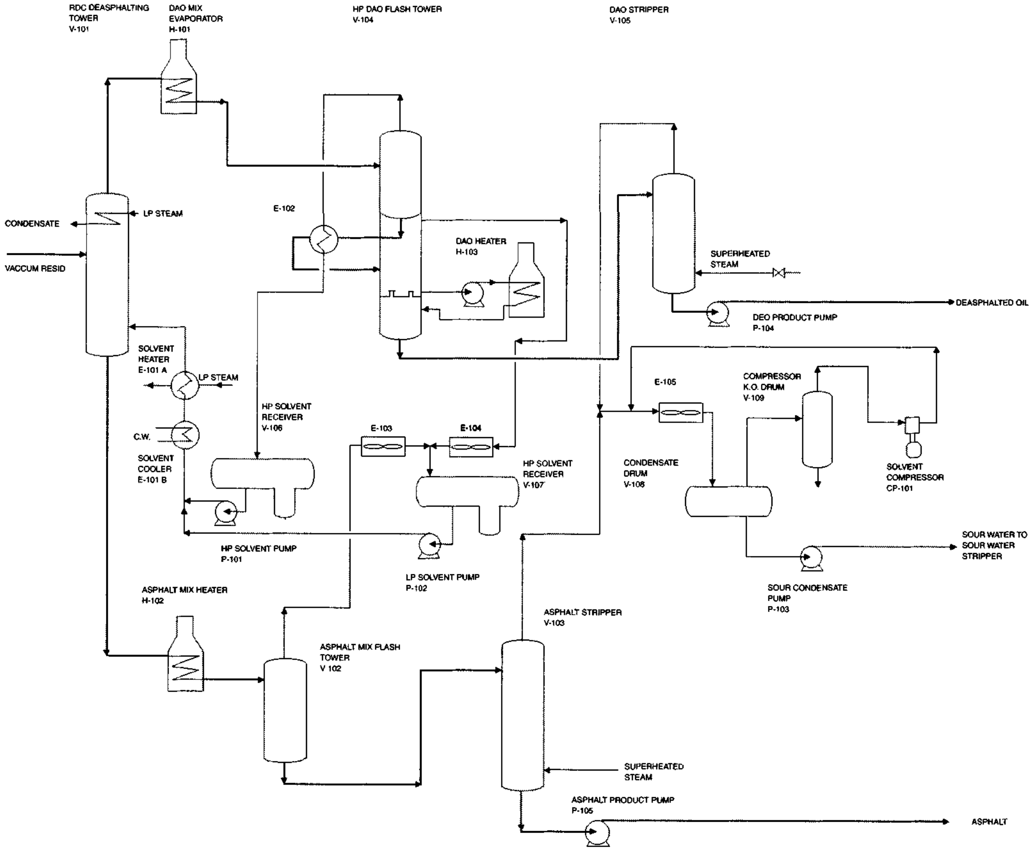

Figure 6-6. Solvent deasphalting unit.

receiver V-106. The DAO mix flows from PVHE to an LP flash tower, where again solvent vapors are taken overhead. The DAO mix flows down the tower, where it is further heated by rising solvent vapors from the reboiler. The remaining DAO mix is circulated through fired heater reboiler H-103 and returns to the bottom of the LP flash tower. The solvent vapor rise through the tower and the liquid mix is held under level control before flowing into DAO stripper V-105.

DAO RECOVERY

The mix enters the top tray of the stripper, and the remaining solvent is stripped overhead with superheated steam, which enters below the bottom tray. The DAO product is pumped from the stripper bottom by P-104 to the battery limits.

ASPHALT RECOVERY

The solvent/asphalt mix from the RDC tower flows at a controlled rate to asphalt mix heater H-102. The hot two-phase asphalt mix from the heater is flashed in asphalt mix flash tower V-102. The solvent vapors are taken overhead. The remaining asphalt mix flows to asphalt stripper V-103 and enters the tower on the top tray. Superheated steam is used to strip the remaining solvent from the asphalt. The wet solvent vapor overhead combines with the overhead vapors from the DAO stripper. The asphalt product is pumped from the stripper bottom by P-105 to the battery limits.

