CHAPTER 2

NAPHTHA

Naphtha is the lightest liquid distillate product of crude distillation consisting of C5 to C10 hydrocarbons boiling in the 100 to 310°F range. It is produced from the atmospheric distillation of crude oil and from many secondary processing units in the refinery. Unlike other petroleum fuels such as kerosene, diesel, or fuel oil, naphtha is not a direct petroleum fuel but is used as a feedstock for the manufacture of plastics and polymers, synthetic fiber, petrochemicals, fertilizer, insecticides and pesticides, industrial solvents for making specialty solvents such as food grade hexane, dyes, and chemicals. In refineries, naphtha is one of the basic feedstocks for the manufacture of gasoline. At locations where natural gas is not available, naphtha is used as a feedstock for producing hydrogen required for hydroprocessing units in refineries. Naphtha is sometimes used as fuel in gas turbines or boilers for power generation units. The worldwide naphtha demand in 2006 was estimated at 900 million tons.

NAPHTHA PRODUCTION

Naphtha is produced from the following units:

- Crude distillation units in the refinery.
- Secondary processing units in the refinery.
- Gas-processing units separating LPG from field gases. Naphtha thus separated is known as natural gas liquid.

Crude Distillation Unit

The yield of naphtha cut from crude distillation depends on the crude oil processed. Lighter crude oils yield larger volumes of naphtha on processing. Table 2-1 lists the yield of naphtha from some Middle Eastern crude oils. Naphtha produced in the refinery is typically a straight C5-310°F cut from the crude distillation unit. Naphtha cut withdrawn from crude column is not a sharp cut because it contains lighter as well as heavier components such as LPG and kerosene.

Naphtha production in the refinery is a two-step process:

1. Production of a broad cut from a crude distillation unit (CDU).
2. Refractionation of the broad naphtha cut to remove light and heavier components.

In the CDU (Fig. 2-1), crude oil is preheated by heat exchange with product streams and enters preflash tower V-100. The preflash tower is a small distillation column with four to five plates that removes most of the LPG gases and some light naphtha as overhead product. The preflash tower top vapors are cooled in exchangers E-101 and E-102 and collected in reflux drum V-103. A part of this preflashed naphtha is sent back to column V-100 as reflux, and the rest is routed to naphtha refractionation section via V-102. The topped crude from the preflash tower is fed to main atmospheric

TABLE 2-1 Yield of Naphtha from Various Crude Oils

Crude	Arab light	Kuwait export	Bahrain	Arab heavy	Bombay high	Safania	Dubai
Crudei API	34.2	30.5	30.4	28.3	39.5	27.1	31.78
Yields, Vol %							
LSR	7.60		4.80	7.30	8.70	4.30	7.10
HSR	10.40		7.60	8.10	15.60	6.90	9.80
Total naphtha	18.00	15.10	12.40	15.40	24.30	11.20	16.90
Kerosene	16.00		19.40	14.60	19.70	20.60	14.40

distillation column V-101. Naphtha is withdrawn from the crude distillation column's reflux drum V-102 and routed to the naphtha refractionation unit. Naphtha liquid withdrawn from the CDU column reflux drum V-102 contains heavy ends that must be removed. Similarly, the LPG gas product from V-102 reflux drum contains some naphtha vapor that must be recovered. Naphtha vapors from V-102 are compressed in compressor C-101 and cooled in a series of water-cooled heat exchangers.

Naphtha Refractionation Unit. The condensed naphtha is collected in naphtha feed drum V-500 (Fig. 2-2). The uncondensed vapors from V-500 enter absorber V-501 near the bottom and are absorbed in a stream of kerosene that enters V-501 near the top. The rich kerosene stream

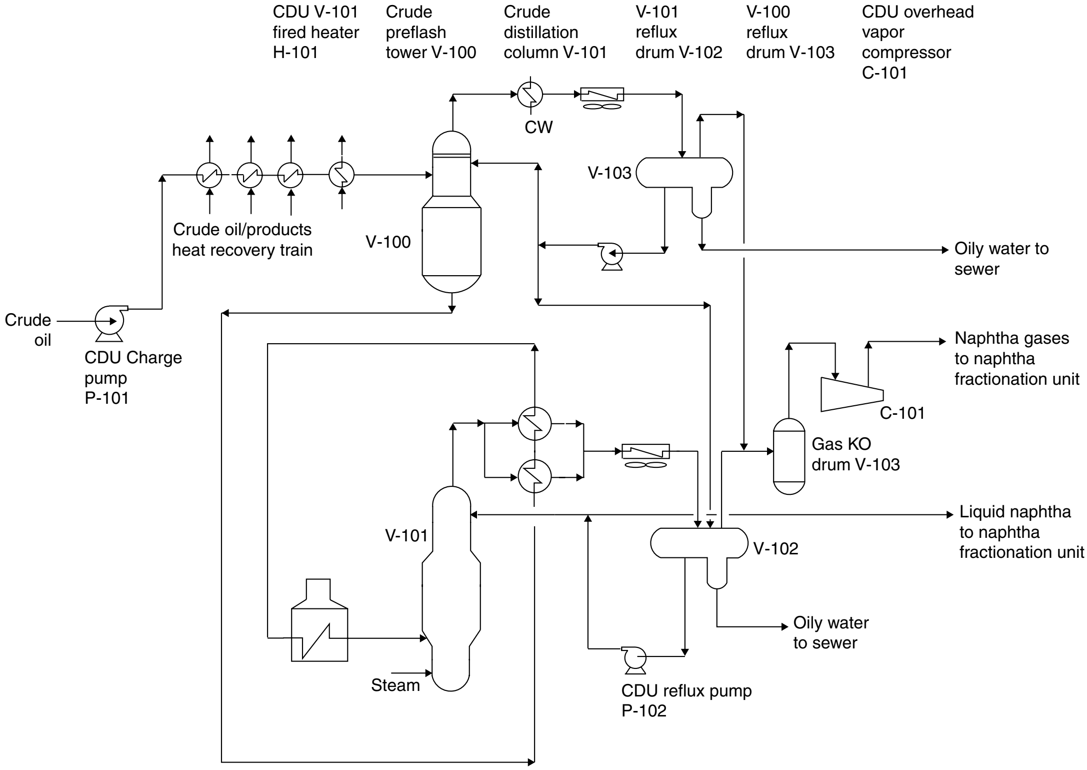

FIGURE 2-1 Simplified process flow diagram for naphtha production from crude distillation unit in refinery.

