

We Process Your Energy

COSWEET™: Deep COS removal from natural gas compatible with all H₂S/CO₂ specifications

**PAPER PRESENTED AT ANNUAL LAURANCE REID
GAS CONDITIONING CONFERENCE**

Oklahoma, USA, 23rd – 26th February 2014



Gauthier Perdu, Laurent Normand,
Géraldine Laborie & François Lallemand
PROSERNAT
Paris, France



Jérémy Gazarian, Jean-Marc Schweitzer,
David Chiche & Sébastien Gonnard
IFP Energies nouvelles
Rueil Malmaison, France

PROSERNAT

Mr Laurent Normand - CO₂ Capture & Amine Business Development Manager

Tel. + 33.1.47.67.19.09 Fax. + 33.1.47.67.20.07

E-mail : lnormand@prosernat.com

COSWEET™ : Deep COS removal from natural gas compatible with all H₂S/CO₂ specifications

Gauthier Perdu, Laurent Normand, Géraldine Laborie & François Lallemand
Prosernat
Paris, France

Jérémy Gazarian, Jean-Marc Schweitzer, David Chiche & Sébastien Gonnard
IFP Energies nouvelles
Rueil Malmaison, France

Abstract

Natural gases, when collected from production wells, are commonly polluted with many contaminants. Among these contaminants are sulfur compounds such as H₂S and COS and unwanted molecules like CO₂. Throughout the oil and gas treatment chain, various steps are used to separate most of the undesired compounds from the profitable part of natural gas. Amine solvents are very often used for this step, as they can be adapted to various specifications and to a wide range of feed gas compositions. However, the amine processes do not provide attractive compromises between investment and operational costs when they target tight COS specifications from gas with large amounts of COS as, for example, (i) When total CO₂ removal is required, conventional amine processes can be adapted to remove COS down to very low levels in treated gas, but this is generally achieved by increasing the solvent flowrate along with expensive absorber arrangements (ii) To achieve selective removal of H₂S, MDEA is required, but since the reaction between MDEA and COS is very slow, the MDEA is not capable of achieving deep COS removal.

IFPEN and PROSERNAT have developed the COSWEET™ process for the removal of COS from natural gases down to 1 ppmv COS or lower. COSWEET™ process is based on a combination of deacidification with an amine solution and of COS destruction on a metal based catalyst. It reaches nearly 100% COS conversion even at low temperature. The COSWEET™ reactor handles most of the COS removal independently of the amine process scheme. Coupled to the adapted solvent, it is possible to tailor the amine scheme for any specifications of acid gas removal, or for selective removal of H₂S. Reduced investment for the deacidification section and positive consequences of the quality of acid gas on the design of the sulfur recovery facilities improve the AGRU + SRU processing scheme.

This paper presents the results obtained on COS conversion, the model and simulation tool, and case studies showing the advantages of coupling COSWEET™ to amine based solvent. In particular, emphasis is made on the performance of COSWEET™ at low temperature and subsequent thermal integration, as well as on the reduced investment and operating costs compared to conventional amine processes (including formulated MDEA units and the quality of acid gas to the Sulfur Recovery) designed to reach the same COS specification. The impact on the SRU chain is therefore evaluated in the case studies.

COSWEET™ : Deep COS removal from natural gas compatible with all H₂S/CO₂ specifications

Introduction

Natural gases, when collected from production wells, are commonly polluted with many contaminants, mainly unwanted sulfur compounds and unworthy molecules like CO₂. Throughout the oil and gas treatment chain, various steps are used to separate most of the unwanted compounds from the profitable part of the natural gas. The desulfurization of natural gas is usually done in generic treatment processes and consists in removing H₂S and /or CO₂ to fulfill the requirements of export gas specifications. Alkanolamine solvents are very often used for this step as they can be adapted to severe specifications and to a wide range of feed gas compositions. When complete CO₂ removal from the gas is required, for instance to achieve LNG plant feed specification, formulated MDEA solvents are more and more used, replacing primary or secondary amines. MDEA, when it is used alone in solution in water, is a selective amine solvent: it targets deep H₂S removal, but leaves part of the CO₂ in the treated gas. This reduces the sweetening cost as some CO₂ is not separated from the feed gas, and also increases H₂S concentration in the separated acid gases to the Sulfur Recovery Units (SRU). MDEA is also used when an additional acid gas enrichment step is required for an optimized design and sulfur recovery efficiency of the SRU.

Commercial gas specifications can include other compounds besides H₂S and CO₂; e.g., specifications have been imposed for many years to also remove most of the other sulfur compounds besides H₂S from the natural gas. Of these compounds, Carbonyl Sulfide (COS) is frequently present in sour natural gases containing both H₂S and CO₂, in quantities that may reach over 200 ppmv.

When total CO₂ removal is required, circulating an increased amine solution flowrate in a taller absorber column is often sufficient to enhance COS removal by the primary or secondary amine or formulated MDEA. This does not work when selective H₂S removal is desired, as MDEA does not efficiently remove COS from the gas.

The severe COS specification in the treated gas consequently impacts the cost of gas treatment when COS removal is done with amines,

- it requires increasing the amine solution flowrate, resulting in a significant increase of the OPEX and of the CAPEX of the regeneration part, as well as the height of the amine/gas contactor, thus maximizing CO₂ removal,
- selective H₂S removal with MDEA is therefore not compatible with efficient COS removal.

IFP Energies nouvelles (IFPEN) and PROSERNAT have developed the COSWEET™ process that combines a very deep COS destruction through the complete hydrolysis of the COS on a catalytic reactor integrated with an amine unit. When integrated with a **MDEAmax** unit used for the selective removal of H₂S, the combination allows deep COS removal and CO₂ slippage from the sweetening unit. When integrated with an *energized* MDEA unit, it reduces the solvent flowrate necessary to perform both H₂S/CO₂ removal and COS removal.

This paper describes the COSWEET™ process and its development by IFPEN/PROSERNAT, and compares this technology against conventional amine processes as well as other COS hydrolysis technologies integrated with amine units. Two cases follow that focus on the implementation of the COSWEET™. First case is bulk CO₂ removal and second case is where acid gas enrichment is necessary for good operation of the SRU.

Solutions for Deep COS Removal from Natural Gases

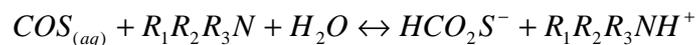
COS absorption

Alkanolamine processes are the most widely used to remove large quantities of H₂S and CO₂ from natural gases.

The basic alkanolamine processes must be modified when deep COS removal is required from gases with large amounts of COS ^[1].

When total CO₂ removal is required, conventional amine processes, using primary or secondary amines or formulated MDEA, must be adapted to remove COS down to very low levels in the treated gas. This is usually achieved by increasing the solvent flowrate along with the number of trays or packing height in the amine absorber. Some processes, such as a specific version of the **HiLoadDEA** process licensed by Prosernat ^[2] have also secured the COS transformation into H₂S and CO₂ by hydrolysis in a specific hot zone of the amine absorber. A very severe COS specification, such as 2 ppmv or lower, might however be difficult to achieve when COS is present in significant concentration in the raw feed gas.

When selective H₂S removal is desired from gases containing COS, the use of selective MDEA faces two difficulties: the reaction between MDEA and COS is very slow, and MDEA is not prone to remove COS. Reaction mechanisms of MDEA with COS are the same as for MDEA with CO₂ : there is no direct reaction between MDEA and COS, and absorption of COS is done through hydrolysis reaction catalyzed by MDEA ^{[3][4][5]} :



This reaction is much slower than the CO₂ hydrolysis reaction, which explains the poor COS removal capabilities of MDEA. When MDEA is used for selective H₂S removal, a reduced fraction of the CO₂ is separated from the feed gas but an even lower fraction of the COS is removed. A severe COS specification cannot be obtained when treating gases with fairly high COS content, even with a higher MDEA circulation rate and/or a higher number of mass transfer units in the contactor (which also would in turn increase CO₂ co-absorption). Some specific MDEA based solvent formulations have been developed which enhance COS removal while maintaining most of CO₂ slip. However, none of these formulations is capable of achieving a very tight COS specification.

