International Journal of Science and Research (IJSR) ISSN (Online): 2319-7064 Impact Factor (2012): 3.358

Recovery of Sulfur in Coke Oven By-Product Plant

Shamik Pushkar

Junior Manager, Energy Management Department, JSW Steel

Abstract: When coal is converted to coke, the volatile matter entrapped in coal escapes. This volatile matter is called coke oven gas, which is collected and cleaned to be used as fuel. One of the impurities of the Coke Oven gas is Sulfur which is extracted using Claus process. The Sulfur thus obtained is 99.5% pure, which can be used commercially.

Keywords: Claus reactor, coke oven gas, carbonization of coal, tar precipitator.

1. Introduction

Tata Steel is increasing its crude steelmaking capacity at the Jamshedpur Works from 6.8 mtpa to 9.7 mtpa via a 2.9 mtpa Brownfield expansion project. Increase in capacity has led to the increase in coke consumption in the plant. To meet the demand of coke, new battery 10 and battery 11 is being set up. The impurities are being separated, converted into by products and either used within the plant or sold to some other organization. Sulfur is the main product of the byproduct plant. Sulfur is produced in solid pellets. Tar is also produced in the byproduct plant and is used within the plant itself. Other gases thus produced in the process are non-toxic and are released in the atmosphere. The capacity of BPP is as follows (including return tail gas from sulfur recovering unit):

- Guaranteed capacity will be 88,000Nm³/h.
- Design capacity will be $97,000 \text{Nm}^3/\text{h}$.
- Capacity of exhauster will be 120% of design capacity, i.e. 116,400 Nm³/h. [4]

2. Process Overview



Overall Process



A.Coke Oven Battery

In a coke oven battery, a number of ovens are built in a row with common walls between neighboring ovens. A battery consisted of many ovens, sometimes hundreds of ovens, in a row [1][2].

Coal is introduced from the top to produce an even layer of about 60 to 90 centimeters deep. Air is supplied initially to ignite the coal. Carbonization starts and produces volatile matter, which burns inside the partially closed side door. Carbonization proceeds from top to bottom and is completed in two to three days. The hot coke is quenched with water and discharged, manually through the side door. The walls and roof retain enough heat to initiate carbonization of the next charge.

B. Primary Gas Cooler/ Primary Cum Deep Cooler

The first step in the treatment of raw coke oven gas is to cool it to remove water vapor and so greatly reduce its volume. This is done in the Primary Cooler. There are two basic types, the spray type cooler and the horizontal tube type cooler [3].

In a spray type cooler the coke oven gas is cooled by direct contact with a re-circulated water spray, with the contact cooling water being itself cooled externally in heat exchangers. In the tubular type, the coke oven gas is cooled indirectly by flowing across horizontally mounted tubes through which cooling water is pumped. In this case, the cooling water does not come into contact with the coke oven gas and so it can be cooled in a cooling tower for example. As the coke oven gas is cooled, water, tar and naphthalene condense out. The condensate collects in the primary cooler system and is discharged to the tar & liquor plant.

Main technical and operating parameters: [4]

1. Gas temperature after primary cooler - 21°C

2. Inlet temperature of circulating water into primary cooler-34°C

3. Outlet temperature of circulating water into primary cooler-45°C

4. Temperature of chilled water into lower stage of primary cooler-15°C

5. Temperature of chilled water out of lower stage of primary cooler-23°C

6. Resistance of primary cooler<1500Pa

C.TAR Precipitator

As the raw coke oven gas is cooled, tar vapor condenses and forms aerosols which are carried along with the gas flow. These tar particles would contaminate and foul downstream processes and would foul gas lines and burner nozzles if allowed to continue in the gas stream. The tar precipitators typically use high voltage electrodes to charge the tar particles and then collect them from the gas by means of electrostatic attraction. The task of the unit is to remove tar droplet entrained in gas after the primary cooler. In order to remove tar mist entrained in gas, three electric tar precipitators are provided, normally three precipitators in operation, in case of one in maintenance two in operation, tar content in gas can also be reduced to 20mg/Nm³ (20mg/Nm³ is the guarantee value while two ETP are in operation).Gas enters into electric tar precipitator from its bottom, via the gas distribution plate gas is uniformly distributed onto the whole section, then flows through high voltage electric field of the honeycomb upward to leave electric tar precipitator and enters into the exhauster unit. When gas passes through electric tar precipitator, solid and tar mist droplet in gas is deposited on surface of honeycomb, the tar flows via the tar outlet at the bottom into water seal pot, from which it flows into underground slop tank.[3][4]