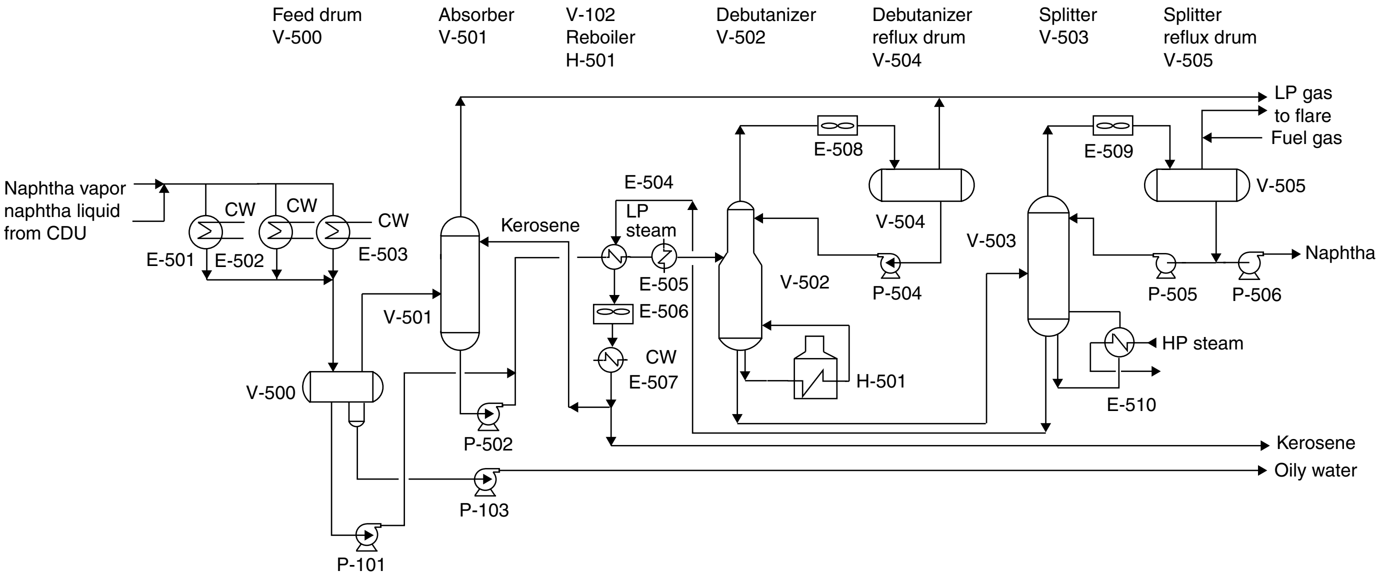

FIGURE 2-2 Naphtha refractionation.

leaving V-501, along with condensed naphtha from V-500 after heating with steam in E-505, enters debutanizer column V-502, which removes all C4 and lighter product from naphtha as overhead product. The bottom product from debutanizer V-502 is sent to a splitter column V-503 where naphtha is removed as a top product and kerosene as a bottom product. A part of kerosene is recycled to absorber V-501 as sponge oil.

Production from Secondary Processing Units

Naphtha is also produced from secondary conversion units such as distillate hydrocrackers, delayed coker units, and resid hydrocrackers. Small quantities of naphtha are also produced by distillate desulfurizer units. However, the distillate hydrocracker is the most important conversion unit, which produces approximately 31 vol % (percentage of volume) naphtha on feed. Compared with straight run naphtha, hydrocracker naphtha has a lower paraffin and higher naphthene content. Hydrocracker heavy naphtha, because of its high naphthene content, is a preferred feedstock for catalytic reformer units. Feed with high naphthene content gives a higher reformate and hydrogen yield.

Production from Associated Gas

Almost 10 percent of total naphtha production comes from associated gas processing. A large quantity of associated gas is also produced as a by-product during crude oil production. Gas separated from oil may contain carbon dioxide, hydrogen sulfide, methane, ethane, propane, normal butane and isobutane, and C5+ hydrocarbons. The typical associated gas composition from a Middle Eastern oil field is listed in Table 2-2. The gas is first processed to remove acid gases (CO_2 and H_2S). Next C3+ components such as propane, butane, and natural gasoline are separated from C1 and C2 gases by cooling with a propane refrigeration system to a low temperature. C3+ hydrocarbons condense as liquid and are separated in a flash drum. The separated hydrocarbons are further separated into propane, butane, and natural gasoline by fractionation in a series of columns. The separated C1 and C2 gases are stripped of any heavier hydrocarbons

TABLE 2-2 Typical Associated Gas Composition

Component	Weight %
H_2	0.00
N_2	0.22
CO_2	2.61
H_2S	0.04
C_1	37.40
C_2	20.97
C_3	19.42
I C_4	3.31
N C_4	8.16
I-C_5	2.00
N C_5	2.63
C_6	2.44
C_7	0.51
C_8	0.20
C_9	0.05
C_{10}+	0.01
Water	0.03
Total	100.00