In other words, it is not possible to design a selective amine unit that deeply removes COS but leaves significant amounts of CO₂ in the treated gas. Therefore, the reduction of the sweetening cost by leaving some CO₂ in the gas, as well as the improvement of the quality of acid gas (H₂S/CO₂ ratio) for a better Claus unit performance, are both unachievable with MDEA when substantial removal of COS is required. The design of such gas treatment plants will likely rely on the use of a primary or secondary amine or of formulated MDEA which will separate the COS and most or all the CO₂ from the feed gas. If CO₂ concentration in the acid gas becomes too high for good operation and performance of the Claus unit, then an acid gas enrichment unit (AGE) using a selective solvent, downstream the main amine unit is compulsory in order to increase the H₂S content of the acid gas.

Physical solvent processes, such as the Selexol[®] or the Morphysorb[®] process can selectively separate H₂S leaving some CO₂ in the treated gas, and may be used to remove mercaptans and COS. However, while deep mercaptans removal is achievable with physical solvents, deep COS removal is more difficult as COS solubility in the physical solvents is lower than that of mercaptans. Physical solvents are effective for treating high pressure gases with very high H₂S concentration, but have a poor selectivity towards hydrocarbons, absorbing most heavy hydrocarbons from the gas, and are not suitable for treating rich gases, as the separated H₂S will contain too much heavy hydrocarbons for good Sulfur Recovery Unit operation. These disadvantages of physical solvents also apply to hybrid solvents such as selective Sulfinol-M.

COS Adsorption

Molecular sieves, often used to remove mercaptans from gases, do not efficiently remove COS when CO₂ or heavy hydrocarbons are present, as COS adsorption is in competition with these components for adsorption by the molecular sieve. Therefore, deep COS removal with molecular sieves becomes extremely difficult and even impractical after a selective amine treatment when contents of CO₂ and COS remain high. Specially formulated activated alumina or silicagels have a better efficiency. It imposes a multilayer arrangement of various adsorbents in the bed, for successive adsorption of pollutants (RSH, COS) and potential co-products (H₂S formed by reaction of COS with CO₂ during mole sieve regeneration). Regardless of adsorbent bed design, regeneration of the saturated bed is done by circulating hot gas, which will pick up the adsorbed sulfur compounds and must be disposed of. One disposal option is to the Claus unit following separation of the sulfur compounds from the regeneration gas with a physical solvent unit. Sending the sulfur compounds of the adsorbent regeneration gas to the Claus unit not only increases the load to the Claus unit with components such as COS (also including the COS formed on the molecular sieve during regeneration), mercaptans, CO₂ and heavy hydrocarbons, but also create operation problems as the concentrations of all these impurities in the regeneration gas, and therefore in the acid gas sent to the Claus unit, vary during the regeneration cycle. This creates component peaks when they are desorbed from the bed, which in turn cause rapid variations in the oxygen demand at the Claus reaction furnace. This phenomenon may be smoothed by passing the solvent used for regeneration gas treatment through a large stirred buffer tank before being fed to the solvent regenerator; however, it is much preferable to remove the COS prior to entering the mole sieve unit.

COS removal in NGLs

If LPG recovery is foreseen from the treated gas, part of the COS will condense with the LPGs. Moreover, when ethane recovery is desired, a substantial part of the COS will also condense with the ethane in the LTS process. For instance, a typical split for COS from a sweetened gas containing 25 ppm vol. COS would be 10% in the NGL free gas, 30% in the ethane, and 60% in the LPG cut. The ethane may be further treated with an amine, and the LPGs as liquids with an amine or caustic soda or molecular sieves to remove the remaining sulfur compounds, including the COS. Here again, it should be noted that when an adsorbent is used to remove organic sulfur impurities, then the production of a sulfur bearing regeneration gas leads to the same drawbacks in the Claus unit.

It should also be noted that a very tight COS specification will not be obtained in the NGL free gas when high amounts of COS are present in the raw gas.

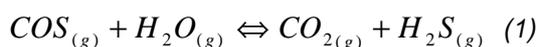
COS destruction by hydrolysis

When a very stringent COS specification must be achieved in the treated gas, upstream COS hydrolysis is probably the best option as it simplifies the design of downstream units.

COS may be hydrolyzed into H₂S and CO₂ in a catalytic reactor prior to absorption with the amine solution. However, the presence of H₂S and CO₂, which are also products of the hydrolysis reaction, in the feed gas to the hydrolysis catalyst reduces the efficiency of the COS hydrolysis. Therefore the hydrolysis reactor must be located after partial or complete removal of H₂S and CO₂. The idea of integrating the hydrolysis reactor with the amine absorber is not new, however most hydrolysis catalysts operate at quite high temperature, which reduces the attractiveness of the process. The COSWEET™ process uses a metal oxide based catalyst which provides virtually complete destruction of the COS at moderate temperature.

COSWEET™ Process Development Work

COSWEET™ is a patented catalytic process developed to deeply remove COS from natural gas. This technology is based on the COS hydrolysis reaction into CO₂ and H₂S on a metal oxide based catalyst, according to the following reaction (1):



The catalytic section is associated with a typical amine sweetening unit. This integration of the COS hydrolysis with H₂S/CO₂ absorption by the amine solution :

- allows almost complete COS destruction by hydrolysis, as the gas entering the catalytic reactor contains very little amounts of H₂S and CO₂, as those components have been partially removed in the first amine absorber. The hydrolysis catalyst is very active, and COS conversion is almost complete at moderate temperature.
- allows reaching the most severe H₂S/CO₂ specifications, as the H₂S and CO₂ produced by the hydrolysis reaction are removed from the gas by the amine solution in the subsequent absorption section.

Coupled to the adapted amine solvent, COSWEET™ enables reaching tight specification on COS (down to less than 1 ppmv COS in sweet gas) and any specification on H₂S and CO₂.

The process was developed and validated by experimental campaigns performed in IFP Energies nouvelles (IFPEN) laboratories^[6].

The specific metal oxide based catalyst was selected from catalysts available on the market. The main criterion was the ability of the catalyst to perform high COS hydrolysis rate at moderate temperature, well below 130°C. Operating the reactor at moderate temperature saves energy and heat transfer area on the exchangers used to heat the sour gas from amine absorption temperature to hydrolysis temperature and to cool the gas leaving the reactor back to amine absorption temperature. Besides catalyst activity, other characteristics were taken into account for final catalyst selection, such as mechanical resistance, pressure drop, market availability and price.

Several residence time tests have been performed to measure the kinetics of COS conversion as a function of the operating parameters: temperature, partial pressure of H₂O, COS, H₂S and CO₂. These data were used to establish a kinetic model and to build a design model of the COS hydrolysis reactor with the selected catalyst.

Moreover, tests showed that the presence of moderate quantities of H₂S and CO₂ has no sensitive impact on the kinetics of the hydrolysis reaction of COS in the tested operating range. However, as the presence of H₂S and CO₂ can decrease the conversion performances due to thermodynamic equilibrium, it is necessary to achieve a bulk acid gas removal in the first amine absorber section before entering the hydrolysis section.

The hydrolysis reaction (1) is exothermic, and therefore thermodynamically promoted by low temperatures. The equilibrium constant was fitted on equilibrium measurements performed at IFPEN laboratories.

The kinetic data were extracted from the literature and from experimental studies performed at IFPEN. The rates of the COS hydrolysis reaction were measured over a large range of temperatures. In order to qualify and quantify the internal diffusional limitations, experimental tests were carried out on the industrial catalysts particle size and on crushed catalyst.

A complete reactor model was developed. The model takes into account the hydrodynamics of the gas phase coupled with the transfer on the external laminar layer around the particles. Diffusional transport in the vicinity of the particle porosity coupled with the reaction is also described for each particle at different reactor levels.

The main assumptions considered were:

- An isothermal reactor (low conversion ≈ 100 ppmv),
- A pressure drop estimated by the relationship from Handley and Heggs^[7] and Ergun^[8],
- A down-flow fixed bed reactor,
- An external transfer resistance estimated by the relationship from Yoshida et al.^[9],
- An internal diffusional transport coupled with the reaction in the particle,
- A plug flow considering an axial dispersion for the gas phase (Gunn^[10])

The reactor model allows establishing the composition profiles of products and reactants along the reactor, but also along the particle radius at different reactor levels. It is then possible to fit the kinetic parameters from experiments carried out on the pilot reactor at various operating conditions and various particle sizes. Then, this intrinsic kinetic rate expression was implemented in the industrial reactor model for design purpose.

