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THE SUPERCLAUS PROCESS

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Presented at the

38th Annual Laurance Reid

Gas Conditioning Conference,

March 7-9, 1988

Norman, Oklahoma, USA

CONTENTS

1. ABSTRACT

The SUPERCLAUS process is a new development of the well-known Claus process and produces elemental sulphur from H_2S. The SUPERCLAUS process implies a modification of the process control system and the use of a newly developed selective oxidation catalyst in the third reactor with the object to yield 99% or 99.5% overall sulphur recovery (two versions) without any further tail gas clean-up.

The catalyst has several unique characteristics:

- Conversion of H_2S with excess oxygen into elemental sulphur for more than 90%.
- No establishment of the reverse Claus reaction

$$\frac{3}{n} S_n + 2\ H_2O \longrightarrow 2\ H_2S + SO_2$$

- High water concentrations in the process gas have hardly any influence on the conversion of H_2S into sulphur.
- Other combustibles are not oxidized.

The SUPERCLAUS process can be applied in new as well as in existing Claus plants.

SUPERCLAUS-99

In the normal Claus process a $H_2S : SO_2$ ratio of 2:1 is essential to reach optimal sulphur recovery rates.

In the SUPERCLAUS-99 process the Claus reaction is carried out with excess H_2S to realize an almost complete conversion of SO_2 after the second reactor stage.

The H_2S concentration downstream the second Claus reactor is controlled between 0.8 - 3.0 vol.%. Air is added to the tail gas which is subsequently passed over the newly developed selective oxidation catalyst for direct conversion of the remaining H_2S into elemental sulphur.

The extra investment or retrofit costs are low. The costs for retrofitting a three stage Claus plant are only 5% of the total investment costs. The extra utility costs are also low.

SUPERCLAUS-99.5

In this version the Claus reaction in the first two reactors is operated at the normal H_2S : SO_2 ratio of 2:1. The tail gas of the second reactor stage is then routed to a hydrogenation reactor for conversion of all remaining sulphur components into H_2S. Subsequently the gas from the hydrogenation reactor is passed directly over the new selective oxidation catalyst to convert the H_2S into elemental sulphur. As the newly developed catalyst is not sensitive to water, there is no need to condense the water downstream the hydrogenation reactor, which is the case in practically all Claus Tail Gas Clean-up processes.

2. INTRODUCTION

On a worldwide scale the exploitation and processing of crude oil and natural gas have increased significantly during the past thirty years. This large expansion has caused severe pollution problems, especially as a result of sulphur dioxide emissions to the atmosphere.

A general public awareness calls for regulations to limit the absolute amount of SO_2 emitted to the atmosphere and thereby the destructive consequences of acid rain. The EEC is preparing legislation that by 1992 Claus plants should have sulphur recovery rates of at least 98.5%.

In the Federal Republic of Germany strict regulations are already prevailing and require recoveries up to 99.5%. In some parts of the world where emissions lead to serious problems, requirements may even be more stringent.

When processing crude oils and sour natural gases, large quantities of H_2S gas are released. In sulphur recovery plants, or so-called Claus plants, this H_2S gas is converted into elemental sulphur. The Claus plants can be blamed for part of the SO_2 emissions, as the sulphur recovery rate is 90-98% depending on the number of reactors. During the last decade a great number of Claus Tail Gas Treating (TGT) processes have been developed to increase the total sulphur recovery efficiency. Removing the last percentages of sulphur by means of these Claus TGT processes is expensive, both in terms of capital investment cost and energy consumption.

The Dutch companies Comprimo and VEG-Gasinstituut, in co-operation with the University of Utrecht, have developed an essentially new version of the well-known Claus process, called the SUPERCLAUS process; this SUPERCLAUS process increases the sulphur recovery rate of a Claus plant to more than 99%.

Two process versions have been developed: the SUPERCLAUS-99 process and the SUPERCLAUS-99.5 process.

