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Dossier

Methodology for Process Development at IFP Energies nouvelles
Méthodologies pour le développement de procédés à IFP Energies nouvelles

COSWEET^{TM}: A New Process to Reach Very High COS Specification on Natural Gas Treatment Combined with Selective H_2S Removal

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Abstract *— COSWEET^{TM}, developed for the treatment of COS containing natural gases, is based on a combination of deacidification with any alkanolamine solution and COS hydrolysis on a metal oxide based catalyst. Nearly complete COS conversion is reached, even at a relatively low operating temperature. Coupled with a classical sweetening unit, in which an adapted alkanolamine solvent is used in order to optimise the removal of H_2S, CO_2, as well as the H_2S/CO_2 selectivity, the high catalyst activity and the original integration of the scheme secure the COS removal at minimum extra cost. Benefits on capital and operating expenditures of the plant result both from the reduction of the absorption column and solvent flow rate and from the quality of the acid gas which has positive consequences on the design of the sulfur recovery facilities units, including Claus unit.*
This paper presents the complete development process approach and the results obtained on COS conversion, the model and simulation tool as well as a case study showing the advantages of coupling COSWEET^{TM} to amine based solvent.

Résumé — COSWEET^{TM} : procédé innovant de traitement du gaz naturel combinant une élimination sélective de l'H_2S et une spécification poussée sur le COS — COSWEET^{TM}, procédé développé pour le traitement du gaz naturel comportant du COS, est une intégration entre un procédé de désacidification à base d'une solution d'alcanolamine et une section catalytique assurant l'hydrolyse du COS à l'aide d'un catalyseur à base d'oxyde métallique. Ce procédé permet d'atteindre des conversions du COS proches de 100 % à basses températures. Lorsque la section catalytique est couplée à une section de désacidification mettant en œuvre un solvant à base d'une alcanolamine adaptée de telle manière à optimiser l'élimination de l'H_2S et du CO_2 et également la sélectivité H_2S/CO_2, la forte activité du catalyseur et l'intégration originale des deux sections permettent de garantir une spécification sur le COS tout en minimisant les coûts de traitement. Les gains sur les coûts d'investissements et opératoires sont dus non seulement à la réduction de la taille de l'absorbeur et du débit de solvant mais également à la qualité du gaz acide, qui impacte la chaîne soufre en aval, comprenant l'unité Claus.

Cet article présente la méthodologie de développement du procédé et les performances obtenues sur la conversion du COS, ainsi que les modèles et outils de simulation qui ont été développés et deux cas d'études qui montrent les gains et avantages du procédé COSWEET^{TM} selon le couplage réalisé avec une colonne d'absorption aux amines.

NOTATION

A_p	Particle surface area (m^2)
a_i	Thermodynamic parameter
b_i	Thermodynamic parameter
T	Temperature (K)
b_7	Water adsorption coefficient in reaction 7 (bar^{-1})
b_8	Water adsorption coefficient in reaction 8 (bar^{-1})
C_i^g	Gas concentration of compound i (mol/m^3)
C_i^p	Particle concentration of compound i (mol/m^3)
D_{ax}^g	Gas axial dispersion coefficient (m^2/s)
$D_{eff,i}$	Effective diffusion coefficient (m^2/s)
d_p	Particle diameter (m)
D_m	Molecular diffusion coefficient (m^2/s)
k_7	Kinetic constant of reaction 7 (SI)
k_8	Kinetic constant of reaction 8 (SI)
k_{gs}	Gas-solid mass transfer coefficient (m/s)
$K_{eq,i}$	i^{th} thermodynamic constant
L	Particle characteristic length (m)
P_{CO_2}	CO_2 partial pressure (bar)
P_{COS}	COS partial pressure (bar)
P_{CS_2}	CS_2 partial pressure (bar)
P_{H_2O}	H_2O partial pressure (bar)
P_{H_2S}	H_2S partial pressure (bar)
P_t	Total pressure (bar)
Re	Reynolds number
r_7	Reaction rate of reaction 7 (mol/s/kg cat)
r_8	Reaction rate of reaction 8 (mol/s/kg cat)
r_j	Reaction rate of reaction j (mol/s/kg cat)
R	Perfect gas constant (SI)
r	Radius coordinate (m)
R_p	Particle radius (m)
Sc	Schmidt number
V_p	Particle volume (m^3)
v_{sg}	Superficial gas velocity (m/s)
z	Reactor elevation (m)

GREEK SYMBOLS

ε_g	Gas holdup
ε_s	Solid holdup
ε_p	Particle porosity
δ	Film thickness (m)
$\mu_{i,j}$	Stoichiometric coefficient
ρ_g	Gas density (kg/m^3)
ρ_s	Solid density (kg/m^3)
τ	Tortuosity

INTRODUCTION: THE GAS TREATMENT CHAIN AND NEW CHALLENGES

Natural gases, when collected from the production wells, are commonly polluted with many contaminants. Among these contaminants are sulfur compounds and CO_2. Throughout the oil and gas treatment chain, various steps intend to separate most of the undesired compounds from the profitable part of the natural gas. The desulfurisation of natural gas is usually performed in generic treatment processes and consists of removing H_2S and/or CO_2 to meet the export gas specifications.