Figure 1 is a diagram of parity between the prediction of the COS via the reactor model and the results of experimental tests on crushed and uncrushed catalyst. This diagram shows a good prediction of the reactor model particularly for high conversions and confirms that intra particle transfer limitations are well integrated in the model, as both crushed and uncrushed catalyst performances are correctly calculated.

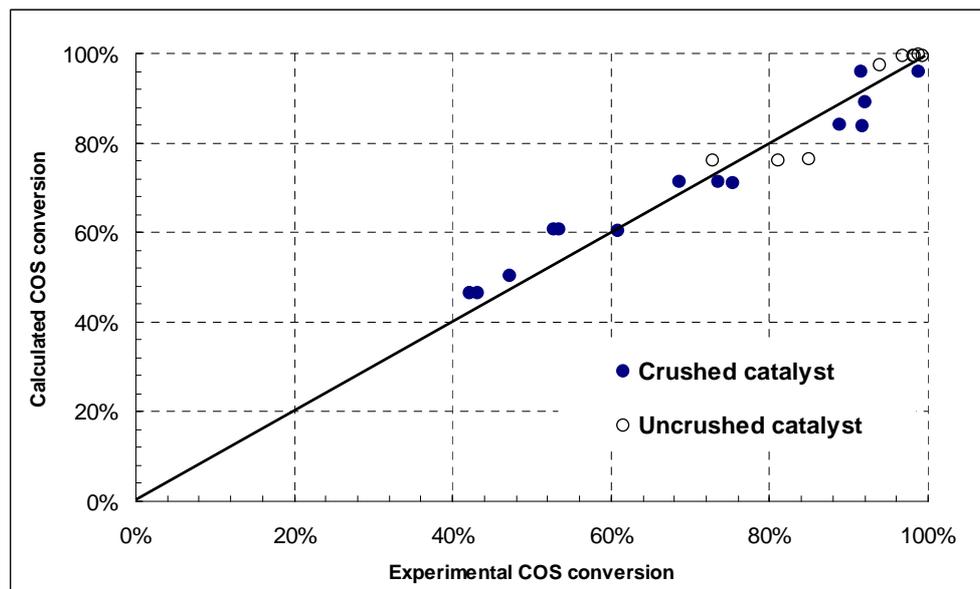


Figure 1: Comparison of reactor model and experimental results

The reactor model highlights intra-particle transfer limitations at the reactor inlet due to high COS kinetic reaction rate and high COS concentration. The pressure effect on diffusional limitations is taken into account in the reactor model through the calculation of the molecular diffusion.

From the Lab towards Industrial Implementation of the Process

Several parameters have an influence on the conversion of COS over the catalyst bed.

The thermodynamic equilibrium is promoted by:

- Low reaction temperature.
- Low H₂S and CO₂ contents in the inlet gas. Even if the thermodynamic equilibrium is favored by minimizing the residual amount of H₂S entering the catalytic reactor, it is possible to achieve a severe specification on COS (down to 1 ppmv in the sweet gas) when the pre treated gas contains up to several tens ppmv H₂S.
- Water content of the inlet gas: water is necessary to favor the thermodynamic equilibrium. As the gas leaving the amine absorption column is water saturated, the water content is already in large excess and sufficient to convert COS at the reactor operating conditions. As a consequence, there is no need to introduce any additional water with the COSWEET™ catalyst.

COS conversion in the reactor is also affected by the kinetics of the hydrolysis reaction in the catalytic bed :

- High temperature increases the kinetics of the hydrolysis reaction. The selected catalyst presents a good activity and provides a high COS conversion at reduced temperature compared to existing usual commercial hydrolysis catalysts. Operating the hydrolysis reactor at a reduced temperature allows some savings on the heating of the process gas, limiting the size of the gas heater as well as the heating energy requirement.
- Size of catalyst particles and pressure drop through the reactor. The larger the diameter of the catalyst particles, the lower the pressure drop through the bed. Larger diameter particles require a higher volume of catalyst to achieve the same COS conversion due to intra particle limitation, however, this has a limited impact on the cost of the reactor.
- It was established that a high water content in the inlet gas has no negative effect on the kinetics as there is no competitive adsorption of water on the catalyst at the process operating conditions.

The COSWEET™ reactor model allows optimizing all the above parameters, and is used to design the hydrolysis reactor and its integration with the amine absorber. The absorption section is simulated with the last version of the amine solvent in-house and proprietary software, used for the design of the AdvAmine™ gas sweetening units. This simulator includes mass transfer rate-based models for acid gas reactions with liquids which have been validated against more than 50 years experience of plant operation and consolidated by process data from running Gas Sweetening Units.

Design and operating conditions of the COSWEET™ reactor are the best compromise between catalyst size, bed pressure drop and mass of catalyst, size and duty of the process gas heater and cooler in order to provide the operator with a sustained high COS conversion at the minimum technical cost. Figure 2 illustrates the relation between the amount of catalyst, reaction temperature and COS conversion, when all other parameters, such as inlet gas composition, catalyst size and bed pressure drop, are kept fixed.

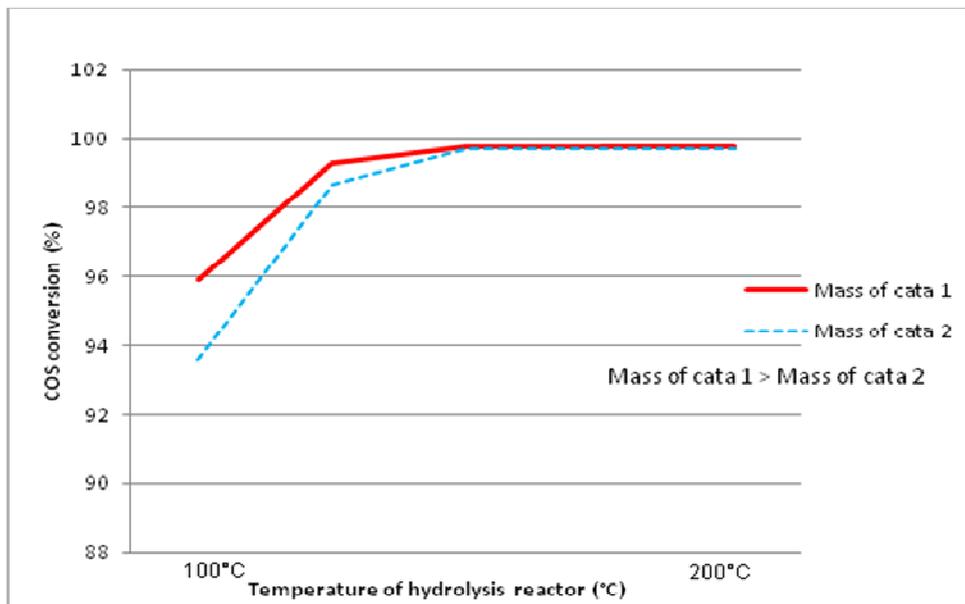


Figure 2: COS conversion rate versus bed temperature and amount of catalyst

COSWEET™ Process Description

Figure 3 presents the process scheme of a COSWEET™ unit for high pressure gas sweetening.

