Increasing the Capacity of Claus Plants with Oxygen

Dr. H.-J. Reinhandt, Dr. M. Heisel, Höllriegelskreuth

1. Introduction and statement of the objectives

Sulfur must be removed from petroleum and natural gas because the average sulfur content of petroleum being refined is from 0.1 to 3.0% by weight, and sometimes higher. (See *Table 1.)*

Components of petroleum	**Percent by weight**
Carbon	85 - 90
Hydrogen	10 - 14
Sulfur	0.1 - 3.0; up to a maximum of 7
Nitrogen	0.1 - 0.5; up to a maximum of 2
Oxygen	0 - 15

Table 1: *Elemental composition of petroleum [!]*

These high sulfur contents cause problems in refining of the petroleum. They also damage the environment, because the main product of the sulfur is sulfur dioxide.

Sulfur is removed from the principal products of petroleum refining by treatment with hydrogen so called hydrotreating. The hydrogen sulfide is usually removed from the gas stream of the hydrotreater by scrubbing and then delivered to Claus plants, which convert the hydrogen sulfide into elementary sulfur.

It is primarily environmental legislation that determines the requirements for the extent of desulfurization. The laws vary regionally. Tables 2 and 3 show recommendations for future gasoline and diesel fuel grades in Europe. The European Parliament has recently accepted these recommendations‘ giving the southern members of the European Union additional two years.

	Units	EN 228 as of 1997	EU-Commission Year 2000	EU-Council of Ministers 2000	EU-Council of Ministers 2005
Sulfur	ppm	500	200	150	50
Benzene	Vol %	5	2	1	1
Aromatics	Vol %	-	45	42	35
Vapor pressure	kPa	70	60	60	60

Table 2: *Recommendations for future gasoline specifications [2]*

	Units	EN 228 as of 1997	EU-Commission Year 2000	EU-Council of Ministers 2000	EU-Council of Ministers 2005
Sulfur	ppm	500	350	350	50
Cetane number	49	51	51	51	
Density	kg/m^3	860	845	845	845
T95	^{0}C	370	360	360	360

Table 3: *Recommendations for future Diesel fuel specifications [2]*

It is apparent from these tables that large quantities of sulfur must be removed, and that desulfurization must extend down to 50 ppm. Therefore, desulfurization capacity will have to be increased in the medium to long term. This includes the capacity of Claus plants to convert hydrogen sulfide to sulfur.

These are the possibilities for increasing the capacity of Claus plants operating with air:

1. Enrichment of the combustion air with oxygen

2. Using industrial oxygen instead of air

In this respect, we must consider that legislation has placed significant limitations on the Claus plants themselves. These limitations refer to the conversion ratio of hydrogen sulfide and to emissions. They differ regionally and depend to some extent on the size of the plant. *Table 4* shows corresponding requirements for refineries in European countries and in the US. US requirements are considerably less stringent for Claus plants desulfurizing natural gas.

As many refineries will get by initially with capacity increases in the range of 20 – 25%**,** and the current earnings situation of the refineries requires keeping investment to a minimum, enrichment of the combustion air with up to about 280/o oxygen by volume is of great interest. This would allow capacity increases of the size stated above, depending on the hydrogen sulfide content, and would require only minimal investment.

Linde has done experimental studies in a Claus plant with oxygen contents up to about 30 vol % and with ammonia contents of up to 5 vol% in the feed gas stream.

The objectives of these studies were:

- determination of the increase of feed gas throughput as a function of the oxygen content of the combustion air and of the hydrogen sulfide concentration
- examination of the influence of ammonia on the combustion and an the composition of the gas leaving the combustion chamber
- measurement of the combustion chamber temperature with various oxygen contents in the combustion air various ammonia contents in the feed gas, and various throughputs.
- determination of the gas composition ahead of the first catalytic reactor at various oxygen contents, ammonia contents, and throughputs
- development of a simulation program for Claus plants, with special consideration of the combustion chamber.

2. Description of the plant technology

The Claus plant in which the tests were carried out *(see Figure 1)* was designed for throughputs of 900 to 2200 standand cubic meters/hour at hydrogen sulfide contents of 70% to 90 vol %.

