

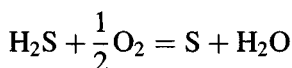
Sulfur Recovery and Pollution Control Processes

Most crude oil contain varying amounts of sulfur. Hydrotreating various distillates from these crudes generate hydrogen sulfide, which is converted to elemental sulfur to minimize atmospheric pollution. In the absence of sulfur recovery, the only option would be to burn this gas in refinery furnaces, releasing huge amounts of sulfur dioxide into the atmosphere, an option no longer acceptable due to environmental concerns.

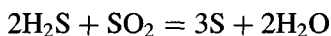
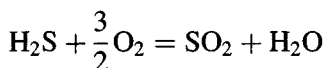
Sulfur recovery processes recover hydrogen sulfide from various refinery gaseous streams by scrubbing with an amine solution and convert it to elemental sulfur by controlled oxidation. Stack or flue gas desulfurization removes sulfur dioxide, generated as a result of burning high-sulfur fuel oil as refinery fuel, from refinery stacks. The process consists of scrubbing stack gases with aqueous ammonia to remove sulfur dioxide, which is reduced to elemental sulfur by reaction with hydrogen sulfide.

SULFUR RECOVERY FROM ACID GAS

The sulfur recovery unit recovers elemental sulfur from the acid gas containing H_2S by the Claus process. The chemical reaction involved is



This reaction is, in fact, a summation of the two following reactions:



The reaction of SO_2 and H_2S also occur in the thermal stage at 2500°F by burning one third of H_2S to SO_2 to obtain $\text{H}_2\text{S}/\text{SO}_2$ stoichiometric ratio of 2 to 1. At high temperature, conversion up to 70% into sulfur may be reached for the Claus reaction. In the presence of inerts (mainly CO_2) in the feed, lower conversion values are obtained.

To increase sulfur recovery, outlet gases from thermal stage are cooled down:

- To condense and remove most of the sulfur, thus shifting the equilibrium of Claus reaction to the right.
- To operate at a lower temperature, in the most favorable thermodynamic range. Under these conditions, a catalyst is needed to ensure an optimum reaction rate.

The exhaust gases from the thermal stage are sent to a sulfur condenser, then to a catalytic converter to increase sulfur recovery. Most Claus units are designed with two or three catalytic converters with activated alumina catalyst to increase sulfur recovery.

The inlet temperature to the catalytic converter is an important variable. The temperature must be high enough to prevent sulfur condensation on the catalyst, which would decrease catalytic activity. But, if the temperature is too high, the exothermicity of the Claus reaction increases the temperature along the catalyst bed, thus limiting conversion.

THE CLAUS SULFUR RECOVERY PROCESS

Acid gas from upstream treating units is mixed with a controlled amount of air and burned in combustion reaction furnace H-01 (see Figure 8-1). The gaseous product emerges from the furnace at 2500°F and passes through waste heat boiler B-01, producing HP steam at 900 psig. After leaving the boiler, the sulfur-laden gas enters first condenser E-01, where sulfur is condensed and collected in a sulfur sump.

The gas leaving the first condenser is reheated by a burning fuel gas to the reaction temperature and passes through a catalyst converter with activated alumina balls, where additional sulfur is formed. Sulfur thus formed is removed again in the second condenser and collected in the sump. The gas is again reheated and passed through a second catalyst converter for further conversion to elemental sulfur, which is removed in the third condenser. The total sulfur recovered is about 90–95% of the

