High sulphur recovery with ease of operation

A process performing sulphur recovery and tail gas treatment in two catalytic reactor units exceeded guaranteed recovery limits from start-up

MICHAEL HEISEL *ITS Reaktortechnik*
FRANK BELA and JORGE PENA LOPEZ *Worley Parsons*
AURELIO SAGARDI-RIVERA and MIGUEL RENDON-SAGARDI *Pemex*

There are thousands of Claus plants worldwide to convert poisonous H_2S into elemental sulphur. A typical two-stage Claus plant reaches 95% to 97% sulphur recovery efficiency. In most countries this is not sufficient to meet environmental protection requirements. Almost always a tail gas treatment has to follow downstream.

In the past, authorities mostly asked for a sulphur recovery efficiency as per local legislation, equivalent to a certain emission level for SO_2. Other emissions, notably CO_2, were of much less or even no concern. However, since the climate change debate focuses on limiting all emissions, CO_2 has become important.

Smartsulf is a relatively new process, but already well proven to minimise sulphur emissions. The only products are bright yellow premium quality sulphur and steam. It does not make by-products. Fuel consumption is limited to the obligatory incineration of the tail gas. In all these aspects it compares very favourably to other, more conventional sulphur recovery and tail gas treatment processes. In addition, the process is easy and reliable to operate. Normal operation is fully on automatic control. Only conditions out of the normal steady state, as in starting up and shutting down, need to be operated on manual control. As a co-licensor with ITS Reaktortechnik GmbH of this sub-dewpoint technology at the time the project was sanctioned, WorleyParsons developed the Basic Engineering Design Package for the SRU at the Pemex Salamanca Refinery. WorleyParsons also provided commissioning, start-up and performance test assistance to Pemex for the new Salamanca SRU under separate contract

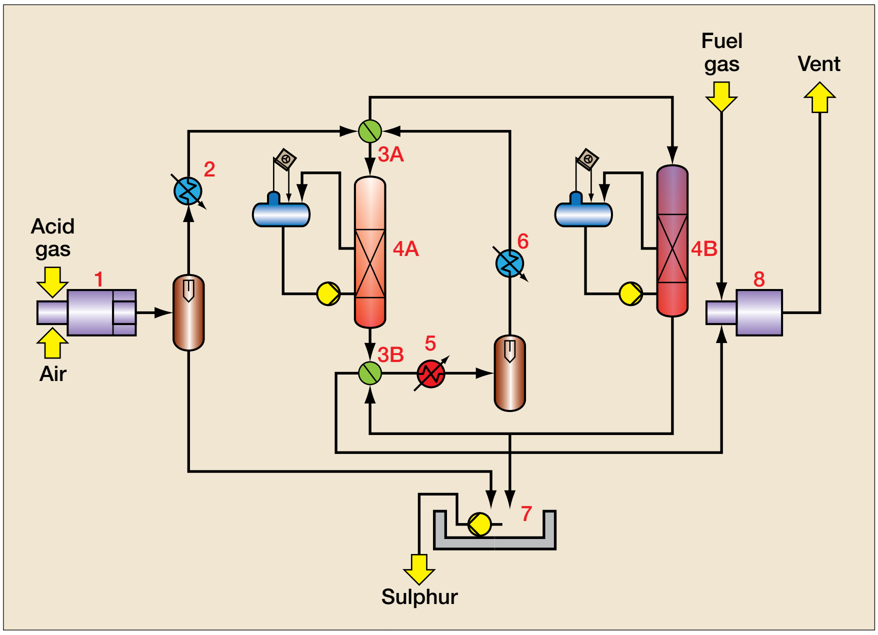

Figure 1 Process flow diagram of a two-stage Smartsulf plant

Process principles

Smartsulf is a sulphur recovery process with an improvement to the catalytic part in contrast to the conventional Claus process. A typical process flow diagram is shown in **Figure 1**.

The fundamental idea of Smartsulf is to remove the heat of the Claus reaction directly in the catalyst bed rather than in a downstream heat exchanger. This controls the temperature throughout the catalyst bed very close to the optimum for chemical equilibrium which results in a substantial increase of sulphur recovery efficiencies. The heat exchanger, applied to absorb the heat of reaction, consists of thermoplates with large clearances. The space in between the plates is filled with catalyst in order to control efficiently its temperature. This is advantageous for a number of reasons.

