

ZERO EMISSION SULPHUR RECOVERY WITH HYDROGEN PRODUCTION

Lucio Molinari

Tecnimont KT S.p.A.
Viale Fulvio Testi, 126
20092 Cinisello Balsamo (MI)
Italy

A kinetic model of the Claus reaction furnace is used to compare a traditional Claus plant with a plant capable to recover hydrogen in addition to liquid sulphur.

To recover hydrogen by partial oxidation of H_2S it is necessary to operate at high temperature with higher $\text{H}_2\text{S}/\text{SO}$ ratio. It has been found that, instead of the traditional value of 2, the best value is 4.4.

1. INTRODUCTION

The request of fuels at very low sulphur content and the increased use of crudes at high sulphur content lead Refineries to increase the capacity of hydrocarbons hydrotreating,

The hydrotreating consists mainly in the transformation of sulphur and organic nitrogen into H_2S and NH_3 by means of the hydrogenation reaction.

The hydrogen sulphide generated by the hydrotreating processes must be transformed into elemental sulphur, that is a non toxic product which may be stored and sold like raw material for other industrial processes.

Similarly, the production of natural gas coming from gas reservoirs at evenly high sulphur content has been increasing.

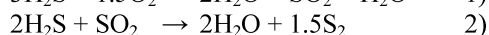
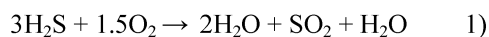
Moreover, the environmental regulations require higher sulphur recovery efficiencies by hydrotreating and desulphurization processes in order to limit the emissions.

The plants of H_2S conversion to elemental sulphur are based on the modified Claus process.

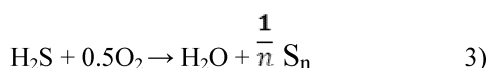
Presently, in order to increase the sulphur recovery efficiency up to 99.8-99.9%, the addition of a Reductive Tail Gas Treatment to the Claus unit is needed.

The first step of the modified Claus process is the Claus reaction furnace, where H_2S is burnt with air to form a mixture of SO_2 , H_2O and H_2S . The quantity of air to be fed is the one necessary to oxidize only one third of H_2S . The not oxidized H_2S and SO_2 produce sulphur and water up to almost equilibrium conditions.

The main reactions occurring in the Claus reaction furnace are:



while the global reaction of the whole Claus plant is:



The reaction furnace is followed by a Waste Heat Boiler and a Condenser, where the process gas is cooled and the sulphur product is condensed.

The sulphur removal and the different temperature conditions allow the progress of reaction 2) with further production of sulphur and water. This further reaction progress happens in two or three catalytic reaction stages. In the Claus reaction furnace, as well as the reactions 1) and 2), other secondary reactions occur, including the reaction of disassociation of H_2S to H_2 :



In a Claus plant fed with a normal acid gas rich in H_2S , 6- 7% of H_2S may decompose in sulphur and hydrogen. ASRL argues that the hydrogen formation does not happen according to the reaction 3) but according to the following reaction:



However, it is proved that the amount of hydrogen produced from the H_2S oxidation may be increased by changing the operating conditions of Claus reaction furnace. It is suggested to investigate the possibility of implementing the sulfur recovery with a different route from the modified Claus, mainly based on the reactions 4) or 5) instead of 1) and 2), so attempting to recover hydrogen to be recycled to the hydrotreating.

The purpose of this article is to evaluate whether, at the current state of technology, it is possible to design a feasible plant flow sheet and to evaluate the energy parameters compared to the ones of a traditional plant.

Therefore, in order to maximize the quantity of hydrogen produced, simulations of a sulphur recovery plant based on the partial oxidation process has been carried out.