TABLE 2-3 C_4+ Natural Gasoline Composition and Properties*

	Vol %
Isobutane	0
Normal butane	0
Isopentane	25.6
Normal pentane	37.7
Cyclopentane	0
2,2 Dimethyl butane	1.2
2,3 Dimethyl butane	2.2
2 Methyl pentane	9.7
3 Methyl pentane	6.3
Normal hexane	2.2
Methyl cyclopentane	5.2
Cyclohexane	5.8
Benzene	1.8
C_7+	2.3
Density, g/mL	0.6568
PONA, vol %	
Paraffins	73.9
Naphthene	15.1
Aromatics	11
Sulfur, ppmw	0.5

*Separated from field gases.

they may contain by absorbing in natural gasoline liquid in an absorber. Naphtha produced from associated gas is called light naphtha. Table 2-3 lists its composition and properties. Light naphtha consisting mainly of C5 and C6 hydrocarbon components is a preferred isomerization unit feed. Isomerization unit isomerizes C5 and C6 normal paraffins to branched chain hydrocarbons and increases the research octane number (RON) from 70 to 83. Isomerate is an important gasoline blend component for controlling the Reid Vapor Pressure (RVP) and distillation specification of blended gasoline.

SECONDARY PROCESSING UNITS

Table 2-4 lists the typical naphtha yield from various secondary processing units. Naphtha properties from secondary processing units such as the distillate hydrocracker and delayed coker are presented in Tables 2-5 and 2-6. Naphthas produced from coker or resid hydrocrackers usually have high nitrogen, sulfur, and olefin content, and they require hydrotreating before blending into the naphtha pool.

TABLE 2-4 Naphtha Yield from Various Refinery Units

Units		Naphtha yield
Distillate hydrocracker	Vol %	31.5
Delayed coker	Vol %	1.9
Resid hydrocracker (H oil)	Vol %	7.3
Resid desulfurizer	Vol %	3.0
Diesel desulfurizer	Vol %	0.9
Kerosene desulfurizer	Vol %	1.3

TABLE 2-5 Light and Heavy Naphtha Properties Ex Hydrocracker

Property	Units	C_5-180°F	180–320°F
Gravity	°API	79	52.5
Density	g/mL	0.672	0.769
Aniline point	°F		107
Distillation	°F		
IBP		110	215
10%		115	225.0
30%		125	245.0
50%		135	260.0
70%		150	270
90%		170	295
EP		195	325
PONA	Vol %		
Paraffins		74	27
Naphthenes		22	58
Aromatics		4	15
Sulfur	ppm	<10	<10
Octane number	Clear, F-1	77	61

TABLE 2-6 Light Coker Naphtha Properties

Property	Units	Value
Gravity	°API	82.1
Density, 60/60°F	kg/L	0.662
Distillation		
IBP		
10 vol %	°F	118
50 vol %	°F	126
90 vol %	°F	147
RON clear		81.8
PONA		
Paraffins	Vol %	36
Olefins	Vol %	56
Naphthenes	Vol %	0
Aromatica	Vol %	8.0
Bromine number		70.0
Nitrogen content	ppm	100.0
Sulfur	Wt %	0.10
Reid vapor pressure	kPa @100°F	91

NAPHTHA DESULFURIZATION

Naphtha produced from crude oil distillation, coking units, or from field gases may contain sulfur, mercaptan, and H_2S as impurities that must be removed or reduced to a low level before naphtha can be used as feedstock in any downstream catalytic process. The naphtha hydrodesulfurization (HDS) unit serves to make naphtha feed suitable for catalytic conversion processes by removing sulfur, nitrogen, trace metals, or other catalytic poisons from feed. This is done by reacting feed

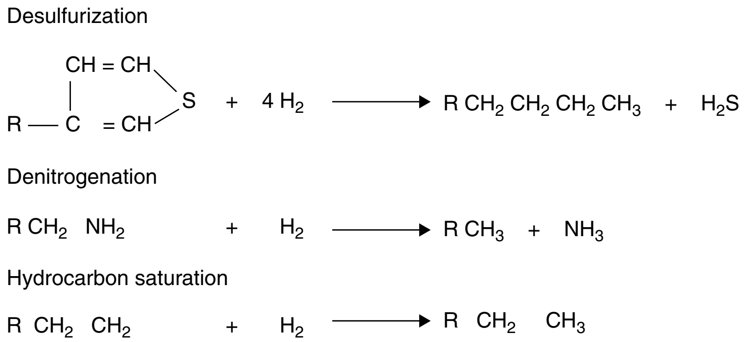

FIGURE 2-3 Hydrodesulfurization reactions.

with hydrogen at high temperature and pressures. Sulfur is converted to H_2S and nitrogen to NH_3, which are removed by distillation. Typical desulfurization reactions occurring in the HDS reactor are shown in Fig. 2-3.

Naphtha feed to cat reformers must meet 1 ppm or lower sulfur level specifications to protect noble metal catalyst in the reforming unit. In the naphtha steam reforming process for the production of hydrogen, naphtha sulfur must be reduced to less than 0.5 ppm in order to prevent poisoning of the nickel catalyst in the reactor. Sulfur is removed from naphtha in a naphtha desulfurization unit. However, if only H_2S is present in the feed, vapor feed is passed over a guard reactor containing ZnO, which absorbs H_2S.