In the catalytic converter, several reactions take place at the same time. Maximum COS and CS_2 hydrolysis require a high temperature, while the Claus reaction needs a low temperature to achieve a favourable chemical equilibrium and thus maximum conversion and recovery of sulphur. The internally cooled Smartsulf reactor can solve this issue: the top layer of the catalyst is not equipped with thermoplates. The feed temperature to this adiabatic section can be adjusted to reach safely the required temperature for COS and CS_2 hydrolysis. The second section

Figure 2 Smartsulf plant at Pemex Salamanca refinery

downstream in the same reactor is cooled and a fixed outlet temperature is set by an external heat sink, for instance by evaporating boiler feed water. This combination of adiabatic and cooled reaction optimises conversion efficiencies.

A second identical reactor is added downstream to take advantage of the thermoplate exchanger and operate at even lower temperature, and thus optimise conditions for the Claus reaction even further. At the outlet of the second reactor, the temperature is below the sulphur dew point or even the sulphur solidification point. The elemental sulphur formed is adsorbed by the catalyst. The evenly low temperature throughout the bed causes a substantial increase in sulphur recovery efficiency up to 99.9%. For such high sulphur recovery efficiency in other processes, much more complex plant configurations are required.

Detailed process description

With reference to **Figure 1**, as in any conventional Claus plant, the feed acid gas is burned substoichiometrically in a Claus furnace and the resulting heat recovered in a waste heat boiler (1), followed by the No. 1 condenser and liquid sulphur separation. Then the process gas is sent via the No. 1 preheater (2) and a first four-way valve (3A) to the first Smartsulf reactor (4A) for continuation of the Claus reaction:

$$2\,H_2S + SO_2 \Leftrightarrow 3/x\,S_x + 2\,H_2O \qquad (1)$$

x = 2,4,6,7,8 indicates the different number of sulphur atoms per molecule

In addition, COS and CS_2 are converted in this reactor.

The outlet gas from the first reactor passes via the second four-way valve (3B) to the No. 2 sulphur condenser (5) which operates at temperatures between 135°C and 150°C and produces low pressure steam. The process gas passes through the sulphur separator. Before entering the second reactor the gas is again reheated (6). In the 2nd reactor (4B) the Claus reaction proceeds towards even more favourable equilibrium at lower temperature. The purified gas flows via the second four-way valve (3B) to an incinerator (8). From there, it is released to the atmosphere.

Switch-over procedure

During operation in the sub-dew-point mode, elemental sulphur is accumulated on the catalyst in the lower bed of the second reactor. Once the pores of the catalyst are saturated with sulphur, it has to be regenerated. Regeneration is accomplished by simply reversing the sequence of the two reactors. What was the first reactor (4A) is free of sulphur and shifts to the adsorber position. The sulphur saturated second reactor (4B) then becomes the first reactor. The sulphur in this reactor will be desorbed in the hot operation condition of the first reactor. A reactor sequence control device calculates and initiates the cyclic switch-over procedure. The sequence runs fully automatic without requiring any operator action. The cycle time is typically 24 hours between switch-overs.

Start-up experience at Pemex Salamanca refinery

The Smartsulf plant

Figure 2 shows the Smartsulf unit installed at the Pemex refinery Ing. Antonio M. Amor in Salamanca, Guanajuato, Mexico.

The equipment

A Smartsulf unit consists essentially of the same equipment as a standard Claus plant. The differences are in the catalytic reactors and the switch-over valves. The reactors contain thermoplates to control the temperature in the reactors in order to optimise reaction conditions and thus maximise conversion and recovery. A cut-out from a thermoplate is shown in **Figure 3**.

A thermoplate is essentially two metal sheets point-welded together across the surface. Between these welded metal sheets high pressure liquid is injected which opens channels through which later boiler feed water can flow as the cooling medium. A number of thermoplates is combined to form a heat exchanger which is then inserted into the reactor. The catalyst particles, which are conventional activated alumina, are poured between the thermoplates.

The thermoplates require very little volume in the reactor. The metal walls of the thermoplates are essentially flat so that filling in the catalyst is easy. Also removing spent catalyst is easy. If there are any crusts or cemented catalyst particles stuck between the metal they can easily be removed from the top of the thermoplates. Actually, the catalyst loading was almost as easy as in any conventional fixed bed. The replacement of the catalyst is planned only at the next refinery turnaround, after about five years in service. Then, the catalyst will be removed by vacuuming it out.

Other proprietary equipment in a Smartsulf unit are the four-way valves for the switch-over of the reactors.

These valves are very compact; they fit easily anywhere suitable in the plant. They are connected by a common drive shaft, so that only one actuator is required to move both valves. This also ensures that they are always actuated at the same time. If the drive fails, the valves can also be moved manually.

In the first unit using these kind of valves, they have been operated for 20 years and the only maintenance required was a change of the valve gaskets at every turnaround, after about five years.