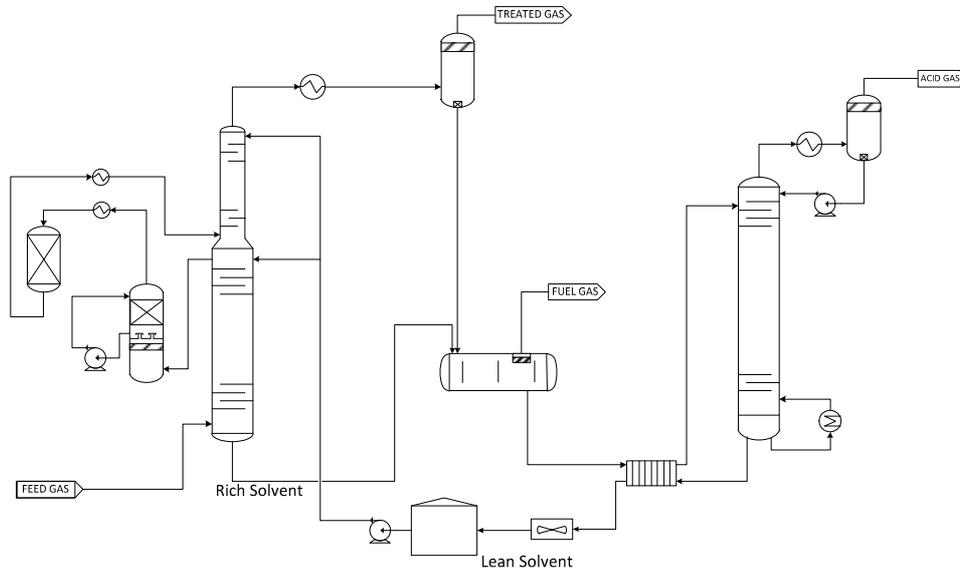


Figure 3: COSWEET™ Process principle

The majority of acid components from the sour gas is removed by the amine solvent in the absorber bulk removal section (bottom of absorber). The gas from this first bulk removal stage is water washed and then heated to the adequate temperature before entering the catalytic reactor where the COS is hydrolyzed into CO₂ and H₂S. The gas exiting the hydrolysis reactor is then cooled and introduced into the final absorption section (top of absorber) to complete H₂S and CO₂ removal down to the required treated gas specifications. Because the gas entering the second amine absorption section contains reduced quantities of acid gases, the solvent flowrate in this section can be reduced compared to that feeding the bulk removal section. A small part of the lean amine solution from the amine regenerator is therefore sent to the top polishing section of the absorber, while the bulk removal section is fed with the rest of the lean amine solution mixed with the solvent from the polishing section.

COSWEET™ does not entail any increase of the amine solution flowrate or of the duty of the amine solution regeneration section.

Due to the almost complete destruction of the COS on the catalyst, the treated gas, the acid gas, and the fuel gas flashed from the rich amine flash drum are virtually COS free.

The catalytic section is integrated with the amine unit and located after removal of the bulk of the acid gases in the first absorption section of the amine unit.

The COSWEET™ catalyst must be protected from any carry-over of amine solution which would be the result of a foaming occurrence due to an always possible upset in the upstream amine absorber. For this purpose, the partially sweetened gas leaving the first absorber column is sent to a short column in which it is washed, using make-up water to the amine unit, before entering the gas heater.

Depending on the economics, a gas/gas exchanger may be used to partially heat the process gas to hydrolysis temperature while cooling the gas exiting the reactor. This will save on the heating and cooling duties of both the gas heater and cooler.

It is worth noting that the COSWEET™ catalyst has been specifically developed to operate at a lower temperature than conventional COS hydrolysis catalysts.

Table 1 illustrates the impact of operation temperature of the hydrolysis reactor, using case study 2 data that is described later. In table 1, the COSWEET™ design is compared to that of a conventional hydrolysis section operating at 170°C for a unit with 550 Sm³/hr circulating amine solvent flow. In this

example, a COSWEET™ temperature of 100°C has been chosen for the comparison. The operating temperature of the COSWEET™ hydrolysis reactor can be optimized on a case by case basis with the corresponding size of the reactor to minimize the life cycle cost of the treatment.

		COSWEET™ hydrolysis reactor	Conventional hydrolysis reactor
Hydrolysis temperature	°C	100	170
Mass of catalyst	% of base	100	35
Gas heating/cooling			
Gas/Gas Exchanger			
Tin/out	°C	46/88	46/136
Duty	MW	11.0	21.0
Gas heater (steam heating)			
Tin/out	°C	94/100	136/170
Duty	MW	1.4	8
Gas/Gas Exchanger			
Tin/out	°C	100/52	170/80
Duty	MW	-11.0	-21.0
Gas cooler			
Tin/out	°C	52/40	80/40
Duty	MW	-2.8	-9.5

Table 1 : Impact of reduced COS hydrolysis temperature

It can be seen that a reduction of the hydrolysis reactor temperature substantially reduces the sizes of the 3 process gas exchangers, as well as the heating and cooling duties, notably reducing the heating steam consumption. With a COSWEET™ reactor operating at low temperature, the design of the gas/gas heat exchanger is also simplified. The heat duty (from LP steam) of the gas heater is reduced to a few % of that of the amine solution regenerator reboiler, compared to 15 – 20% in the case of high temperature hydrolysis. A high temperature hydrolysis reactor would also require using HP steam to heat the gas upstream the reactor, entailing additional expensive piping and interconnection of the Acid Gas Removal Unit (AGRU) to the HP steam network of the plant. On the other hand, the mass of catalyst is higher, due to the reduced kinetics of reaction at lower temperature. The life cycle cost is obviously substantially reduced in the COSWEET™ solution.

Case study 1 : Deep COS removal with bulk CO₂ removal

Case study 1 presents the COSWEET™ process for a CO₂ bulk removal application that also requires removing a few ppm COS down to very low level. The solvent used for acid gas removal is formulated MDEA. Based on selection from the AdvAmine™ series licensed by Prosernat, the solvent is effective to absorb CO₂ and some of the COS.

Component	Vol. %
CO ₂	6.80
H ₂ S	0.0002
COS	0.0005
C ₁	84.2
C ₂	6.70
C ₃	1.44
i+nC ₄	0.40
i+nC ₅	0.12
C ₆ ⁺	0.10
H ₂ O	0.24
Dry gas flowrate (MMm ³ /d @ 1atm. 15°C)	4.0
Pressure (bar g.)	93

Table 2: Feed gas composition & conditions

The feed gas composition on a wet basis and conditions are given in table 2 above.

The treated gas has to meet typical pipeline gas specifications for H₂S (< 4ppmv) and CO₂(< 2vol%), The COS specification is less than 0.5 ppm vol.

Approximately two thirds of the CO₂ present in the feed gas needs to be removed. Destruction of the COS by hydrolysis in a COSWEET™ catalytic section allows slipping the required amount of CO₂ with the treated gas, substantially reducing the size and the energy consumption of the amine section that would be designed with formulated MDEA, such as *energizedMDEA* from the AdvAmine™ series licensed by Prosernat.

The process scheme of the acid gas absorption is as described in figure 3 above, and the main sizing data are summarized in table 3 below.

		COSWEET™
Amine solvent		non proprietary formulated MDEA
Bulk removal section		
Amine solution flowrate	m ³ /hr	150
Packing height	mm	4000
COSWEET™ catalytic section		
Mass of catalyst	tons	16.3
Gas heater duty	MW	1.0
Gas cooler duty	MW	-2.9
"on-spec" section		
Amine solution flowrate	m ³ /hr	65
Packing height	mm	3000
Amine reboiler duty	MW	12.2
H ₂ S guaranteed specification	ppmv	4
CO ₂ guaranteed specification	% vol.	2
COS guaranteed specification	ppmv	0.5

Table 3: Sizing data for Case Study 1 – COSWEET™

The extra heat duty needed for the removal of COS is less than 6% of the amine solution regenerator reboiler duty. The pressure drop of the COSWEET™ hydrolysis section is less than 1 bar.

CO₂ spec is 2% vol. in treated gas. Selection of optimized formulation of AdvAmine™ *energizedMDEA* (non proprietary solvent using open market chemicals) accelerates the transfer of CO₂ into the amine solvent, allowing the use of an absorber fitted with a low number of transfer stages. However, the bulk removal of CO₂ does not allow complete removal of COS, even when the initial content is very low. The absorber operates at relatively high temperature (85-90°C) because there is constant and intensive reaction of CO₂ with amine occurring on every stage of the column. The need for heating the extracted gas prior to entering the hydrolysis reactor is minimized, and no gas/gas exchanger is necessary, reducing the overall pressure drop.