Fig. 1: Claus plant at Leuna

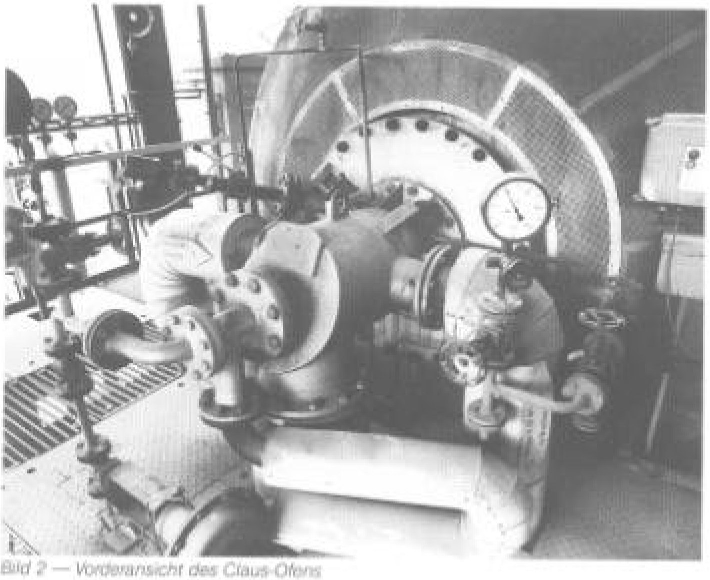


Bild 2 — Vorderansicht des Claus-Ofens

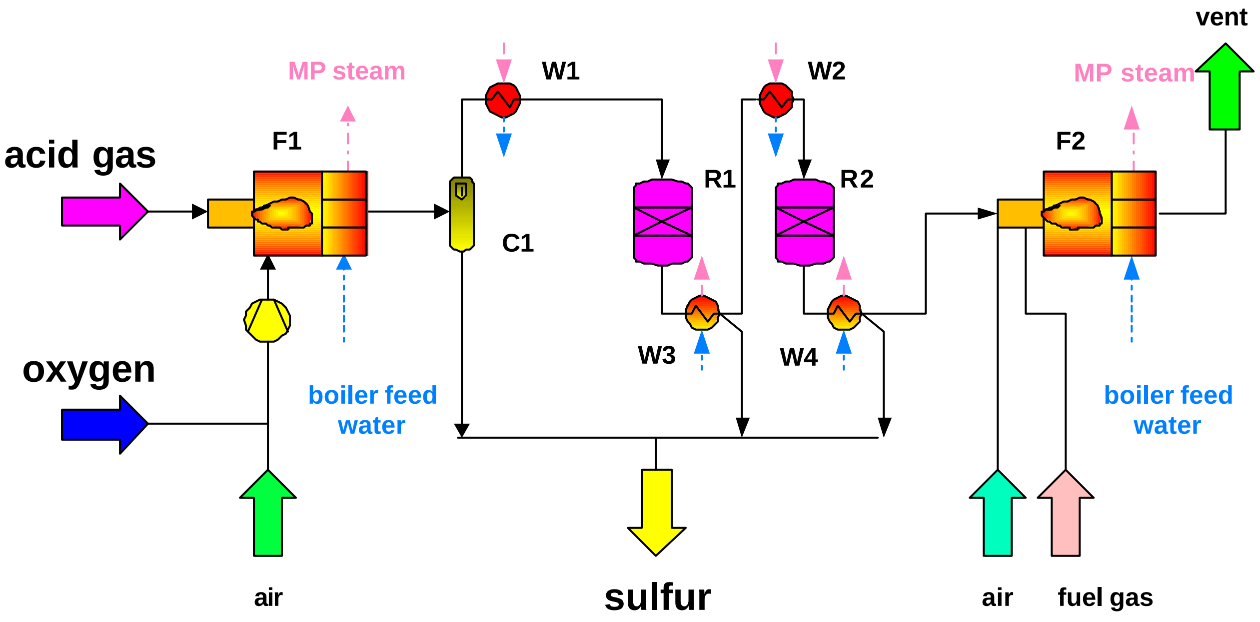
Figure 2 shows the front of the Claus furnace with the feed lines for feed gas, air, and fuel gas.