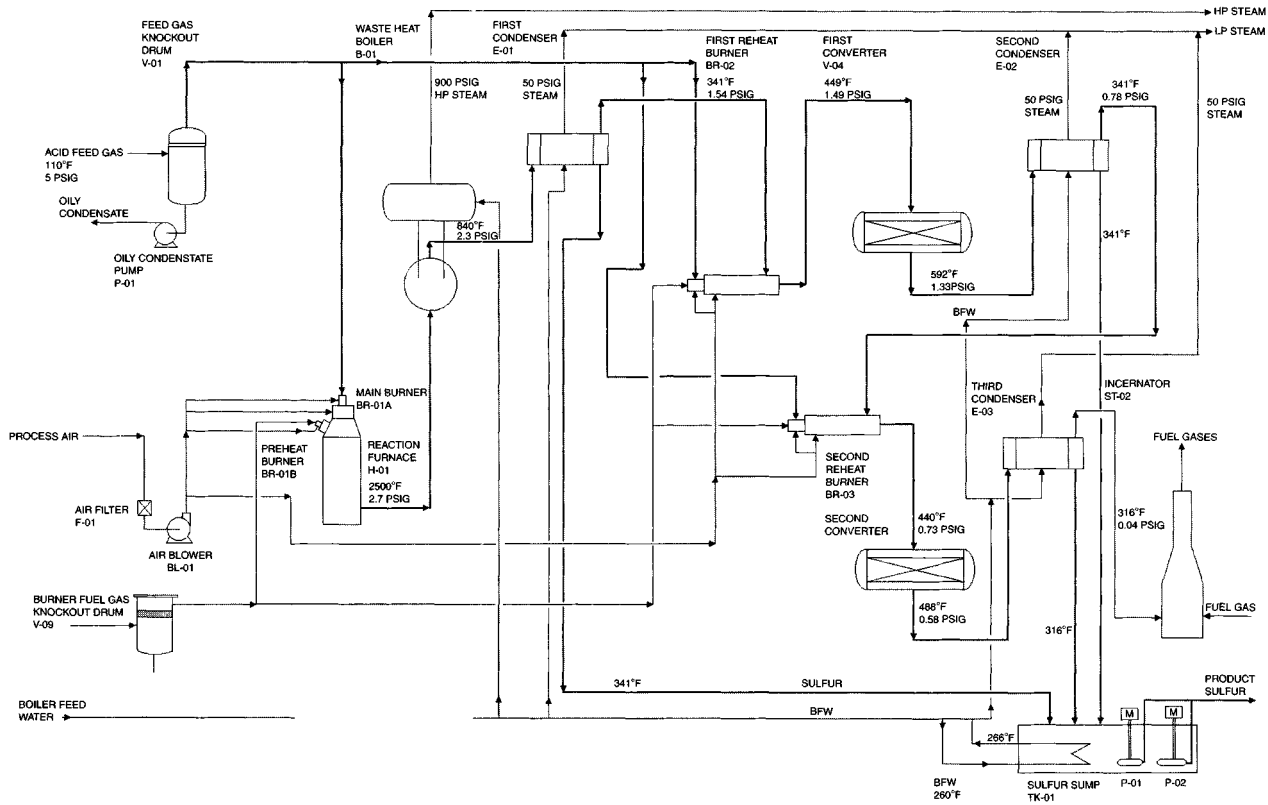


Figure 8-1. Sulfur recovery unit.

sulfur in the feed to the unit. After leaving the final condenser, the gas is burned in waste gas incinerator ST-02.

The sulfur from the waste heat boiler and all condensers is drained into sulfur sump TK-01, where it is kept in molten condition. From the sulfur sump, sulfur is transferred to liquid sulfur storage tanks. From the tanks, sulfur may be shipped in molten condition or pumped to a sulfur flaking unit to produce solid sulfur for shipments.

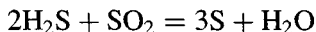
Operating conditions and feed composition of a Claus sulfur unit are shown in Table 8-1. The unit yield and utility consumption are shown in Tables 8-2 and 8-3.

CLAUS TAIL GAS TREATMENT

Sulfur recovery in a conventional Claus sulfur unit depends on the number of catalytic stages in the unit. An average Claus plant with three catalytic stages may recover approximately 95–97% of the sulfur contained in the acid gas fed to the unit, letting off as much as 3–5% of sulfur in the air in the form of stack gases after incineration. With increasing concern for environmental air quality, this practice is becoming unacceptable. Tail gas treatment removes most of the sulfur contained in the tail gas of a sulfur recovery unit in the form of elemental sulfur. The treated gas after incineration contain less than 1500 ppm SO₂.

THE CHEMISTRY OF THE SYSTEM

The Claus tail gases are contacted with solvent polyethylene glycol (PEG) containing a dissolved catalyst for accelerating Claus reaction:



The reaction is exothermic, the heat of reaction being 35,000 kCal/kg mole SO₂ reacted. The catalyst used is a 22% solution of benzoic acid, sodium, and potassium hydroxides in water. A typical composition of the catalyst solution is shown in Table 8-4.

The reaction occurs in the liquid phase between dissolved H₂S and SO₂ in the PEG by way of a catalyst complex. It is carried out at approximately 250–300°F, thus ensuring continuous elimination of sulfur and water of reaction (sulfur's melting point is 246°F).

Table 8-1
Sulfur Recovery Unit Operating Conditions

	UNITS	
ACID GAS FEED TEMPERATURE	°F	110
ACID GAS FEED PRESSURE	psia	19.7
THERMAL STAGE		
FURNACE GASES OUTLET TEMPERATURE	°F	2520
FURNACE GASES OUTLET PRESSURE	psia	17.41
WASTE HEAT BOILER		
EFFLUENT GASES OUTLET TEMPERATURE	°F	840
EFFLUENT GASES OUTLET PRESSURE	psia	16.98
FIRST SULFUR CONDENSER		
INLET TEMP	°F	840
OUTLET TEMP	°F	341
INLET PRESSURE	psia	16.98
OUTLET PRESSURE	psia	16.24
FIRST REHEATER		
INLET TEMPERATURE	°F	341
OUTLET TEMPERATURE	°F	449
INLET PRESSURE	psia	16.98
OUTLET PRESSURE	psia	16.24
FIRST CONVERTER		
INLET TEMPERATURE	°F	449
OUTLET TEMPERATURE	°F	592
INLET PRESSURE	psia	16.19
OUTLET PRESSURE	psia	16.03
SECOND SULFUR CONDENSER		
INLET TEMP	°F	592
OUTLET TEMP	°F	341
INLET PRESSURE	psia	16.03
OUTLET PRESSURE	psia	15.48
SECOND REHEAT BURNER		
INLET TEMP	°F	341
OUTLET TEMP	°F	449
INLET PRESSURE	psia	15.48
OUTLET PRESSURE	psia	15.43
SECOND CONVERTER		
INLET TEMPERATURE	°F	449
OUTLET TEMPERATURE	°F	488
INLET PRESSURE	psia	15.43
OUTLET PRESSURE	psia	15.28
THIRD SULFUR CONDENSER		
INLET TEMP	°F	488
OUTLET TEMP	°F	316
INLET PRESSURE	psia	15.28
OUTLET PRESSURE	psia	14.8

ACID GAS FEED COMPOSITION:H₂S 86.03 mol%CH₄ 0.51 mol%CO₂ 5.92 mol%H₂O 6.99 mol%C₂H₆ 0.28 mol%C₃+ 0.27 mol%

Table 8-2
Sulfur Recovery Unit Yields

STREAM	YIELD WT%
FEED	
H ₂ S GAS	1.0000
TOTAL FEED	1.0000
PRODUCT	
SULFUR	0.8478
LOSS	0.1522
TOTAL	1.0000

Table 8-3
Sulfur Recovery Unit Utility Consumption (per Ton Feed)

UTILITY	UNIT	CONSUMPTION
FUEL	mmBtu	2.8
POWER	kWhr	65
STEAM	mmBtu	-7.5
DISTILLED WATER	MIG*	0.02
COOLING WATER	MIG*	0.2

*MIG = 1000 IMPERIAL GALLONS.