SOLVENT SYSTEM

The solvent evaporated in the LP flash tower is condensed and flows to the LP solvent receiver. Solvent from the asphalt flash tower, which operates at the same pressure, is condensed in a separate condenser and flows to LP solvent receiver. The reason for segregating the two solvent streams is the potential for the accidental fouling by asphalt carried over from the flash tower.

Vapor overhead from the two strippers is cooled, and most of the water is condensed and recovered in stripper condensate drum V-108. The water collected is considered sour and pumped from the unit to the sour water stripper. The noncondensed solvent vapor from this drum flows to solvent compressor suction drum V-109, where any entrained liquid is knocked out. The vapor is then compressed by solvent compressor CP-101 and joins the vapors from the asphalt flash drum, upstream of asphalt solvent condenser. Makeup solvent is pumped to the LP solvent receiver from the off-site solvent tank as required.

BITUMEN BLOWING

Industrial grades of bitumen with industrial uses, such as road paving, waterproofing, insulation, are manufactured from heavy crudes, either by vacuum reduction alone or air blowing of vacuum resids. However, the vacuum resids from all crudes are not suitable for making bitumen.

Vacuum distillation of some crudes under specified conditions may yield resid that meets the specifications of a bitumen for certain paving grades, but for low penetration and higher softening point grades, air blowing the vacuum resid under specified operating conditions is required. Pilot plant tests are generally necessary to establish whether a given crude can yield good-quality bitumen and determine the optimum operating conditions for a given bitumen grade. Subjecting the bitumen to high temperatures during processing can affect the ductility of the product and care is taken not to subject asphalt to more than approximately 750°F.

In the air blowing operation, the aromatic and polar compounds in the feed are condensed to form higher-molecular-weight chemical species. The process increases the asphaltene level, while the level of aromatics and polar aromatics are reduced. The change is also indicated by a significant increase in the average molecular weight of the blown asphalt. The saturates in the feed, consisting mainly of cyclosaturates, are not affected by the air blowing step.

When certain additives, such as ferric chloride, are added to the air blowing step, the cyclosaturates are dehydrogenated. There is increase in the level of aromatics, which is a major contributor to higher penetration values. These aromatics, in turn, are converted to asphaltenes.

It has been shown that the weight percentage of material with molecular weight 490 is related to the softening point of the asphalt, while the weight percent of material at molecular weight 2160 is related to penetration. The relationship between the softening point and lower-molecular-weight material (490) contained in asphalt and also between high molecular weight (2160) and penetration has been presented by Dark.[5] A balance of material at these two molecular weights is required to obtain air blown asphalts with desired final characteristics. Composition of asphalts, however, is also important. The ratio of saturates to asphaltenes determines the weathering characteristics of asphalts. Good-quality asphalts generally have a saturates/asphaltene ratio of between 2 and 3.