Commercial gas specifications also focus on compounds other than H_2S and CO_2. New specifications have been imposed for many years to also remove most of other sulfur compounds from the natural gas. One of these, Carbonyl Sulfide (COS) is usually present in sour natural gases containing both H_2S and CO_2, in quantities which may reach 150 to 1 000 ppm vol., due to the exploitation of gas fields with an increase in acid gas compounds.

The market for natural gas is in constant increase, +3%/year for natural gas and +7%/year for Liquefied Natural Gas (LNG), and we can assume that there is a correlation between H_2S content and COS content such that 70% of raw acid gas world reserves are affected by this problem.

In addition to the total sulfur specification on the treated gas, there are some specific constraints with COS:

- after fractionation of the treated gas, 90% of residual COS will be recovered in the C3 fraction and 10% in the C2 fraction because of the respective boiling point (−50.2°C for COS and −44.5°C for propane) which could entail problems on downstream petrochemical units,
- if the treated gas is aimed to be transformed into LNG, the liquefaction process does not admit COS.

For H_2S and CO_2 deacidification combined with COS constraint, different treatment processes can be envisaged. Hybrid or physical solvents present the advantage of achieving both H_2S, CO_2 and COS elimination in one unit. However, for a selective application, it is not possible to respect the required H_2S/CO_2 selectivity and hydrocarbon co-absorption leads to economically unattractive processes. In addition, some of these solvents are not stable at high temperatures. Regarding these disadvantages, chemical solvents are in most cases more attractive solutions.

Amine solvents are very often used for natural gas deacidification purposes as they can be adapted to various specifications and to a wide range of feed gas compositions.

When complete CO_2 removal from the gas is required, for instance to achieve LNG plant feed specifications, formulated MDEA solvents are more frequently being used, replacing primary or secondary amines. MDEA, when it is used without activator, is a selective amine solvent. It targets H_2S removal, but leaves some CO_2 in the treated gas. This reduces the sweetening cost as some CO_2 can be left in the treated gas, and increases H_2S concentration in the produced acid gases to Sulfur Recovery Units (SRU). MDEA is also used for an additional acid gas enrichment step to prepare the feed load of SRU for an optimised design of the Claus unit.

When MDEA is used for a selective H_2S removal from the gas, a reduced fraction of the CO_2 is separated from the feed gas but an even lower fraction of the COS is removed. It is well known that MDEA has poor COS removal capabilities. Severe COS specification cannot be reached for gases with fairly high initial COS content even with higher solvent circulation rate and/or high number of mass transfer units in the contactor.

In other words, it is not possible to design a selective removal plant that removes COS and leaves amounts of CO_2 in the treated gas, as a selective plant should aim to do. Therefore, the reduction of the sweetening cost by leaving some CO_2 in the gas, so as to improve the quality of acid gas, is equally unachievable. The design will likely rely on the use of a primary or secondary amine or a formulated MDEA. If acid gas enrichment is needed to efficiently design the Claus unit, then a second acid gas enrichment unit using selective solvent is compulsory to improve the quality of acid gas and increase its H_2S content.

The severe COS specifications in the export gas consequently affect the cost of gas treatment when this is carried out with amines solvents, especially when a selective H_2S removal unit should help to minimise the number of units of the Sulfur Recovery Facilities or to reduce the size of the high pressure acid gas removal unit.

Regarding this process analysis and following a review of catalytic solutions, *IFP Energies nouvelles (IFPEN)* has developed the COSWEET^{TM} process that combines a very deep COS removal through the complete hydrolysis of the COS in a catalytic reactor integrated within the selective removal of H_2S by a MDEA amine unit. The COSWEET^{TM} reactor can also be integrated with an Energized **MDEA** unit as it reduces the solvent flow rate to perform both acid gas removal and COS removal.

At the screening phase, IFPEN has selected a specific metal oxide based catalyst that is able to operate at moderate temperatures. Numerous data have been acquired in the laboratory on the thermodynamics and the kinetics of the hydrolysis reaction taking place on the catalyst. Based on these data, a specific prediction model (and an in-house simulator) has been developed to allow the precise and optimal design of the catalytic reactor. Details of these developments are presented in this paper.

The last part of the paper focuses on the interest of the COSWEET^{TM} process when selective acid gas removal is required through a representative case study. The paper also discusses interest in the COSWEET^{TM} process in terms of capital and operating expenditures (CAPEX and OPEX) compared to a formulated amine application.

1 IDENTIFICATION OF THE CONCEPT AND PROCESS DEFINITION

1.1 Existing Sweetening Processes: Advantages and Disadvantages

The solvents based on alkanolamines are the most generally accepted and widely used of the many available solvents for removal of acid gas H_2S and CO_2 from natural gas streams. However, alkanolamine based processes do not provide technological solutions and attractive compromises between investment and operational costs when they target tight COS specifications from gas containing large amounts of COS [1]. When total CO_2 removal is required, conventional amine processes can be adapted (using for instance primary and secondary amines or formulated MDEA), to remove COS down to very low levels in treated gas. This is generally achieved by increasing the solvent flow rate along with the absorber height.

Some processes have also secured the COS transformation into H_2S and CO_2 by hydrolysis in a hot zone of the amine absorber, as this is performed in a specific version of the HiLoadDEA process licensed by *Prosernat* [2].