Table 8-4
Catalyst Composition

COMPONENT	WT%
PURE BENZOIC ACID	15.20
PURE POTASSIUM HYDROXIDE	1.00
PURE SODIUM HYDROXIDE	5.80
DEMINERALIZED WATER	78.00
TOTAL	100.00

NOTE: THE CATALYST IS A 22% SOLUTION OF BENZOIC ACID, SODIUM HYDROXIDE, AND POTASSIUM HYDROXIDE WITH THIS COMPOSITION. INDUSTRIAL-GRADE CHEMICALS CAN BE USED.

The level of catalytic activity of the system is characterized by a soluble sodium and potassium (Na⁺ and K⁺) content and free acidity (H⁺) of the solvent. With the gas at steady conditions (flow and

temperature) and a predetermined $\text{H}_2\text{S}/\text{SO}_2$ ratio, these levels can be maintained by catalyst makeup.

Sodium and potassium salts (K^+ and Na^+ content) in the PEG are maintained in the range of 20–50 millimole/kg. Free acidity of PEG (H^+ content) is maintained at 30–70 millimole/kg.

The benzoic acid consumption corresponds to its losses in off gases by vapor pressure. Sodium and potassium hydroxides are finally degraded to sodium and potassium sulfates, which are insoluble and deposited on the packing. The amount of sodium sulfate deposited on the catalyst can be estimated from the cumulative amount of pure KOH and NaOH injected into the solvent since the last washing. The washwater required is approximately 3.3 times the amount of sodium sulfate to be washed off the packing.

For a given packing volume and catalyst composition, the operating variables are

1. Total acid gas flow.
2. ($\text{H}_2\text{S} + \text{SO}_2$ content) in the acid gas flow.
3. The ratio $\text{H}_2\text{S}/\text{SO}_2$.
4. Solvent flow rate.

The temperature is held constant at the design value for optimum operation and to minimize PEG loss.

Any increase in acid gas flow decreases conversion. The optimum performance of the unit is reached by minimizing the SO_2 content in the off gas. This is achieved by a molar ratio $\text{H}_2\text{S}/\text{SO}_2$ equal to or greater than 2.3 in the feed gas by controlling operation of the upstream Claus unit operation. Any excess SO_2 decreases conversion, increases potassium and sodium consumption, and affects the color of the product sulfur. Long-duration SO_2 excess can damage the solvent, which may require charcoal treatment to restore its quality and required conversion rates. Flow of the solvent has an effect on the interfacial area available for mass transfer and conversion: Increasing the solvent flow increases interfacial area and conversion.

THE TAIL GAS TREATMENT PROCESS

The acid gas is introduced in reactor R-101 near the bottom (see Figure 8-2). The reactor, where gas/liquid contact is effected, is a packed column designed for a low pressure drop while ensuring the interfacial area

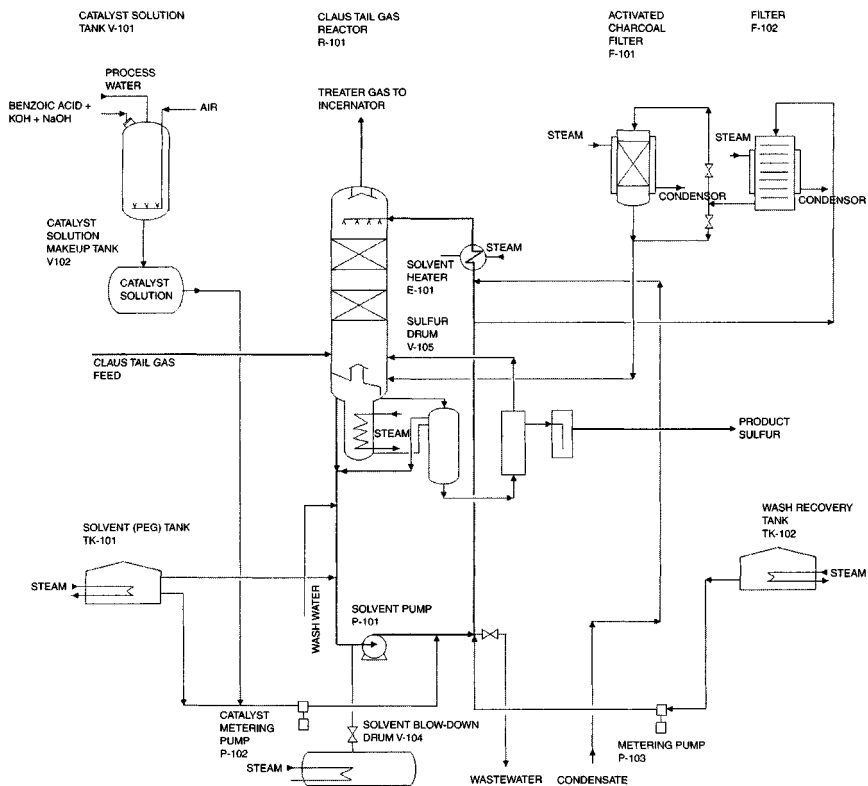


Figure 8-2. Claus tail gas treatment unit.

necessary for the desired conversion. The packing volume is divided into a number of beds separated by liquid redistributors and packing support plates to ensure maximum packing efficiency all along the reactor. At the top of the tower, a deflector plate is provided to minimize solvent entrainment in the off gases.

