

SULPHUR PLANT CONFIGURATIONS TO CUT COSTS AND CO₂ EMISSIONS

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The sulphur recovery is considered a mature technology with minor possibilities of improvements. During the last years the new Refineries built in the world have installed sulphur plants with tail gas treatment suitable to achieve the maximum of recovery efficiency. In general these plants have a similar process scheme with minor differences between the various technologies available on the market.

The importance to cut operating costs and reduce the CO₂ emissions has been seen as a target of lower importance for sulphur plants being the efforts of the designers directed to the maximization of the recovery efficiency.

It is instead possible to obtain high recovery efficiency with lower operating and investment costs by selecting the best plant configuration for each particular situation and there are rules which may be applied to any plant design to optimize the system.

The evaluation of the various plant configurations is of high importance for the implementation of low cost sulphur plants environmentally more friendly.

The paper describes the options which may minimize the sulphur recovery plant operating cost and quantifies the achievable benefits in terms of CO₂ emissions.

1. WORLDWIDE CO₂ EMISSIONS

The quantities of CO₂ emissions pro capite are largely dependent on the development of the economy of the country involved. Table 1 shows the emissions in some of the most populated countries:

Table 1: CO₂ emissions in the world – Overall (year 2008) – Reuters/Financial Times

China	6.81×10^9 T/Y	\approx	5 T/Y per man
U.S.A.	6.37×10^9 T/Y	\approx	20 T/Y per man
Europe (EU27)	3.92×10^9 T/Y	\approx	10 T/Y per man
Russia	1.69×10^9 T/Y	\approx	12 T/Y per man
India	1.41×10^9 T/Y	\approx	1.2 T/Y per man
Very poor countries	-	\approx	<0.1 T/Y per man

The sources for the energy production in the world are as follows:

Oil, gas, coal	79%
Biomasses	13%
Water	3%
Nuclear	3%
Others	2%

The oil and gas industries are therefore the major energy generators and CO₂ emissions producers.

The CO₂ emissions for different types of energy production are shown in Table 2.

Table 2: CO₂ emissions for energy productions

Source of energy	Emitted CO ₂ (gr/kW)
Coal, fuel oil (old plants)	950-1000
Clean coal	750-770
Fuel oil (modern plants)	650
Natural gas	460
Natural gas (combined cycle)	350-400
Renewable (wind turbines, photovoltaic solar cells, solar power, biofuels)	0

Depending on the Refinery configuration, the average CO₂ emissions are as follows:

Hydroskimming	0.08-0.15 kg CO ₂ /kg crude oil
Fluid Catalytic Cracking + Visbreaking	0.20 kg CO ₂ /kg crude oil
Hydrocracker + Coker	0.20-0.35 kg CO ₂ /kg crude oil
Resid Desulphurization + Resid FCC	0.30-0.40 kg CO ₂ /kg crude oil

The average CO₂ emissions of European Refineries (EU 27) is 0.22 kg CO₂/kg crude oil treated.

The CO₂ generation for energy production is depending on the technological level of any country. For instance, the figures of USA and China are as follows (Reuters – Financial Times – 2007 average):

USA	0.549 kg CO ₂ /kW generated
China	0.758 kg CO ₂ /kW generated

The above data help to better understand and evaluate the achievements which can be reached adopting the strategies finalized to cut the CO₂ emissions in sulphur recovery plants.

2. TYPICAL SULPHUR PLANT CONFIGURATION

The environmental concerns and consciousness of the necessity of the greenhouse gases reduction are now and shall be in the near future the driving factor for the selection and the improvement of any industrial activity, starting from the Refineries technologies.

The main and more easy way to reduce the CO₂ emissions is to boost the thermal efficiency of the plants and this may be very often obtained without additional or with low investment. In most cases the CO₂ emissions may be reduced even with lower investment.

Examples of reconfiguration of sulphur plants finalized to improve the thermal efficiency and reduce the carbon footprints are discussed in this paper.

The typical flow sheet of sulphur recovery is shown in Figure 1.