The Claus plant consists of the following process units:

1. partial combustion of hydrogen sulfide in the Claus furnace
2. conversion of hydrogen sulfide and sulfur dioxide in 3 catalytic stages
3. tailgas treatment to minimize emission of sulfur compounds (Sulfreen plant)
4. thermal-catalytic incineration of H_2S, CS_2, COS and sulfur vapor to comply with TA Luft [Air Quality Specifications].

The further discussion refers to the Claus furnace and to the 2 catalytic reactors, with main emphasis an the Claus furnace.

Figure 3 shows the basic flow chart of the Claus plant.



F1	Claus furnace with waste-heat boiler	C1	Sulfur separator
W1, W2	Preheaters	R1, R2	Catalytic reactors
W3, W4	Sulfur condensers	F2	Incinerator

Figure 3 Basic flow diagram for the Claus plant (process units 1 and 2)

The feed gas containing H_2S (sour gas) comes from refinery desulfurization. It is burned with a substoichiometric amount of air in the Claus furnace (A) at temperatures in the range of 920 to 1400^0C. The oxygen input must not exceed 1/3 of the quantity that would be required to burn the hydrogen sulfide completely.

The main reaction is**:**

$$H_2S \pm 3/2\ 02 \sim SO_2 + H_2O$$

As a result of the partial combustion, the 2:1 ratio of $H_2S:S0_2$ needed for the Claus reaction is attained. Depending on the reaction conditions, the conversion is 65% to 75% The waste heat boiler is linked directly to the Claus furnace F1. Most of the heat of the gas is transferred to water boiling under pressure. The cooling to about 370^0C results in condensation of sulfur vapor. The liquid sulfur is separated in separator C1. Heat exchanger W1 then heats the gas up to the working temperature of the catalyst in reactor R1, which is about 290°C. The sulfur is condensed and separated out in Sulfur condensor W3.

The main reaction in the catalytic reactors is**:**

$$2H_2S+SO_2 = 3/xS_0+2H_2O$$

where x indicates the number of sulfur atoms in the sulfur molecule, which depends on the temperature and can be S2, S6, or S8.

Most of the carbonyl sulfide and carbon disulfide formed in the Claus furnace is hydrolyzed in reactor R1.

The gas stream from W3 is reheated in heat exchanger W2. The temperature of the gas stream entering reactor R2 is about 200°C. The gas stream is cooled in sulfur condensor W4 and sulfur is removed. The remaining hydrogen sulfide, carbonyl sulfide, carbon disulfide and sulfur vapor are burned in the following thermal-catalytic incineration F2.

The sulfur from the separators is pumped through a sulfur collection system to a sulfur tank It must be noted that the temperature is higher than 119°C, the melting point of sulfur, at every point in the collection system.

Table 4 shows typical teed compositions during the tests.

H_2S	**H_2**	**NH_3**	**CO_2**	**N_2**	**Ar**	**Hydrocarbons**
89.5	0.32	0.34	4.6	3.3	0.28	360 vpm
70.7	1.2	0.12	23.9	2.2	0.12	150 vpm

Table 4: *Typical feed gas input compositions. (Values without units are in vol %)*

County	**Plant size**	**Sulfur recovery rate**
Germany	< 20 t/d 20 to 50 t/d > 50 t/d	Min. 97 % Min. 98 % Min. 99,5 %
Italy	<20 t/d 20 to 50 t/d > 50 t/d	95 % 96 % 97,5 %
England		98%
France		97,5%
The Netherlands	Old plants New plants	98,5% 99,8%
Spain		97%
USA	In refineries	99,9%

Table 5: *Specifications for sulfur recovery rates in* Claus *plants [3,4]*

3. Test program

The evaluation of the experiments and development of a simulation model require the following measurements and analyses:

1. Throughputs

- Feeds to the combustion chamber
  - feed gas
  - air
  - oxygen
  - ammonia
- Outlet of the combustion chamber
  - process gas

2. **Temperatures**

- Temperatures at the input streams
- Temperatures in the combustion chamber
- Temperatures downstream from the combustion chamber

3. Pressure drops

4. Concentrations

Table 6 shows the concentrations which had to be determined for the individual gas streams. The concentration of the process gas was measured upstream reactor R1