NAPHTHA HDS UNIT

Referring to the process flow diagram in Fig. 2-4, naphtha feed from storage tanks is pumped by charge pump P-101 through reactor effluent-feed exchangers E-101 to E-103 and fired heater H-101 into the top of reactor V-101. The reactor is loaded with a desulfurization catalyst consisting of cobalt-molybdenum (Co-Mo) metals on an alumina base. Hydrogen from the catalytic reformer or hydrogen plant is compressed by centrifugal compressor C-101 and sent to the feed stream upstream of the reactor effluent-feed exchanger. The reactor effluent is cooled in effluent-feed exchangers E-101, E-102, E-103, in air cooler E-104, and in trim water cooler E-105 before flowing into high-pressure (HP) separator V-102. Hydrogen-rich vapors from a HP separator are routed back to compressor C-101. A small part of this stream is purged off to prevent buildup of H_2S in the hydrogen stream. HP separator liquid is flashed in low-pressure separator V-103 where H_2S and lighter hydrocarbons are separated from liquid. The liquid from V-103 is pumped to stabilizer column V-104 through feed/bottom exchanger E-106. Stabilizer column V-104 overhead vapors are condensed in air cooler E-107 and in water trim cooler E-108 and flow into accumulator V-105. The vapor from the accumulator (C4 and lighter) along with gas from the flash drum is sent to an amine unit for H_2S removal and gas recovery. The liquid from the V-105 is returned to the stabilizer column as total reflux. Stabilizer bottoms flow through E-106 to dehexanizer column V-106. The objective of dehexanizer column V-106 is to split desulfurized naphtha into light and heavy naphtha. Heavy naphtha is used as a feed for the catalytic reforming unit. The dehexanizer overhead vapors are condensed in E-109 and flow into reflux drum V-107. A part of the condensed liquid is sent back to the column as reflux, and the remainder is pumped through water trim cooler E-113 to storage as light naphtha (C5/C6) product. Dehexanizer bottoms (heavy naphtha) are cooled by pumping through air cooler E-111 and water trim cooler E-112 and routed to storage tanks. Table 2-7 lists the key operating conditions for a naphtha HDS unit.

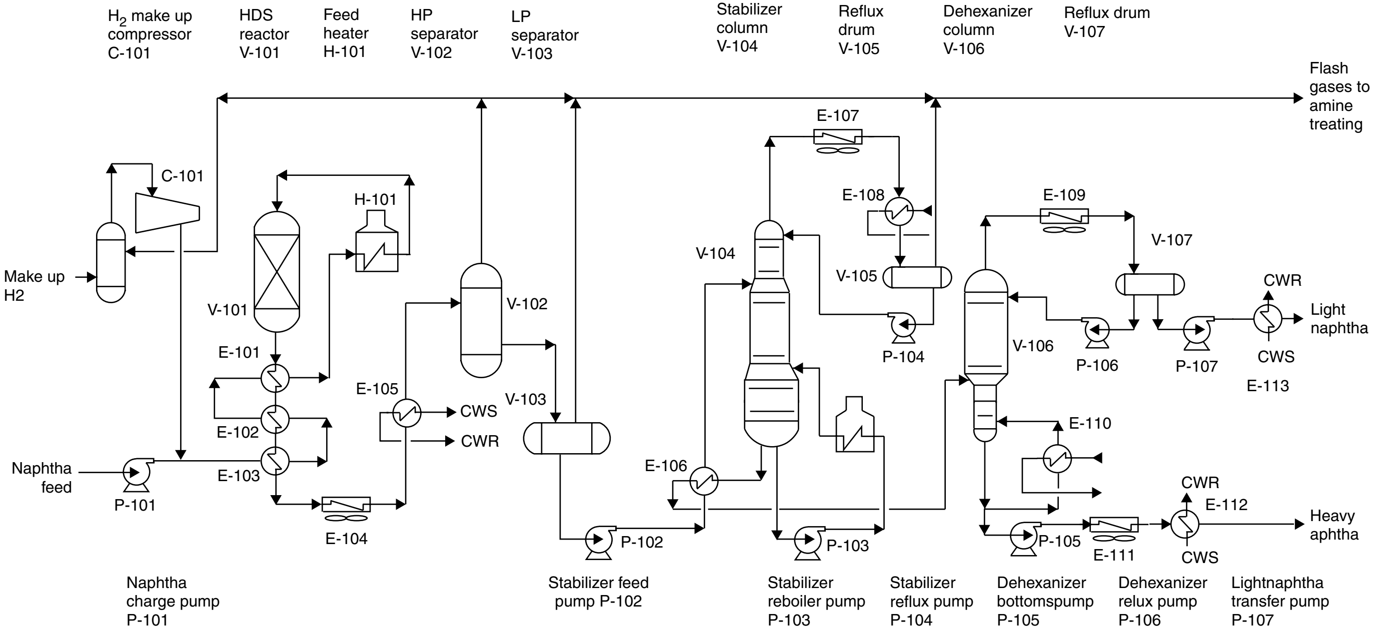

FIGURE 2-4 Naphtha desulfurization and fractionation.

TABLE 2-7 Naphtha HDS Unit Operating Conditions

Property	Units	Value
Reactor inlet temperature @ SOR/EOR	°F	608/698
HP separator pressure	kg/cm^2	21.3
Hydrogen partial pressure at reactor outlet	kg/cm^2	11.2
VVH (m^3/h naphtha/m^3 catalyst)	15°C	4.00

NAPHTHA SPECIFICATIONS

Naphtha may be classified by its boiling range or by its end use:

- Light straight run (LSR) naphtha
- Wide straight run (WSR) naphtha
- Petrochemical naphtha

LSR NAPHTHA

LSR naphtha is a light naphtha cut produced from crude oil distillation with a boiling range of C5 to180°F. It consists mainly of C5 and C6 hydrocarbons. It is highly paraffinic. The paraffin content of light naphtha is greater than 80 vol %. Table 2-8 lists the specifications of light naphtha, which is typically blended from hydrocracker light naphtha, meroxed coker light naphtha, and natural gasoline separated from associated gas. Specifications limit blending of light cracked naphtha such as light coker naphtha in LSR blends to an olefin content of 1.0 vol % maximum. LSR naphtha, because of its volatility, is a preferred feedstock for refinery isomerization unit to make a light gasoline blending component. LSR naphtha has a low RON of approximately 60. In the isomerization unit, feed is vaporized, mixed with hydrogen, and passed over a platinum-impregnated chlorinated