Main Technical Parameters

Temperature of insulator box of ETP~60°C

Resistance of ETP500Pa

D.Exhauster

The exhauster is a large blower that provides the motive force to induce the coke oven gas to flow from the coke oven battery and through the by-product plant. The exhauster is of prime importance to the operation of the coke oven battery. It allows the close control of the gas pressure in the collecting main, which in turn affects the degree of emissions, for example door emissions, from the battery. A failure of the exhauster will immediately result in venting to atmosphere, through the battery flares, of all of the raw coke oven gas produced. The task of the unit is to boost crude gas from coke oven to the downstream gas purification system, for this purpose three electric driven gas exhausters are installed, two in operation and one as stand by.

The gas exhauster is located after electric tar precipitator and before H_2S scrubber. In order to stabilize the pressure of the gas suction main before primary gas cooler, the gas pressure regulation before primary cooler is realized by means of regulating speed of exhauster through VVVF.

The condensate deposited in gas pipe at inlet and outlet of gas exhauster and exhauster flows via water seal pot into the slop tank from which it is sent to the decanter.

Water seal pot and slop tank are connected with the pressure equalizing system.[3]

Main Technical Parameters [4]

Gas temperature after exhauster~45°C Pressure after exhauster-14.5kPa

E.H₂S/NH₃ Scrubing Unit

Coke oven gas from exhauster is first fed into the final cooling stage at lower part of H_2S scrubber. Gas is cooled down to ~22°C by spraying with the circulating water. After the circulating water out of H_2S scrubber is cooled with the cooler for circulating water, the circulating water is sent back again to the final cooling stage at the lower part of H_2S scrubber for circulating cooling. At the upper part of H_2S scrubber, H_2S in gas is absorbed with enriched ammonia water from ammonia scrubbing and lean solution from deacidifier and ammonia stripping unit. At the same time of H_2S removal in H_2S scrubber, also CO₂, HCN and NH₃ are absorbed. Because the absorption process of H_2S , CO₂, HCN and NH₃ is the exothermic process, therefore both upper stage and lower stage of H_2S scrubber are provided with the coolers for H_2S circulating scrubbing solution [1].

In ammonia scrubber, ammonia in gas is washed with soft water and the stripped water from deacidifier and ammonia stripping unit. In addition to these, coal water from coal water filtering system is added to the bottom of ammonia scrubber after cooled with coal water cooler so as to increase ammonia scrubbing effect. If the concentration of free ammonia in coal water is very high, part of or all coal water is directly sent to ammonia stripper. Enriched ammonia liquor out of the sump of ammonia scrubber is first cooled with ammonia liquor cooler, then sent to the top of H_2S scrubber [3].

The upper stage of ammonia scrubber is provided with soda washing stage, where the diluted soda lye, can be added for further absorbing H_2S and HCN in gas. Soda lye out of ammonia scrubber flows to soda lye tank in deacidifier and ammonia stripping unit.

Soft water is used for ammonia scrubbing on top stage of ammonia scrubber. Ammonia content in purified gas is 0.04 g/Nm^3 .

Except soda lye, all scrubbing solutions are finally gathered at the sump of H_2S scrubber, from which they are pumped to enriched solution tank in deacidifier and ammonia stripping unit. In order to keep continuous running and high efficiency of H_2S/NH_3 removal, H_2S/NH_3 scrubber is provided as standby that is there are three scrubbers: H_2S scrubber, H_2S/NH_3 scrubber and ammonia scrubber.[2]

F. Deacidifier and Ammonia Stripping Unit

Two de-acidifiers and two ammonia strippers are provided in the unit with one in operation and one as standby. The solution in enriched solution tank is pumped to lean solution/enriched solution heat exchanger for heat exchange with lean solution from the sump of de-acidifier and then sent to the top of de-acidifier where enriched solution is stripped with ammonia-containing vapor out of ammonia stripper; most of H₂S, HCN, CO₂ in solution are stripped out.