3. THE CLAUS PROCESS

The Claus process was developed around 1890 and was based on passing H_2S and air over a catalyst. In that period, its application was extremely difficult due to the technical problem of handling the large amount of heat generated by the process. In 1938 this problem was basically solved by I.G. Farben by the introduction of a thermal stage in which the reaction heat is used to generate steam.

Nowadays a Claus plant consists of a thermal stage followed by two or three catalytic reactor stages. In the thermal stage, which consists of an H_2S burner with combustion chamber and waste heat boiler, one-third of the H_2S gas is combusted at a temperature of about 1200°C to SO_2 according to the reaction

$$3\ H_2S + 1.5\ O_2 \longrightarrow 2\ H_2S + SO_2 + H_2O \qquad \text{(a)}$$

and the major part of the H_2S reacts subsequently with the SO_2 to elemental sulphur, according to the Claus reaction

$$2\ H_2S + 1\ SO_2 \rightleftharpoons 1.5\ S_2 + 2\ H_2O \qquad \text{(b)}$$

The heat generated by the reactions in the H_2S burner and by cooling the gases in the waste heat boiler is used to produce steam. The gases are cooled to about 160°C so that the formed sulphur is condensed (fig. 1) and separated as liquid sulphur. The Claus reaction is an equilibrium reaction and in the thermal stage 65 - 70% of the total H_2S is converted into sulphur (1). Thus the gases leaving the thermal stage still contain a rather large quantity of sulphur. To reach higher conversions the Claus reaction has to continue with the aid of a catalyst. The gases are passed through two or three reactor stages, each consisting of a heater, reactor and sulphur condenser.

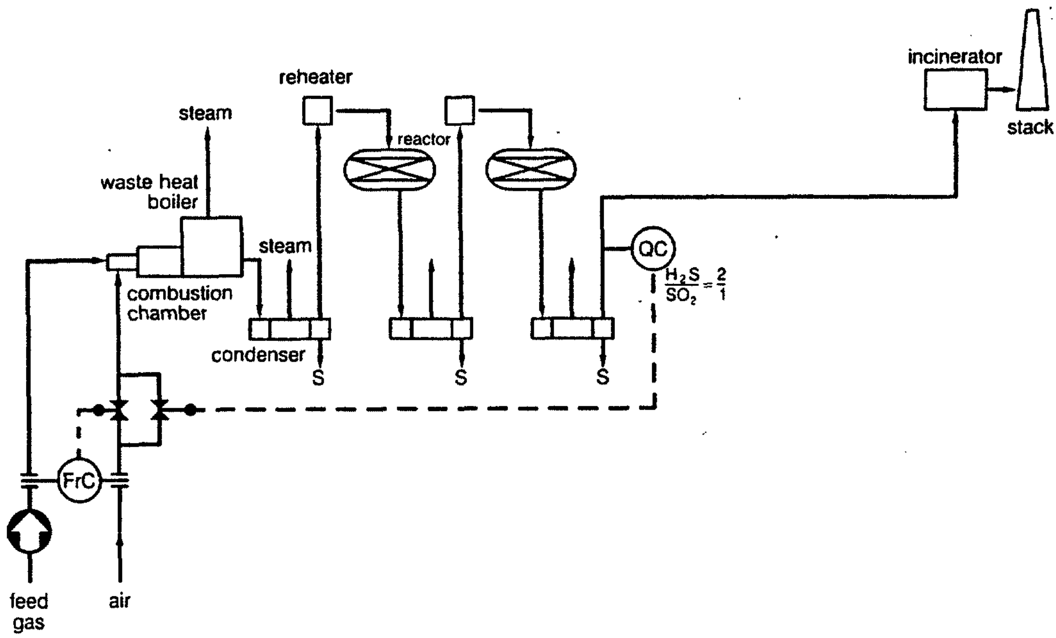

Figure 1 Claus process

The gases are heated up to about 200-250°C and as soon as equilibrium conditions have been reached, the sulphur is removed before the gases are passed to the following reactor stage.