Some competitors [3] propose the use of physical solvents in selective treating by using differences in equilibrium constants (*i.e.* solubility), the advantage being the good absorption of COS component but the two major drawbacks are:

- hydrocarbon coabsorption which represents a loss of valuable hydrocarbons into the acid gas (lost sales of natural gas components (C_1, C_2) and lost sales of C_3+, NGL, condensate;
- required high partial pressure of acid gas.

Other competitors propose the use of hybrid solvents [4] to remove the COS and mercaptans and maintaining the selectivity. However, the application of hybrid solvents is adapted to acid gas enrichment units and these solvents have the same problem of hydrocarbon coabsorption as physical solvents.

MDEA is the attractive solution for maintaining the selectivity but for gases containing COS, the use of selective MDEA processes faces two difficulties. The reaction between MDEA and COS is low and MDEA is not prone for removing COS. Reaction mechanisms of COS with MDEA are the same as those of MDEA with CO_2.

There is no direct reaction between MDEA and CO_2. Absorption of CO_2 is achieved through hydrolysis (Reaction 2) catalysed by MDEA. This reaction is very slow and this is the reason why MDEA solvent is selective:

$$CO_{2(aq)} + HO^- \rightarrow HCO_3{}^-$$

Reaction 1

$$CO_{2(aq)} + R_1R_2R_3N + H_2O \leftrightarrow HCO_3{}^- + R_1R_2R_3NH^+$$

Reaction 2

As noted by Sharma [5], reactions between COS and MDEA are based on the same mechanism. COS undergoes hydrolysis to yield carbon dioxide and hydrogen sulfide [6] according to Reaction 3:

$$COS_{(aq)} + HO^- \rightarrow HCO_2S^-$$

Reaction 3

Al-Ghawas *et al*. [7] proposed that tertiary amines act as base catalyst for the hydrolysis reaction of COS according to Reaction 4:

$$COS_{(aq)} + R_1R_2R_3N + H_2O \leftrightarrow HCO_2S^- + R_1R_2R_3NH^+$$

Reaction 4

Reaction 4 is even slower than the CO_2 hydrolysis in Reaction 2.

The existing sweetening processes do not have the capability to remove all COS while maintaining high CO_2/H_2S selectivity. The presence of the COS in the sour gas is a major problem in the case of natural pipe gas specification. Most of the time, a total acid gas removal unit is designed to achieve COS elimination.

1.2 Evaluation of Different Schemes to Reach High COS Elimination

Based on its experience of catalyst development, *IFPEN* has investigated the possibility to remove the COS by hydrolysis (Reaction 5) through heterogeneous catalysis. Reaction 5 implies the removal of acid gases formed by the hydrolysis reaction:

$$COS_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_2S_{(g)}$$

Reaction 5

The philosophy of the development is to keep the high selective performance of MDEA solvent with a conventional acid gas (CO_2 and H_2S) absorption and achieve significant COS removal through a dedicated catalytic reactor. Both catalytic and process schemes were investigated to find the suitable configuration.

1.2.1 First Configuration: COS Hydrolysis Followed by Amine Treatment

The first configuration investigates the possibility to perform the hydrolysis upstream of the absorber as a pretreatment. Figure 1 represents the first process scheme in which feed gas is sent into a feed/effluent heat exchanger and enters to the reactor final a last heating step so as to reach the temperature required by the process. The COS free exhaust gas is sent to the absorber to remove acid gas.

The feed gas composition treated by the hydrolysis reactor contains the highest quantity of acid gas. A typical acid gas composition in natural gas (Tab. 1) was taken into account for the preliminary investigation of the process scheme.

The water content is 1 200 ppm vol. (saturation of the natural gas). Due to high acid gas content (COS and H_2S), and as COS hydrolysis reaction is an exothermic equilibrium reaction, either low temperature and/or higher water content would be required to reach high COS conversion. This is however unacceptable as in these conditions operating temperatures required to reach high COS conversion would be below gas dew point. At process scale, this would lead to capillary condensation inside catalyst porosity. This is illustrated in Figure 2, which represents the COS conversion at thermodynamic equilibrium for different water contents. These calculations underline that is not possible to reach high COS conversion by adding a huge amount of water (10 vol.%).

This explains the necessity to remove the CO_2 and H_2S content upstream the COS hydrolysis reactor due to the thermodynamic constraint.

1.2.2 Second Configuration: Amine Treatment Followed by COS Hydrolysis

The second configuration proposes to hydrolyse the COS downstream of the absorber contactor (Fig. 3). This configuration favours the thermodynamic equilibrium of the