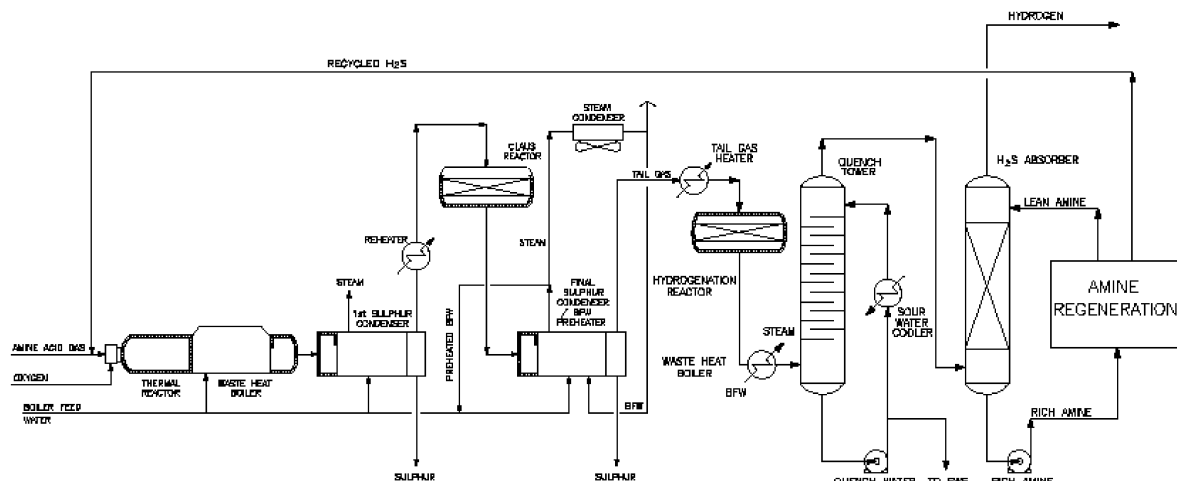
2. DESCRIPTION OF A SULPHUR PLANT WITH HYDROGEN RECOVERY

A possible plant configuration is the following.

Acid gas and oxygen are fed to a reaction furnace where the oxidation reactions take place. The reaction products are partially quenched and enter a Waste Heat Boiler for the recovery of the reaction heat. After heat recovery, the process gas enters a Sulphur Condenser for the separation of the produced sulphur and for a further heat recovery.

The completion of the reactions is obtained in one catalytic block, which consists of a process gas preheater, a catalytic reactor and a final sulphur condenser.

From the final condenser the tail gas is sent to a traditional reductive Tail Gas Treatment.



Fi

g. 1: Sulphur Plant Flow Sheet

The heat and material balance of the plant has been executed with a tool normally used for the SRU unit simulation, with the exception of the reaction furnace, which is the core of the process.

For the simulation of the reaction furnace a mathematical model developed by Politecnico of Milano has been employed. This model considers more than 100 simultaneous reactions.

This model has been successfully tested in many operating units and resulted also consistent with the laboratory results of H₂S partial oxidation carried out with an H₂S/O₂ ratio of 4.

Using this tool, the operating conditions of the reaction furnace have been optimized in order to maximize the hydrogen production.

The selected conditions are the following:

- H₂S/O₂ ratio 4.4
- Adiabatic temperature 1200°C

The feedstock has been preheated to 240°C.

Considering these operating conditions, the H₂S conversion is 56%, where

- 15.8% is converted to H₂ and S₂ according to reaction 4)
- 39.9% is converted to H₂O and S₂ according to reaction 3)
- 0.3% is converted to SO₂ and H₂O according to reaction 1)

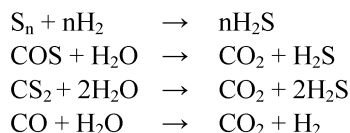
while 44% of H₂S remains unconverted.

These figures take into account the recombination of hydrogen and sulphur during the process gas cooling in the Waste Heat Boiler.

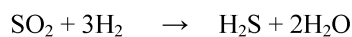
SO₂ is a big hydrogen consumer in the Hydrogenation Reactor and in order to reduce it to very low concentration, a Claus catalytic reactor has been considered downstream the Waste Heat Boiler and the Sulphur Condenser.

The tail gas, coming out from the final condenser, after preheating is fed to the Hydrogenation Reactor, where the sulphur vapors are transformed to H₂S, COS and CS₂ are hydrolyzed and CO is shifted to hydrogen.

The reactions are the following:



The remaining small concentration of SO_2 shall react as follows:



The tail gas coming from the Hydrogenation Reactor is cooled down in a Quench Tower where the water generated in the oxidation reactions is condensed.

Finally, the cool gas is washed in an Amine Absorber. From the top of the Amine Absorber a hydrogen rich stream, containing impurities such as H_2S , CO_2 and N_2 , is released.

The rich amine from the bottom of the Amine Absorber is sent to the Amine Regeneration section generating an H_2S and CO_2 stream, which is recycled to the reaction furnace.

Therefore, the sulphur lost is only the H_2S contained in the hydrogen stream leaving the Amine Absorber, so the sulphur recovery efficiency can be higher than 99.9%.