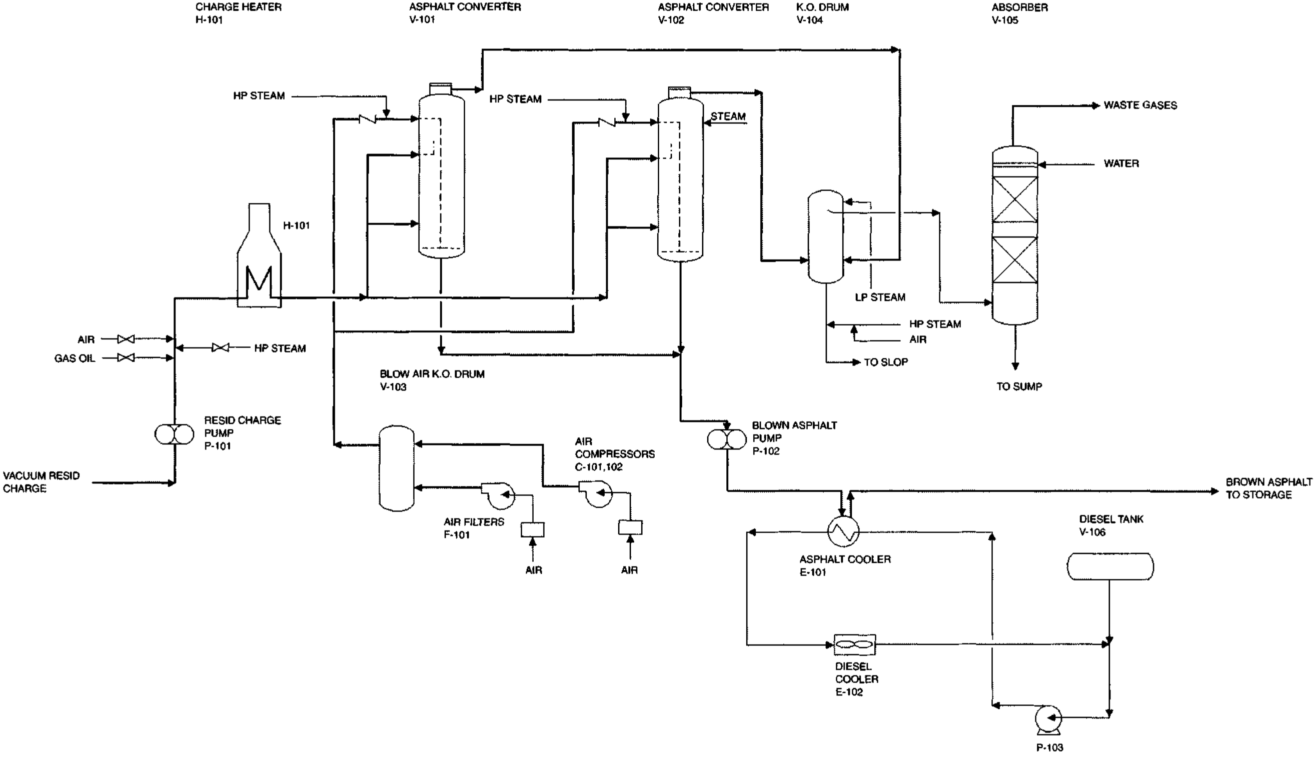

Figure 6-7. Bitumen blowing unit.

THE BITUMEN BLOWING PROCESS

Vacuum resid from the vacuum distillation unit is charged to asphalt converters V-101 and V-102 through steam-jacketed gear pump P-101 and charge heater H-101 (see Figure 6-7). The temperature of the feed to asphalt converters is controlled at 390–410°F. Compressed air at 100 psig mixed with HP steam is bubbled at a controlled rate through the vacuum resid using an internal sparger, causing exothermic reactions in the asphalt converter. The temperature of the bed is controlled by the air/steam injection rate in the range of 500–520°F. Approximately 2% of the charge is carried overhead as fumes and vapor. The waste gases pass through knockout drum V-104, where any condensed liquid separates out and is sent to slop. The vapors from V-104 are scrubbed with water in absorber V-105 and sent to refinery flare.

Finished blown asphalt from the asphalt converter is pumped through E-101, where its temperature is brought down to approximately 250°F by heat exchange with a closed-circuit diesel stream. The diesel stream, in turn, is cooled in an air cooled exchanger. The asphalt stream at 250°F is sent to storage through steam-jacketed pump P-102.

OPERATING CONDITIONS

The typical operating conditions for a bitumen blowing unit processing a 24 API Middle Eastern crude are listed in Table 6-15. The properties of the feed and product from the bitumen blowing unit are shown in Table 6-16. The overall yields from the unit and utility consumption are listed in Tables 6-17 and 6-18. The product specifications for various end uses and test methods used are shown in Tables 6-19 and 6-20.

Table 6-15
Bitumen Blowing Unit Operating Conditions

OPERATING VARIABLE	UNITS	
VACUUM RESID (FEED) TEMPERATURE	°F	390–410
BED TEMPERATURE	°F	500–520
CONVERTER PRESSURE	psig	95
AIR BLOWING RATE*	scft/bbl	166

*FOR 60/70 PEN. ASPHALT.