TABLE 2-8 Light Naphtha Specifications

Property	Units	Limit	Value	Test method
Color, saybolt			+20	ASTM D 156
Density	kg/L	Min.	0.645	ASTM D 1298
		Max.	0.700	
Distillation				ASTM D 86
IBP			Report	
10 vol %	°F	Max.	131	
50 vol %	°F	Max.	149	
90 vol %	°F	Max.	239	
End point	°F	Max.	320	
Lead content	ppb	Max.	50	IP 224
PONA				Chromatography
Paraffins	Vol %	Min.	80	
Olefins	Vol %	Max.	1.0	
Naphthene	Vol %	Max.	18.0	
Aromatics	Vol %	Max.	5.0	
Sulfur	Wt %	Max.	0.03	ASTM D 1266
Vapor pressure, Reid	kPa @100°F	Max.	91	ASTM D 323

alumina catalyst in an isomerization reactor. Isomerization of C5 and C6 normal paraffins to isoparaffins increases RON by 18 to 22 numbers. Isomerate is a very useful blend component to control gasoline distillation and to reduce high aromatic content reformate blending in gasoline.

WSR Naphtha

WSR is a (C5-310°F) cut from crude distillation units. Typical product specifications for WSR naphtha are listed in Table 2-9. A significant part of WSR is used as petrochemical naphtha or as a feedstock for the catalytic reforming unit for the production of a motor gasoline blend component.

TABLE 2-9 Wide Straight Run (WSR) Naphtha Specifications

Property	Units	Limit	Value	Test method
Color, Saybolt			Report	ASTM D 156
Density	kg/L	Min.	0.690	ASTM D 1298
		Max.	0.735	
Distillation				ASTM D 86
IBP			Report	
10 vol %	°F	Min.	109	
		Max.	210	
50 vol %	°F	Min.	174	
		Max.	270	
90 vol %	°F	Min.	230	
		Max.	351	
End point	°F	Max.	399	
Lead content	ppb	Max.	200	IP 224
Olefins	Vol %	Max.	1.0	ASTM D 1319
or				
Bromine number		Max.	1.0	ASTM D 1159
PONA			Report	
Sulfur	Wt %	Max.	0.07	ASTM D 1266
Vapor pressure, Reid	kPa @100°F	Max.	75	ASTM D 323

Petrochemical Naphtha

In refineries, petrochemical naphtha is blended from the straight run naphtha ex-crude distillation column and hydrocracker naphtha. Naphtha used as petrochemical feedstock must be highly paraffinic (minimum 70 vol %) with low aromatic content (less than 11 vol %). Table 2-10 lists the typical specifications of petrochemical naphtha.

Naphtha is widely used in the fertilizer and petrochemical industries (naphtha crackers for production of ethylene, propylene, etc.) as feedstock. The most important criteria for the selection of naphtha as feedstock in petrochemical and fertilizer plants are its paraffin and aromatic content. This is because high-paraffin naphtha is an excellent cracking feedstock in naphtha cracker and yields higher volumes of ethylene and other olefinic products. In the fertilizer plant, naphtha is mixed with steam passed over a nickel catalyst at high temperature (steam reforming) to synthesis gas ($CO + H_2$). The synthesis gas is further converted to ammonia and urea. Paraffinic naphtha requires lower steam reformer severity, whereas high aromatic feed is basically resistant to the steam reforming reaction requiring a higher severity operation. Aromatics also produce more coke lay-down on catalyst with a resultant shorter catalyst life.

TABLE 2-10 Petrochemical Naphtha Specifications

Property	Units	Limit	Value	Test method
Color, Saybolt		Min.	+20	ASTM D 156
Density, 60/60°F	kg/L	Min.	0.680	ASTM D 1298
		Max.	0.725	
Distillation				ASTM D 86
IBP			Report	
10 vol %	°F	Min.	Report	
		Max.		
50 vol %	°F	Min.	122	
		Max.	248	
90 vol %	°F	Min.	167	
		Max.	320	
End point	°F	Max.	356	
Lead content	ppb	Max.	200	IP 224
Olefins	Vol %	Max.	1.0	ASTM D 1319
PONA				
Paraffins	Vol %	Min.	70	Chromatography
Olefins	Vol %	Max.	1.0	
Naphthene	Vol %		Report	
Aromatics	Vol %		Report	
Sulfur	Wt %	Max.	0.07	ASTM D 1266
Vapor pressure, Reid	kPa @100°F	Max.	91	ASTM D 323

NAPHTHA USES

Catalytic Reforming

Catalytic reforming is an important refinery process for the manufacture of gasoline from naphtha. Straight run naphtha from crude oil distillation consists mainly of paraffins and naphthenes. It has a low octane number and cannot be used for gasoline blending.

The catalytic reformer unit converts low-octane heavy naphtha to high-octane catalytic reformate. Reformate is used as a blend component for gasoline blending. The reformate octane number can be increased by increasing the process severity, that is, increasing the reactor temperature or decreasing the space velocity. Increasing severity decreases reformate yield. Most cat reformers for gasoline manufacture operate in the 95 to 100 RON severity range. The manufacture of aromatics requires catalytic reforming units with continuous catalyst regeneration, operating in a higher severity RON range (100 to 102).