Component	**Air**	**Feed gas**	**Process gas**
Hydrogen sulfide		X	X
Hydrocarbons		*X*	*X*
Ammonia		X	X
Hydrogen		*X*	*X*
Carbon dioxide		X	X
Nitrogen	X	X	X
Argon	X	X	X
Oxygen	X		X
Sulfur dioxide			X
Sulfur trioxide			X
Sulfur			X
Carbon disulfide			X
Carbonyl sulfide			X
Nitrogen oxides			X

Table 6: Components and gas streams in which the components had to be determined

4. Experimental procedure and analysis

Oxygen and ammonia were supplied by liquid storage tanks with vaporizers and appropriate measurement and control equipment. The connection of the oxygen led to the air supply line, ammonia to the feed gas line for the Claus plant. The oxygen and ammonia concentrations were increased by steps so that the plant operation could be maintained within specified limits. The measurements were collected through the Claus plant process control system.

The combustion produces a complex gas mixture containing principally H_2S, CS_2, COS and SO_2 along with nitrogen and water. Gas sampling was done with the sampling valve shown in *Figure 4.*

Bild 4 — Probenahmeventil

After sampling, which was necessarily linked with reduction of the temperature and removal of water, gas chromatographic methods were used principally to determine the concentrations. Other methods were used in special cases, as in determining traces of NO and SO_3.

5. Experimental results

Table 6 shows a typical composition of the dry sulfur-free process gas ahead at reactor R1.

H_2S	H_2	NH_3	CO_2	CO	N_2	SO_2	SO_3	SO_3	CS_2	COS	NO
6	1	9	28vpm	12.1	16	72.3	3.1	45vpm	<500vpm	410vpm	18vpm

Table 6: *Typical composition of the dry sulfur-free process gas after the Claus furnace at an oxygen content of 27% by volume. (Figures without units are in vol %)*

Oxygen enrichment increases the combustion chamber temperature, resulting in higher reaction rates. *Figure 5* shows the correlation found for the combustion chamber temperature as a function of the oxygen content of the combustion air with hydrogen sulfide concentrations of 35, 70, and 90 vol %.

The higher combustion chamber temperature also results in a faster approach to equilibrium and higher ammonia conversion. The oxygen requirement of the combustion reaction is determined by the composition of the feed gas, and especially by its hydrogen sulfide content, and by the composition established for the process gas entering the first fixed-bed reactor ($H_2S:SO_2 = 2:1$). The nitrogen in the combustion air is not needed for the reaction.

The sulfur conversion in the tests was 77% and above. It is almost independent of the oxygen concentration.

The ammonia content in the feed gas was varied between 20 ppm and 5 vol % to obtain more information about the effect of the ammonia content an the combustion process and the composition of the process gas. Care was needed in the combustion to make sure that virtually all the ammonia was converted, because of the risk of forming ammonium sulfate and ammonium sulfide, which cause clogging and corrosion problems in the subsequent steps of the process.

There are two possibilities for reaction of ammonia:

1. Decomposition:

$$2\ NH_3 \Leftrightarrow N_2 + 3\ H_2$$

2. Combustion:

$$2\ NH_3 + 3/2\ 02 \Leftrightarrow N_2 + 3\ H_20.$$

Heat is absorbed in the endothermic decomposition, while the combustion is exothermic and releases heat. The temperature increases with the ammonia content, so combustion is the preferred reaction path. The measured temperature increases vary from 0°C to 50°C, depending on the ammonia concentration. The analytical results show that the ammonia conversion was high. The ammonia conversion also increases somewhat with increasing oxygen content.

Increasing the oxygen content results in slightly higher concentrations of sulfur trioxide, carbonyl sulfide, and nitric oxide. These changes are so slight that they have no negative effects.

The hydrogen content in the process gas was higher than in the feed gas; but the hydrogen has no negative effect on the subsequent process steps. For instance, it can be used as fuel gas in incineration.

The pressure drop in the plant is the first limitation on increasing capacity. The feed gas throughput can be increased substantially by reducing the proportion of air and adding oxygen as a replacement for the air oxygen. Figure 6 shows the potential capacity increase,

i. e., the increase in feed gas throughput, for hydrogen sulfide concentrations of 30, 50, 70 and 90 percent by volume.