Table 6-16
Properties of Feed and Products

PROPERTY	FEED	PRODUCT
PENETRATION	220	60–70
SPECIFIC GRAVITY	1.016	1.028
KINEMATIC VISCOSITY		
210, Cst	800–1100	6400
250, Cst		1400
300, Cst		335
400, Cst		35
520, Cst		5

Table 6-17
Bitumen Blowing Unit Yields

STREAM	WT FRACTION
FEED	
VACUUM RESID	1.0000
TOTAL FEED	1.0000
PRODUCTS	
BITUMEN, 60/70 PEN.	0.9800
LOSSES	0.0200
TOTAL PRODUCT	1.0000

Table 6-18
Bitumen Blowing Unit Utility Consumption *(per Ton Feed)*

		CONSUMPTION	
UTILITY	UNITS	60/70 PEN.	40/50 PEN.
ELECTRICITY	kWhr	7	10
FUEL	mmBtu	0.04	0.06
STEAM	mmBtu	0.09	0.09
AIR	scft	1500	2300
DISTILLED WATER	MIG*	0.11	0.11
COOLING WATER	MIG*	1.3	1.3

*MIG = 1000 IMPERIAL GALLONS.

Table 6-19
Properties of Penetration Grade Bitumens

PROPERTY	TEST METHOD	GRADE									
			15 PEN.	25 PEN.	35 PEN.	40 PEN.	50 PEN.	70 PEN.	100 PEN.	200 PEN.	300 PEN.	450 PEN.
PENETRATION AT 25°C	IP 49	10–20	20–30	28–42	30–50	40–60	60–80	80–120	170–230	255–345	385–515	
SOFTENING POINT, MIN.	IP 58		63	57	52	58	47	44	41	33	30	25
MAX.		76	69	64	68	58	54	51	42	39	34	
LOSS ON HEATING FOR 5 HOURS AT 63°C	IP 45											
(A) LOSS BY MASS, MAX		0.1	0.2	0.2	0.2	0.2	0.2	0.5	0.5	1.0	1.0	
(B) DROP IN PENETRATION, %, MAX		20	20	20	20	20	20	20	20	25	25	
SOLUBILITY IN TRICHLORO ETHYLENE	IP 47											
% BY MASS, MIN.		99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	
PERMITTIVITY AT 25°C AND 1592 Hz, MIN.				2.630	2.65	2.65	2.65					

Table 6-20
Properties of Cutback Bitumen

PROPERTY	TEST METHOD	GRADE		
		50 SEC.	100 SEC.	200 SEC.
VISCOSITY (STV)* AT 40°C, 10 mm CUP	IP 72	40–60	80–120	160–240
DISTILLATION				
(A) DISTILLATE AT 225°C (vol%, MAX.)	IP 27	1	1	1
DISTILLATE AT 360°C (vol%, MAX.)		8–14	6–12	4–10
(B) PENETRATION AT 25°C OF RESIDUE	ASTM D5-73	100–350	100–350	100–350
FROM DISTILLATION TO 360°C	IP 49			
SOLUBILITY IN TRICHLORO ETHYLENE, % MASS, MIN.	IP 47	99.5	99.5	99.5

*STANDARD TAR VISCOMETER

NOTES

1. B. P. Castiglioni. “How to Predict Coke Yield.” *Hydrocarbon Processing* (September 1983), p. 77.
2. R. Deblane and J. D. Elliot “Delayed Coking; Latest Trends.” *Hydrocarbon Processing* (May 1982), p. 99.
3. H. R. Jansen. “Conoco Coking/Calcining Process.” Kellogg Symposium on Heavy Oil Upgrading, Nice, France, September 1982.
4. A. Rhoe and C. DeBlignieres, *Hydrocarbon Processing* (January 1979); H. Martin, “Visbreaking, a Flexible Process”, *Oil and Gas Journal* (April 13, 1981); F. Stolfa, *Hydrocarbon Processing* (May 1982); R. Hournac, Kuhn, *Visbreaking; More Feed for FCCU Hydrocarbon Processing* (December 1979).
5. W. A. Dark. *“Asphalt Tests are Correlated.” Hydrocarbon Processing* (September 1983), p. 104.