Case study 2 : Deep COS removal with selective sweetening

The COSWEET™ process main application is for the removal of COS with the use of selective gas sweetening schemes using amine solvent that must produce sufficiently H₂S rich acid gas to sulfur recovery, while achieving at the same time a severe COS specification on the sweetened gas. Case study 2 is intended to show the benefits of COSWEET™ in selective sweetening schemes that also require the deep removal of COS in the treated gas.

As shown in table 4 below, the raw sour gas contains almost equivalent H₂S and CO₂ contents together with some COS. The gas must be treated to typical pipeline gas specification, but with a very severe COS specification in export gas. The case study, based on different AGRU schemes that remove COS (COSWEET™ or *energizedMDEA*) focuses on the impact of the different AGRU design on the design of the sulfur recovery chain, considering high sulfur recovery efficiency from H₂S in acid gas.

The acid gases are sent to a Claus Sulfur Recovery Unit (SRU) followed by a selective amine Tail Gas Treatment Unit (TGTU) based on the Prosernat Sultimate™ technology. The overall sulfur recovery (in term of H₂S conversion) must be higher than 99.9%. The H₂S from the TGTU is recycled to the inlet of the Claus unit. Destruction of the aromatic hydrocarbons (BTX) must be maximized in the Claus unit reaction furnace. For this purpose, the Claus design requires a minimum furnace temperature of 1100°C in order to complete their destruction and reduce the deactivation of Claus catalyst. Acid gas feed to SRU does not contain any COS. Presence of mercaptans corresponds to their absorption within the AGRU.

If the amine unit is designed for deep COS removal, necessary to achieve the severe COS specification of the treated gas, then virtually all the CO₂ will also be removed from the gas, and the acid gas will not have the minimum H₂S concentration necessary to achieve the required overall sulfur recovery efficiency. Because of lower H₂S content, an acid gas enrichment step (AGEU) is required prior to sulfur recovery, while the COSWEET™ process with a selective amine solvent allows deep COS destruction together with selective H₂S removal. No acid gas enrichment is required with COSWEET™ to achieve high sulfur recovery efficiency, and it results in a substantial simplification of the sulfur recovery facilities.

The sulfur recovery facilities are therefore included in the economic evaluation of the different treating options. However, all subsequent treated gas processing units, such as possible mercaptans removal or NGL recovery units, are not included in the economic comparison, as they are deemed to be equivalent or similar for the different options.

Design bases

The feed gas composition on a wet basis and conditions are given in table 4 below.

Component	Vol. %
CO ₂	4.4000
H ₂ S	4.6000
N ₂	0.3948
COS	0.0025
C ₁	79.3916
C ₂	5.1586
C ₃	2.4191
iC ₄	0.4728
nC ₄	1.0025
i+nC ₅	0.2872
nC ₆	0.3202
Benzene	0.0349
nC ₇	0.0708
Toluene	0.0341
mXylene	0.0100
C ₈ +	0.0634
C ₁ SH	0.0075
C ₂ SH	0.0050
H ₂ O	0.0030
Dry gas flowrate (MMm ³ /d @ 1atm. 15°C)	12.98
Pressure (bar g.)	67.75
Temperature (°C)	25.0

Table 4: Feed gas composition & conditions

The treated gas has to meet typical pipeline gas specifications for H₂S and CO₂: less than 4 ppm vol. H₂S and less than 2.0 vol. % CO₂. The COS specification is less than 1 ppm vol. The incinerator effluent specifications impose a good destruction of all hydrocarbons and reduced sulfur compounds, and low sulfur emissions. Treated gas and incinerator effluent specifications are summarized in table 5.

			Max content
Treated Gas Specifications	H ₂ S	ppm vol.	4
	CO ₂	% vol.	2
	COS	ppm vol.	1
Incinerator Effluent Specifications	H ₂ S	(mg/Nm ³)	15
	Total reduced S (CS ₂ , COS, H ₂ S)	(mg/Nm ³)	50
	Unburnt hydrocarbons	(mg/Nm ³)	20
	SO ₂	(mg/Nm ³)	500

Table 5: Treated Gas and SRU Incinerator effluent specifications

The plant is located in a hot humid, Middle East area country with limited cooling water availability. Available utilities and ambient air conditions are indicated in table 6.

HP steam	bar g.	43
LP steam	bar g.	6
Cooling Water (limited availability)		
Temperature In/Out	°C	35 / 45
Ambient air		
Maximum temperature	°C	52
Average annual maximum temperature	°C	49
Minimum temperature	°C	0
Absolute maximum humidity	%	100

Table 6 : Ambient conditions and utilities data

Treatment schemes

In the 3 options presented below, the acid gas from AGRU is sent to sulfur recovery units. The base scheme of SRU/TGT is presented in figure 4. For all cases, it consists of a Claus unit (SRU) with a thermal stage followed by two catalytic stages and a TGTU with hydrogenation reactor, quench and amine section.

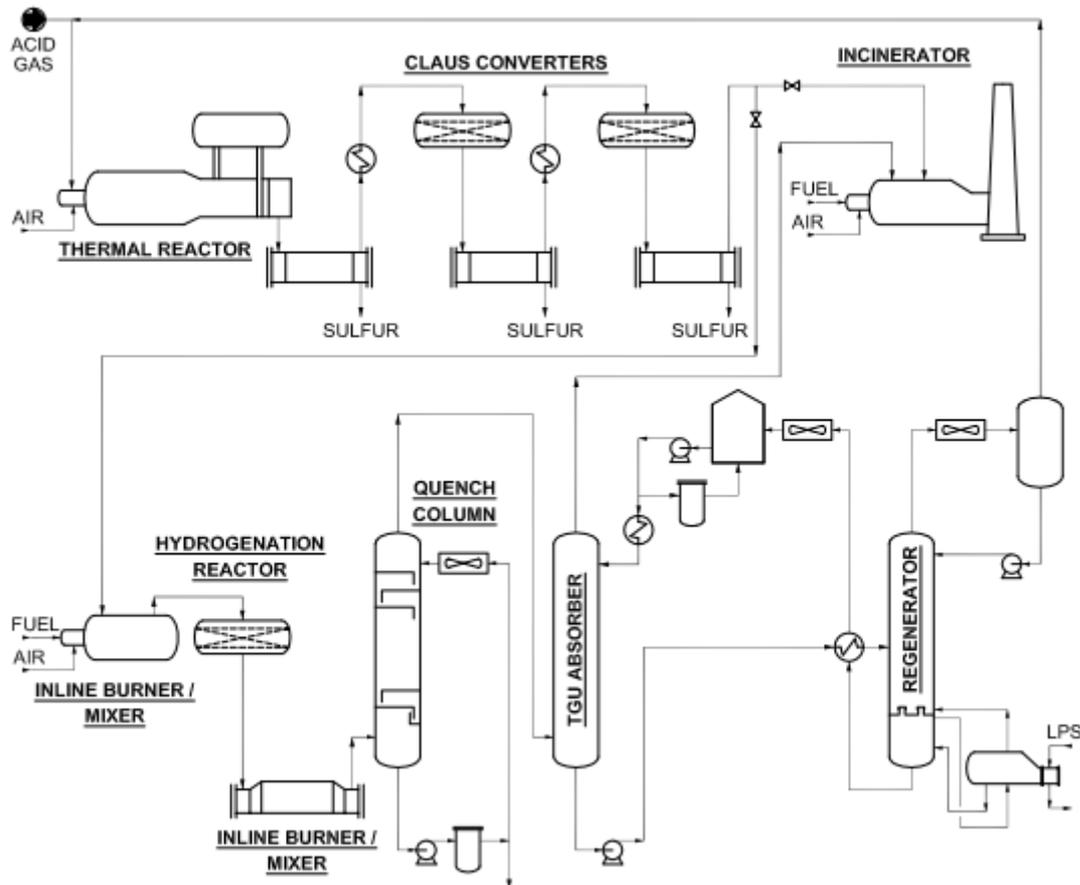


Figure 4 : Conventional SRU and TGTU

Three treatment options are considered:

- Option 1** (figure 5) : sweetening of the gas with a selective process using MDEA as solvent (e.g., MDEAmax process from the AdvAmine™ technology portfolio). Selective H₂S removal allows direct treatment of the acid gas in a conventional Claus unit. The Claus unit is followed by an MDEA based Tail Gas Treatment Unit (e.g., Sultimate™ process using generic MDEA solvent), and the recovered H₂S is recycled to the upstream Claus unit. The sulfur degassing pit exhaust gas is also routed to the inlet of the Claus unit to minimize sulfur emissions.