Quite a number of different types of Claus processes have been developed during the last twenty years (2).
The principle control variable in all these Claus processes is the air to acid gas ratio. The plant efficiency or sulphur recovery is quite depending on the two components H_2S and SO_2 being in the correct ratio of 2:1 for the Claus reaction (b).
As a result the air control becomes more critical for plants to be operated with high efficiencies as is illustrated by figure 2.

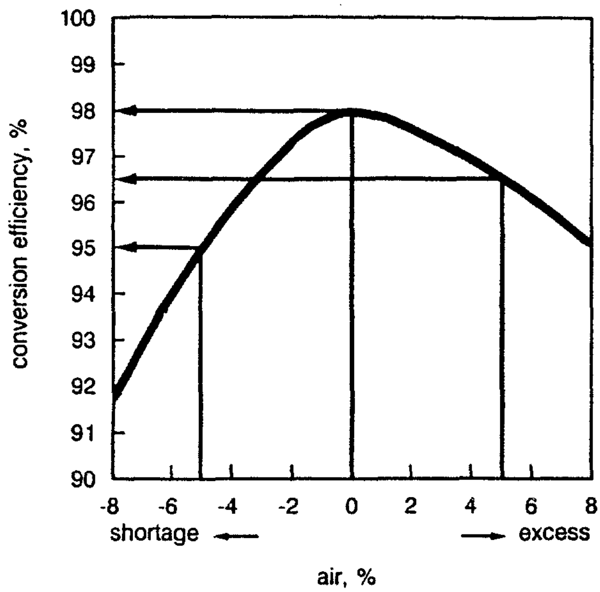

Figure 2 Conversion $H_2S + 0.5\ O_2 \rightleftharpoons S + H_2O$

Figure 2 shows that for a Claus plant with a sulphur conversion of 98% the loss in conversion efficiency due to 5% deficiency of air, is about 3% and 1½ % for 5% excess air operation.
As the plant efficiency depends on the exact H_2S : SO_2 ratio of 2:1 for the Claus reaction

$$2\ H_2S + SO_2 \rightleftharpoons \frac{3}{n} S_n + 2\ H_2O \qquad \text{(b)}$$

it is clear that, notwithstanding the fact that modern Claus plants are equipped with H_2S/SO_2 tail gas analysers to control the air demand, the process control is very sensitive.

Water is produced by the reactions (a) and (b) and the concentration in the process gas increases proportionally to the overall conversion of the H_2S. As the water cannot be removed from the Claus process gas because of practical reasons such as sulphur plugging and corrosion, the steady increasing water concentration has an opposite effect on the conversion of H_2S and SO_2 in the Claus equilibrium reaction (b).
This process water hinders the conversion to sulphur and limits the total sulphur recovery.

4. THE SUPERCLAUS PROCESS

The Claus process indeed has limitations that hinder higher conversion efficiencies.

Firstly the establishment of the Claus equilibrium

$$2\ H_2S + SO_2 \rightleftharpoons \frac{3}{n} S_n + 2\ H_2O$$

which is thermodynamically limited and secondly the increasing water content in the process gas during conversion into sulphur with the simultaneous decrease of the H_2S and SO_2 concentration. The Claus process also calls for an accurate H_2S/SO_2 ratio control in the tail gas.

The basic condition for the development of the SUPERCLAUS process was to overcome the limitations of the Claus process.

The new process should have

- a simpler and more flexible air to acid gas control
- a new catalyst for selective oxidation of H_2S directly to sulphur.

The principle of the new SUPERCLAUS process is that the well-known critical $H_2S : SO_2 = 2:1$ ratio control has been left and replaced by an operation with excess H_2S. The excess H_2S suppresses the SO_2 concentration in the Claus tail gas after the second reactor stage. The H_2S left in the tail gas is then oxidized with air to sulphur by means of a newly developed catalyst.

Although the total quantity of air for oxidation of the H_2S gas according to reaction (a) is the same, the air in the SUPERCLAUS process is divided into two parts.