Acid gas flows countercurrently to the solvent to ensure the concentration gradient between the bottom and top of the reactor. An incorporated system of decantation at the bottom of the tower separates the liquid sulfur produced from the solvent. The sulfur is next sent to a sulfur pit by way of a seal leg. To keep sulfur in a liquid state, sulfur lines and valves are steam-jacketed.

The solvent at the bottom is recycled back to the top of the reactor by pump P-101. This pump is designed to operate on pure liquids or crystal-

line sulfur slurries. Steam-heated mechanical sealing with seal liquid taken at pump discharge is used. This pump is also used for filling and emptying the unit with solvent.

A sidestream is drawn from the solvent loop to filter a small part of the solvent through filter F-102 and the activated charcoal bed in F-101.

Although the Claus reaction is exothermic, the precise heat balance of the unit depends mainly on the heat losses in the reactor system. The reactor temperature is controlled by either additional condensate injection or steam-heating in exchanger E-101. The catalyst consumption is compensated by continuous injection of catalyst solution from V-102 through metering pump P-102.

Heat exchanger E-101 on the solvent circulation line heats the packed reactor and its PEG content to the reaction temperature in a period of 48 hr during start-up. It is placed at a level above the reactor bottom solvent inlet to prevent solid sulfur deposits between E-101 and the reactor. This exchanger is also used to compensate for heat losses during normal operation. It is used during shutdown to cool the unit and during washing to heat the washwater.

Solvent let-down tank T-101 is provided for PEG storage during filling and emptying and as a reserve for makeup solvent. Washing recovery tank T-102 is provided to recover the PEG/water mixture during the unit washing. The mixture is stored in the tank by solvent pump P-101 and reinjected intermittently in the system by metering pump P-103 to compensate for solvent losses and deposits on the packing.

Underground solvent blow-down drum V-104 is used for PEG recovery during purges of pumps, lines filters, and the like. Steam coils are used to heat the solvent in the tanks to reduce viscosity for pumping.

Operating conditions and feed composition of a Claus sulfur unit are shown in Table 8-5. The catalyst composition, unit yield, and utility consumption are shown in Tables 8-6 to 8-11.

FLUE GAS DESULFURIZATION

Flue gas desulfurization aims to reduce sulfur oxides emissions from the stack gases of the refineries and power plants to 150–1500 ppm range, for pollution control. The process is particularly useful for refineries and power plants burning high-sulfur heavy fuel oil.

Table 8-5
Sulfur Plant Tail Gas Treatment
Operating Conditions

OPERATING VARIABLE	UNITS	
REACTOR TEMPERATURE		
INLET GAS	°F	285–300
OUTLET GAS	°F	248–252
REACTOR INLET PRESSURE	psig	0.5–2.0
REACTOR OUTLET PRESSURE	psig	0.1–1.6
SOLVENT CIRCULATION RATE*	GPM	700

*BASIS ACID GAS FEED RATE OF 180 MSCF/HR.

Table 8-6
Catalyst Component Properties

PROPERTY	BENZOIC ACID	SODIUM HYDROXIDE	POTASSIUM HYDROXIDE
CHEMICAL FORMULA	C ₆ H ₅ COOH	NaOH	KOH
MOLECULAR WEIGHT	122	40	56
MELTING POINT, °F	252	604	752
SOLID SPECIFIC GRAVITY	1.266	2.13	2.04

Table 8-7
Solvent

SPECIFICATIONS	UNITS	
MOLECULAR WEIGHT		380–420
FREEZING POINT	°F	39–46
SPECIFIC GRAVITY		1.125
REFRACTIVE INDEX		1.466
VISCOSITY	122°F, cst	27.85
	212°F, cst	6.5–8.2
	275°F, cst	3.94
SULFUR SOLUBILITY	68°F, gm/liter	2–10
	248°F, gm/liter	27
	275°F, gm/liter	35

NOTE: THE SOLVENT USED IS POLYETHYLENE GLYCOL WITH AN AVERAGE MOLECULAR WEIGHT OF 400.

Table 8-8
Claus Tail Gas Treatment Unit Yields

STREAM	WT%
FEED	
ACID GAS FEED	1.0000
CONDENSATE	0.0481
TOTAL FEED	1.0481
PRODUCT	
SULFUR	0.0463
TREATED GAS	1.0019
TOTAL PRODUCT	1.0481

Table 8-9
Utility Consumption, per Tons Sulfur Produced

UTILITY	UNITS	CONSUMPTION
ELECTRICITY	kWhr	463
CONDENSATE	TONS	2.23

Table 8-10
Claus Tail Gas Treatment Unit Feed and Treated Gas Composition

COMPONENT	MOL WEIGHT	ACID GAS FEED, WT%	TREATED GAS, WT%	SULFUR, WT%
H ₂ S	34	0.0370	0.0053	
SO ₂	64	0.0298	0.0000	
CO ₂	44	0.1171	0.1168	
C ₃	44	0.0089	0.0089	
N ₂	28	0.6019	0.6005	
H ₂ O	18	0.2035	0.2678	
S ₆₋₈	246	0.0019	0.0008	
LIQUID SULFUR	32			1.0000
TOTAL		1.0000	1.0000	1.0000

The process can be divided into four steps:

1. Ammonia scrubbing of flue gas.
2. Sulfitic brine treatment: recovery of gaseous SO₂ and NH₃ from aqueous sulfite/sulfate solution.