The feed gas to the Claus Unit (SRU) is a mixture of the acid gas from the AGRU, the recycled acid gas from the TGTU, and the off-gas from the sulfur degassing pit. Due to limited cooling water availability, the overhead of AGRU and TGTU regenerators are air cooled and the corresponding acid gases are produced water saturated at 60°C. H₂S content in the feed gas mixture to SRU is 48% (wet basis), The temperature in the Claus reaction furnace is 1100°C, allowing a good destruction of the aromatic compounds present in the feed gas, with a minimal preheating of air and acid gas.

The TGTU is designed to produce a tail gas containing less than 250 ppm vol. H₂S, which allows meeting the target of 99.9% overall sulfur recovery. The use of high efficiency catalyst in the hydrogenation section of the TGTU reduces the levels of COS and CS₂ in the tail gas. The calculations are based on end of run conditions.

However, this scheme does not meet the severe COS specification of the treated gas, as MDEA cannot efficiently remove COS. COS may be present in acid gas in those cases where it is recovered separately from gas or NGLs and rejected to SRU to limit the sulfur emissions of the plant. The destruction of COS, considering the high performance of SRU, should not be a problem. This option is presented to quantify the cost associated with the deep removal of COS with alternate technologies of AGRU's in options 2 and 3.

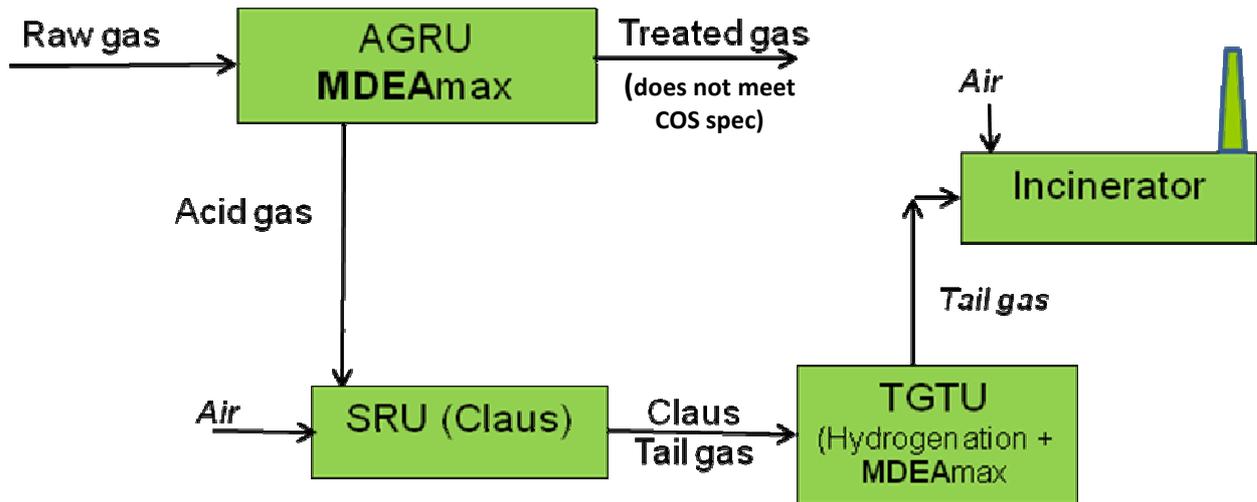


Figure 5: Option 1 - Selective MDEA / No COS removal

- **Option 2** (figure 6) : This treatment scheme achieves all requirements, and is therefore considered as the base treatment case.

Sweetening of the gas is done with formulated MDEA (e.g., *energizedMDEA* process from the AdvAmine™ technology portfolio, using non proprietary solvent). The *energizedMDEA* unit is designed to achieve the COS specification: the solvent flowrate and number of stages in the absorber are increased to enhance COS removal. This results in an almost complete co-absorption of CO₂ from the gas.

At first look, as a consequence of the increased CO₂ absorption in the AGRU, the H₂S content of the acid gas feeding the Claus unit is lower than for case 1. In case of direct feed to SRU, the mixture of the separated acid gas in the AGRU with the recycled gas from the TGTU and the sulfur degassing pit off-gas, would only contain 42% H₂S (wet basis), which does not allow achieving the required overall sulfur recovery. The BTX content of acid gas is higher than case 1, mainly because of the higher solvent flowrate needed to absorb COS (and CO₂) down to 1 ppm vol. This higher BTX content can increase Claus catalyst deactivation rate if some aromatics are not completely destroyed in the reaction furnace. An Acid Gas Enrichment Unit (AGEU), using selective MDEA (e.g., **MDEAmax** process), is installed to produce an acid gas of adequate quality to achieve the targeted sulfur recovery efficiency together with good BTX destruction in the Claus unit reaction furnace. The H₂S content in off gas to incinerator is 250 ppm vol. The TGTU and AGEU share a common amine regenerator and the reuse of the semi lean solvent from TGTU absorber to the AGEU absorber, because the TGTU absorber is lowly loaded, allows significant savings in term of solvent flow. The acid gas produced from the common regenerator is recycled back to SRU thermal chamber. The low loading of solvent from TGTU allows its full recycle to AGEU absorber for much higher H₂S loading.

Alternative solutions have been considered instead of AGEU:

- Preheating of acid gas and air does not allow reaching 1100°C in the Claus unit reaction furnace,
- Fuel gas co-firing in the Claus unit reaction furnace can achieve 1100°C in reaction furnace with a limited impact on the size of the equipment of the Claus unit. However, this process option does not provide better economics than an AGEU.

The tail gas from the TGTU contains < 250 ppm vol. H₂S, which allows meeting the target of 99.9% overall sulfur recovery. The overall sulfur recovery % takes into account the H₂S contained in the CO₂-rich stream from the AGEU, which is directly sent to the incinerator.

In this scheme, most of the BTX however bypasses the Claus unit and is sent directly to the incinerator with the CO₂-rich stream from the AGEU. A solution to limit BTX emissions to the atmosphere would be to increase incineration temperature up to 800°C. In that case it is possible to produce more HP steam from incinerator effluent. Mercaptans also bypass the SRU thermal chamber and escape destruction. Considering sulfur emission specs and mercaptans content in the acid gas, it is not an issue for the case.

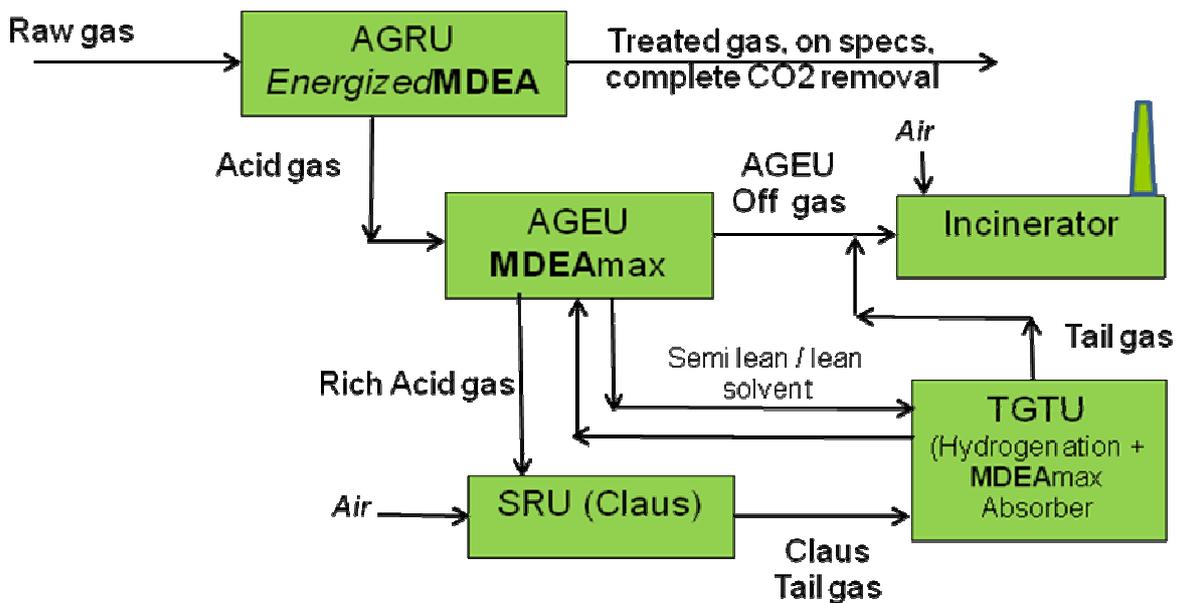


Figure 6: Option 2 - energized MDEA and AGEU

- **Option 3** (figure 7) : Sweetening of the gas is done with a COSWEET™ process combined with the use of MDEA as amine solvent. This process achieves the severe COS specification and provides a sufficient CO₂ slippage with the treated gas to eliminate the need for an AGEU prior to sulfur recovery. The sulfur recovery and tail gas treatment units are the same as in option 1, as the acid gas composition is very close to that of option 1.