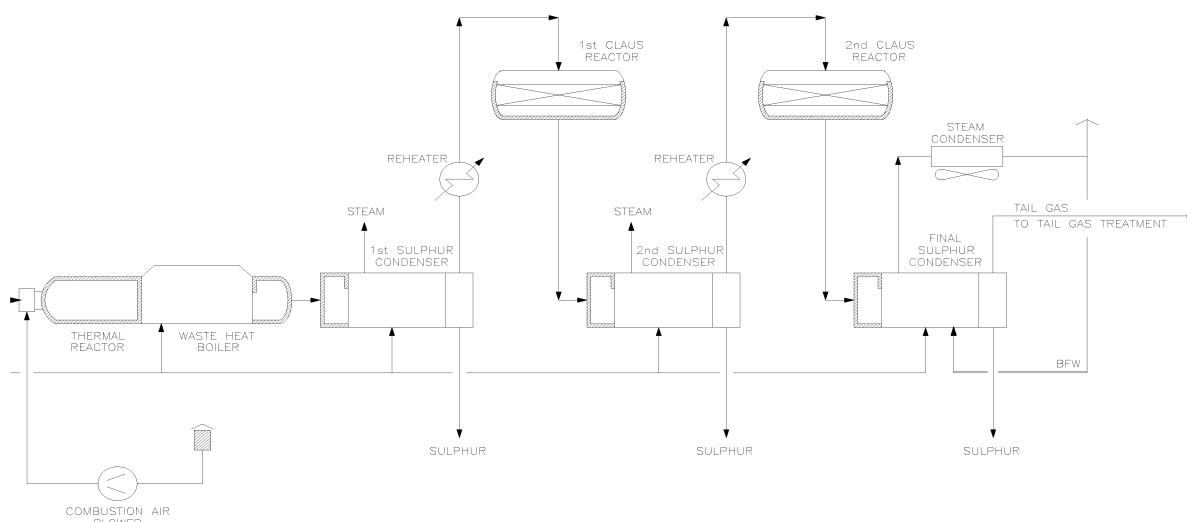
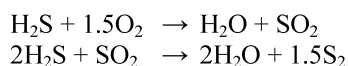


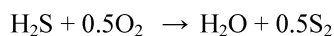
Fig. 1: Sulphur recovery typical flow sheet.

The sulphur recovery process is based on the Claus reaction to produce elemental sulphur from the H_2S contained in the feedstock.

The main reactions in the Claus plant are:



The overall reaction of H_2S is:



Hydrocarbons contained in the feedstock are transformed in CO/CO_2 , H_2O , COS and CS_2 .

Part of the CO_2 contained in the feedstock reacts with $\text{H}_2\text{S}/\text{SO}_2$ and S producing COS and CS_2 .

The Claus plant consists of a thermal stage, in which H_2S is partially burnt with air, followed by two (or three) conventional Claus catalytic reactors.

The Claus reaction is achieved with molar ratio air/ H_2S in the feed gas to the thermal conversion stage in order to obtain a tail gas containing H_2S and SO_2 in a molar ratio 2:1-

The Claus reaction is exothermic, so enhanced by the low temperature. The most common catalyst used in the Claus reactors is alumina. More expensive Titanium oxide catalyst is used to promote the hydrolysis of COS and CS_2 to H_2S in the First Claus Reactor.

The hydrolysis reaction are enhanced by the high temperature ($\geq 300^{\circ}\text{C}$), which is achievable in the first catalytic converter.

In certain cases of treatment of H_2S very lean feedstocks, titanium oxide replaces or is mixed with alumina even in the Second Claus Reactor in order to balance the alumina sulphation, which reduces the catalyst lifetime.

The correct ratio of feed gas and air is maintained by two flow controllers acting on two parallel control valves in the discharge line of the Combustion Air Blower. One flow controller maintains the ratio of air and sour gas. The other flow controller is reset by the signal coming from the $\text{H}_2\text{S}/\text{SO}_2$ analyzer mounted on the Claus tail gas outlet line.

The total air sent to the main burner is exactly sufficient to accomplish the complete oxidation of all hydrocarbons present in the feed gases and to burn as much H_2S as required to obtain an $\text{H}_2\text{S}/\text{SO}_2$ ratio equal to 2 in the tail gas.

The waste heat contained in the process gas leaving the Thermal Reactor is recovered by rising high pressure steam in the Waste Heat Boiler (typical pressure is 40÷45 bar g).

The process gas leaving the WHB is sent to the First Sulphur Condenser in which the sulphur is condensed and collected to a sulphur pit via a sulphur seal.

The process gas leaving the First Condenser is heated up in the First Reactor Reheater to typical temperature of 240°C .

The process gas enters the First Claus Reactor where the reaction between the H_2S and SO_2 continues until equilibrium is reached. The effluent gas from the First Reactor at temperature of $300\text{-}310^{\circ}\text{C}$ enters the Second Sulphur Condenser, where the sulphur is condensed and drained via a sulphur seal to a sulphur pit.

