

Hydrogen Production and Recovery

Hydrogen is required in refineries for a large number of hydrotreating and hydrocracking processes, to remove sulfur, nitrogen, and other impurities from hydrotreater feed and to hydrocrack the heavier gas oils to distillates. A limited quantity of hydrogen is produced in the catalytic reforming of naphthas, but generally the quantity is insufficient to meet the requirements of hydrocracker and hydrotreating units. As hydrogen production is capital intensive, it is always economical to recover hydrogen from low-purity hydrogen streams emanating from hydrotreating and hydrocracking units and minimize production from hydrogen units. In the absence of hydrogen recovery, these streams end up in fuel gas or sent to flare.

Most refinery hydrogen is produced by the steam reforming of natural gas. The conventional hydrogen production in the refineries involve the following steps: natural gas desulfurization, steam reforming, high- and low-temperature shift conversion and trace CO and CO₂ removal by methanation.

NATURAL GAS DESULFURIZATION

Compressed natural gas at 110°F and 480 psig, after passing through knockout (K.O.) drum V-101, flows to the bottom of sulfinol absorber C-101 (see Figure 5-1). Here, the gas is treated with sulfinol solvent flowing down from the top to remove most of the H₂S and CO₂ contained in the feed. The treated gas, which contain less than 1 ppmw H₂S, passes through knockout drum V-102 and is washed with water in C-102 to remove any traces of the sulfinol solvent. The sulfinol solvent is regenerated in sulfinol regeneration column C-103 with a steam reboiler. The rich sulfinol solvent flows down the column and the acid gas leaves the column at the top.

Table 5-1
Primary Reformer Operating Conditions

OPERATING CONDITIONS	UNITS	
GAS INLET TEMPERATURE	°F	700
GAS OUTLET TEMPERATURE	°F	1575
GAS INLET PRESSURE	psig	360
GAS OUTLET PRESSURE	psig	310
ESTIMATED HEAT TRANSFER	Btu/hr ft ²	23317
THEORETIC H ₂ SPACE VELOCITY	hr ⁻¹	2627
TYPICAL FEED AND PRODUCT COMPOSITION	INLET % MOL	OUTLET % MOL
CH ₄	79.10	2.6
C ₂ H ₆	1.49	
C ₃ H ₈	0.33	
C ₄ H ₁₀	0.18	
C ₅ H ₁₂	0.10	
CO	0.00	7.882
CO ₂	0.00	12.324
H ₂	5.90	73.703
N ₂	12.90	3.49
AR	0.00	0
TOTAL	100.00	100.00
STEAM/GAS MOLAR RATIO	5.6	1.19

CATALYST

HIGH GEOMETRIC SURFACE RINGS

SIZE: DIAMETER 0.59–0.65 IN.

COMPOSITION:

Ni = 12–14 WT%

Al₂O₃ = 80–86 Wt%BULK DENSITY, lb/ft³ = 70SURFACE AREA, m²/gm = 1.5–5.0PORE VOLUME, cm³/gm = 0.10–0.20

The desulfurized feed gas is next heated in the convection section of primary reformer H-101 to 700°F, mixed with a small quantity of hydrogen (about 5%), and flows to sulfur absorbers R-101 and R-102, containing mainly zinc oxide with a small quantity of desulfurization catalyst. For the steam reforming process, it is essential to remove all sulfur in the feedstock before it enters the primary reformer, to prevent poisoning the catalyst. If only H₂S is present, there is no need to employ the hydrogenation step. In this case, H₂S is adsorbed on ZnO, which can pick up to 20% of its weight when operated at 750°F.