International Journal of Science and Research (IJSR) ISSN (Online): 2319-7064 Impact Factor (2012): 3.358

The lean solution out of deacidifier is pumped out with the lean solution pump, part of it is heat exchanged in lean/enriched solution heat exchanger with enriched solution, then cooled with the lean solution cooler and sent to H_2S scrubber in H_2S/NH_3 scrubbing unit. The rest is directly sent to ammonia stripper.

At the upper stage of ammonia stripper, free ammonia in lean solution from deacidifier is further stripped out, and part of stripped water is taken after free ammonia stripped out, the stripped water is first cooled with the cooler and then sent to ammonia scrubber in H₂S/NH₃ scrubbing unit for absorbing ammonia in gas. The rest liquor is reached to the lower stage of ammonia stripper, where soda lye is added for decomposition of fixed ammonia. Ammonia-containing vapor out of ammonia stripper enters into deacidifier for stripping enriched solution. The stripped water out of the sump of ammonia stripper is pumped to the cooler for stripped water for cooling, after that, it is pumped and a small part of it is used for diluting soda lye, the rest, namely waste water is sent to bio-chemical waste water treatment plant. The mixed vapor contained with NH₃, H₂S, HCN and CO₂ discharged from the top of deacidifier is first partially condensed and then sent to the sulfur recovery unit.

The deacidifier and ammonia stripping unit is provided with one enriched solution tank, one lean solution tank and one stripped water tank [2].

Main Technical Parameters [4]

Gas temperature into final cooling stage of H_2S scrubber~45°C Gas temperature out of final cooling stage of H_2S scrubber ~22°C

Gas temperature into ammonia scrubber~23°C

Gas temperature out of ammonia scrubber $\sim 24^{\circ}$ C Pressure loss of gas in H₂S scrubber < 2000Pa Pressure loss of gas in H₂S/NH3 scrubber < 2500Pa Pressure loss of gas in ammonia scrubber < 1750Pa

G. Sulfur Recovery System

1.Feed Gas Composition

Typical feed gas composition					
Component	Mol %	Wt %	Component	Mol %	Wt S
From an amine process:			From a sour water stripper:		
H ₂ S	82.1	80.8	H ₂ S	26.7	40.2
CO2	11.9	15.1	CO2	2.6	5.1
NH ₃	nil	nil	NHa	39.4	29.7
H ₂ O	4.0	2.1	H ₂ O	31.3	25.0
HC	2.0	2.0	HC	nil	nil

3. Reactions

Overall Reactions:

H₂S+1.5O₂ \rightarrow SO₂+H₂O; Δ H= -518.4KJ/kg H₂S (exothermic Reaction)

2H₂S + SO₂ →3/X S_X + 2H₂O (X=1- 8); Δ H= -146.7KJ/kgH₂S (at 260°C)

General Reaction:

 $3H_2S+1.5 O_2 = (3/X)S_X+3H_2O + 664KJ$

 $CO_{2}+H_{2}S = COS+H_{2}O$ $COS + H_{2}O = H_{2}S + CO_{2}$ $2H_{2}S+CO_{2} = CS_{2}+2H_{2}O$ $CS_{2} + 2H_{2}O = 2H_{2}S+CO_{2}$ $NH_{3} = 1.5H_{2}+0.5N_{2}$ $HCN+H_{2}O = 1.5H_{2}+0.5N_{2}+CO$ $2H_{2}S+SO_{2} = 1.5S_{2}+2H_{2}O$

Catalyst used in Claus kiln "NICKEL CATALYST" over inert ball. Catalyst used in Claus reactor "ALUMINA CATALYST" over inert ball [2].

The reaction furnace pressure and temperature is maintained at about 1.5 bar gauge (barg) and about 1,000 °C. At those conditions, the Claus reaction occurs thermally in the reaction furnace (i.e., without requiring any catalyst). About 70% of the H_2S in the feed gas is thermally converted into elemental sulfur in the reaction furnace.