The process gas flow from the Second Sulphur Condenser passes to the Second Reactor Reheater before entering to the Second Claus Reactor, operating at typical temperature of $210\text{-}215^{\circ}\text{C}$.

The gas leaving the Second Reactor at temperature of $230\text{-}240^{\circ}\text{C}$ enters the Final Sulphur Condenser where the sulphur is condensed and drained via a sulphur seal to a sulphur pit.

The waste heat contained in the process gas passing through the first and second condensers is utilized to raise steam at typical pressure of 3-4 bar g.

The waste heat contained in process gas passing through the third condenser generates steam at typical pressure of 1.2 bar g. The process gas (tail gas) leaving the Final Sulphur Condenser at temperature of 130°C is sent to the Tail Gas Treatment.

The sulphur recovery achievable by a well designed Claus plant is with two catalytic converters ranges from 95 to 97%, depending on the feedstock composition; with three catalytic converters the recovery may be boosted to 97÷98%.

The recovery efficiencies imposed by the Authorities governing the air pollution worldwide is generally between 98.5% and 99.9% plus. This requires installing additional facilities, named tail gas treatment, downstream the Claus plants.

Several tail gas treatment technologies are available on the market, but the most widely used in Refineries and gas fields is the reductive amine based process, which is considered the Best Available Technology, capable to achieve 99.9% plus aggregate recovery efficiency.

The typical flow sheet of tail gas treatment is shown in Figure 2.

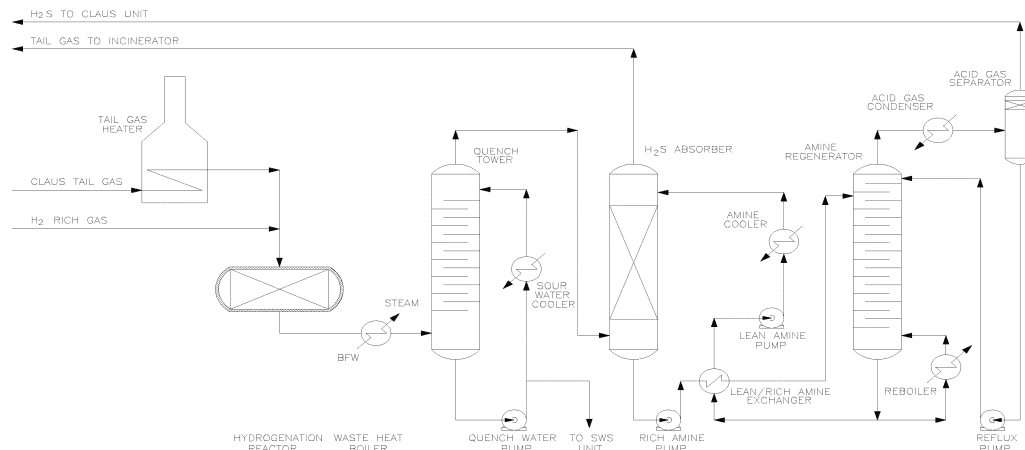


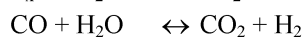
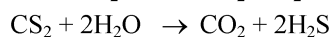
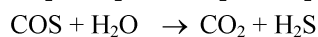
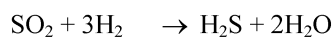
Fig. 2: Tail gas treatment typical flow sheet.

In Refineries, the Claus tail gas is added with hydrogen rich gas, as necessary, and it is sent to the hydrogenation reactor, where all components containing sulphur are reduced or are hydrolyzed to H_2S over a CoMox catalyst. In gas fields, where hydrogen is not always available, the hydrogen (and CO) necessary for the sulphur compounds hydrogenation is produced by substoichiometric combustion of natural gas in an inline burner.

The H_2S formed in the Hydrogenation Reactor is absorbed by amine solution. The amine solution is regenerated in amine regeneration facilities, which may be dedicated or common to other facilities installed in Refineries or gas fields.

The off gas leaving the H_2S Absorber is finally treated in a Thermal Incinerator for the conversion of the residual sulphur compounds to SO_2 before they are released to the atmosphere.

The main reactions in the TGT section are:



The tail gas coming from the Claus plant is heated up to a temperature of 280-290°C in a Tail Gas Heater, the hot process gas is mixed with hydrogen rich gas and sent to the Hydrogenation Reactor, which is filled with a specific CoMox reduction/hydrolysis catalyst.

Here all the sulphur compounds contained are hydrogenated or hydrolyzed to H_2S .

Due to the exothermic reactions the process gas temperature increases.