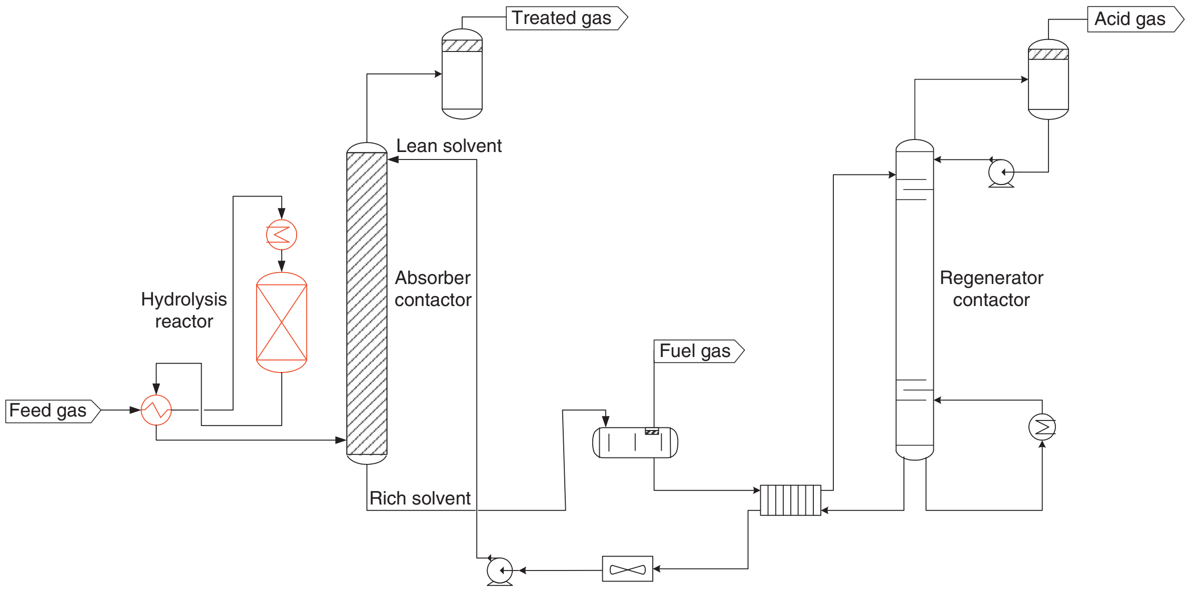

Figure 1

Process scheme 1: COS hydrolysis followed by amine treatment.

TABLE 1

Natural gas composition

	Molar fraction (%)
CO_2	9.6
H_2S	6.0
N_2	0.23
C_1	76.8
C_2	4.2
C_3	1.3
C_4	0.96
C_5	0.43
C_6	0.25
COS	0.0075

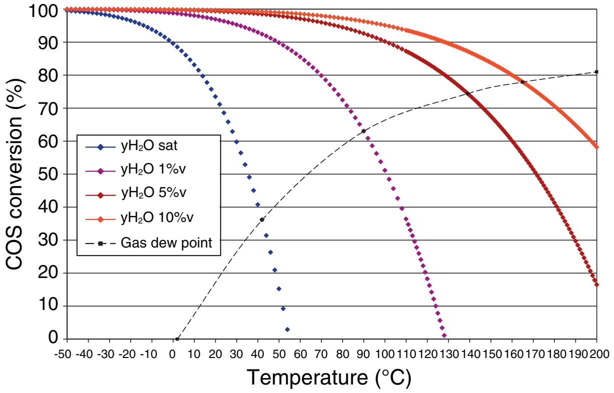

Figure 2

Thermodynamic COS conversion *versus* temperature.

hydrolysis reaction because the absorber removes CO_2 and H_2S compounds by MDEA absorption.

The natural gas enters at the bottom of the absorber and flows upward through the column and is contacted at counter current with the lean solvent MDEA. At the top of the column the gas has reached CO_2 and H_2S specifications. The gas is heated to the operating temperature of the process (100-180°C) and is sent to the hydrolysis reactor. The exhaust gas contains H_2S produced by the hydrolysis reaction which should be removed by an additional reactor step. The typical purification reactor to remove low H_2S concentration (≈ 100 ppm vol.) from a gas is a zinc oxide fixed bed reactor. Reaction 6 takes place at higher temperature than the hydrolysis reaction and requires an additional heater:

$$H_2S_{(g)} + ZnO_{(s)} \rightarrow ZnS_{(s)} + H_2O_{(g)}$$

Reaction 6

Additionally, a lead-lag configuration is mandatory because zinc oxide is non-regenerable.

Figure 4 represents the COS conversion at equilibrium as a function of the temperature with the acid gas composition at the inlet of the hydrolysis reactor. Contrary to the first configuration, there is no thermodynamic limitation to reaching high COS conversion.