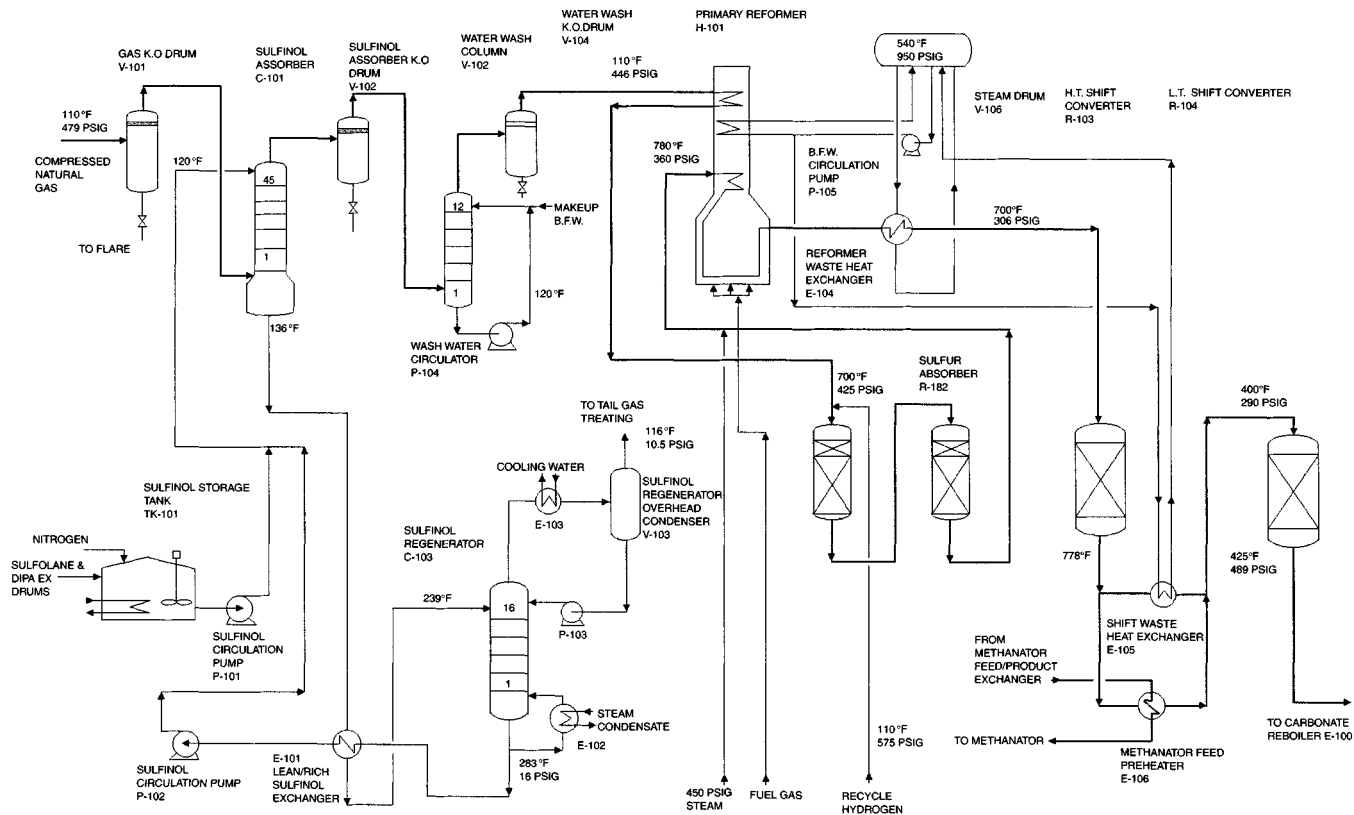


Figure 5-1. Hydrogen plant (reforming and shift conversion). H.T. = high temperature; L.T. = low temperature; B.F.W. = boiler feedwater.

Table 5-2
High-Temperature Shift Converter

OPERATING PARAMETER	UNITS	
FEED INLET TEMPERATURE	°F	700
EFFLUENT FROM HT CONVERTER	°F	770
FEED INLET PRESSURE	psig	306.0
REACTOR OUTLET PRESSURE	psig	304.0
DRY GAS INLET SPACE VELOCITY	hr ⁻¹	1638
REACTOR FEED AND EFFLUENT COMPOSITION	INLET MOL%	OUTLET MOL%
CH ₄	3.70	3.40
CO	8.88	2.00
CO ₂	11.42	15.90
H ₂	72.76	75.10
N ₂	3.23	3.60
AR	0.00	0.00
DRY TOTAL	100.00	100.00
H ₂ O	0.921	0.8
TYPICAL CATALYST COMPOSITION	WT%	
Fe ₂ O ₃	89-91	
CuO	2	
Cr ₂ O ₃	8-10	

If mercaptans and some other easily hydrogenated sulfur compounds, such as disulfides, are present, then by adding 2-5% hydrogen to the natural gas, ZnO alone both hydrogenates and adsorbs sulfur compounds. If nonreactive sulfur compounds like thiophene are present, a Co-Mo or Ni-Mo hydrogenation catalyst plus 5% recycle hydrogen is used to ensure complete conversion to H₂S, which is fully absorbed on ZnO. Any trace of chloride, which is another catalyst poison, is also removed in this step.

STEAM REFORMING

In the desulfurization stage, the sulfur in the feed is reduced to less than 0.5 ppm. The purified gas is mixed with superheated steam and further heated to about 900°F before entering the catalyst-filled tubes of primary reformer H-101. A steam/carbon molar ratio of 3-6 is used. The steam/carbon ratio is an important process variable. A lower steam/carbon

Table 5-3
Low Temperature Shift Converter

OPERATING PARAMETER		UNITS
FEED INLET TEMPERATURE		°F
EFFLUENT FROM HT CONVERTER		°F
FEED INLET PRESSURE		psig
REACTOR OUTLET PRESSURE		psig
DRY GAS INLET SPACE VELOCITY		hr ⁻¹
REACTOR FEED AND EFFLUENT COMPOSITION		REACTOR IN MOL% REACTOR OUT MOL%
CH ₄		3.47 3.40
CO		2.00 0.00
CO ₂		17.02 15.50
H ₂		74.48 77.90
N ₂		3.03 3.30
AR		0.00 0.00
DRY TOTAL		100.00 100.10
H ₂ O		0.8 0.767
CATALYST FORM	PALLETS	
Dimensions	5.2 mm × 3.5 mm	
Composition	wt%	
CuO	33.0	
ZnO	33.0	
Al ₂ O ₃	33.0	

ratio requires higher operating temperatures of the reformer and higher fuel consumption per unit hydrogen. The reforming furnace is fired with natural gas. The hot flue gases leave the radiant section of the reforming furnace at 1740–1830°F. The reformed natural gas exits the reformer tubes at 1560°F and 270 psig. The waste heat in the flue gases leaving the radiant section of the reformer are used to preheat reactants and superheat steam in a waste heat reboiler. The flue gas from the primary reformer is discharged to the atmosphere at approximately 300°F. The operating conditions of primary reformer are listed in Table 5-1.

CARBON MONOXIDE CONVERSION

The hot gas leaving the reforming tubes of H-101 is cooled to 650–700°F in waste heat boiler E-104 and enters a high-temperature shift converter R-103. In this reactor, about 75% of the CO is converted into CO₂ over an iron and chromium oxide catalyst. The gas from the high-temperature

Table 5-4
Methanator Reactor

OPERATING VARIABLE		UNITS
FEED INLET TEMPERATURE		°F 600
EFFLUENT FROM METHANATOR REACTOR		°F 660
REACTOR INLET PRESSURE		psig 274.0
REACTOR OUTLET PRESSURE		psig 273.9
DRY GAS INLET SPACE VELOCITY		hr ⁻¹ 5927
REACTOR FEED AND EFFLUENT COMPOSITION	REACTOR IN MOL%	REACTOR OUT MOL%
CH ₄	4.17	4.50
CO	0.18	0.00
CO ₂	0.10	0.00
H ₂	91.90	91.82
N ₂	3.65	3.69
AR	0.00	0.00
DRY TOTAL	100.00	100.00
H ₂ O	0.011	0.015
CO		<0.45 ppm
CO ₂		<9.55 ppm
CATALYST FORM	SPHERES	
Dimensions	3/16–5/16 in. diameter	
Composition,	wt%	
Ni	34.0	
Al ₂ O ₃	50–55	
CaO	5–7	
Life	4–5 Years	

shift converter is cooled to 430°F by raising steam in E-105 and preheating the methanator feed in E-106 and boiler feed water before it enters the low-temperature CO converter R-104 at approximately 400°F. In this reactor, most of the remaining carbon monoxide is converted to CO₂ over a copper-base catalyst. The operating conditions of high and low temperature shift converters are listed in Tables 5-2 and 5-3.