The hydrogenated gas leaving the Reactor is sent to the Quench Tower after being cooled down to typical 170°C in the TGT Waste Heat Boiler. The heat contained in the process gas is used to raise low pressure steam. In the Quench Tower the process gas quench and cooling is achieved by circulation of the condensate generated in the gas cooling.

The Quench Water Pump provides the water circulation to the tower. The sensible heat of the process gas and the steam condensation heat are removed in the Sour Water Cooler. The sour condensate containing H₂S generated are recycled to a Sour Water Stripper, if available, or are stripped with air in a packed tower. The air containing H₂S is sent to the Claus main burner.

The cooled gas, leaving the top of the Quench Tower is sent to the H₂S Absorber.

The absorption of the H₂S contained in the gas is accomplished using amine solution. The H₂S rich amine solution leaving the Absorber is pumped to the amine regeneration facilities. The acid gas released in the amine regeneration is sent to the Claus main burner.

The treated (sweetened) tail gas leaving the top of the Absorber enters the Incinerator, where all the sulphur species contained are oxidized to SO₂.

The final incineration of the TGT tail gas is typically achieved in a forced draft combustion chamber with waste heat recovery to generate steam at 40-45 bar g and, in most cases, to superheat the steam to 400-430°C.

The amine solution used in the Tail Gas Treatment must be H₂S selective with minimum coabsorption of the CO₂ contained in the process gas.

The selection of the amine solution type determines the recovery efficiency of the Tail Gas Treatment.

Using diisopropanol amine (DIPA) or plain methyldiethanolamine (MDEA) solutions it is possible to achieve an aggregate recovery efficiency of 99.8-99.9%. Higher efficiencies (99.9% plus) are achievable using formulated amine solutions, MDEA based, or hindered amine solution. An important factor for the H₂S removal is the temperature of the lean amine solution; with max 32°C it is possible to reduce the H₂S concentration in the process gas leaving the H₂S Absorber to less than 50 ppm vol, using plain MDEA solution and to less than 10 ppm vol using formulated or hindered amine solutions.

Also the selectivity of the solution is affected by the temperature. However, the CO₂ coabsorption ranges from 5% with hindered amines to 15-20% with plain MDEA.

3. ENHANCED SULPHUR PLANTS CONFIGURATIONS

The possible energy savings here presented are referred to sulphur plants installed in Refineries and in gas fields and having capacity of 750 T/D sulphur, which is typical for Refineries treating 10x10⁶ T/Y crude oil.

This Refinery size is the minimum acceptable in certain countries such as China and Saudi Arabia.

The capacity of the sulphur plants in megaprojects now in construction in gas fields in Middle East is in the range of 4000-6000 T/D sulphur split in multiple trains.

The figures presented are based on the following assumptions:

Steam generation	70% thermal efficiency
Electric power generation	35% thermal efficiency

3.1 Final Sulphur Condenser Replaced by Boiler Feed Water Preheater

The Final Sulphur Condenser of the Claus plants has the scope to cool the process gas to typical 130-135°C temperature so to minimize the sulphur content in the Claus tail gas and the gas cooling is achieved generating

steam at 1.2 bar g pressure. The generated steam has no use in the factory and is condensed with waste of energy.

As an alternative to the low low pressure steam generation, it is possible to preheat the boiler feed water, which is necessary for the overall steam generation in the plant, generally available at 110°C temperature.

Due to the risk of the sulphur solidification in the tail gas at temperature below 119°C, the boiler feed water temperature to the preheater must be increased to 125°C.

With this plant configuration, in addition to the higher production of high and low pressure steam and lower power requirements, there is a certain saving in the installation cost.

3.2 Conventional Hydrogenation Catalyst Replaced by Low Temperature Catalyst in the Tail Gas Treatment

The conventional hydrogenation catalyst operates at typical inlet temperature of 280°C at Start of Run up to 320°C at End of Run.

The reheating of the process gas is achieved using furnaces fired with fuel gas in Refineries or using inline burners in gas fields if hydrogen rich gas is not available.

The conventional catalyst may be replaced by low temperature catalyst, operating at inlet temperature of 230-240°C at SOR up to 255°C at EOR. The minimum operating temperature at SOR can be as low as 210°C with moderate concentration of SO₂ in the process gas. The 255°C temperature at EOR is suitable to treat gas with higher SO₂ concentration even with not fresh catalyst.

