

1.0 Treatment of SWS off gas in the SRU 2

Introduction

Historically operators have been concerned about introducing SWS off gas into the Claus unit because of possible problems such as the potential for blockage and corrosion, the need for good control of the SWS and the increase in the SRU 2 throughput.

Modern advances in control and improved understanding of the ammonia destruction mechanisms have meant that SWS can be reliably processed in the SRU. This means that the SWS off gas can be disposed of without additional NO_x or SO_x emission and sulphur and heat can be recovered from the SWS off gas.

The existing combustion chamber can be modified if it is suitable or a new combustion chamber installed. Normally only a single furnace and burner are used.

Claus plants have followed similar flow schemes for more than 50 years and a revamped design can embody modern design features, for instance, if the furnace is replaced a modern explosion resistant design would be used.

The use of SWS off gas in the Claus unit increases the throughput of the unit, which is an advantage in this case because the operation of control systems should be improved.

This study is to define modifications to the existing SRU 2 to process the SWS off gas with the minimum of changes to the unit.

Basis of Revamp

The Claus unit at Tamoil Cremona Refinery is to be revamped to process SWS off gas with the amine acid gas. The amine acid gas flow rate is a minimum of 185 kg/h when Cremona Refinery treats Crude Oil (71% ELSHARARA, 29% ELEPHANT Wafa) with very low sulphur content (0.07% wt.) and a maximum of 860 kg/h when treating Crude Oil (100% ES SIDER) containing 0.39% wt. of sulphur.

1.1 Description of the adopted solution

Discussion.

The SRU 2 uses a hot gas reheat system with supplementary electric heating for the first reactor and a gas-gas exchanger also with supplementary electric heating for the second reactor.

For good operation of a hot gas bypass and gas-gas exchange reheat system the gas flow through the unit needs to be more than approximately 35% of the design rate.

This means that for the low flow cases considered fuel gas co-firing is needed to provide the necessary volume flow through the unit. Ideally this fuel gas should be a constant composition (natural gas is recommended), but if this is not the case then the control system should compensate for the change in air demand with the composition of the fuel gas.

There is a conventional limit of 25 dry volume % of ammonia in the total stream fed to the Claus unit. For the low flow case of 185 kg/h of acid gas with the average flow of SWS off gas (127 kg/h) this limit is reached.

Increasing the SWS off gas flow in this case may not cause problems, especially with fuel gas support, but the operation should be treated with caution as it is beyond the normal limits for good destruction of ammonia.

Process Description

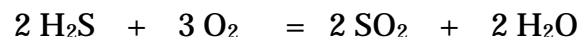
The SRU 2 downstream of the reaction furnace remains unchanged but the system upstream of the reaction furnace is modified to introduce all of the SWS off gas mixed with some of the amine acid gas (and all the combustion air) to the single main burner.

The remaining amine acid gas (50%) is bypassed to the (modified) second section of the furnace.

This operation ensures that high temperatures (above 1300°C) occur in the first section of the reaction furnace so that all the ammonia is decomposed either by thermal disassociation (to N₂ and H₂), by combustion or by reaction with SO₂ as follows:



SO₂ is formed by combustion of H₂S in this section as follows:

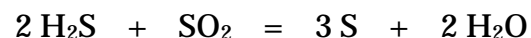


An important feature of this design of this first section is that significant H₂S (about 1/3) remains un-burnt and strongly sub-stoichiometric conditions exist.

This reducing environment suppresses the formation of NO_x and SO₃ which are easily formed if the combustion of NH₃ or H₂S approaches stoichiometric or (worse) oxidising conditions. Even traces of NO_x and SO₃ are damaging to Claus plants because of catalyst damage and corrosion.

The total air flow to the SRU 2 is controlled to achieve the correct 2:1 ratio of H₂S:SO₂ for the Claus process downstream of the waste heat boiler, but the reaction furnace is operated with two sections with different stoichiometric conditions to achieve ammonia destruction in the first section.