CARBON DIOXIDE REMOVAL

CO₂ from the process gas from the shift reactors is removed by a Benfield CO₂ removal system (see Figure 5-2). This process has two conversion

Table 5-5
Hydrogen Plant Overall Yield

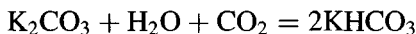
STREAM	YIELD WEIGHT FRACTION
FEED	
NATURAL GAS	1.0000
TOTAL FEED	1.0000
PRODUCT	
HYDROGEN	0.5640
LOSS	0.4360
TOTAL PRODUCT	1.0000

Table 5-6
Utility Consumption (per Ton Feed)

UTILITY	UNITS	CONSUMPTION
POWER	kWhr	450.80
FUEL	mmBtu	35.90
STEAM	mmBtu	1.70
COOLING WATER	MIG*	16.10

*MIG = 1000 IMPERIAL GALLONS.

steps: an absorption step at elevated pressure, in which CO₂ is absorbed in an aqueous solution of potassium carbonate, and a regeneration step at near atmospheric pressure, in which CO₂ is stripped from the carbonate solution to make it suitable for reuse in the absorption step. The basic reaction involved is as follows:



On absorption of CO₂, potassium carbonate in solution is converted into potassium bicarbonate, as shown by the equation. The reaction is reversed in the regenerator by steam stripping the solution and lowering the pressure.

After leaving the low-temperature CO converter, the gas is cooled to approximately 335°F by reboiling in Benefield solution regenerator E-109. The gas leaves this reboiler at approximately 265°F and enters a knockout drum, where the condensed water is removed. The gas next enters CO₂ absorber C-104, where CO₂ is reduced to 0.2% by contacting

Table 5-7
Feed and Product Properties, Natural
Gas Feed

COMPONENT	MOL%
COMPOSITION	
CARBON DIOXIDE	2.20
NITROGEN	0.65
METHANE	89.10
ETHANE	6.31
PROPANE	0.34
ISOBUTANE	0.30
N-BUTANE	0.60
ISOPENTANE	0.20
N-PENTANE	0.20
HYDROGEN SULFIDE, ppmv	400
MERCAPTANS, ppmv	600
TOTAL	100.00
TEMPERATURE, °F	110
PRESSURE, psig	480

Table 5-8
Product Hydrogen

COMPONENT	
HYDROGEN, MOL%	97
CO + CO ₂ , ppmv MAX.	20
CO, ppmv MAX.	10
METHANE & NITROGEN	REMAINDER

with Benfield solution flowing from the top of the column. CO₂ is removed from the gas stream by a solution of potassium carbonate, promoted by DEA and containing a vanadate corrosion inhibitor (approximately 25.7% potassium carbonate and 4.76% diethanol amine).

Part of the potassium carbonate is converted to bicarbonate on each pass. Since the cooler solution has a lower carbon dioxide vapor pressure, the top part of the CO₂ absorber is provided with a cooled stream of solution. The remainder of the solution enters the absorber lower down with no cooling.

The hot, rich solution flows to the top of CO₂ stripper C-105 (Benfield solution regenerator), where it is regenerated by contact with steam rising