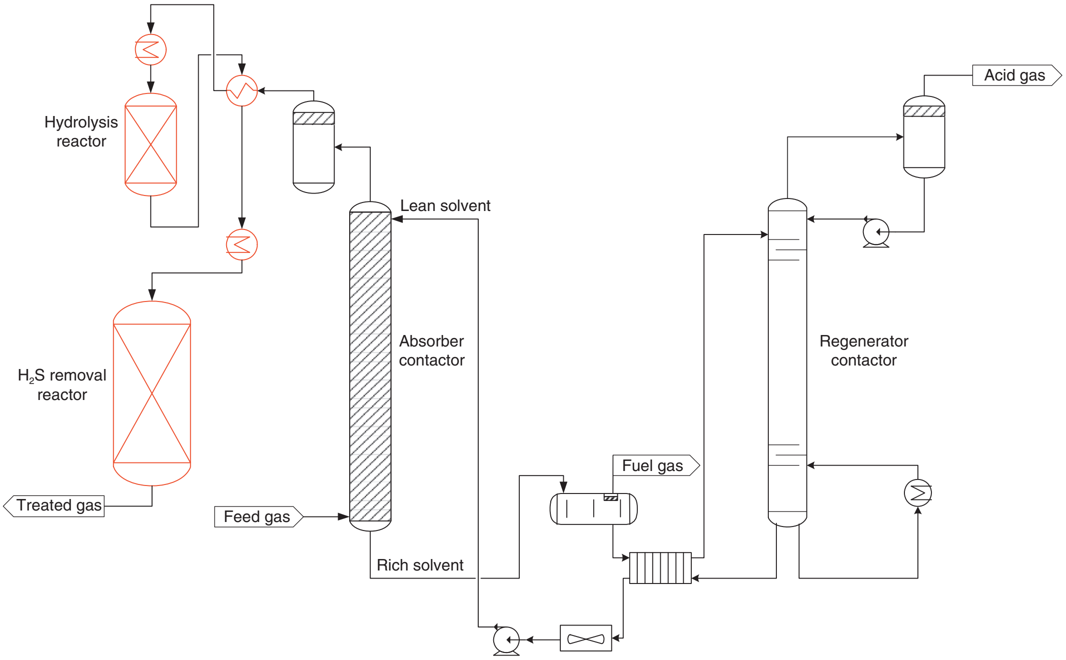

Figure 3

Process scheme 2: amine treatment followed by COS hydrolysis.

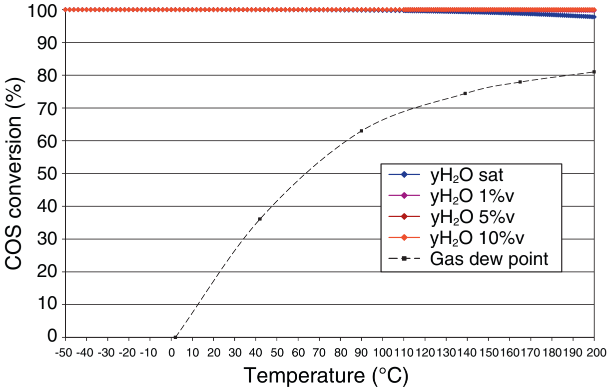

Figure 4

Thermodynamic COS conversion *versus* temperature.

A preliminary design of the hydrolysis reactor and ZnO reactor was performed based on this configuration. A shortcut reactor model for the hydrolysis reactor was developed by *IFPEN* for the preliminary design based on a catalyst and a kinetic law from the literature [8]. The composition of the hydrolysis feed gas reactor is summarised in Table 2. The hydrolysis reactor design is presented in Table 3 and the ZnO reactor design is presented in Table 4.

The shortcut model validates the feasibility of the hydrolysis reactor in term of performance and the design is acceptable.

The zinc oxide reactor was designed with another shortcut model. The results of the design show that the configuration is not suitable for the H_2S removal. Indeed, the huge amount of solid is not economically acceptable and implies a considerable size of the reactor. In fact, the residual H_2S content (several tens of ppm) to be treated downstream of the hydrolysis reactor is too important due to the huge natural gas flow rate. The CAPEX of hydrolysis section plus zinc oxide reactor and heat exchanger equipment could not be envisaged.

An alternative solution to remove H_2S reformed by COS conversion should be envisaged. Other processes exist on the market but the associated costs are not acceptable. The suitable solution will be to re-introduce the exhaust gas of the hydrolysis reactor into the upper part of the amine absorber in order to remove the last trace of the H_2S.

1.2.3 Third Configuration: Combined COS Hydrolysis and Amine Treatment

The third configuration (Fig. 5) proposes to sweeten the acid gas from the hydrolysis reactor inside the absorber. The feed

TABLE 2
Hydrolysis feed gas reactor

Molar flow rate (kmol/h)	2721
Molar fraction (%)	
CO_2	1.97
H_2S	0.0002
H_2O	0.17
N_2	0.26
C1	89.2
C2	4.9
C3	1.5
C4	1.1
C5	0.5
C6	0.3
COS	0.0083

TABLE 3
Hydrolysis reactor design

CO_2 outlet (mol%)	1.98
H_2S outlet (ppm mol)	83
COS outlet (ppm mol)	1
Mass of the catalyst (kg)	3500
Reactor diameter (mm)	1100
Reactor length (m)	4.2

TABLE 4
ZnO reactor design

Mass of the ZnO (T)	472
Volume of ZnO bed (m^3)	410.3
Diameter (m)	3.2
High (m)	50.7

natural gas enters at the bottom of the absorber column in order to remove the bulk CO_2 and H_2S acid gases. The objective is the same as configuration 2 (amine treatment followed by COS hydrolysis) which is to avoid thermodynamic limitation. In a second step, the gas is withdrawn from the absorber and sent to the catalytic reactor after two heating steps. At the outlet of the hydrolysis reactor, the gas no longer contains COS and is sent back to the upper part of the absorber. H_2S formed by the COS conversion is sweetened by MDEA lean solvent in countercurrent.

The advantage of this configuration is the use of the same absorber column to remove the acid gas to reach the natural gas specifications and to remove the last decades of H_2S ppm vol. present at the outlet of the catalytic hydrolysis reactor. This configuration implies two dedicated sections of the absorber, due to the pressure drop of the heat exchanger and the hydrolysis reactor.