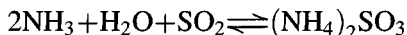
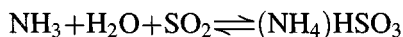
Table 8-11
Product Sulfur Properties

PROPERTY	
CARBONILE MATTER (PEG CONTENT)	<1000 ppm
ASH CONTENT	<200 ppm
SULFUR PURITY	>99.7%
COLOR	BRIGHT YELLOW

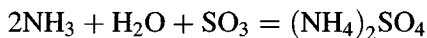
- Reduction of a part of the SO₂ produced to H₂S, a step avoided if an outside source of H₂S is available.
- Conversion of SO₂ into sulfur by reacting it with H₂S.

AMMONIA SCRUBBING

In the scrubbing step, absorption of SO₂ by aqueous ammonia solution takes place according to the following chemical reaction;



Owing to the presence of SO₃ in the flue gas or oxidation of a part of SO₂, sulfate may also be formed.

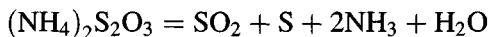
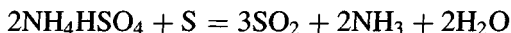


Ammonia scrubbing of flue gas results in a treated flue gas leaving the stack with less than 150 ppm SO₂. Also an aqueous ammonium sulfate/sulfite solution is generated.

SULFITIC BRINE TREATMENT

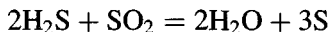
Sulfitic brine is partly decomposed back into NH₃, SO₂, and H₂O in an evaporator according to the preceding equations.

The bottom liquid containing the bulk of sulfates is fed to a sulfate reduction reactor, where sulfates, thiosulfates, and remaining sulfites are reduced to SO_2 , NH_3 , and H_2O by reaction with molten sulfur:



This reaction takes place in a liquid bath at a temperature of approximately 660°F, using a molten salt bath. The reaction is endothermic; so heat must be supplied from external sources. The gases in the molten bath contain a certain amount of SO_3 . This gas is reduced to SO_2 by reaction with fuel gas containing CO plus H_2 contained in the fuel gas. The reaction is carried out over a solid catalyst.

If refinery H_2S stream is available, the sulfur dioxide produced from sulfate reduction and sulfite decomposition is reacted with H_2S in liquid phase to produce elemental sulfur. The ratio of H_2S to SO_2 must be greater than 2.3 for this reaction to proceed to completion:



High-purity liquid sulfur is produced as final product. If H_2S stream is unavailable (as in power plants), a part of SO_2 can be reduced to H_2S using a reducing gas ($\text{CO} + \text{H}_2$) in a catalytic converter.

PROCESS DESCRIPTION

The stack gases of the refinery are scrubbed with an aqueous solution of ammonia in column C-101 (see Figure 8-3). The ammonia solution is introduced into the column at the top, while flue gases enter the column near the bottom. The rich effluent containing dissolved sulfur oxides, called *sulfitic brine*, enters tank TK-101, where any dust contained in the stack gases is separated out by settling.

The sulfitic brine is pumped by P-101 to heat exchanger E-101, heated by medium-pressure steam, and flashed in drum V-101, where partial decomposition of sulfites take place at 300°F and 30 psia pressure. The gases produced as a result of decomposition of ammonium sulfites, SO_2

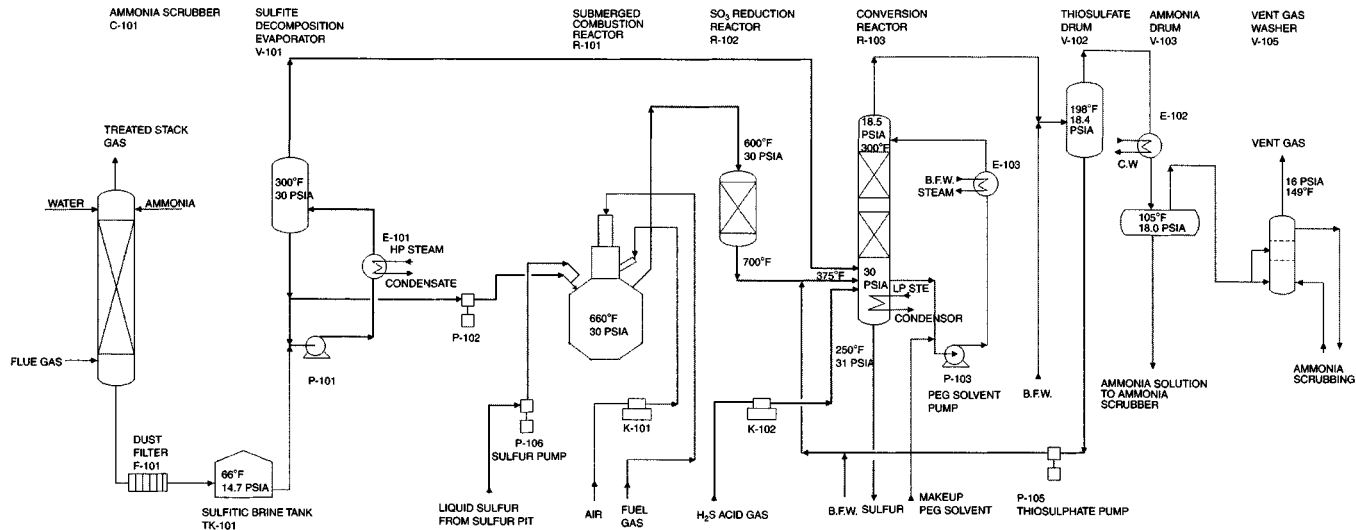
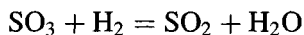
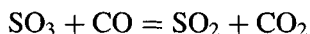


Figure 8-3. Flue gas desulfurization. B.F.W. = boiler feedwater.

and NH_3 , are sent to R-103, the conversion reactor. The concentrated brine is sent by P-102 to R-101.