Owing to the lower temperature level to be achieved for the process gas reheating, the furnace is replaced by a shell and tube heat exchanger using the steam produced in the sulphur plant for the gas reheating with a considerable reduction of operation and installed costs. For gas fields, in addition to the saving in fuel gas consumption, there is a smaller size of the plant downstream the inline burner due to the smaller flue gas generation.

This improvement may be applied even to existing plants, being the space velocity of the Low Temperature catalyst not lower of that of the conventional catalyst.

3.3 Recycle of Sulphur Degassing Air to the Claus Burner

The liquid sulphur produced in the Claus plant contains H₂S, which must be removed to avoid health risks and hazard risks to the operators during the handling.

Many sulphur degassing processes are based on the use of stripping air in facilities erected inside or outside the sulphur storage pit. The stripping air containing H₂S is generally disposed to the incinerator for the oxidation to SO₂.

By designing sulphur degassing facilities operating under pressure it is possible to recycle the air containing H₂S to the Claus burner, where it shall be transformed in sulphur, with two alternative benefits: higher recovery efficiency or lower amine circulation in the TGT.

3.4 Optimization of Amine Circulation in the TGT

The amine system of TGT is designed for operation between SOR and EOR of the Claus catalysts. This means that the amine circulation in the TGT is oversized at SOR and during the most part of the Claus catalyst lifetime. The over sizing factor may even exceed the 30% of the circulation rate.

The circulation rate and the corresponding regeneration steam rate may be optimized in order to satisfy the sulphur recovery efficiency prescribed by the Authorities by installing an H₂S analyzer at the outlet of the H₂S

Absorber. The analyzer results are used in line or offline to optimize the amine and the steam rates to the plant, with a substantial saving in the operating cost of utilities such as steam, electric power and cooling water.

3.5 Optimization of Thermal Incinerator Operation

The incinerators of sulphur plants are designed for a typical operating temperature of 650°C, which is suitable to achieve the total oxidation of COS-CS₂-H₂S contained in TGT tail gas to SO₂ with a residual content of max 10 ppm vol H₂S.

Despite there are legislations of certain countries prescribing max 5 mg/Nm³ H₂S in the incinerator effluents or incineration operating temperatures of more than 800°C and with large O₂ excess, the total residual sulphur in the incinerator effluents allowed by USA and Canada legislations is of 300 ppm.

With such higher H₂S allowable limit the incinerator may be operated at 550-600°C, unless the tail gas contains high concentration of CO, which may not be fully oxidized at temperatures lower than 800°C.

The lower incinerator temperature, where possible and applicable, is beneficial both for utilities saving and for investment cost, even considering the larger size of the waste heat recovery system due to the lower temperature of the flue gas.

4. BENEFITS OF IMPROVEMENTS

The sulphur recovery units are net steam producers with a benefit in CO₂ emissions of -69,500 T/Y, referred to the capacity of 750 T/D sulphur.

The effect of the proposed improvements as above detailed is shown in Table 3.

Table 3: Effects of the proposed improvements

Improvement	Investment Cost Impact, %	CO ₂ Emission Reduction, T/Y
BFW Preheater	-0.4	-4300
HT Catalyst/Furnace in Refineries	-2.0	-13200
HT Catalyst/Inline Burner in Gas Fields	-3.8	-20200
Degassing Air Recycle	+0.5	-8000
Amine Circulation Rate Reduction (20%)	-	-7300
Incinerator Temperature (600°C)	-2.3	-1500
Incinerator Temperature (560°C)	-3.4	-4700

The possible CO₂ emission reduction due to the proposed improvements in Refinery ranges from min. 25000 T/Y to max 37500 T/Y, equivalent to 1.1 – 1.7% of the total CO₂ emissions of the Refinery, or 35-53% additional CO₂ credit with the further benefit of a reduction of the investment cost, which may exceed the 5% of the total plant cost.

Better results are expected in gas fields due to the different configuration of the TGT.

If similar strategies were adopted in other Refinery units, such as Catalytic Cracking, hydrotreaters and hydrocrackers and in utilities generation, it shall be possible to achieve sensible emission reduction, estimated in more than 20% of the actual emissions without the implementation of expensive carbon-capture-and-storage (CCS) technologies.

5. CONCLUSIONS

The reduction of CO₂ emissions in sulphur recovery units does not necessarily cause a negative impact on the new plant cost. Existing units may be easily retrofitted with small inexpensive modifications.

The application of appropriate energy saving strategies to all the process and utilities generation units in Refineries is a crucial tool for the abatement of the CO₂ emissions to the level which tomorrow shall be probably imposed by the legislations of many countries to fight the climate changes.

6. REFERENCES

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