3. COMPARISON WITH A TRADITIONAL PLANT

The main differences between a hydrogen recovery plant and a traditional plant are summarized here below:

- While in a traditional plant the oxidation of H_2S is done with combustion air, in a hydrogen recovery plant it is done with oxygen. The reason of this choice is that it is necessary to reach a high temperature with high H_2S/SO_2 ratio. The high temperature pushes H_2S dissociation reaction towards hydrogen formation, while the high H_2S/SO_2 ratio reduces SO_2 formation. With air only the reaction temperature would be much lower. In addition, the H_2 rich gas produced shall be practically nitrogen free.
- Only one catalytic reactor is provided instead of two or three. Considering the low SO_2 content in the process gas generated in the reaction furnace, one catalytic reaction is sufficient to reduce the SO_2 content to low values.
- The amount of H_2S not converted is 20 times the amount of a traditional plant, therefore the amine regeneration section shall have a higher capacity and the H_2S recycled shall be much greater. The higher partial pressure of H_2S in the tail gas consents a higher amine loading and therefore the amine solution circulation shall be not more than 2.5 times the circulation of a traditional plant.
- Considering that the hydrogen is recovered, it is not necessary to install the tail gas incinerator. During start-up and shut down, the process gas hydrogen rich may be sent to the flare.

The balance shows that from a feedstock containing 100 kmol of H_2S , 30 kmol of hydrogen can be recovered, leading to a good saving in hydrogen consumption of the hydrotreating. It has to be noted that a traditional plant has instead a hydrogen consumption of about 1-2 kmol per 100 kmol of H_2S for the Tail Gas hydrogenation step.

Other differences between a traditional plant and a plant with hydrogen recovery can be noted by the comparison of the relevant heat and material balances. For this purpose the material balance of the two plant configurations has been carried out for a capacity of 100 T/D of sulphur product.

The relevant process gas flow rates in crucial parts of the plant are shown in Table 1.

Table 1: Process gas flow rates

	Traditional Plant		H ₂ Recovery Plant	
	Kg/h	Kmol/h	Kg/h	Kmol/h
Reaction Furnace	14425	481	9900	314
Final Condenser	10255	422	5729	256
Quench Tower Outlet	8087	304	3938	157
Absorber Outlet	7832	295	335	48

Table 1 shows that the process gas flow rates of the hydrogen recovery plant are lower compared to the one of the traditional plant. Therefore, equipment sizes will be smaller and less expensive.

From the heat and material balance it is possible to compare the energy balance summarized in Table 2:

Table 2: Energy consumptions and recoveries

	Traditional Plant	H ₂ Recovery Plant
	kW	kW
Heat recovered	9775	6612
Heat consumption	-2476	-5057
Electric power (1)	-881	-1568
Fuel gas	-2606	0
Hydrogen	-68	2717
Total	3316	2704

- (1) The electric power consumption has been multiplied by 2.5 to compare it with transferred heat and reaction heat. For the H₂ Recovery plant the electric power consumption figure is comprehensive of the power necessary for the oxygen production.
The efficiency considered for the electric power generation is 40%.

4. CONCLUSIONS

The plant with hydrogen recovery has at least the same sulphur recovery of a traditional plant but generating a saving in the hydrogen plant, considering that about 30% of hydrogen can be recovered as process fluid. In case the recovered hydrogen is compressed and recycled directly to the hydrotreating, without any purification, the system shall be at zero emissions.

The investment cost of the plant with hydrogen recovery is cheaper than the cost of the traditional plant, while the overall energy balance is slightly better for the traditional plant.

Considering that the proposed flow sheet is based on the use of the same equipment of the traditional Claus process, this alternative route for sulphur recovery and hydrogen production is immediately available for the implementation in industrial plants.

5. REFERENCES

- Clark P.D., Dowling N.I., Huang M., Hyne J.B., Moon D.A. and Ehlers P., 1997, High Temperature Cracking of H₂S to hydrogen in Ceramic Reactor Systems, ASRL Report for Fourth Quarter 1997.
- Clark P.D., Dowling N.I. and Huang M., 2002, A New Generation of Sulfur Recovery Processes: Sulfur and Hydrogen by Partial Catalytic Oxidation, ASRL Report for First Quarter 2002.
- Clark P.D., Dowling N.I. and Huang M., 2004, Production of H₂ from catalytic partial oxidation of H₂S in a short-contact-time reactor, *Catalysis Communications* 5 (2004), 743-747.
- Pierucci S., Ranzi E. and Molinari L., 2004, Modeling a Claus Process reaction furnace via a radicalic kinetic scheme, *Computer Aided Chemical Engineering*, 18, 463-468.
- Pierucci S., Molinari L., D'Arcangelo P., Peviani W. and Manenti F., 2005, Kinetics and Fluid-dynamic Modeling of the Claus Reaction Furnace, *Chemical Engineering Transactions*, 6(1):115-120.