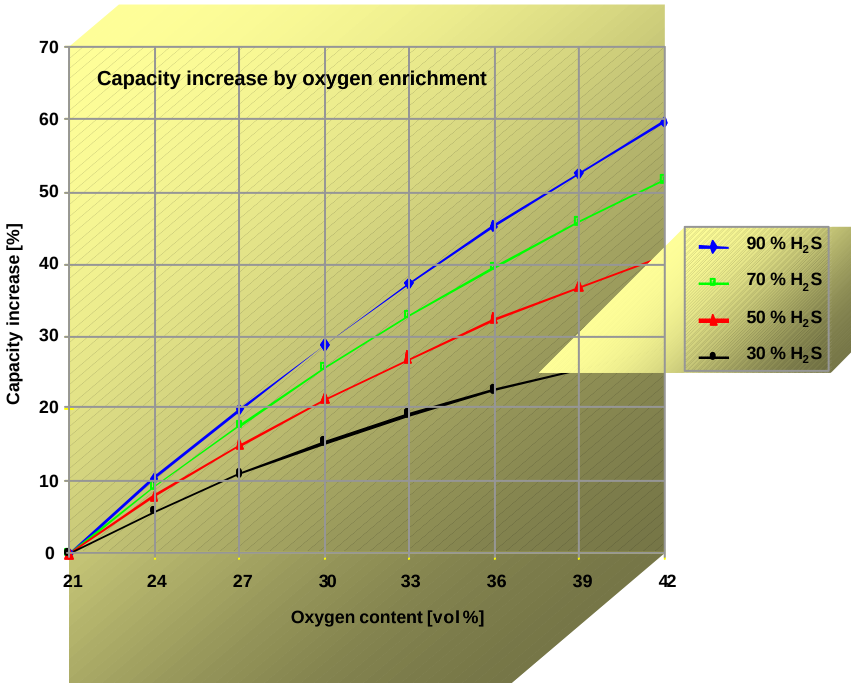


Figure 6 — Capacity increase in a Claus plant as a function of oxygen enrichment

6. Simulation

The mathematical simulation of the Claus plant was done with the Linde MultiPhase Flow Pack System. This system constructs a plant for the simulation from components which correspond approximately to unit operations. These are, for instance, heat exchangers, furnaces, and catalytic reactors. The Gibbs free energy is determined to compute the chemical equilibria. With this program system, based an a materials data base, It is possible to predict chemical conversions, temperatures, and other factors with excellent accuracy.

For the simulation of the Claus plant, the Claus furnace was computed as an equilibrium reaction on the basis of the components shown in *Figure 7.* The actual reaction temperature is lower than the computed one because of insulation losses. The losses must either be drawn from measurements in the plant, or plausibly assumed and then compared with measured values.

When the gases from the Claus furnace cool in the waste heat boiler new chemical compositions appear. However these do not correspond to the equilibrium at the outlet temperature from the waste heat boiler. Instead, the equilibrium freezes between the furnace temperature and the waste heat boiler outlet temperature. The correct compositions are found from equilibrium temperatures determined empirically in operating plants.

The downstream equipment, such as the sulfur condensers, heat exchangers, and catalytic reactors, were also simulated.

Temperatures and concentrations of the process gases were simulated well.