The concentrated brine, which consists of all ammonium sulfates, thio-sulfates, and unconverted sulfites, is fed by metering pump P-102 to a sulfate decomposition reactor R-101, which is a bath of molten ammonium sulfates, where sulfate reduction takes place. Also, a stream of molten sulfur is pumped by metering pump P-106 to R-101. The temperature of the molten bath is maintained at 660°F. The reactions in the sulfates reduction reactor are endothermic. The heat is supplied to the system by submerged flame combustion of fuel gas and air. The hot gases are sent from a special burner directly into the molten bath via a graphite tube. This combustion takes place under slightly reducing conditions, implying that air/fuel gas inlet ratio is maintained slightly lower than stoichiometric (90%). The reduction of sulfates start at 570–590°F. The operating temperature is not allowed to exceed 750°F, when ammonia starts to react with medium. The operating temperature of the bath can be adjusted according to the thiosulfate/sulfate ratio in the bath. The molten salt in the bath is very corrosive. The reactor is therefore lined with acid-resisting refractory.

The gases above the molten bath (80% NH_4HSO_4 and 20% $(\text{NH}_4)_2\text{SO}_4$) contain a certain amount of SO_3 due to vapor pressure. The SO_3 is reduced to SO_2 by the following exothermic reactions. The CO and H_2 originate from unburned fuel gas. The reactions are carried over a solid state (Co-Mo on alumina) catalyst:



The off gases from reactor R-102 at about 700°F are quenched to 375°F by injection of boiler feedwater.

The SO_2 -rich gases coming from V-101, R-101, and R-102 are mixed with H_2S from an outside source, such as a refinery amine plant, through compressor K-102 and enter conversion reactor R-103 near the bottom. The $\text{H}_2\text{S}/\text{SO}_2$ feed ratio must be maintained higher than 2, to protect the chemical system.

The reactor is an absorber column with 13 perforated trays. The solvent polyethylene glycol (PEG) is circulated by pump P-103 through cooler E-103 to remove the heat of reaction, feed enthalpy, and to keep the tower temperature at 300°F. Heat is removed by thermosyphon recirculation of boiler feedwater through E-103 and raising LP steam.

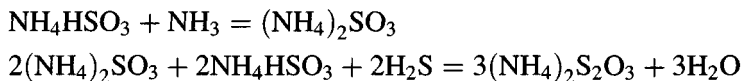
The PEG solvent flows down the column. The Claus reaction takes place in a liquid solvent PEG (polyethylene glycol, mol. wt. 400). Ammonia in the gas stream acts as a catalyst. The molten sulfur produced is collected by decantation at the bottom of the reactor. Makeup solvent is added to the cooling loop to compensate for the solvent losses.

As the Claus reaction in R-103 does not reach 100% completion, gases coming out from R-103 overhead contain NH_3 , H_2S , SO_2 , CO_2 , inerts, sulfur vapors, and entrained PEG. These are quenched with boiler feedwater and sent to thiosulfate drum V-102. Water quenching lowers the temperature to the dew point of the gases. SO_2 reacts with sulfur in the presence of NH_3 to give thiosulfates, which are dissolved in water. This solution, also containing traces of PEG, is sent back by P-105 to the gas line coming from R-102. The temperature being higher than 190°F , the thiosulfates are cracked into gaseous SO_2 , NH_3 , and sulfur.

The off gases from V-102 at approximately 200°F are cooled in exchanger E-102. Most of the water is condensed and collected in drum V-103 with some ammonia, H_2S , and CO_2 dissolved in it.

The top gases from V-103 are washed in drum V-105 by bubbling contact with brine from the ammonia scrubber bottom to further reduce pollutant release into atmosphere.

The following reaction takes place:

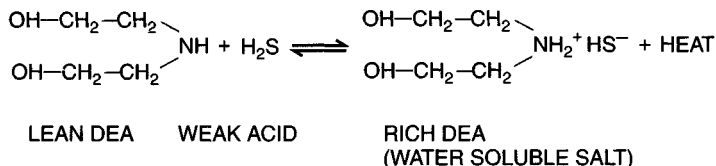


The operating conditions and feed composition of a flue gas desulfurization unit are shown in Table 8-12. The feed and product compositions and utility consumption are shown in Tables 8-13 to 8-15.

AMINE TREATMENT

The objective of an amine treatment unit is to remove H_2S , CO_2 , and mercaptan compounds from various gas streams, such as recycled gas in hydrotreating and hydrocracking processes, hydrogen plant feed, and fuel gas systems. The H_2S recovered is used as feed for the sulfur recovery unit.

Hydrogen sulfide is removed from a gas stream by contact with an aqueous solution (18 wt%) of monoethanol amine (MEA) or diethanol amine (DEA) according to the following reaction:



The amount of H₂S that can react depends on the operating conditions. Low temperature, high pressure, and high concentration of H₂S in the H₂S absorber favor the reaction.