The hot reaction product gas, containing gaseous sulfur, is used to produce steam in a boiler (called a waste heat boiler) which results in cooling the gases. The gas is then further cooled and condensed in a heat exchanger while producing additional steam. The condensed liquid sulfur is separated from the remaining unreacted gas in the outlet end of the condenser and sent to product storage.

The separated gas is then reheated and enters the first catalytic reactor maintained at an average temperature of about 305 °C where about 20% of the H₂S in the feed gas is converted into elemental sulfur. The outlet product gas from the first reactor is cooled in another condenser while also producing steam. Again, the condensed liquid sulfur is separated from the remaining unreacted gas in the outlet end of the condenser and sent to product storage.

The separated gas from the second condenser is sent to another reheater and the sequence of gas reheat, catalytic reaction, condensation and separation of liquid sulfur from unreacted gas is repeated for the second and third reactors at successively lower reactor temperatures.[1] About 5% and 3% of the H₂S in the feed gas is thermally converted into elemental sulfur in the second reactor and third reactors, respectively. For a well-designed and operated Claus sulfur recovery plant having three catalytic reactors (as shown in the flow diagram), an overall conversion of at least 98% can be achieved. In fact, the latest modern designs can achieve up to 99.8% conversion of hydrogen sulfide into product sulfur that is 99+% saleable "bright yellow sulfur" [2].

The remaining gas separated from the last condenser is referred to as "tail gas" and is either burned in an incinerator or further desulfurized in a "tail gas treatment unit" (TGTU).

4. Process Description



Sour vapor containing H_2S/NH_3 from de-acidifier and ammonia stripping unit is first regulated for pressure and then fed into the burner located at upper part of Claus furnace. The partial oxidation is adopted, in which one-third of H_2S is burnt with air to form SO₂, the rest two-third H_2S is reacted with SO₂ to form elemental sulfur.

The whole reaction is an exothermic reaction. The high temperature in furnace is maintained by chemical reaction. When H_2S in sour vapor is lower, the released heat is not sufficient to keep temperature necessary for reaction, small amount of coke oven gas must be introduced into the furnace so as to maintain heat amount necessary for reaction in furnace.

 NH_3 and HCN in sour vapor is decomposed into $H_2,\,N_2$ and CO under

~1150°C catalytic cracking. Hydrocarbon in sour vapor also can be fully decomposed or burnt. Secondary air is introduced into the bottom of Claus furnace; the process gas is further oxidized. The amount of secondary air is controlled with H_2S/SO_2 proportional monitor after sulfur separator. High temperature process gas out of Claus furnace is passed through waste heat boiler for heat recovery, and then continuously passed through two stages of clause reactor to form elemental sulfur, then passed through sulfur condenser and sulfur separator to separate liquid sulfur. The tail gas is sent to the cooler, where it is sprayed and cooled with condensate from upper stage of primary cooler, after cooling it is sent to the gas suction main before downcomer.

Liquid sulfur condensed at waste heat boiler together with liquid sulfur from sulfur separator are merged and then fed into liquid sulfur tank, then sent by pump into sulfur solidification unit, where it forms pellet solid sulfur by cooled, then slide down along chute, packing and finally transported out with truck.

The process gas intermediate heater is provided between Claus reactors. The process gas into second stage Claus reactor is heated with the process gas out first stage Claus reactor, enabling second stage reached to the temperature required by reaction.

0.4MPa steam produced in waste heat boiler is used for heating of air heater and heating, tracing and purging of equipment and pipe. The surplus one is sent to the 0.4MPa steam net. 0.15MPa steam produced in sulfur condenser is used for degassing of the treatment tank for boiler feed water.

The cleaned gas used for Claus furnace heating comes from downstream of naphthalene scrubber. Gas is boosted to Claus furnace with gas blower. Air for combustion is boosted with air blower and passed through heater to Claus furnace.

Boiler feed water necessary for waste heat boiler and sulfur condenser enters into boiler feed water treatment tank, after degassed with steam, is sent into the waste heat boiler and sulfur condenser by water feed pump.