Figure 2-5 presents the chemical reactions that take place during catalytic reforming. Important chemical reactions are dehydrogenation, dehydrocyclization, isomerization and hydrocracking. Dehydrogenation reactions convert naphthenes to aromatics with higher octane number. Dehydrocyclization reactions convert normal paraffins to naphthenes, and isomerization of normal paraffins convert n-paraffins to branched hydrocarbons with high RON. Hydrocracking of paraffins decreases molecular weight and increases the volatility of reformate. The yield of reformate is a function of feed paraffin, olefin, naphthene, and aromatic (PONA) and cat reformer operating conditions. Naphthas with high naphthene content are the preferred feed for the catalytic reformer unit. The cat reforming process also produces hydrogen gas, which can be used for various desulfurization units in the refinery.

Naphtha feed for the reformer unit comes from the naphtha desulfurization unit where naphtha, sulfur, and nitrogen are both reduced to below 0.5 ppm.

Referring to the process flow diagram in Fig. 2-6, in the reforming unit, naphtha feed from the naphtha HDS unit or storage tank is mixed with hydrogen from recycle compressor K-101

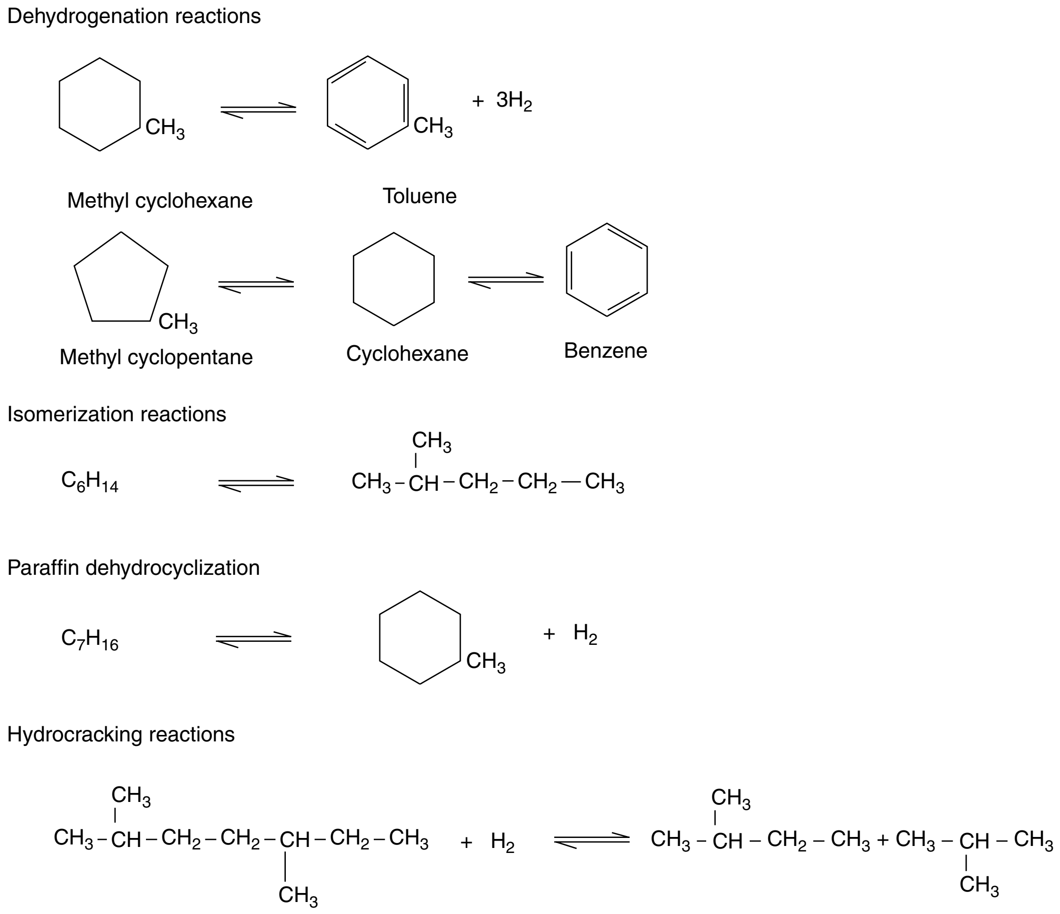

FIGURE 2-5 Catalytic refforming reactions.

and is preheated in feed-effluent exchanger E-101. The feed-hydrogen mix is next heated to reaction temperature by first fired heater H-101 and passed over reforming catalyst in first reactor R-101. Due to the endothermic nature of reactions, the temperature of the effluent coming out of the first reactor drops. It is reheated in the second fired heater H-102 after which the effluent from the first reactor enters the second reactor R-102. Effluent from the second reactor is reheated in third fired heater H-103 after which it enters the third reforming reactor R-103. Effluent from third reforming reactor is cooled first by heat exchange with incoming feed in E-101, next in air cooler E-102, and finally in trim water cooler to 104°F before entering HP separator drum V-103. Pressure in V-103 is controlled at 170 lb/in^2. High-pressure gas, mainly hydrogen, is sent to recycle compressor K-101 and recirculated to incoming fresh feed. Reforming reactions produce large volumes of hydrogen. Excess hydrogen from a flash drum is sent to other refinery units via knockout (KO) drum V-105 and compressor K-102.

Liquid effluent from HP Separator V-103 is pumped via P-102 to stabilizer column V-106, which separates fuel gas and LPG as top product; reformate is the bottom product. Reformate is cooled by heat exchange with incoming feed in E-105, E-106, and next cooled in water cooler E-108 before sending it to storage.