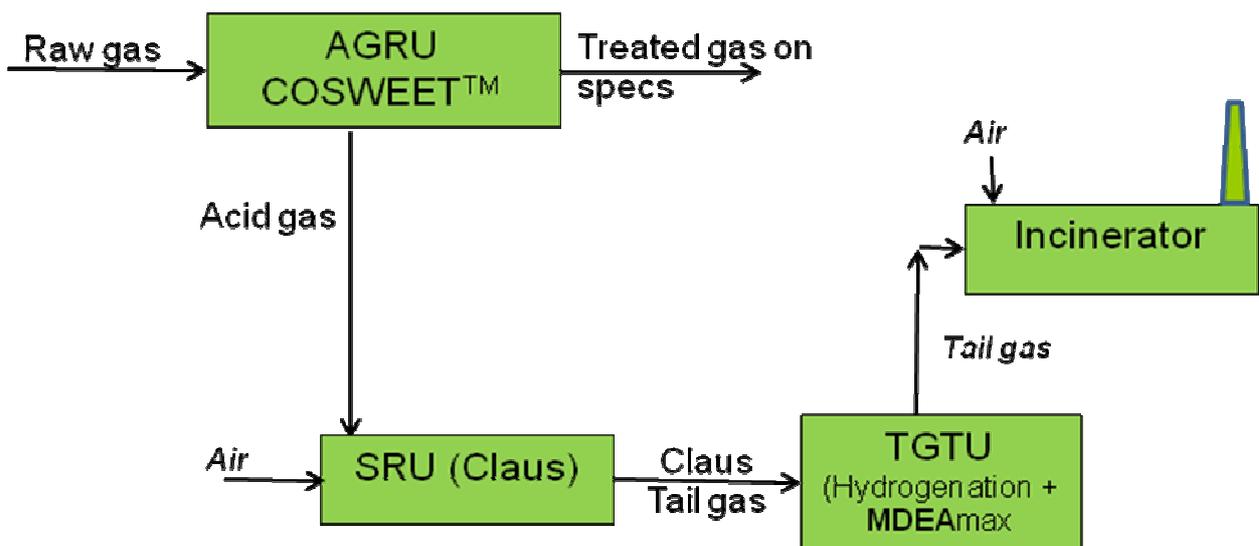


Figure 7: Option 3 - COSWEET™ / MDEA

Figure 8 details the flow scheme of the COSWEET™ section integrated to the AGRU. Due to the pressure drop through the hydrolysis reactor and gas heater / cooler, it has been found more practical to install two separated absorption columns, rather than a single absorber with two sections. Bulk acid gas removal is done in the first absorber section of the AGRU, which includes a water section on top to protect the COSWEET™ reactor from any amine carry-over. The partially sweetened gas is heated to hydrolysis temperature by heat exchange with the gas exiting the COSWEET™ reactor followed by a steam heater, The gas then enters the hydrolysis reactor, and is subsequently cooled in the gas/gas exchanger followed by an air cooler, prior to entering the second absorption section.

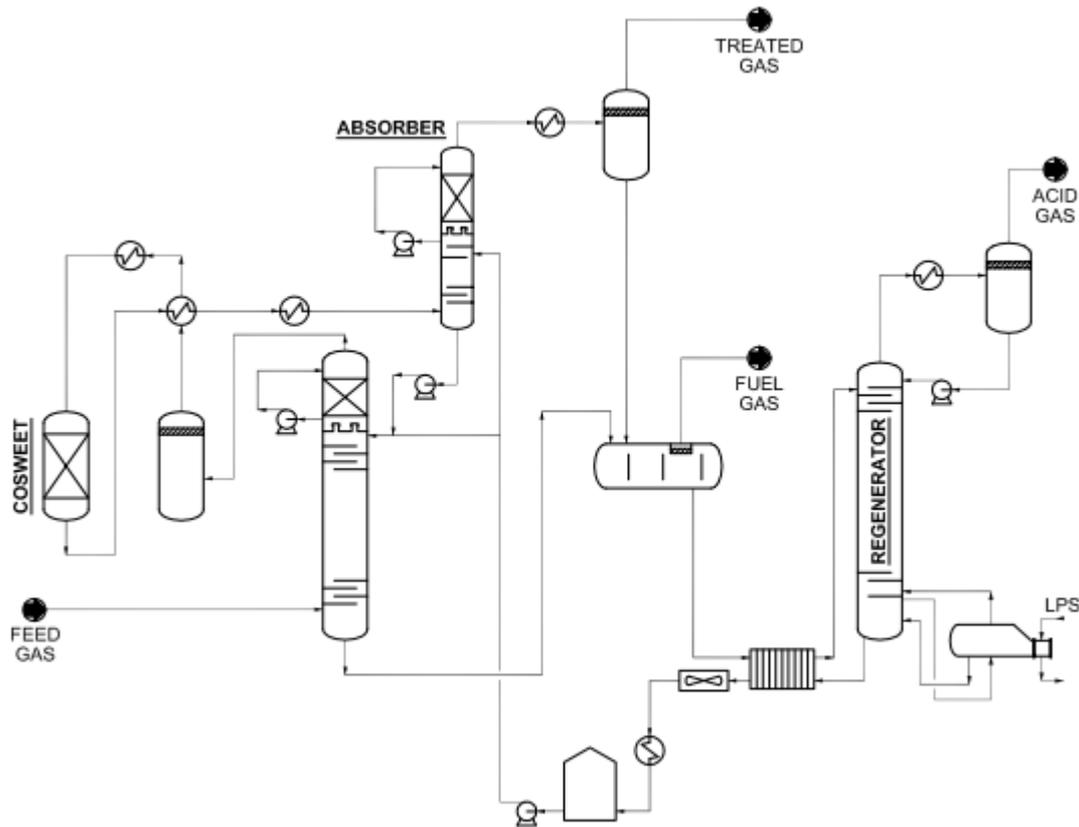


Figure 8: Option 3 - COSWEET™ with hydrolysis reactor integrated to AGRU absorber

Units design & performances

Table 7 presents significant sizing data and performances of the AGRU for the 3 options. Selective units of case 1 and case 3 are fitted with trays to control CO₂ slippage. The *energizedMDEA* unit of case 2 is fitted with structured packing.

Option		1	2 (base)	3
AGRU	Units	Selective H ₂ S absorption No COS removal	Total H ₂ S/CO ₂ absorption Absorption of COS	COSWEET™
Solvent		MDEAmax	<i>energized</i> MDEA	MDEA
Bulk AG removal section				
Solvent flow	% of base	59	100	61
ID	mm	3800	4000	3800
Height (T/T) water wash section included	mm	25000	30500	19500
COSWEET™ reactor				
ID	mm	-	-	3700
Polishing section				
ID	mm	-	-	3100
Height (T/T) gas scrubber & water wash section included	mm	-	-	19500
Treated gas quality				
H ₂ S	ppm vol.	4	4	4
CO ₂	ppm vol.	20000	< 20	20000
COS	ppm vol.	15	1	1

Table 7: AGRU - Sizing data & performances

Main performance data of the sulfur recovery facilities are summarized in table 8 below:

Option		1	2 (base)	3
SRU/AGEU/TGTU	Units	Selective H ₂ S absorption No COS removal	Total H ₂ S/CO ₂ absorption Absorption of COS	COSWEET™
AG from AGRU	kmol/hr	1890	2290	1860
H₂S content				
AG from AGRU	Vol.% wet basis	55.7	46.6	55.5
AG to SRU	Vol.% wet basis	48	58	47.8
BTX content				
AG from AGRU	ppm vol.	300	550	300
Solvent flow AGEU/TGTU	% of base	45	100	45
Overall sulfur recovery	%	99.9	99.9	99.9
Overall sulfur production	Tons/d	809	809	809

Table 8: Sulfur recovery - Sizing data & performances

Economic comparison

The capital costs of the treatment units for the 3 options are given in table 9 below.