Amine acid gas is introduced into the second section of the furnace to re-establish the correct stoichiometry for the Claus reaction as follows (sulphur is shown as S₁)



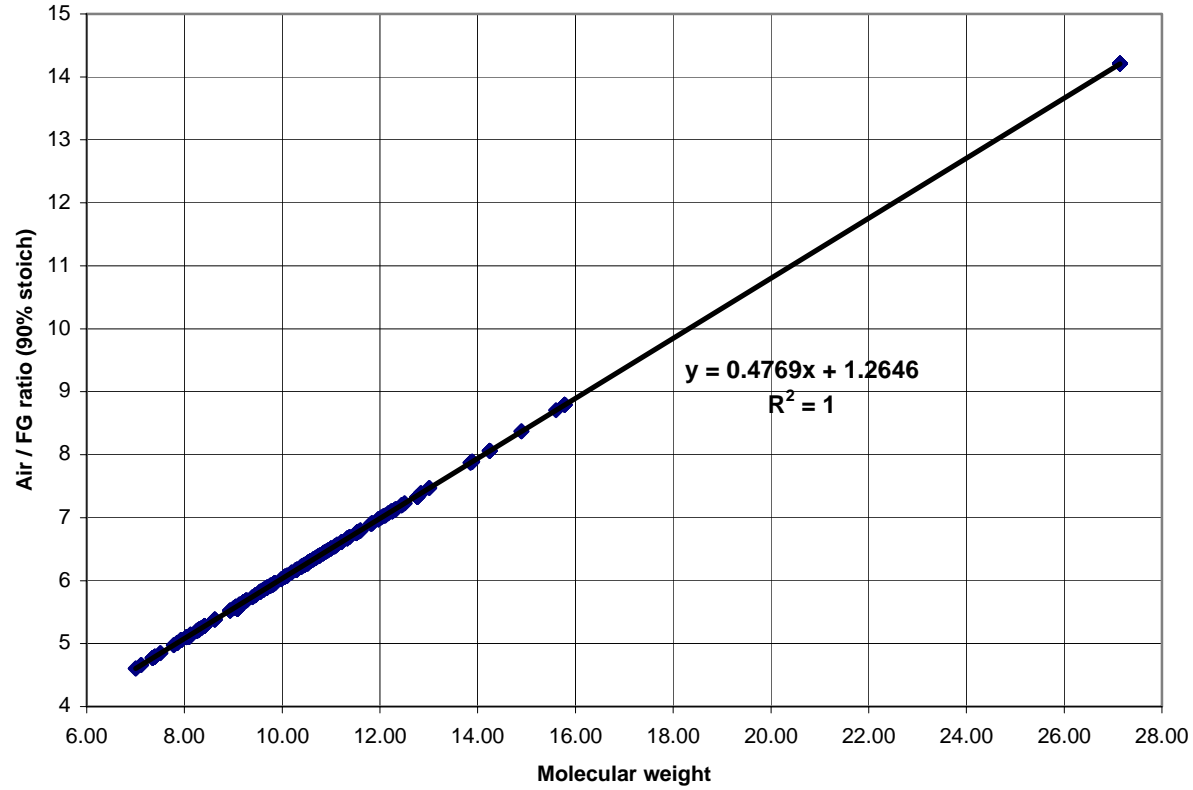
The process gases are cooled in the waste heat boiler and processed in the catalytic stages of the Claus unit as per the present operation.

Use of fuel gas

The fuel gas can change in molecular weight and the air requirement changes with the molecular weight. The fuel gas molecular weight has a linear relationship with the air demand as in the graph below. This information can be used to help compute an accurate air / FG ratio (vol.) for good control of the SRU 2 when fuel gas is being burnt.

SRU / SWS Revamp and TGTU Feasibility Study for Tamoil Raffinazione S.p.A.

Air / FG ratio vs FG MW.



SWS off gas flow measurement.

The SWS off gas forms solid deposits at temperatures below approximately 75°C and the impulse lines to flow orifices need to be heated and purged with nitrogen in order to avoid blockages.

The SWS overhead temperature should be constant. If the temperature of the SWS off gas changes then the water vapour content changes and the control system for combustion air will not be correct.

2.0 Addition of TGTU to achieve 99.5% overall sulphur recovery

An amine based HCR unit can be added to the existing SRU to increase the overall sulphur recovery efficiency to more than 99.5%. If the SRU is operating at turndown there would be pressure available for gases to flow through the tail gas unit without the need for a tail gas blower. However as the design of the TGTU will be based on the full design rate of the SRU (30 t/d) then a booster blower shall be provided.

Basis of Design

The TGTU design is based on the maximum flow of tail gas from the SRU based on the original design for the SRU of 30 t/d. The proposed design of the TGTU does not use a fired heater so it will be capable of operation at low turndown. The overall sulphur recovery of the SRU and TGTU will be at least 99.5%

2.1 Description of adopted solution

Discussion

The Tail Gas treatment Unit (TGTU) Process uses HCR type amine based technology to remove sulphur species from the SRU tail gas.