The preliminary design of this last process scheme, with a combined COS hydrolysis and amine treatment, presents the best performance and it is the preferable configuration.

1.3 Definition of the COSWEET^{TM} Process

The COSWEET^{TM} process (Fig. 6) is based on the preferred process scheme 3 (combined COS hydrolysis and amine treatment) and is presented in the final configuration.

Most of the acid compounds from the sour gas are removed by the solvent in the lower section of the absorption column. The gas from this first bulk removing stage is heated to an optimised temperature before entering the catalytic reactor where the COS is hydrolysed into CO_2 and H_2S. The produced gas is introduced into the upper part of the absorption column to complete the H_2S removal. Therefore the absorption column needs two solvent feeds. Because of the low acid gas content in the upper section, the solvent flow rate in this section can be strongly decreased, allowing a reduction in column diameter.

The COSWEET^{TM} section is integrated to a very simple and conventional amine unit. The configuration can be adapted to any arrangement of Acid Gas Removal Unit (AGRU):

– the solvent used in a COSWEET^{TM} unit is the one produced by the regenerator of the AGRU unit, with no need for extra duty or modified configuration of the stripping section;
– the absorber can be fitted with trays or with packing beds;
– the hydrolysis of COS in a reactor destroys COS, and it almost completely reduces the COS content in the flash gas and in the acid gas.

Some special arrangements of the reactor section, especially some dedicated arrangements to knock out the liquids upstream of the reactor, mitigate the risk of any solvent carry-over which could drastically reduce the hydrolysis catalyst activity.

2 PROCESS DEVELOPMENT AND FIRST TECHNO-ECONOMIC EVALUATION

2.1 Validation of the Concept: Catalyst Choice and First Techno-Economic Evaluation

The first techno-economic comparison (Tab. 5) is based on the COSWEET^{TM} scheme *versus* a total removal absorption scheme by use of the solvent DEA (reference case).

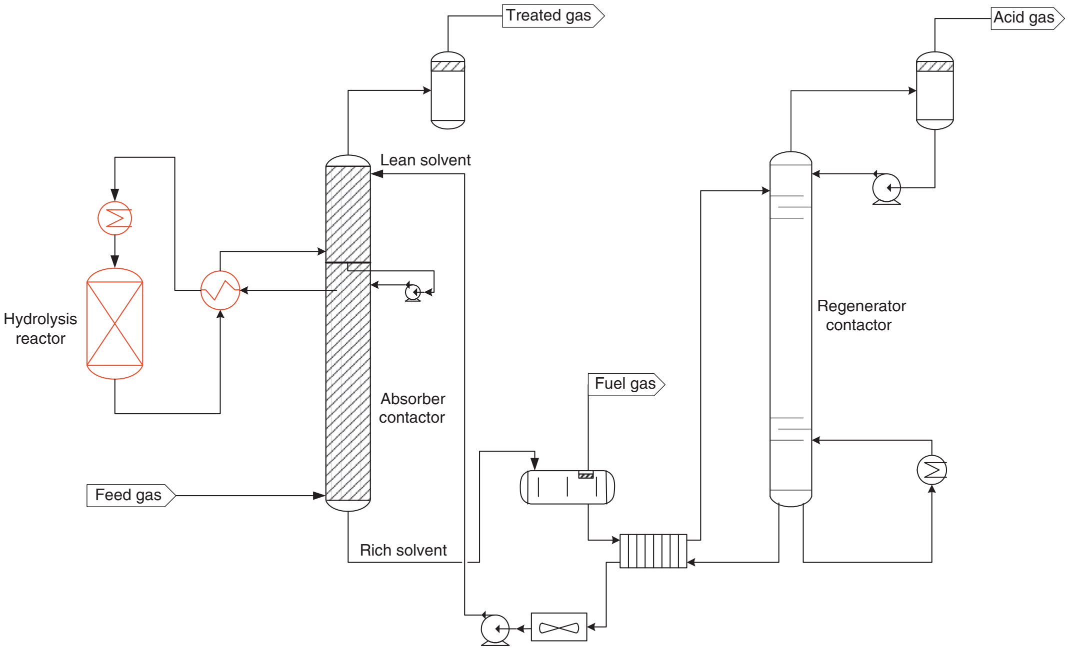

Figure 5

Process scheme 3: Combined COS hydrolysis and amine treatment.