The main advantages of these valves are:

- No dead pipes in the whole unit under all operating conditions. This avoids under-deposit sulphurous acid corrosion typically experienced when solid sulphur deposits on pipe walls
- Saving of cost and area requirement in comparison to eight on/off valves.

Figure 3 Cut-out from a thermoplate

Operation

The Smartsulf unit at Salamanca refinery was installed by the Spanish company Isolux Corsan. After mechanical completion in November 2013, pre-commissioning started in December of that year. The usual activities followed, such as dry-out of refractory in the incinerator, checking functionality of pumps, valves, instruments, and so on. The dry-out of the refractory of the Claus furnace was done earlier by the refractory supplier. When the plant was considered ready for heating up, natural gas was fed to the Claus furnace and hot off-gas started flowing through the unit, heating the equipment in the process. Note that no extra piping is required for the start-up procedure, as is required for a number of more conventional sulphur recovery processes. This saves cost and avoids corrosion in pipes which would be used only rarely under conditions of start-up and shut-down.

The cooling system of the reactors was additionally heated by injecting low pressure steam in order to speed the temperature rise. When the required temperature at the inlet was reached in the first reactor, acid gas was introduced to the furnace; then, the plant started working as a sulphur recovery unit. In March 2014 the plant was operated reliably and with no incidents, and different parameter changes were tested to observe the effects. For example, the pressure and hence the temperature in the cooling cycles of the reactors was modified to check the gasket performance up to the design pressure. The plant operated perfectly throughout this period.

It was therefore decided that the plant was ready for the guarantee run. The conditions planned were:

- Start guarantee run on 16 March. Measurements of the sulphur recovery rate and stack emissions to be done by sulphur experts
- The plant load might be up to 110% of design as the existing two Claus plants might drop below operability level if the new Smartsulf unit receives acid gas as per design
- The plant has to deal with the typical fluctuations of feed gas amount and composition if the parallel Claus plants have to be shut down.

In this way, the guarantee run started. The load was actually about 110% of design on acid gas. No sour water stripper gas was added, since only minor quantities were available. Two independent methods of calculating the sulphur recovery efficiency were applied: sulphur experts made chemical analyses of the sulphur species in the feedgas and the tail gas. They also analysed the gas out of stack. The second method used data from plant instrumentation to determine the H_2S content in the feedgas and the residual H_2S and SO_2 in the tail gas from the ADA online data. The results from both methods coincided very well. The guarantee run went on as planned for 72 consecutive hours. The maximum sulphur recovery rate measured was 99.7%, the average was 99.5% (using the ADA data) and 99.4% according to analyses. The required guarantee value was 99.2%; at the first attempt, the guarantee run was successful.

Note that the temperature at the outlet of the sub-dew-point reactor was kept at 125°C, relatively high. Lowering the temperature would have further increased the sulphur recovery efficiency. However, since the recovery efficiency was already safely above guarantee, lowering the temperature was not necessary. Comments from the operators were that “the plant was kind of boring to operate”, as it functioned absolutely automatically. This is especially true for the complete switch-over procedure which is triggered automatically and also executed without any operator action. In consequence, the plant fulfilled completely the demands required by Mexican environmental standards and by the authorities.

The Salamanca refinery is very close to populated areas of the city. Therefore it was a welcome effect that immediately after the start-up of the Smartsulf unit the smell of SO_2 disappeared. The new unit reduced the emissions in comparison to the old Claus plants by more than 90%.