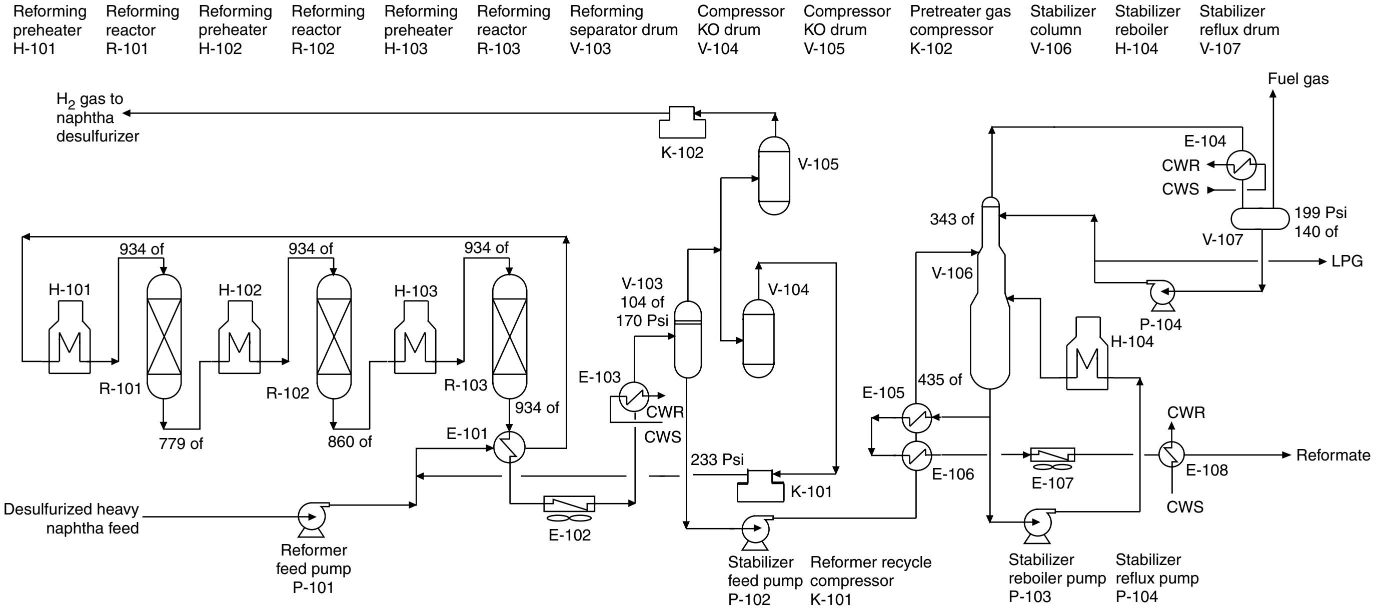

FIGURE 2-6 Process flow diagram: Catalytic reforming unit.

Operating Conditions

Reforming catalyst is a high-purity alumina catalyst impregnated with platinum and other noble metals. Reforming reactions are favored by high temperature and low pressure. The yield of reformate is a function of feed PONA and process severity. Typical operating conditions, feed, and product properties are shown in Tables 2-11 and 2-12. Motor gasoline blends typically contain 30 vol % or more reformate. Considering the large volumes of motor gasoline blended, the volumes of heavy naphtha feedstock consumed are a significant fraction of total naphtha production.

TABLE 2-11 Catalytic Reformer Operating Conditions

Operating conditions	Units	Value
Reactor inlet temperature (SOR/EOR)	°F	934/1013
HP separator temperature	°F	104
HP separator pressure	lb/in^2	170
Space velocity	WHSV	2.75
Recycle ratio (moles of H2/moles of feed)		4.5
Catalyst distribution	Wt %	
First reactor		15
Second reactor		25
Third reactor		60
Stabilizer column		
Column top/Bottom temperatures	°F	180/435
Column top pressure	lb/in^2	205

TABLE 2-12 Catalytic Reformer Feed and Product Properties

Property	Units	Feed	Reformate C5+
API gravity	°	61.3	47.8
Specific gravity		0.734	0.789
Octane number		38	96
TBP distillation	°F		
IBP		194	140
10%		203	
30%		221	194
50%		239	230
70%		257	257
90%		275	
FBP		284	311
PONA	Vol %		
Paraffins		69	
Naphthenes		20	
Aromatics		11	
Sulfur	Wt %	0.015	
Mercaptan	Wt %	0.008	
Nitrogen	ppm	1.00	

Aromatics Production

Benzene, toluene, and xylene are important feedstocks for the petrochemical industry. Benzene ranks in the top-20 chemicals worldwide in terms of production volumes. Benzene is used in the manufacture of plastics and resins, nylon and synthetic fiber, in rubber, lubricants, dyes, detergents, drugs, and pesticides, and in many other industries. Paraxylene, a basic raw material for the polyester fiber industry, is

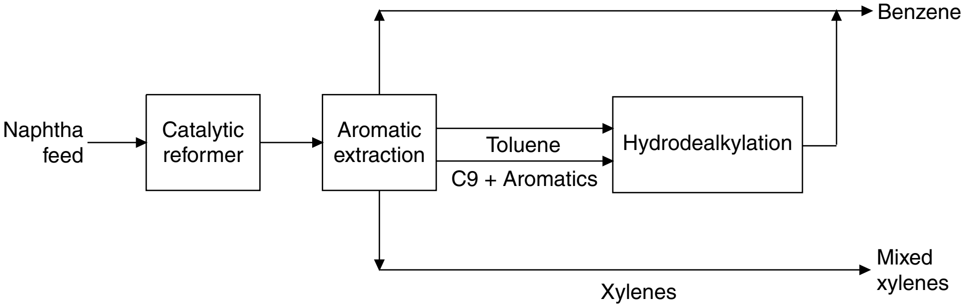

FIGURE 2-7 Aromatics production from naphtha.

used for the manufacture of terephthalic acid (TPA) and dimethyl terephthalate (DMT). Both TPA and DMT are used in the manufacture of polyethylene terephthalate (PET) resin. The major uses of PET are fiber, film, and engineering resins.