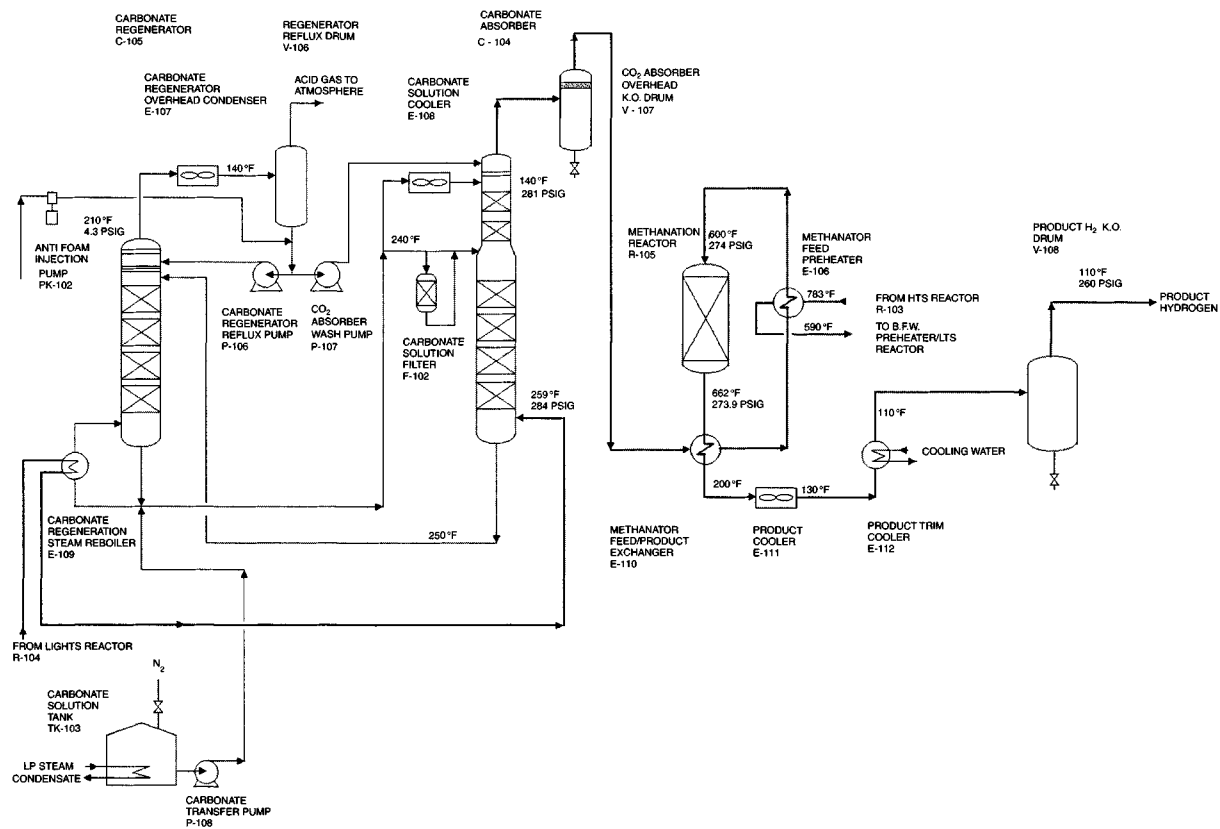


Figure 5-2. Hydrogen plant CO₂ removal and methanation. LP = low pressure.

from solution reboilers attached to the base of the column. A large proportion of the reboiler heat is provided from the gas stream, and the remainder is obtained from low-pressure steam (65 psia) condensed in the steam reboiler.

CO₂ and steam leaving the top of the column is cooled sufficiently to maintain the system water balance and vented to atmosphere. In locations where visible plume is not permitted, it is cooled 20–30°F above ambient temperature before venting it to atmosphere. Surplus condensate in this situation is degassed and sent to an off-site area for treatment.

The solution from the base of the CO₂ stripper is pumped to a CO₂ absorber. A part of the solution is cooled and sent to the top of the column, while the remainder enters the bottom half of the column with no cooling. Both columns are packed with metal pall rings packing.

METHANATION

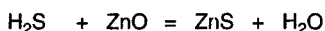
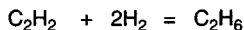
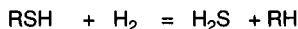
The gas that leaves the carbonate absorber at about 160°F is heated to 600°F by heat exchange with the process gas in two exchangers, E-110 and E-106, before entering methanation reactor R-105. Here, any remaining oxides of carbon are catalytically converted to methane over a nickel-alumina catalyst. The exit gas, the product hydrogen, is used to partially preheat the feed before being cooled to 20–30°F above ambient temperature. A small quantity of water is condensed and removed before the gas is sent to the battery limit for use. Operating conditions of methanation reactor are shown in Table 5-4.

Figure 5-3 shows the chemical reactions involved in H₂ manufacture. Tables 5-5 to 5-8 show process yield, utility consumption and feed/product qualities.

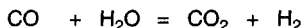
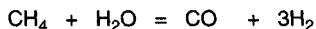
PRESSURE SWING ADSORPTION ROUTE

The pressure swing adsorption (PSA) route is simpler than the conventional route, in that the low-temperature CO conversion, CO₂ removal by liquid scrubbing, and methanation to catalytically remove the remaining oxides of carbon are replaced by a molecular sieve system. This system works by adsorbing CO₂, CO, CH₄, N₂, and H₂O at normal operating pressure while allowing hydrogen to pass through. The molecular sieve is regenerated by lowering the pressure and using some of the product to sweep out the desorbed impurities. Due to this pressure cycling, it is commonly referred to as a *pressure swing adsorption system*.

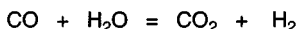
A FEED GAS PURIFICATION



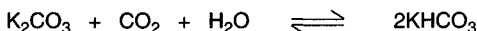
B STEAM REFORMING



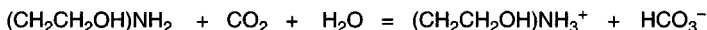
C HIGH TEMPERATURE & LOW TEMPERATURE SHIFT REACTIONS

D CO₂ ABSORPTION & REGENERATION

(with Benfield solution)



(with monomethanolamine)



E METHANATION

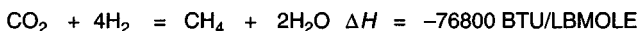


Figure 5-3. Chemical reactions involved in H₂ manufacture.

Steps involved in PSA route are as follows;

DESULFURIZATION

The natural gas is heated to 750°F and desulfurized in exactly the same way as in the conventional route. The only variation being that recycle gas used must be pure hydrogen.

REFORMING

The desulfurized natural gas is mixed with superheated steam to give a molar ratio of 3.0 moles of steam for each mole of carbon in the natural gas. The mixture is preheated to 895°F before being distributed to the catalyst-filled tubes of the reforming furnace. The reformed gas leaves the tube at 1562°F and approximately 315 psia and enters the waste heat boiler, where it is cooled to 660–680°F before it enters the high-temperature CO converter.

The bulk of the fuel gas for the reformer is obtained from the purge gas from the PSA unit.

REMOVAL OF IMPURITIES

When gas leaves the high-temperature CO converter, it contains about 4 mol% carbon monoxide and 5 mol% of CO₂ plus methane. As the gas is cooled down to ambient temperature, most of the water vapor is removed by condensation. The gas then enters one of the adsorption vessels, where all the carbon compounds, residual water vapor, any nitrogen, and a small amount of hydrogen are adsorbed.

Most of the hydrogen passes through, leaving as a very pure gas. After some time, the molecular sieve adsorber becomes saturated, and the feed is switched to another vessel, containing a freshly regenerated molecular sieve.