The major part is introduced into the Claus burner, while the rest is charged to the third reactor filled with this new catalyst. The introduction of an additional amount of air to the third reactor will create the requested flexibility in the air to acid gas control.

The requirement for this new catalyst was that H_2S should be completely converted, with a high selectivity to elemental sulphur so that formation of SO_2 should be very small even in the presence of excess air. Moreover, the catalyst should not be sensitive to high water concentrations present in the process gas. In other words, this catalyst should have no Claus reaction activity, so that the reverse Claus reaction

$$\frac{3}{n} S_n + 2\ H_2O \rightleftharpoons 2\ H_2S + SO_2$$

would not take place.

Other requirements were no $CO/H_2/CH_4$ oxidation, no COS/CS_2 formation, and the catalyst should be chemically and thermally stable with sufficient mechanical strength.

5. SUPERCLAUS-99

The SUPERCLAUS-99 process consists of a thermal stage followed by three catalytic reactor stages (fig. 3).
Reactors no. 1 and no. 2 are loaded with standard Claus catalyst, while reactor no. 3 is filled with the newly developed selective oxidation catalyst. In the thermal stage the acid gas is burnt with a substoichiometric amount of air in such a way that the tail gas leaving the second reactor stage will contain 0.8 - 3 vol.% H_2S. The combustion air is controlled by both a flow ratio controller with the incoming acid gas feed and an H_2S analyser controller located downstream the second reactor stage, acting on a trim valve in the combustion air supply.

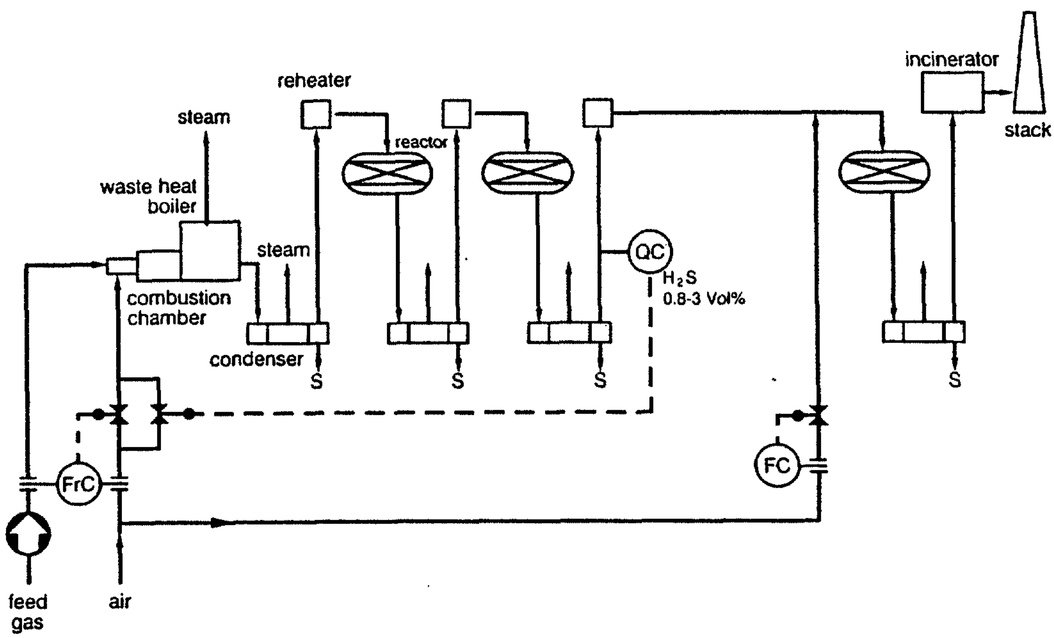

Figure 3 SUPERCLAUS-99 process

The H_2S burns according to reaction (a) with now a substoichiometric amount of air, resulting in a gas mixture in which H_2S is in excess of SO_2 for the continuation of the Claus reaction (b). The excess H_2S will practically consume all SO_2 in the process gas.