Tail Gas from the existing SRU flows via a booster blower to the Hydrogenation section of the Tail Gas Unit which converts all sulphur compounds, including sulphur vapour and entrained sulphur to hydrogen sulphide (H₂S). The H₂S is subsequently removed from the tail gas by absorption in a selective amine (MDEA) and then passed to the existing incinerator.

H₂S is recovered from the solvent in the amine regenerator and recycled to the SRU. If the refinery amine unit uses a selective amine, (either at present or at a future time when the TGTU is implemented) then considerable cost savings can be made by integrating the TGTU amine regeneration system with the refinery amine system.

As the SRU tail gas flows through the TGTU the following processes are carried out:

Hydrogenation and hydrolysis

The SRU tail gases are heated using an electric heater. If the proposed power of the electric heater does not suit the refineries needs then the power can be reduced by adding a feed – effluent exchanger to the hydrogenation reactor.

There are sufficient reducing gases (H₂ and CO) present in the tail gas because of the SRU high ratio operation (HCR) The tail gas is then fed to the hydrogenation/hydrolysis reactor. The gases pass over a Co/Mo catalyst, where almost all sulphur compounds (COS, CS₂, S_x and SO₂) react with hydrogen to form hydrogen sulphide (H₂S). The catalyst also serves to convert carbon monoxide to additional hydrogen (and carbon dioxide) by reaction with water vapour.

Water Removal

The hydrogenated hot gas leaving the Reactor is sent to the Water Removal Tower to be cooled by direct contact with water.

The treated tail gas enters the bottom of the tower after mixing with a spray of water in the pipeline, which serves to de-superheat the gas, and flows upward through a packed section where it comes in contact with the circulating cooling water. The cooled tail gas leaves the tower at about 40°C.

The circulating cooling water is filtered through the Water Removal Filter and cooled in the Water Removal Cooler.

As tail gas cools down, water vapour is condensed and is removed from the system to maintain a constant water level in the contact condenser tower. The water leaving the contact condenser is sour and is exported to the existing sour water facilities. If the present SWS cannot handle more water then a small stripper can be integrated with the contact condenser.

The pH of the circulating water is monitored and ammonia can be added to maintain the water pH at about 7 to 8. As well as reducing the potential for corrosion this also reduced the occurrence of a SO₂ breakthrough which would damage the amine in the following absorber.

Automated by-pass facilities around the amine contactor are provided to ensure that damage to the amine caused by SO₂ breakthrough can be avoided.

A hydrogen analyser on the contact condenser overhead stream determines excess H₂, which can guide the operation of the SRU.

An inline blower is used because the TGTU is designed for the maximum SRU plant design rate. At low flow rates there is sufficient pressure in the SRU tail gas to flow through the TGTU. For start-up and shutdown operations the blower can be used to recycle gas around the TGTU.

H₂S Removal

The cooled gas from the Contact Condenser enters the Absorber which removes the hydrogen sulphide from the gas stream. The gas is contacted by a counter-current flow of a 50 wt% solution of MDEA in water. The use of MDEA solution allows the removal the H₂S from the process gas without removing all the CO₂.

The lean amine passes through a lean amine filter before entering the absorber.

The MDEA H₂S rich solution leaving the bottom of the Absorber is pumped by the Rich Amine Pump to the Amine Regeneration Section.

The treated gas containing some hundreds of ppm of H₂S, leaves the top of the Absorber and is sent to the existing incinerator.

Stripping of rich amine

The rich amine from the amine absorber is preheated by exchange with lean amine through the Lean/Rich amine exchanger before entering the regenerator.

The hydrogen sulphide is removed from the rich amine solution in the Regenerator. Heat required to regenerate the rich amine is supplied by the reboiler. The steam flow rate to the amine reboiler is controlled in ratio with the amine circulation rate.

The stripped hydrogen sulphide is then recycled to the SRU.

A direct contact condenser is used in the amine regenerator to reduce pressure drop and regenerator bottom temperature as well as reduce the potential for corrosion.

The bottom of the regenerator tower is used for surge volume for the system.

The concentration of the amine is controlled by either make up steam or water blowdown to or from the regenerator.

The lean amine solvent is recycled to the absorber after being cooled through the lean-rich amine exchanger and the lean amine cooler.

An amine sump tank is used for collecting amine drains, as a make-up vessel and to hold the amine inventory during maintenance operations.

Tail gas incineration

The tail gas has to be incinerated to oxidize remaining H₂S and COS before release to atmosphere. This is carried out using the existing incinerator and stack.