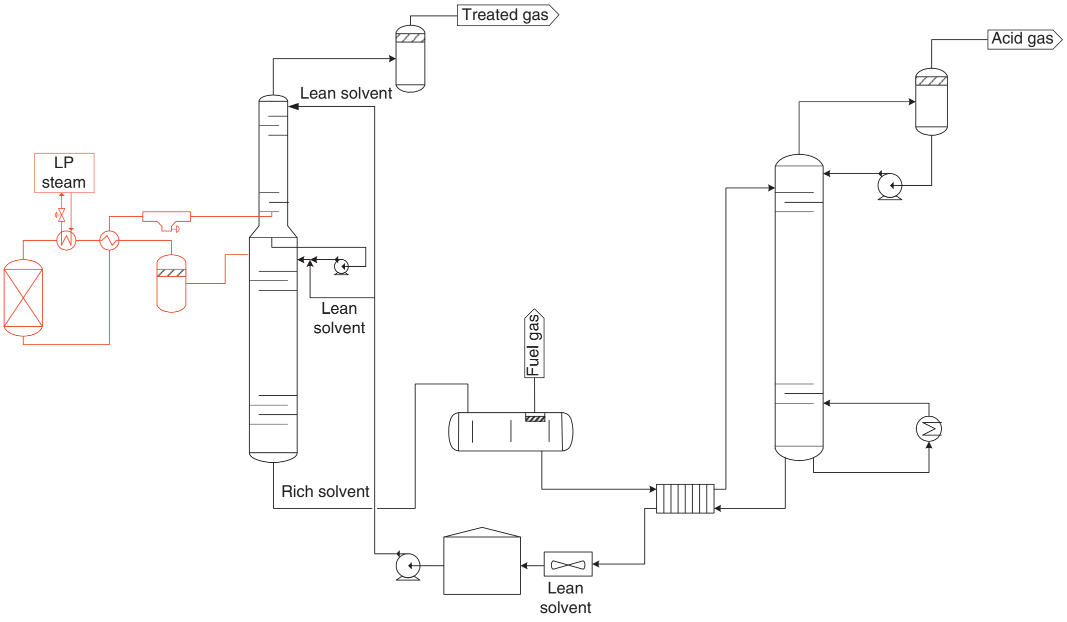

Figure 6

COSWEET^{TM} process scheme.

TABLE 5
First techno-economic evaluation

	Hi*Load*DEA	COSWEET™
CO_2 outlet (mol%)	0	1.8
H_2S outlet (ppm mol)	0	4
COS outlet (ppm mol)	1	1
CAPEX (%)	100	83
OPEX (%)	100	91

The COSWEET™ process allows to maintain 1.8% of CO_2 in the treated gas by achieving a deep COS removal (1 ppm vol.). To reach 1 ppm vol. of COS in the treated gas with DEA process implies the total removal of CO_2. The CAPEX reduction is significant even when considering the cost increase due to the additional reactor and heat exchanger. Indeed, the reduction of the size of the column and of the solvent flow rate balances the CAPEX increase of the COSWEET™ equipments.

2.2 Definition of the Process Phase Development

The preliminary study resulted in high interest in the COSWEET™ process for natural gas application to remove COS to meet very severe specifications (< 1 ppm vol.) allowing high H_2S/CO_2 selectivity to be kept. The process development approach could be illustrated by Figure 7.

Based on a commercial catalyst, a shortcut reactor model has been developed to identify the best process scheme to remove COS in parallel to the AGRU. The technical evaluation allowed the determination of the suitable scheme that could be economically investigated. If the economic aspect is acceptable, the scheme is protected with a registered patent and a more thorough study could start.

Catalyst laboratory tests should be performed to determine the activity of the catalyst in the process operating condition and a rigorous kinetic model should be developed. Based on the kinetic and process constraint a fixed bed reactor model was developed. Additional experimental lab tests were performed to validate the model at low and high conversion for several operating conditions.

Based on the preferred scheme a patent was registered to protect the COSWEET™ process [9] (Fig. 8).

3 EXPERIMENTAL STUDY

Following techno-economic evaluation, an experimental study has been carried out in order to obtain data on catalyst activity toward the COS hydrolysis reaction. Objectives were primarily to validate the feasibility of COS conversion reaction under the industrial COSWEET™ process conditions. Experiments were also performed to obtain information on reaction kinetics to determine the critical parameters that may affect COS conversion and to get data to be used to develop a kinetic modeling tool. From these experiments, the dependence of reaction kinetics toward a set of parameters that have to be considered for the COSWEET™ process design has been underlined.

3.1 The Pilot Plant

A schematic representation of the experimental set-up used for kinetics measurements is reported in Figure 9.

This equipment can be divided into three sections, as represented in Figure 9:

1. a feed preparation zone where the different gas are mixed to build the feed gas. COS, CO_2, He and H_2S are supplied from gas tanks with specific gas compositions provided by *Air Liquide*. An helium and water mixture is prepared using a water saturator set-up where a helium flow bubbles in water heated at a controlled temperature. This controlled water saturated helium flow is mixed to the mixture of dry COS-H_2S-CO_2-He gas to reach the desired water content;
2. a reaction zone, which basically consists of a cylindrical fixed bed reactor filled with the COS hydrolysis catalyst and heated at the desired temperature;
3. an analytic set-up to analyse and quantify the reactions products through mass spectrometry. Initial COS gas contents and COS gas contents downstream of the hydrolysis reaction zone are measured to determine COS conversion rates as a function of the operating conditions.

3.2 Experimental Results

COS hydrolysis is thermodynamically very favoured at low temperature as shown in Figure 10. Preliminary long residence time tests have been first carried out to measure the occurrence of any inhibition effect or lack of catalyst activity under the industrial COSWEET™ process conditions. COS conversion rates have been measured for different temperatures from 100 to 200°C. These experiments show that the selected catalyst exhibited highly satisfactory activity toward the operating conditions imposed as it allowed nearly complete COS conversion close to thermodynamic equilibrium to be reached.