The saturated vessel is depressurized very slowly to a low pressure of approximately 3–5 psig. The gas is then swept out using the smallest possible quantity of hydrogen product. The vessel is then repressurized by hydrogen, and it is ready to be swung on-line for its next period as adsorber. Commercial systems have a minimum of three or four vessels to give a smooth operation. With this number, about 74% of hydrogen in the raw gas can be recovered.

The purged gas flow is intermittent and of varying composition over the cycle. A surge vessel is required to ensure good mixing and even outflow. The purge gas is used as fuel in the reforming furnace.

PARTIAL OXIDATION PROCESS

Partial oxidation is a noncatalytic process¹ for the manufacture of hydrogen from heavy feedstocks, such as vacuum residues and asphaltic

pitch. The heavy feed is partially burned using oxygen in a reactor. Due to high temperature, the remaining part of the feed is cracked. The composition of the hot synthesis gas leaving the reactor is mainly CO and H₂, with smaller quantities of CO₂, Ar, N₂, CH₄, and H₂S along with some soot and ash. All the sulfur in the feed is converted to H₂S. Argon in the synthesis gas originates from air from which oxygen is separated. Ash comes from the metals in the residual feed. Tables 5-9 to 5-11 list the parameters of this process.

Table 5-9
Typical Operating Conditions,
Synthesis Gas Reactor

PARAMETER	UNITS	
TEMPERATURE	°F	2000–2800
PRESSURE	psig	1200–2000

Table 5-10
Patrial Oxidation Process, Overall Yields

PROPERTY	
FEED ORIGIN	VACUUM RESID FROM WAFRA CRUDE
API	4.3
SPECIFIC GRAVITY	1.0420
SULFUR, WT%	6.2
VISCOSITY, 210°F CST	4000
STREAM FEED	YIELD WT FRACTION
VACUUM RESID	1.0000
OXYGEN	1.1140
BOILER FEEDWATER	1.7154
TOTAL	3.8294
PRODUCT	
HYDROGEN	0.2105
CH ₄	0.0504
A	0.0061
N ₂	0.0031
CO ₂ + WASTE	3.4956
H ₂ S	0.0637
TOTAL	3.8294

Table 5-11
Utility Consumption (per Ton Feed)

UTILITY	UNITS	CONSUMPTION	
		1*	2*
POWER	kWhr	102.4	0
FUEL	mmBtu	4.2	9.3
STEAM	mmBtu	-3.7	0
COOLING WATER	MIG	12.2	49.7

1* = OXYGEN IMPORT AT 1400 psig.

2* = IN-PLANT GENERATION OF OXYGEN. AIR SEPARATION UNIT ON STEAM DRIVE.

The synthesis gas is cooled by either direct quenching or raising steam in waste heat boilers. The cooled synthesis gas from the partial oxidation reactor is sent to a single-stage shift converter,² which converts most of the carbon monoxide to carbon dioxide over a Co-Mo catalyst, by reaction of the carbon monoxide with steam. Using a single-stage shift prevent relying on low-temperature shift catalysts, which are sensitive to water, sulfur, and chlorides. Acid gas removal and separation are carried out next. The H₂S recovered is sent to a Claus unit for production of elemental sulfur. The final purification step is methanation, which reduces carbon oxides to less than 10 ppm.

SYNTHESIS GAS GENERATION

The feed is heated to 500°F by high-pressure steam and pumped to the synthesis gas reactor at a pressure of 500–2000+ psig, depending on the required product hydrogen pressure (see Figure 5-4). Major improvement results from operating at a pressure of 2000 + psig, eliminating product gas compression. Oxygen from an air separation plant with a purity of 99.5% or more is preheated, mixed with process steam, and fed through a special burner to a refractory-lined combustion chamber in pressure vessel V-101. In the reactor, the heavy fuel oil is partially burned in an atmosphere of pure oxygen. Steam acts as moderator. CO₂ or N₂ can also be used as moderator. Due to the high temperature (2000–2800°F) in the reactor, the remaining part of the feed is cracked. The gas leaving the reactor consists of CO, H₂, CO₂, CH₄, Ar, H₂S, and some carbon in the form of soot. The hot synthesis gases