The blow down water from waste heat boiler and sulfur condenser is mixed with the cooling water from sulfur solidification unit and cooled, then discharged into the water drainage system.

After two batteries put into operation, that is four coke ovens in production, two sets of Clause system can be operated, the actual running capacity of each is ~50%, hot standby each other. If only one battery in production, one Clause system will be in operation, the actual running capacity is ~50%, the other one serves as clod standby [2].

5. Main Technical Data[4]

Flow rate of sour vapor containing $H_2S/NH_3 \sim 3400Nm^3/h$ Temperature of catalyst bed in Claus furnace ~1150°C Temperature of process gas out of waste heat boiler: 220~240°C Temperature of process gas into 2nd stage Claus reactor: 210~220°C Temperature of process gas after sulfur condenser -135°C Tail gas temperature after tail gas cooler ~80°C Resistance of catalyst bed of Claus furnace <5 KPa Resistance of catalyst bed of Claus reactor <4.5 KPa Steam pressure produced by waste heat boiler- 0.4MPa

Steam pressure produced by sulfur condenser- 0.15MPa Sulfur purity -99. 5% (w/w)

6. Waste Heat Recovery Unit (Waste Heat Boiler)[1]

A waste heat recovery unit (WHRU) is an energy recovery heat exchanger that recovers heat from hot streams with potential high energy content, such as hot flue gases from a diesel generator or steam from cooling towers or even waste water from different cooling processes such as in steel cooling. Waste heat boiler produce steam at a pressure of 0.4 mpa with a capacity of 6 ton/hr. These systems have many benefits which could be direct or indirect.

- Direct benefits: The recovery process will add to the efficiency of the process and thus decrease the costs of fuel and energy consumption needed for that process.
- Indirect benefits:
- a. Reduction in Pollution: Thermal and air pollution will dramatically decrease since less flue gases of high temperature are emitted from the plant since most of the energy is recycled.
- b. Reduction in the equipment sizes: As Fuel consumption reduces so the control and security equipment for handling the fuel decreases. Also, filtering equipment for the gas is no longer needed in large sizes.
- c. Reduction in auxiliary energy consumption: Reduction in equipment sizes means another reduction in the energy fed to those systems like pumps, filters, fans...etc.

• Disadvantages

- a. Capital cost: The capital cost to implement a waste heat recovery system may outweigh the benefit gained in heat recovered. It is necessary to put a cost to the heat being offset.
- b. Quality of heat: Often waste heat is of low quality (temperature). It can be difficult to efficiently utilize the quantity of low quality heat contained in a waste heat medium. Heat exchangers tend to be larger to recover significant quantities which increases capital cost.

7. Degasifier [3]

Degasification is the removal of dissolved gases from liquids, especially water or aqueous solutions. There are numerous possible methods for such removal of gases from solids.

Generally speaking, the higher the temperature of a solution becomes, the less a gas dissolves provided it doesn't react with the solvent. Consequently, heating a solution can expel the remaining gas. This method is used in the degasifier, along with chemical dosing. Degasification is done to reduce corrosion and increase heat transfer in the waste heat boiler. A temperature of 104° C is maintained in the degasifier and chemical used are tri sodium phosphate (TSP) and hydrazine hydrate.

8. Material Energy and Product [4]

Crude Coke Oven Gas

a) Temperature: 82°C (saturated with water).

b) Content of impurities in crude coke oven gas (excluding tail gas, charging gas and Respiration gas):

H₂S 5~6.5g/Nm³ NH₃-10~11 g/Nm³ BTX -30~35 g/Nm³ Tar -35~45 g/Nm³ C₁₀H₈(naphthalene)- 6~10 g/Nm³ HCN- 1~1.5 g/Nm³ PURIFIED COKE OVEN GAS

a) Pressure (97,000 Nm³/h at battery limit)-3.5kPa (min.) b) Gas composition (vol %): CO₂ -3~4 CnHm- 2~2.6 O₂- 0.6 CO - 6~9 H₂- 52~56 CH₄- 24~26 N₂- balance c) Temperature: ~28°C (saturated with water). d) Content of impurities (the figures are valid for gas flow $88,000 \text{Nm}^3/\text{h}$ $H_2S-0.5 \text{ g/Nm}^3$ NH3-0.04 g/Nm³ $C_{10}H_8$ - 0.12 g/Nm³ Tar -0.02 g/Nm³ CRUDE TAR