Sulphur is produced in the thermal as well as in the two catalytic Claus reactor stages and steam is generated in the waste heat boiler and sulphur condensers like in the standard Claus process.

The H_2S concentration in the tail gas leaving the second reactor stage will be controlled between 0.8 - 3 vol.%. Air is added to the tail gas for the selective oxidation of the H_2S directly to elemental sulphur. The quantity of air is set in excess of this H_2S to cover fluctuations of the H_2S concentration in the tail gas.

Sulphur is produced according to the reaction

$$H_2S + 0.5\ O_2 \longrightarrow \frac{1}{n}\ S_n + H_2O \qquad (c)$$

The third reactor stage consists of a heater, reactor and sulphur condenser. However, the normal operating conditions i.e. oxidation of H_2S with SO_2 have been replaced by oxidation of H_2S with oxygen.
Due to the operation with excess H_2S in the thermal, first and second reactor stages, the efficiency of conversion into sulphur decreases about 1-2%. However, the loss of conversion efficiency is more than compensated in the third reactor stage by the selective oxidation of the H_2S to elemental sulphur.

The new catalyst installed in this third reactor has an oxidation efficiency of H_2S to elemental sulphur of more than 90%. Because the new catalyst hardly oxidizes H_2S to SO_2 and has no Claus activity for the reverse reaction of sulphur and water to H_2S and SO_2, a total sulphur recovery rate of more than 99% can be reached (fig. 4).

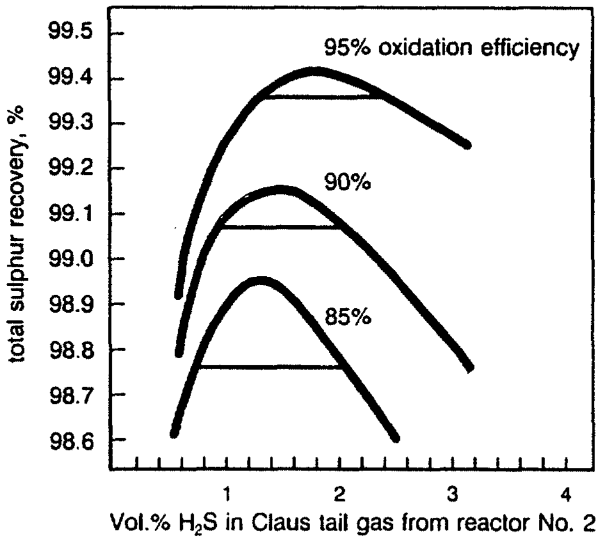

Figure 4 Total recovery SUPERCLAUS-99 process

6. <u>SUPERCLAUS-99.5</u>

If a sulphur recovery rate of more than 99.5% is required, a hydrogenation stage has to be added between reactor no. 2 and the selective oxidation reactor.
The SUPERCLAUS-99.5 process therefore consists of a thermal stage, two Claus reactors, a hydrogenation reactor and a selective H_2S oxidation reactor (fig. 5).