The catalytic reforming of naphtha is also used for the production of aromatics such as benzene, toluene, and xylenes (Fig. 2-7). The only difference from the cat reformer for motor gasoline (mogas) is that reforming operations are carried out at a higher severity (98 to 102) in a continuous catalyst regeneration configuration. Feed is 183 to 313°F cut. It is used for the production of benzene, toluene, and mixed xylenes. Aromatics from reformate are separated from nonaromatics by solvent extraction. Aromatic extract is separated into benzene, toluene, and xylene by fractionation or other separation processes. Because there is little demand for toluene, it is converted to benzene by a hydrodealkylation process.

Fertilizer/Petrochemical Industry

Naphtha is used as a feedstock for the manufacture of nitrogen fertilizers such as urea, ammonium nitrate, ammonium sulfate, and so on. In regions where natural or associated gas is not available, naphtha is the preferred feedstock. Naphtha is also used for the manufacture of methyl alcohol with a large industrial demand.

Naphtha is gasified and next reacted at high temperatures (1575°F) with steam over a nickel catalyst that converts naphtha to carbon monoxide and hydrogen (Fig. 2-8). Carbon monoxide reacts with more steam to produce more hydrogen and carbon dioxide. Hydrogen is reacted with nitrogen from the air to ammonia. Ammonia in turn is reacted with CO_2 to manufacture urea. Methanol is manufactured by reacting carbon monoxide with hydrogen over a catalyst.

Steam reforming reaction

$$C_5H_{12} + 5\,H_2O = 5\,CO + 11\,H_2$$

Low-temperature shift reaction

$$CO + H_2O = CO_2 + H_2$$

FIGURE 2-8 Steam reforming of naphtha.

Naphtha Steam Cracker

Naphtha is one of the basic raw materials for the production of ethylene and propylene. Ethylene is the largest volume petrochemical produced worldwide (estimated at 95 million tons in 2002). Ethylene has no direct use but is used exclusively as a chemical building block. Ethylene, propylenes, and C4 olefins are used for the production of plastics, fibers, films, textiles, pharmaceuticals, detergents, and so on.

The bulk of the worldwide commercial production of olefin is based on the thermal cracking of naphtha or heavier hydrocarbons with steam. The process is called pyrolysis, or steam cracking.

Naphtha is pumped through the convection section of the pyrolysis furnace where it is heated by heat exchange with flue gases. It is then mixed with steam and further heated to incipient cracking temperature (approximately 950°F) depending on feedstock. This stream next enters the radiant heating section of the furnace where it is heated under controlled conditions (residence time and temperature profile) to 1380 to 1607°F for 0.1 to 0.5 seconds. Final heating temperature depends on feed properties. Pyrolysis converts heavier hydrocarbons into lighter fractions, primarily ethylene and propylene, by removing hydrogen. Ethylene yield is roughly 33 wt % of the naphtha feed. The hot gas effluent from the furnace is then passed through a quench section where it is rapidly cooled to retard further cracking and to condense heavy fractions. Heavy fractions are subsequently processed into fuel oil, light cycle oil, and pyrolysis gasoline. The pyrolysis gasoline produced from naphtha cracker has a high benzene, toluene, and xylene content (Table 2-13). It also has a high olefin and diolefin content. It is first hydrotreated to saturate diolefins and monolefins. Aromatics are next extracted by a selective solvent such as sulfolane and separated by fractionation. Steam generated in the quench section is recycled back to the furnace for reuse.

TABLE 2-13 Pyrolysis Gasoline Properties and Composition Ex Naphtha Steam Cracker

ASTM distillation		°F
IBP		95
10	Vol %	133
30		160
50		187
70		221
90		298
EP		392
Density	g/mL, 60°F	0.770
Bromine number		71
Diene number		57
Total sulfur	ppm	800
Mercaptan sulfur	ppm	100
Molecular weight		85.73
Organic nitrogen	ppm	10
Existing gums	ppm	33
Composition	Wt %	
C_4 diolefins	0.50	
C_4 mono olefins	0.40	
C_4	0.10	
C_5 cyclopentane	1.00	
N-C_5	5.30	
I -C_5	3.60	
C_5 mono olefins	4.50	
C_5 diolefins	8.30	
N C_6	1.30	
Methyl cyclopentane	0.10	
Cyclohexane	0.10	
I-Hexane	1.50	
C_6 mono olefins	1.90	
C_6 diolefins	3.70	
Benzene	22.30	
C_7 naphthene	0.60	
N-Heptane	0.55	
ISO heptane	0.26	
C_7 mono olefins	0.90	
C_7 DI Olefins	1.70	
Toluene	14.40	
N-Octane	0.25	
Iso octane	0.25	
C_8 monolefins	0.30	
C_8 diolefins	0.60	
Xylene+ethyl benzene	6.80	
Styrenes	3.10	
C_9+	15.69	

Power Plant Fuel

Naphtha is increasingly being used as a fuel in gas-based power plants in place of natural gas, associated gas, or liquefied natural gas (LNG). Naphtha as a fuel cannot compete with natural gas due to its higher price, but because of the shortage of natural gas feedstock, power producers in many regions of the world use naphtha as fuel to meet electric power output requirements. Naphtha with high aromatic content (less than 20 vol %) can be used. Net heat of combustion is 20,000 Btu/lb or 11,300 kcal/kg, which is much more than natural gas on a per unit volume basis. Using naphtha in place of gas requires adjustment of operating conditions to avoid high boiler temperatures of 2000°F or more. Also, use of naphtha results in higher corrosion rates due to the sulfur in naphtha, which in turn causes shorter run length or more plant maintenance.