(After centrifuge)

Specific gravity 1.14~1.22

Moisture3% (W/W) Solid matters (>100 µm) 0.3% (W/W) Without Centrifuge Specific gravity 1.14~1.22 Moisture4% (W/W) Solid matters (>100 µm) NA

Stripped Waste Water

Total ammonia content: 150mg/l Quantity: 105m³/h (DN200) Pressure at T.O.P 0.45MPa

Temperature 40°C

Sulfur

Sulfur purity 99. 5% (W/W)

9. Conclusion

The new by product plant established in Tata steel would house two batteries (#10,#11). Each battery is equipped with 44 coke ovens. Approx 44,000 m³/hr coke oven gas will be produced by each battery. Each battery is followed by tar ammonia H_2S and naphthalene removal system. Tar is used within the plant as a fuel. Tar produced is approx 70,610 ton/yr. Ammonia is broken down into n_2 and H_2O in Claus process while sulfur is recovered from H_2S in liquid form. This liquid sulfur is then sent to the pelletization plant where liquid sulfur is converted into solid sulfur pellets by cooling.

The main aim of establishing such a plant was not to attain financial benefits but to keep a check on environmental pollution in Jamshedpur. The SO_2 and NO_2 levels have increased in the city and 2 new batteries producing 44,000 m³/hrcog would have take these gases to extreme levels. Tata

Volume 3 Issue 8, August 2014

Steel has always been know for uplifting social and environmental causes and keeping this in mind, the new by product plant came in. Moreover, the sulfur produced has a purity of 99.5%. H_2S concentration is brought down by 87% while ammonia BTX and HCN are removed entirely from the tail gas.

Heat is recovered from the waste heat boiler as well as the two condensers. Waste heat boiler produces steam at 0.4 mpa and has a capacity of 6 ton/hr while the condenser produces steam at .14 mpa and has a capacity of 1 ton/hr.

Sulfur recovery is done by Claus process. Claus process is a two step process for sulfur recovery. The first step is a thermal step in which the sour gas(mixture of NH₃ and H₂S) is heated to 1150^{0} C where ammonia cracks down to N₂ and H₂O while H ₂S breaks down to give liquid sulfur. The second step is a catalytic step in which the exit gas from the first step is treated with a catalyst (Al₂O₃) which break the remaining H₂S to give sulfur.

Acknowledgement

First of all, I would like to thank the department of SNTI for giving me to the opportunity to visit the plant and attain some industrial experience. Secondly I would like to thank my guide Mr. Sujit Sinha who has helped me throughout the project and without who, completion of my project would have been very difficult. Finally I would like to thank the whole tata steel management for rendering such a trainee program through which budding engineers can gain some experience. Without the support of all of them, the project would not have been a success.

Reference

- [1] UDHE brochure for Schwelgern coke plant.
- [2] TECHNICAL OFFER of By Product Plant & Facility for COB10 & 11 for JSR Project of TATA STEEL DOCUMENT NO.424EC05 Sep. 2009
- [3] ACRE Coking and Refractory Engineering Consulting Corporation, MCC
- [4] Sulfur recovery unit tatasteeel
- [5] THE COKE OVEN MANAGERS'ASSOCIATION 197
- [6] Generic Methods for Coke Oven Gas Desulphurization by WilfriedSeyfferth Rainer Dittmer, Dr. HolgerThielert ThyssenKrupp EnCoke GmbH, Bochum, Germany (nowUhde GmbH, Dortmund, Germany)

Author Profile



Shamik Pushkar was born on 27th march 1992 in Jamshedpur. He did his schooling from Loyola School Jamshedpur. HE joined MIT Manipal in 2010 in Dept of Chemical Engineering and passed

out in 2014. He is currently working in JSW Steel as a junior manager in Energy Management Department. This research was done in June 2013 in TATA STEEL'S Coke oven byproduct plant. The main aim of the project was to get an insight of the process.