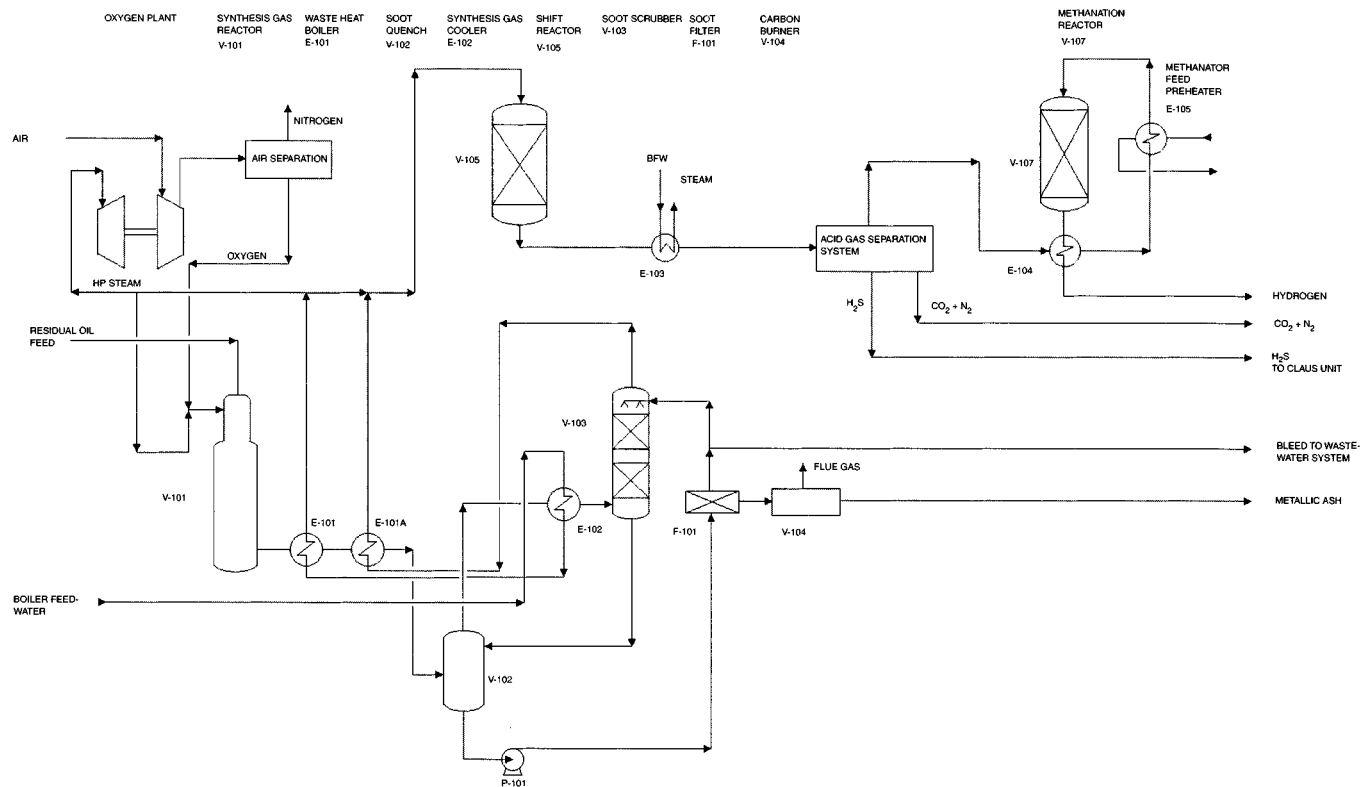


Figure 5-4. Partial oxidation process for hydrogen production.

are cooled in waste heat boiler E-101A and 101B, by incoming boiler feedwater, and a large quantity of high-pressure steam is generated in this step. Direct quenching can also be used if gas is required at higher pressures due to elimination of hydrogen compression and increased effectiveness of steam generation in the quenching.

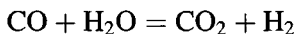
The synthesis gas contains approximately 0.5–1 wt% of the feed as carbon particles or soot. Synthesis gas is next quenched with water coming from soot scrubber V-103, in soot quencher V-102. This removes the bulk of solids, such as carbon particles and ash (consisting mostly of metals in the form of oxides) entrained in the reactor effluent. The synthesis gas still contains entrained carbon particles and enters a soot scrubber, where the synthesis gas is washed with water to remove the remaining entrained soot. Synthesis gas leaving scrubber contains less than 1 ppmv soot.

The water/soot slurry is filtered in F-101 to remove carbon particles and ash, and the clear water is recycled to the soot scrubber. The filter cake is incinerated to burn off carbon, leaving only ash (mainly metallic oxides), which is disposed off-site.

In some process configurations,³ the soot/water slurry is contacted with extraction naphtha and decanted into a soot/naphtha stream and gray water stream. The gray water is flashed off and returned to the soot scrubber. A small bleed stream of gray water is removed from the system to control dissolved solids and chloride ions. The soot/naphtha slurry is contacted with a portion of reactor feed, and the naphtha is stripped from the resulting stream for recycling. The feed/carbon mixture is sent back to the reactor feed tank. In this manner, the soot is entirely consumed.

SHIFT CONVERSION

The synthesis gas consists mainly of carbon monoxide, hydrogen, carbon dioxide, H_2S , and water vapor, with minor amounts of impurities such as methane, argon, and nitrogen. The synthesis gas is passed over a catalytic bed in shift converter V-105, where carbon monoxide reacts with steam over a sulfur-resistant catalyst to produce carbon dioxide. The reaction is exothermic:



ACID GAS REMOVAL

Carbon dioxide and H_2S are next removed from the synthesis gas by absorption in a variety of solvents such as MEA solution, cooled metha-

nol (Rectisol process),⁴ or potassium carbonate solution (Benfield process).⁵ The process removes essentially all H_2S and CO_2 from the synthesis gas and delivers a mixture of H_2S and CO_2 to the Claus unit, recovering about 95–97% of the sulfur contained in the feedstock as saleable sulfur.

METHANATION

The absorber effluent is heated by heat exchange with the methanation reactor effluent and enters methanation reactor V-107, where the remaining small quantities of carbon oxides in the feed are converted to methane by passing through a methanation catalyst.

Gas leaving the methanator is product hydrogen of 98+% plus purity. The hydrogen purity depends on the oxygen purity, generator pressure, and conversion level in the shift reactors.

The principle advantages of the partial oxidation process over that of steam reforming are these:

- Good feedstock flexibility. The process can operate on feedstocks from natural gas to residual fuel oil, whereas the steam reforming process is limited to hydrocarbons no heavier than naphtha.
- No catalyst required in the synthesis gas generation, which also increases feedstock availability by tolerating impurities in the feedstock.
- Fewer process heat requirements.
- Hydrogen generation at much higher pressure than in a steam-reforming unit.

The principle disadvantage is that process requires a supply of high-purity oxygen, necessitating capital investment in the oxygen plant. Also, large quantities of high-pressure steam are generated, for which there may be no use, unless steam is used to drive the air separation unit compressor. Therefore, the cost of hydrogen production by the partial oxidation process does not compare favorably with that of gas based steam-reforming units.