The temperature of the lean amine solution to the H₂S absorber is controlled by a temperature controller on E-101. The temperature of lean amine is maintained at least 10°F above H₂S feed to the absorber to

Table 8-12
Flue Gas Desulfurization Operating Conditions

OPERATING VARIABLE	UNITS	
SULFITE EVAPORATOR		
TEMPERATURE	°F	300
PRESSURE	psia	30
SULFATE REDUCTION REACTOR		
TEMPERATURE	°F	660
PRESSURE	psia	32
SULFUR CONVERSION REACTOR		
TEMPERATURE	°F	300
PRESSURE	psia	18.4
SOLVENT (POLYETHYLENE GLYCOL), FOR SULFUR CONVERSION REACTOR		
MOLECULAR WEIGHT		380-420
FREEZING POINT	°F	39-46
SPECIFIC GRAVITY		1.125
VISCOSITY	122°F, cst	28
	212°F, cst	6.5-8.2
	275°F, cst	3.9
SULFUR SOLUBILITY		
	68°F, gm/liter	2-10
	248°F, gm/liter	27
	248°F, gm/liter	35
SO₃ CONVERSION REACTOR CATALYST		CO-MO ON ALUMINA BASE
TEMPERATURE	°F	660
PRESSURE	psia	31

Table 8-13
Utility Consumption, per Tons Sulfur Recovered

UTILITY	UNITS	AMMONIA		TOTAL
		SCRUBBING	CONVERSION	
ELECTRICITY	kWhr	1883	974	2857
FUEL, mm Btu	mmBtu	14.2	41.2	55.4
STEAM	mmBtu	0	-36.7	-36.7
DISTILLED WATER	MIG	0	0.057	0.057
COOLING WATER	MIG	0	2.86	2.86
PROCESS WATER	MIG	0.095	0	0.095

Table 8-14
Feed and Product Properties

PROPERTY	UNITS	FEED FLUE	TREATED	SULFUR
		GAS	FLUE GAS	
SO ₂	ppm	1600	200	
SO ₃	ppm	75	0	
AMMONIA LOSSES	ppm		10	
CARBONILE MATTER	ppm			<1000
SULFUR PURITY	Wt%			99.7
COLOR				YELLOW

prevent condensation of gas, which results in foaming in the absorber or hydrocarbon contamination of the H₂S product.

Rich amine solution is fed to a flash and surge drum. The object of the flash drum is to separate liquid hydrocarbons and dissolved gases from rich amine solution. A hydrocarbon skim is provided to remove any liquid hydrocarbons. This prevents foaming in the amine regenerator and contamination of the sulfur plant where the sulfur plant catalyst is coked. The drum also serves as surge volume for circulating the amine solution. Pressure in this drum is maintained as low as possible to release hydrocarbons from the rich amine solution.

H₂S is removed from the amine solution in an amine regenerator, where high temperature and low pressure are used to strip H₂S from amine solution.

At low temperature (<180°F), aqueous amine solutions are not too corrosive to carbon steel. Organic acids and decomposition products of DEA contribute to corrosion where surface temperatures are high enough to decompose the salts and release acid.

Table 8-15
Product Composition

COMPOSITION	
AMMONIA SOLUTION (RECYCLE) TO AMMONIA SCRUBBER, WT%	
(NH ₄) ₂ CO ₃	18.9
NH ₄ OH	2.2
(NH ₄) ₂ S	0.3
H ₂ O	78.6
SULFITIC BRINE FROM AMMONIA SCRUBBER, WT%	
NH ₄ HSO ₃	17.39
(NH ₄) ₂ SO ₃	12.12
(NH ₄) ₂ S ₂ O ₃	13.40
(NH ₄) ₂ SO ₄	7.10
H ₂ O	49.99
TOTAL	100.00
TREATED VENT GAS, VOL%	
H ₂ S	0.47
H ₂ O	11.70
NH ₃	0.12
CO ₂	22.20
UNCONDENSABLES	65.51
TOTAL	100.00

In amine plants, provisions are made to allow additions of chemicals such as sodium carbonate to neutralize acids and reduce acid-type corrosion. Sometimes, a DEA solution can promote severe H₂S corrosion. A filming amine corrosion inhibitor is usually added to prevent contact between corrosive material and metal.

THE AMINE TREATMENT PROCESS

Most refineries have more than one amine contactor, one for low pressure H₂S contaminated gases for treating refinery fuel gas and another for treating high pressure recycle gas from units such as hydrocrackers and hydrotreaters.

In LP absorber V-104, the gas feed enters the absorber at the bottom and the circulating amine solution enters the column at top (see Figure 8-4). The amine absorber has approximately 24 plates or a packed column of equivalent length. An aqueous amine solution (18%) enters the column at top, while

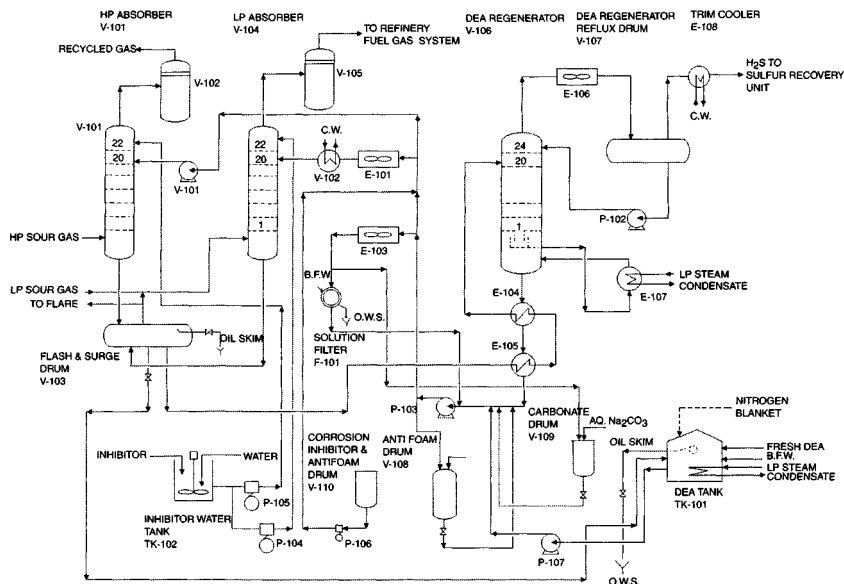


Figure 8-4. Amine treatment unit. B.F.W. = boiler feedwater; O.W.S. = oily water sewer.

sour gas enters the column at the bottom. Treated gas leaves the column at the top after passing through knockout drum V-105 and is sent out of battery limits. Rich amine solution is collected in flash and surge drum V-103. HP sour gas is similarly treated in column V-101 with 24 plates.