	1	2	3
CAPEX (Relative cost units)	Selective H ₂ S absorption No COS removal	Total H ₂ S/CO ₂ absorption Absorption of COS	COSWEET™
AGRU	111	137	143
AGEU	-	69*	-
SRU + Incinerator	103	94	103
TGT	31	-	31
Total	245	300	277

*: including TGTU amine absorber section

Table 9: CAPEX comparison

The overall steam and power balances are shown in table 10. In this utility balance, negative figures indicate a production and positive figures indicate a consumption of the related utility. Other utilities, such as cooling water or fuel gas, are not indicated, as there is no substantial difference between the 3 treatment options. Table 11 indicates the yearly cost of steam and power, in the same relative cost unit as used in table 9.

		1	2	3
	Units	Selective H ₂ S absorption No COS removal	Total H ₂ S/CO ₂ absorption Absorption of COS	COSWEET™
Steam	MW	15.3	56.5	16.8
AGRU		57.3	69.7	58.8(**)
AGEU			49.0*	
SRU/Hydrogen/Quench		-58.3	-62.2	-58.3
TGT		16.3	-	16.3
Power	MW	2.4	4.1	2.5
AGRU		1.9	3.3	2.0
AGEU			0.5*	
SRU/Hydrogen/Quench		0.3	0.3	0.3
TGT		0.2	-	0.2

*: including TGTU amine absorber section

** : including LP steam to preheat COSWEET™ reactor

Table 10: Utilities balance

	1	2	3
OPEX (Relative cost units)	Selective H ₂ S absorption No COS removal	Total H ₂ S/CO ₂ absorption Absorption of COS	COSWEET™
Steam	3.7	13.7	4.1
Power	1.4	2.6	1.5
Total	5.1	16.3	5.6

Table 11: Utilities cost comparison – expressed in same relative cost unit as table 9

The above demonstrates that COSWEET™ offers an attractive solution for deep COS removal when selective H₂S removal is desired. It reduces the necessary amine solution circulation rate and simplifies the sulfur recovery facilities. If the comparison is restricted to the AGRU boundary, it is worth noting that COSWEET™ AGRU unit has a much lower energy consumption (mainly because of a lower steam demand by solvent reboiler) than the alternate COS on specs AGRU using formulated amine.

For the AGRU design, solvent flow and reboiler duty of the COSWEET™ unit are very similar to that of conventional selective AGRU, with a gap of less than 5%. The acid gas is also similar in terms of H₂S and BTX content. It allows directly feeding the SRU unit without acid gas enrichment step or any other needs to achieve the thermal chamber temperature necessary to destroy BTX and achieve high H₂S conversion rates.

Finally, the main difference between the COSWEET™ / selective amine integrated scheme and the traditional selective amine unit is that the treated gas specification can be fully achieved with limited increase of CAPEX and OPEX compared to the selective scheme which does achieve the COS specification.

COSWEET™ lowers the cost of the gas treatment compared to traditional formulated MDEA solution, including the sulfur recovery facilities, with 9% saving on total CAPEX and 65% savings on energy cost. The extra cost for deep COS removal, compared to option 1, is reduced to 13% additional CAPEX and 9% additional energy consumption, which is low compared to the cost of additional process units which would be needed to remove COS from treated gas in option 1.

When all treated gas and sulfur specifications are fully achieved, CAPEX and OPEX savings of the COSWEET™ / selective amine integrated scheme compared to the formulated MDEA scheme are quite substantial. This is due to the fact that amine circulation rate in the AGRU is maintained low, the H₂S selectivity in the AGRU is still achieved and no modification of the SRU and TGTU units are necessary, and finally because of the high efficiency of the hydrolysis catalyst at low temperature. This low temperature catalyst allows a good heat integration of the COS removal section minimizing energy consumption.

Conclusions

COS removal can become an issue in natural gas treatment essentially when the export gas specification calls for deep removal in the range of 1 ppm vol. Among the solutions for deep COS removal, upstream COS hydrolysis is probably the best option as it simplifies the design of downstream units.

COSWEET™ is a process developed for the treatment of natural gases containing COS, supported by extensive laboratory measurements and reactor modeling. It is based on a combination of deacidification with any alkanolamine solution and of COS hydrolysis on a metal oxide based catalyst.

A characteristic of the COSWEET™ process is that it achieves almost complete COS hydrolysis at moderate temperature, making the process more attractive due to substantial heat transfer savings from lower heating of the gas to hydrolysis temperature and reduced cooling of the hydrolyzed gas back to amine absorber temperature.

The COSWEET™ process can be combined with any amine, such as MDEA or formulated MDEA. This allows removing COS down to very low specification while maintaining some CO₂ in the treated gas. When sulfur recovery is associated to the gas sweetening, using COSWEET™ to convert COS allows keeping a high H₂S/CO₂ selectivity required to optimize the gas treatment chain, including SRU. COSWEET™ removes COS in gas phase, it achieves strict COS specification without increase of the amine solvent flowrate and the reboiler duty. Evaluations have been done on CAPEX and OPEX and they show that COSWEET™ allows reducing the investment cost as well as the operating cost compared to a formulated MDEA unit sized to reach the same COS specification.

When selectivity is required on a gas treatment, COSWEET™ is an attractive and efficient solution as it improves the design of selective amine plant, while still ensuring the quality of the acid gas. Significant savings can be expected for the high pressure AGRU and also at the SRU since the SRU feed has an increased H₂S content and reduced hydrocarbons contaminants, without needing a dedicated acid gas enrichment unit.

References

- [1] Kohl, A.L. and Nielsen, R.B. (1997), Gas Purification, 5th Edition, Houston, Gulf Publishing Company.
- [2] Cadours, R., Magné-Drisch, J., Normand, L., Roquet, D., and Perdu, G., "COS removal from natural gases by absorption in alkanolamine solutions", paper presented at the 85th Annual GPA Convention, Grapevine, Texas, Marsh 5-8, 2006
- [3] Sharma, M. M. (1965). Kinetics of reactions of carbonyl sulphide and carbon dioxide with amines and catalysis by Brönsted bases of the hydrolysis of COS. Trans. Faraday Soc., 61, 681-688.
- [4] Svoronos P. D. N. , Bruno T. J. (2002), Carbonyl sulfide: A Review of its chemistry and properties, Ind. Eng. Chem. Res., 41, 5321-5336
- [5] Al-Ghawas, H. A., Ruiz-Ibanez, G., & Sandall, O. C. (1989), Absorption of carbonyl sulfide in aqueous methyldiethanolamine. Chemical engineering science, 44(3), 631-639.
- [6] Perdu G., Normand L., Laborie G., Magné-Drisch J., Gazarian J., & Gonnard S. (2012), COSWEETTM makes COS removal compatible with selective H₂S removal, paper presented at the GPA Europe annual conference, March 2013.
- [7] Handley, D., Heggs, P. J. (1968), Momentum and heat transfer mechanisms in regular shaped packings. Trans. Inst. Chem. Eng. , 46 (9), T251.
- [8] Ergun, S. (1952), Fluid flow through packed columns. Chem. Eng. Prog, 48, 89.
- [9] Yoshida, F. and Koyanagi, T. (1962), Mass transfer and effective interfacial areas in packed columns. AIChE J., 8: 309–316.
- [10] Gunn, D. J. (1987), Axial and Radial Dispersion in Fixed Beds, Chem. Eng. Sci., 42, 363.