The partial oxidation process is suitable for refineries and petrochemical plants that must process heavy, high-sulfur, high-metal crude oils and, at the same time, meet the environmental pollution standards. In this case, the partial oxidation process can convert its heavy resid into clean synthesis gas for use in furnaces and also convert a part of this synthesis

gas into hydrogen. An alternative for these plants or refineries would be investment in the stack gas-cleanup units to control SO_2 emissions from burning high-sulfur resids. Also, the partial oxidation process may be of greater interest for ammonia and urea manufacture where by-products nitrogen (from the oxygen plant) and CO_2 can be used.

The typical operating conditions, feed properties, yields, and utility consumption for a partial oxidation unit are shown in Tables 5-9 to 5-11. Stoichiometry and product yields vary with the rate of water or CO_2 fed to reactor.

HYDROGEN RECOVERY

The objective of hydrogen recovery unit (see Figure 5-5) is to recover hydrogen from hydrogen-rich off gases released from several units in a refinery; for example, the hydrocracker, various desulfurizing units (naphtha, kerosene, diesel, and fuel oil), or the cat reformer.

Hydrogen-rich gas recovered in a hydrogen recovery unit (HRU) is gathered into a hydrogen header together with hydrogen gas manufactured by the hydrogen production unit to supply makeup hydrogen to several hydrogen-consuming units. See Tables 5-12 to 5-15 for the unit's operating parameters and yields.

The HRU consists of four sections: feed gas treatment, feed gas compression, the pressure swing adsorption system, and tail gas compression.

FEED GAS TREATMENT

The feed gas coming from various desulfurization and hydrocracking units (purge gases, stripper off gases, etc.) usually contain a high volume percentage of H_2S (2.9 vol% max, which must be brought down to less than 50 ppmv to prepare the feed for the PSA unit. The feed gas is first fed to feed gas knockout drum V-102, at 240 psig, where any condensed liquid is separated out.

The hydrogen sulfide is next removed by scrubbing with ADIP solution in Adip absorber column V-101. The ADIP solution is a 2-molar solution of DIPA (di-isopropyl amine) in water. The ADIP solution enters the top of the column at 114°F and 290 psig pressure. The following reactions take place.

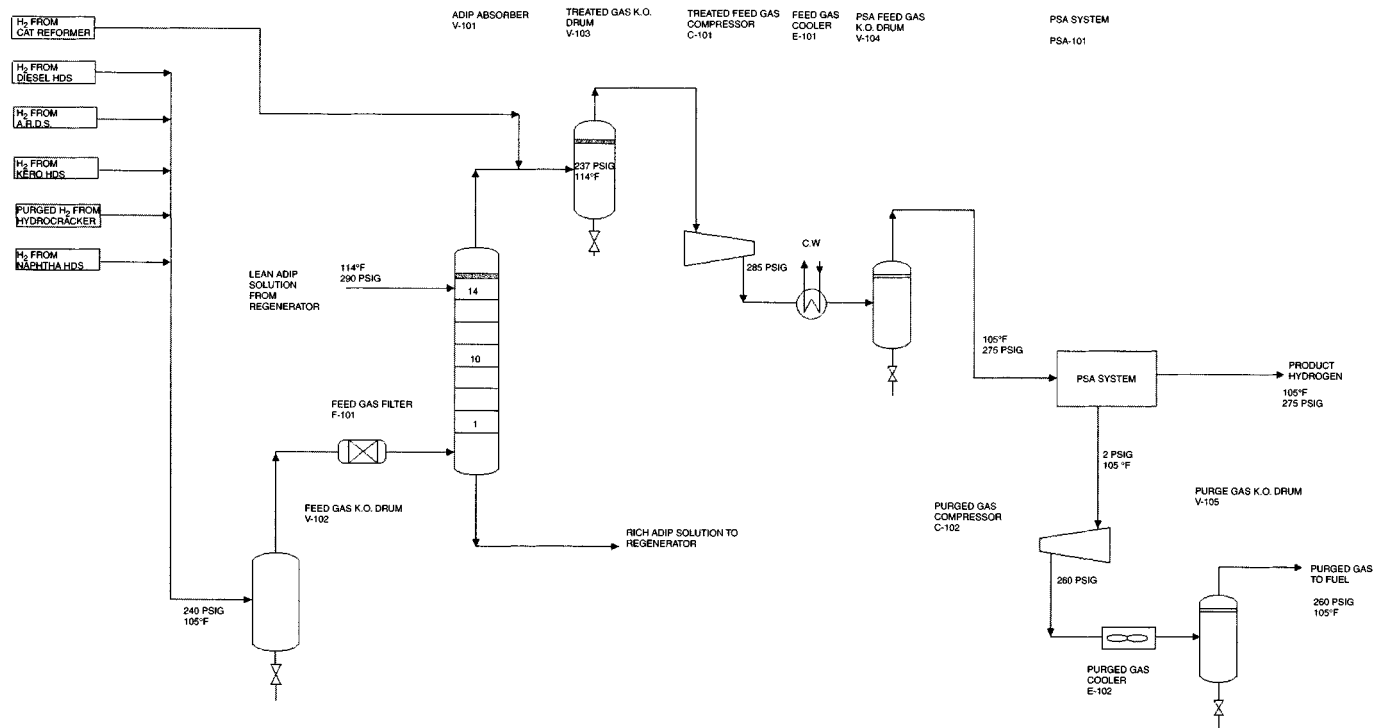


Figure 5-5. Hydrogen recovery unit.