Rich amine from both columns V-101 and V-104 is collected in V-103, which acts both as a flash and a surge drum. Liquid from V-103 exchanges heat with regenerator column V-104 bottoms in E-104 and E-105 and enters the amine regenerator column V-104 at the top. The regenerator column has 24 plates and a steam reboiler. In this column, acid gases, such as H_2S and CO_2 , are separated as the overhead stream while the regenerated amine solution is pumped with recirculation pump P-103 to high- and low-pressure absorber columns V-101 and V-104. Acid gas from amine regeneration is sent to the sulfur recovery plant as feed. Liquid collected after condensation of V-106 vapor in E-106 is collected in V-107 and sent back to the column as reflux.

The amine solution is cooled in exchangers E-101 and E-102 before entering contactor V-104. The circulating amine solution is dosed with sodium carbonate and antifoaming additives to prevent foaming and corrosion in the contactors.

Table 8-16
Amine Treatment Unit Operating Conditions

OPERATING VARIABLE	UNITS	
LOW-PRESSURE AMINE ABSORBER		
INCOMING LEAN DIETHANOL AMINE TEMPERATURE	°F	150
INCOMING SOUR GAS TEMPERATURE	°F	140
ABSORBER BOTTOM PRESSURE	psig	27
NUMBER OF PLATES IN ABSORBER		24
HIGH-PRESSURE AMINE ABSORBER		
INCOMING LEAN DEA TEMPERATURE	°F	150
INCOMING SOUR GAS TEMPERATURE	°F	140
RICH AMINE LOADING	MOLES H ₂ S/ MOLE DEA	0.35–0.45
ABSORBER BOTTOM PRESSURE	psig	2410
NUMBER OF PLATES		24
DEA REGENERATOR		
REGENERATOR COLUMN TOP TEMPERATURE	°F	220
REGENERATOR COLUMN TOP PRESSURE	psig	13
REFLUX DRUM TEMPERATURE	°F	140
REFLUX DRUM PRESSURE	psig	9
REGENERATOR FEED TEMPERATURE	°F	215
REGENERATOR COLUMN BOTTOM TEMP.	°F	253
REGENERATOR COLUMN BOTTOM PRESSURE	psig	14

A small, lean amine slipstream is sent to amine filter F-101 to remove undesirable salts that contaminate the system. The slipstream filtration system is provided to maintain the cleanliness of the circulating amine.

Makeup amine, received in drums, is emptied in an amine sump and diluted with water to about an 18% solution. The aqueous amine solution is pumped to amine storage tank TK-101. The tank is blanketed with nitrogen gas to prevent air oxidation of the amine. Fresh amine is pumped into the circulating amine system as required.

Table 8-17
Amine Unit Utility Consumption, (per Ton Feed)

UTILITY	UNITS	CONSUMPTION
FUEL	mmBtu	
POWER	kWhr	13
STEAM	mmBtu	2.2
COOLING WATER	MIG	2.2
DISTILLED WATER	MIG	0.003

The operating conditions and feed composition of an amine treatment unit are shown in Table 8-16. The properties of amine, feed and product, and utility consumption are shown in Tables 8-17 to 8-19.

Table 8-18
Feed and Product Composition

COMPONENTS	FEED, mol%	TREATED GAS, mol%	ACID GAS, mol%
H ₂	11.24	14.97	
H ₂ S	24.89	0.00	91.45
C ₁	19.07	25.39	0.54
C ₂	11.02	14.68	0.30
C ₃	12.99	17.30	0.25
IC ₄	5.15	6.86	0.05
NC ₄	13.46	17.92	
IC ₅	0.06	0.08	
NC ₅	0.32	0.43	
C ₆₊	0.41	0.54	
H ₂ O	1.37	1.83	7.42
TOTAL	100.00	100.00	100.00

Table 8-19
Typical Properties of Amines*

PROPERTY	UNITS	MONOETHANOL AMINE	DIETHNANOL AMINE
FORMULA		H ₂ NCH ₂ CH ₂ OH	HN(CH ₂ CH ₂ OH) ₂
MOLECULAR WEIGHT		61.08	105.14
BOILING POINT	760 mm Hg, °F	338.7	498.2
	50 mm Hg, °F	213.8	359.6
	10 mm Hg, °F	159.8	302
FREEZING POINT	°F	50.9	82.4
SPECIFIC GRAVITY	68°F	1.017	1.092
VISCOSITY	CP, 86°F	16.2	380
REFRACTIVE INDEX	n _D ³⁰	1.4539	1.4747 ⁽¹⁾
SURFACE TENSION	dynes/cm	48.3 ⁽⁴⁾	48.5 ⁽⁵⁾
FLASH POINT	°F	205	375
HEAT OF VAPORIZATION	Btu/lb	390 ⁽²⁾	300 ⁽³⁾
CRITICAL TEMPERATURE	°F		827.8
CRITICAL PRESSURE	Atm		32.3

(1) AT 30°C. (2) AT 212°F. (3) AT 302°F. (4) AT 77°F. (5) AT 86°F.

*DOW CHEMICAL COMPANY DATA.