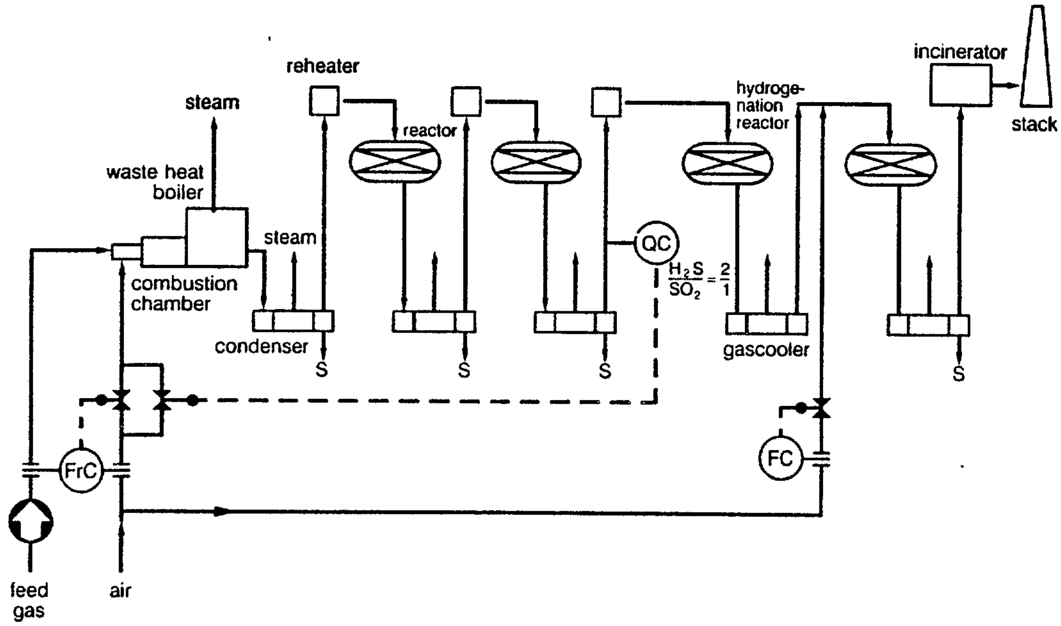

Figure 5 SUPERCLAUS-99.5 process

As the newly developed selective oxidation catalyst is not sensitive to water, there is no need to condense the water downstream the hydrogenation reactor as is the case in practically all Claus Tail Gas Clean-up processes.
The gas from the hydrogenation reactor is cooled to the optimum inlet temperature of the selective oxidation reactor.

Since all sulphur components like SO_2, COS, CS_2 and S-vapour are converted into H_2S in the hydrogenation reactor, there is no need to operate the thermal stage and reactors no. 1 and no. 2 with excess H_2S, and the normal H_2S : SO_2 ratio of 2:1 can be applied, but is less critical than for normal Claus operation.
The desired flexibility is again obtained by introducing excess air to the selective H_2S oxidation reactor.

7. THE SUPERCLAUS CATALYST

The newly developed catalyst has some unique properties compared to the conventional Claus catalyst. The catalyst consists of a carrier on which active metal oxides have been brought. With newly developed preparation techniques it is possible to cover the carrier completely with active metal oxides, resulting in the following specific properties of this catalyst:

- H_2S is completely converted with a high selectivity into sulphur, while the formation of SO_2 is very small even in the presence of an overstoichiometric amount of oxygen.
- The catalyst does not establish the Claus equilibrium reaction. This means that the equilibrium reaction of sulphur with water to H_2S and SO_2 does not occur.
- A high water concentration in the process gas has hardly any influence on the conversion of H_2S into sulphur.
- The catalyst is selective for H_2S oxidation. Other components like hydrogen, CO and other combustibles are not oxidized.

In case of misoperation when the catalyst is subjected to reducing gas conditions due to shortage of oxidation air, H_2S will react with the metal oxides of the catalyst to metal sulfides. However, with excess oxygen the catalyst can be easily regenerated.

8. INVESTMENT COSTS

The SUPERCLAUS process can be applied in new as well as in existing Claus plants.
Because of the simplicity of the process and the limited amount of equipment parts required, the extra investment costs are low.
For retrofitting an existing three stage Claus plant the extra investment costs are only 5% of the total original costs.
For a two stage Claus plant the extra costs amount to 17% of the toal original costs.

In case a sulphur recovery rate of 99.5% is required, the addition of a hydrogenation step is necessary and the extra investment costs will then be 30% of the price of a two stage Claus plant.

9. EXPERIENCE

The SUPERCLAUS catalyst was developed and tested on laboratory bench scale for more than three years. As the results were very promising, it was decided to test the SUPERCLAUS process directly in a commercial unit.

A three stage 100 t/d Claus plant in a natural gas plant in the Federal Republic of Germany has been retrofitted to SUPERCLAUS, and since 21st January 1988 the SUPERCLAUS process is being successfully in operation.
The stage has been reached that the SUPERCLAUS process is available for natural gas Claus plants.

10. REFERENCES

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