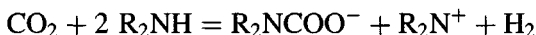
Table 5-12
Operating Conditions

OPERATING PARAMETER	UNITS	
ADIP ABSORBER		
FEED GAS INLET H ₂ S CONTENT	VOL%	2.9
TREATED GAS H ₂ S CONTENT	ppmv	10
FEED GAS TEMPERATURE	°F	105
FEED GAS INLET PRESSURE	psig	240
ADIP SOLUTION INLET TEMPERATURE	°F	114
ADIP SOLUTION INLET PRESSURE	psig	290
PSA SYSTEM		
ADSORPTION CYCLE		
PRESSURE	psig	275
TEMPERATURE	°F	105
DESORPTION CYCLE		
PRESSURE	psig	2
TEMPERATURE	°F	105
TAIL GAS COMPRESSION		
GAS INLET PRESSURE	psig	2
GAS OUTLET PRESSURE	psig	260

With H₂S, a hydrosulfide is formed:



With CO₂, a carbamate is formed:



The absorber has 14 trays. The treated gas passes out of the column to a knockout drum at 114°F and 237 psig, where any entrained adip solution is separated from the gas. Hydrocarbon liquid collected in the feed knockout drum is discharged to the flare by draining.

The rich ADIP solution leaves the bottom of the absorber under level control. Because of the exothermic nature of the reaction, the rich adip solution is at 16°F higher temperature than the lean ADIP solution temperature.

To prevent the condensation of hydrocarbons in the absorber, the temperature of the lean solution fed to the absorber is at least 10°F higher

Table 5-13
Feedstock Properties at the Inlet of the PSA System

UNITS		
COMPOSITION		
H ₂	vol%	78.46
C ₁	vol%	11.56
C ₂	vol%	4.30
C ₃	vol%	3.00
IC ₄	vol%	0.73
NC ₄	vol%	0.86
C ₅	vol%	0.24
C ₆	vol%	0.46
C ₇	vol%	0.33
C ₈	vol%	0.05
C ₉ +	vol%	0.01
TOTAL		100.00
IMPURITIES		
H ₂ O CONTENT		SATURATED
H ₂ S	ppm	50
MERCAPTANS & COS	ppm	2
HCL	ppm	3
NH ₃	ppm	100
CO	ppm (MAX)	50
CO ₂	ppm (MAX)	50
BENZENE	ppm	1000
TOLUENE	ppm	1000
XYLENE	ppm	500
PRODUCT HYDROGEN		
HYDROGEN	vol%	99
CO + CO ₂	ppmv	20
CH ₄	ppmv	1

than that of the feed gas temperature. The rich ADIP solution is sent to a regenerator column, where H₂S and other absorbed impurities are stripped off. The regenerated apip solution is returned to the absorber.

THE PSA SYSTEM

The feed gas, after leaving the knockout drum of the ADIP absorber is compressed from 225 psig to 285 psig by feed gas compressor. After

Table 5-14
Overall Hydrogen Recovery Unit Yields

STREAM	YIELD WT%
FEED	
HYDROGEN-RICH GAS	1.0000
PRODUCTS	
HYDROGEN	0.1510
RICH PURGE GAS TO FUEL	0.8420
LOSS (H ₂ TO FUEL)	0.0070
TOTAL	1.0000

Table 5-15
Unit Utility Consumption (*per Ton Feed*)

UTILITY	UNITS	CONSUMPTION
POWER	kWhr	1.08
STEAM	mmBtu	2.25
COOLING WATER	MIG	13.24

removing the heat of compression by the feed gas aftercooler and knocking out condensate in the feed gas cooler knockout drum, the feed gas is routed to the PSA system at 105°F and at 275 psig.

The pressure swing adsorption system works on the principle of physical adsorption, in which highly volatile compounds with low polarity (as represented by hydrogen) are practically unadsorbable compared to light and heavy hydrocarbon molecules, which are adsorbed on molecular sieves. Thus, most impurities contained in the hydrogen-containing feed stream are selectively adsorbed and a high-purity hydrogen product obtained.

The pressure swing adsorption works at two pressure levels: The adsorption of impurities is carried out at high pressure (275 psig, 105°F); and the desorption or regeneration of the molecular sieves is carried out at low pressure (2.8–5.6 psig).

Typically two batteries, each containing six adsorbers working as an integral unit, are used. Out of six adsorbers, two (in parallel) are continuously on adsorption, while remaining adsorbers perform different regeneration steps.

After the adsorption step, the adsorber is regenerated in the following manner:

- The adsorber is depressurized to a low pressure level, usually 2 psig. The gas is then swept out by smallest quantity of hydrogen product.
- The vessel is then repressurized with hydrogen and ready to be swung on-line for its next period as adsorber.

All absorption, desorption, and depressurization cycles are controlled and optimized by a microprocessor. The low-pressure tail gas is collected in a surge drum and boosted to 260 psig by a compressor.

The hydrogen recovery is about 83% of the hydrogen contained in the feed.

TAIL GAS COMPRESSION

The HRU tail gas is routed to a tail gas compressor suction drum and compressed from 2 psig to 260 psig. In the first compressor stage, the gas is compressed to 60 psig and cooled to 105°F by the compressor inter-cooler to knock out condensate in the tail gas to intercooler knockout drum. In the second stage, the tail gas is compressed to 260 psig, cooled to 105°F to knock out condensate, and sent to the refinery fuel gas system or the hydrogen plant.

NOTES

1. C. P. Marion and W. L. Slater. "Manufacture of Tonnage Hydrogen by Partial Combustion, the Texaco Process." Sixth World Petroleum Congress, Frankfurt, Germany 1963.
2. W. Auer. "A New Catalyst for the Co Shift Conversion of Sulfur-Containing Gases." 68th National Meeting of American Institute of Chemical Engineers, Houston, Texas, February 1971.
3. J. M. Brady and L. Nelson. "Heavy Residue Gasification Schemes." Conference on New Opportunities for Fuel Oil in Power Generation, Institute of Petroleum, London, February 19, 1990.
4. Process licensors are Linde A. G. and Lurgi GmbH.
5. H. E. Benson and R. E. Parrish. "Hi Pure Process Removes CO/H₂S," *Hydrocarbon Processing* 53, no. 4 (April 1974), p. 81.