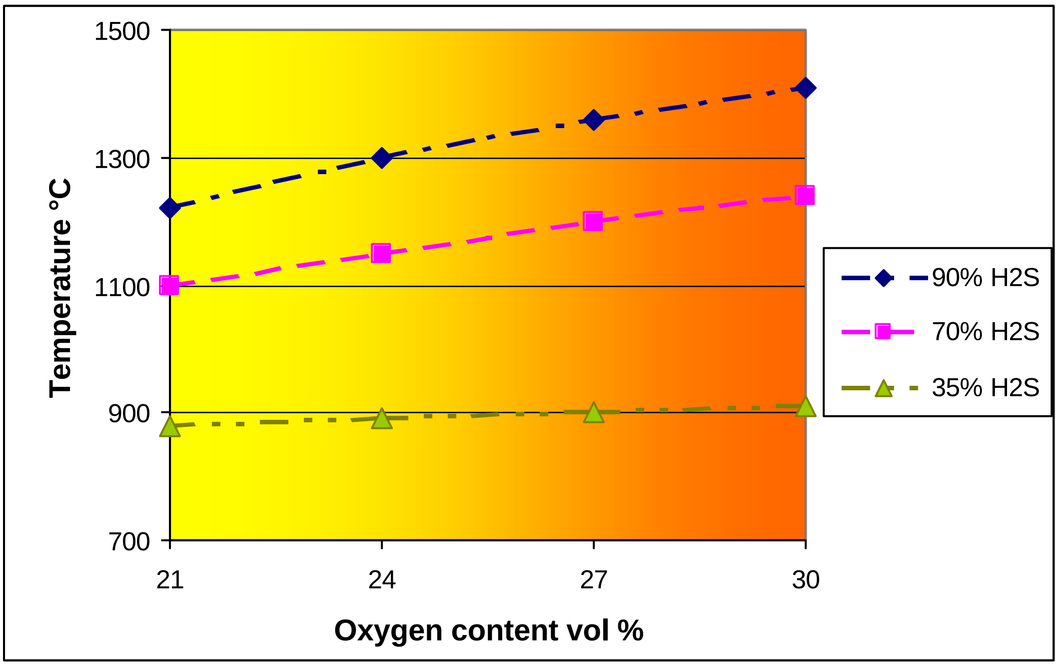


Figure 5 — *Combustion chamber temperature as a function of the oxygen content of the combustion air at different hydrogen sulfide concentrations.*

This simulation model can be used to compute Claus plants of various types. Only the specific data need to be entered. Such data are:

- Feed gas volume, composition, and inlet pressure
- Enrichment of combustion air with oxygen for the Claus furnace
- Insulation losses from the Claus furnace
- Combustion gas composition, boiler feed water pressure and temperature
- Main dimensions of the apparatus being considered.

The simulation program computes all internal gas flows in the Claus plant and all product streams, with their compositions, temperatures and pressures. One can also get a computation of the consumption figures.

7. Advantages and effects of oxygen enrichment

Combustion air enriched with oxygen is used primarily when the capacity of a Claus plant has to be increased without great investment, or if the combustion chamber temperature must be increased to born ammonia almost completely.

The advantages at oxygen enrichment are:

- increased plant capacity with very minor investment
- increased combustion chamber temperature
- increased throughput without increased pressure drop.

The higher temperature of the combustion chamber not only makes If possible to burn gas streams with high ammonia concentrations, but may also allow reduction or even omission of gas preheating. Therefore a saving of energy is also possible.
As a general rule, only the following measures are needed for oxygen enrichment up to 28%

oxygen by volume *(see Figure 8):*

- Connection of the oxygen line to the air inlet pipe
- Integration of the oxygen supply in the plant safety system
- Oxygen supply.