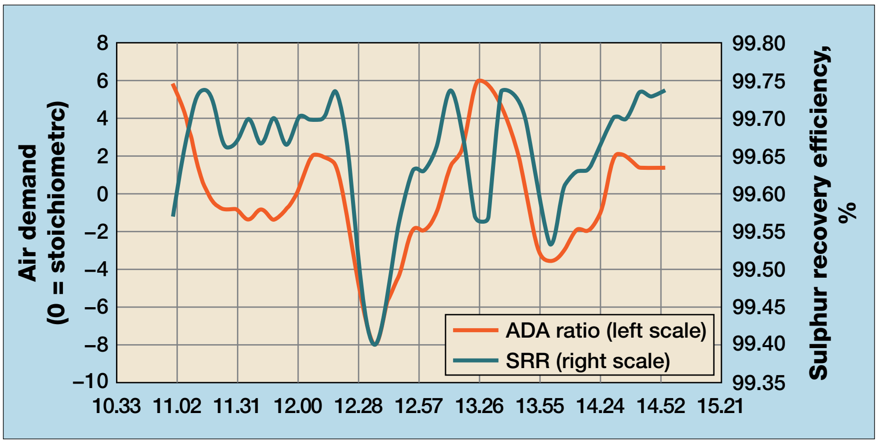

Figure 4 Air demand versus sulphur recovery efficiency

Figure 4 shows jointly the sulphur recovery efficiency and the air demand. An air demand of zero corresponds to stoichiometric addition of air to the unit. This entails the optimal sulphur recovery efficiency. The figure shows that air demand fluctuated around the ideal value and therefore the sulphur recovery efficiency fluctuated as well. This behaviour is normal in refineries where the feed gas flow and composition to the sulphur recovery unit vary. In the Salamanca unit, nevertheless, the sulphur recovery efficiency remained safely above the guarantee value of 99.2% and if the air demand came close to zero the sulphur recovery efficiency was close to 99.7%.

Smartsulf in context

The conventional three-stage Claus process nowadays does not meet most environmental requirements, typically requiring secondary tail gas treatment to achieve >99% recovery.

Essentially there are three types of tail gas treatment processes:

- The direct oxidation processes convert residual H_2S in Claus tail gas by selective catalytic oxidation into elemental sulphur, for instance Superclaus
- The recycle processes convert any remaining sulphur species into either H_2S or SO_2, scrub these materials off and recycle the enriched fraction to the Claus front end. The vast majority of these recycle processes choose the H_2S route. However, recently the Cansolv process has been sold several times which scrubs off SO_2 and recycles that to the Claus front end.
- The sub-dew-point processes continue the Claus process at lower temperature which shifts the chemical equilibrium to the sulphur side.

When the operation of Smartsulf is compared to a direct oxidation tail gas treatment, it enables a higher sulphur recovery efficiency; 99.5% recovery efficiency can be guaranteed if the plant is designed accordingly, while for a direct oxidation unit typically 99.2% is the limit. In addition, normal operation of Smartsulf is completely automatic. Even fluctuations or even failure of the air demand analyser (ADA) cause no major problems. Obviously, the sulphur recovery efficiency drops if the ADA is out of operation or not functioning well. However, no risk results for the catalyst or the equipment. Once the ADA is back in operation, the plant within minutes returns to optimal sulphur recovery efficiencies. This is different for direct oxidation units where failure of the ADA may cause a substantial increase in catalyst temperature. This is detrimental to the catalyst's active component which may be damaged irreversibly. Also corrosion in downstream piping may occur due to overheating and SO_3 generation. That is especially true in the presence of traces of ammonia which have not been destroyed in the Claus furnace.

Very high recovery efficiencies can be achieved using tail gas treatment processes which recycle H_2S downstream of the Claus plant following hydrogenation over a CoMo catalyst. This step converts SO_2, sulphur vapour and other sulphur species into H_2S. These reactions are highly exothermic and therefore the catalyst becomes very hot if more than normal SO_2 is present. If the ADA is not working properly, say due to a lack of maintenance, the H_2S/SO_2 ratio deviates from the ideal value of 2. Under these conditions, the CoMo catalyst will undergo wide temperature fluctuations. Even though these catalysts are very robust, they cannot withstand this situation often or for an extended period. The result is that they lose activity or fail completely. Then, unreacted SO_2 may pass onto the scrubbing step where it damages the amine solvent. Also, sulphur vapour that is not hydrogenated may condense in the quench column leading to plugging. If this happens, costly catalyst and solvent replacements, as well as repairs become necessary. In Smartsulf, an ADA not functioning results only in lower sulphur recovery efficiency, but in no damage to catalysts or equipment.

In other types of sub-dew-point processes a failing ADA will also not damage the plants. However, they suffer typically from other difficulties. Their reactors for regeneration need to be switched into different positions in the process. This typically is done by on/off valves. As a result, the piping with a closed valve becomes cool and sulphur and salts may deposit leading to corrosion. In a Smartsulf unit, the applied four-way valves ensure piping with continuous flow of process gas at any time. Thus the risk of pipe corrosion is minimised.

In summary, the lessons learned from problems known in tail gas treatment units have been used to provide solutions avoiding those problems. The result is a process of simple set-up, high sulphur recovery efficiency that is easy and reliable to operate and requires little maintenance.

Michael P Heisel has over 35 years' experience in sulphur recovery. He founded ITS-Reaktortechnik GmbH, which was sold to Prosernat in 2014.

Frank Bela is a Process Engineer and Plant Operations Specialist, Sulphur Technology, at WorleyParsons.

Jorge Peña López is a Senior Process Engineer, Sulphur Technology, at WorleyParsons.