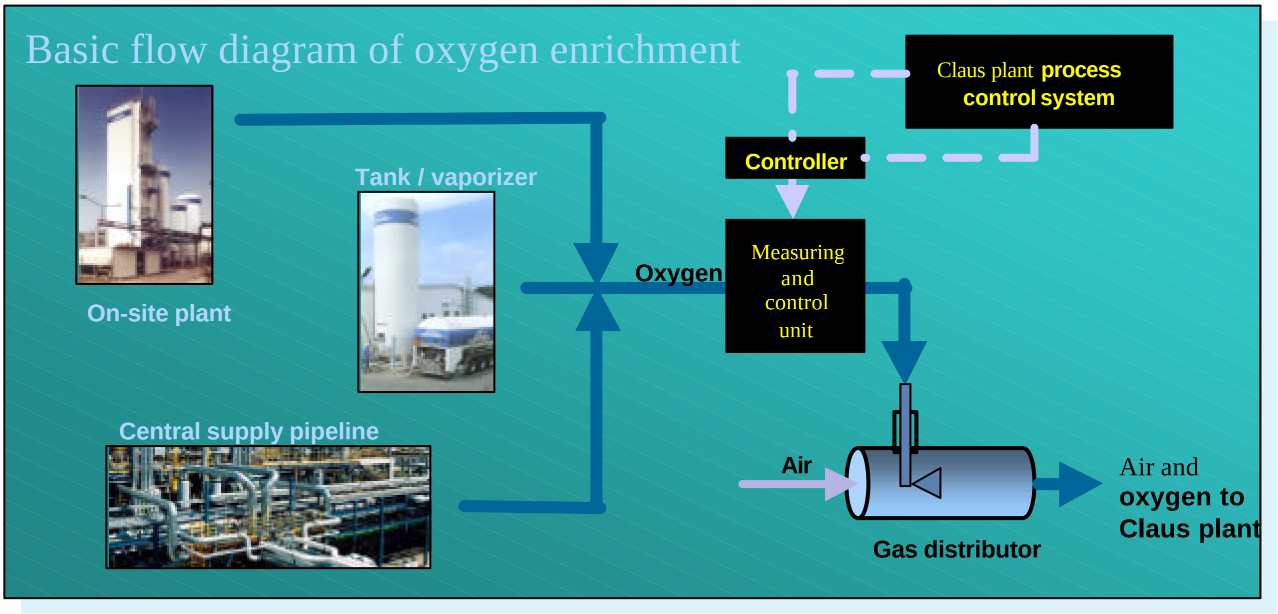
$H_2S + 0,5\ O_2 \Leftrightarrow 1/x\ S_x + H_2O$	Direct oxidation to sulfur
$2\ H_2S + 3\ 02 \Leftrightarrow 2\ SO_2 + H_20$	Combustion of the H_2S
$H_2S \Leftrightarrow H_2 + S$	Thermal decomposition of H_2S
$CH_4 + 2\ O_2 \Leftrightarrow CO_2 + 2\ H_2O$	Methane combustion
$2\ CO_2 \Leftrightarrow 2\ CO + O_2$	Dissociation of 002
$2\ CO \Leftrightarrow C + CO_2$	Boudouard reaction
$CO_2 + H_2S \Leftrightarrow COS + H_2O$	Formation of carbonyl sulfide
$CO_2 + 2\ H_2S \Leftrightarrow CS_2 + 2\ H_2O$	Formation of carbon disulfide
$4\ NH_3 + 5\ O_2 \Leftrightarrow 4\ NO + 6\ H_2O$	Direct oxidation of ammonia to nitric oxide
$2\ NO + 2\ H_2S \Leftrightarrow N_2 + 2\ H_2O + 2/x\ S_x$	Reaction of the nitric oxide
$4\ NH_3 + 3\ O_2 \Leftrightarrow 2\ N_2 + 6\ H_2O$	Direct oxidation of ammonia to nitrogen
$2\ NH_3 \Leftrightarrow N_2 + 3\ H_2$	Decomposition of ammonia

Figure 7 — Reactions in the combustion process in the Claus furnace

8. Available oxygen supply systems

There are three oxygen supply systems available *(see Figure 8):*

Fig. 8: Supply options for oxygen enrichment



1. Liquid tank with vaporizer
2. On-site plant
3. Pipeline, if there is an appropriate pipeline grid for oxygen nearby, as is the case in same refineries.

Cryogenic plants and VPSA plants can be considered as on-site plants. Selection of the supply system is determined primarily by the need for oxygen.

If the oxygen requirement fluctuates, the decision would be in favor of liquid tank supply. Tanks containing up to 64,000 m^3 and vaporizers with capacities up to 600 m^3/hour are available and for higher demands special standardized vaporizers can be provided.

For continuous use of oxygen and throughputs greater than 300 standard m^3/hour, an an-site plant would be used. A PSA plant producing oxygen purity of 90 % to 94% is adequate.

9. Summary

Use of combustion air enriched up to 30% oxygen was investigated in a large industrial Claus plant with a processing capacity of up to 2,200 standard cubic meters of raw gas per hour. Ammonia was added up to 5% by volume to assure input gas compositions typical for various refineries. The plant was operated without problems, and ammonia was almost completely converted. The following results were determined:

- increase in plant capacity
- combustion chamber temperatures
- composition of process gas downstream of the combustion chamber and sulfur separation
- effects on subsequent process steps.

A simulation model and a program were developed an the basis of the experimental data. They describe the experimental results and can be transferred to other Claus plants. So it is possible to make well-founded recommendations an operation of plants with oxygen-enriched air.

In addition, technical efforts ta be taken for oxygen enrichment were estimated, and an overview of the available oxygen supply systems is presented.

Literature

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