Lower residence time tests have been performed to evaluate the kinetics of COS conversion as a function of experimental parameters: temperature, GHSV (Gas Hourly Space Velocity) or residence time, pressures H_2O, COS, H_2S, CO_2. The operating condition ranges explored are summarised in Table 6. These data were used to produce a design

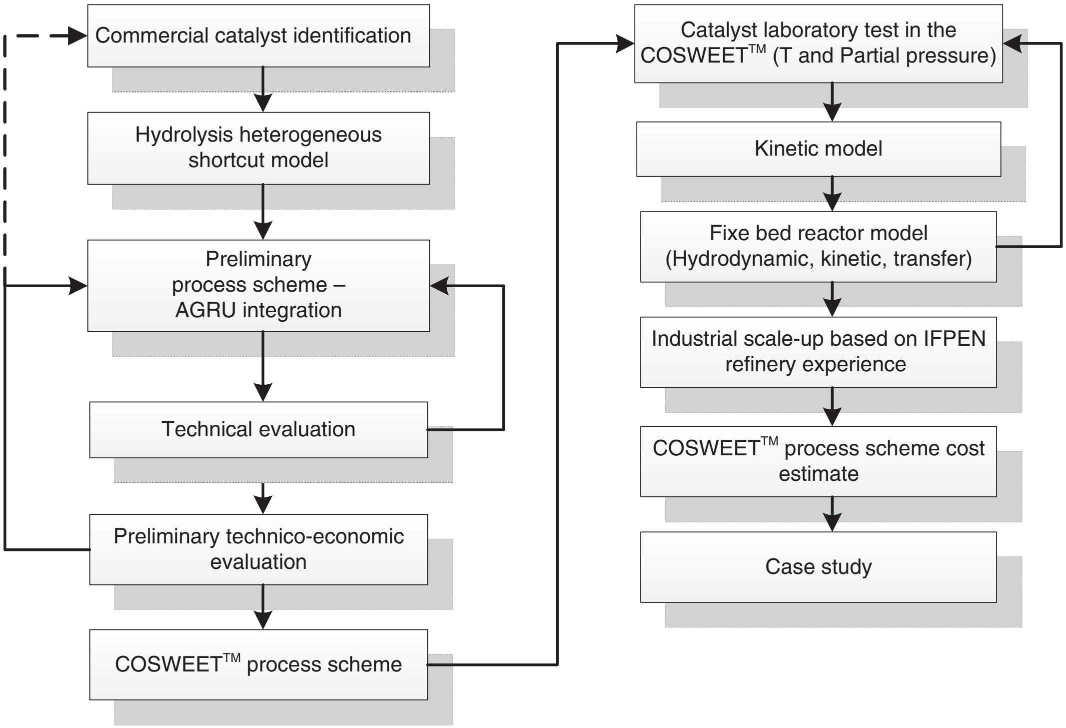

Figure 7

Process phase development.

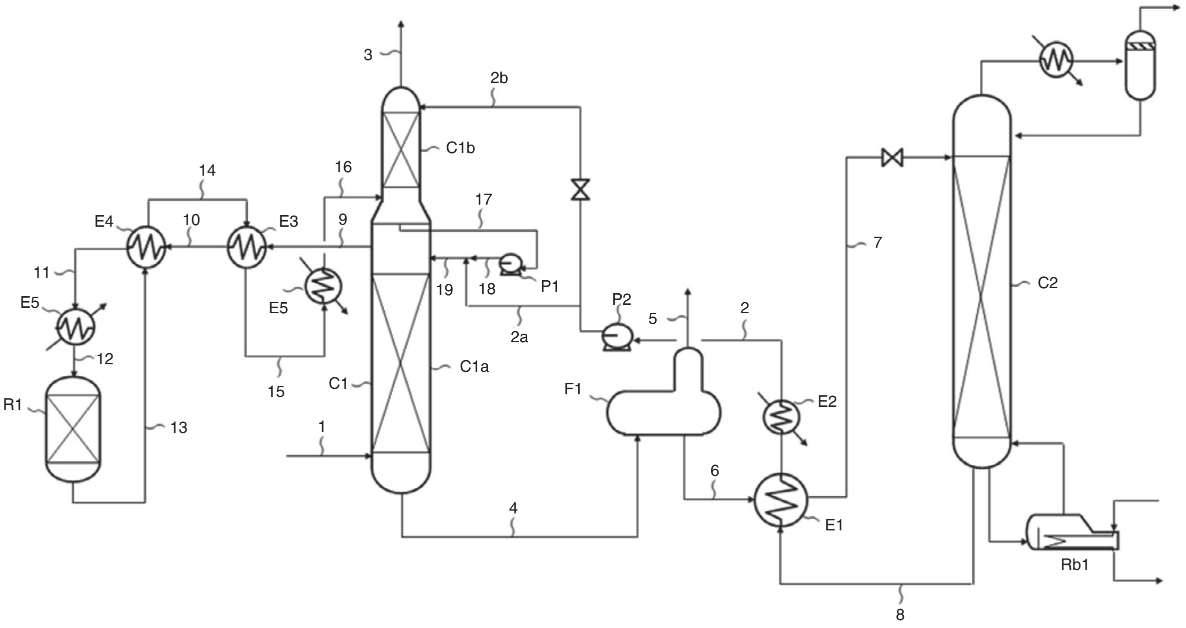

Figure 8

COSWEET^{TM} process scheme [9].

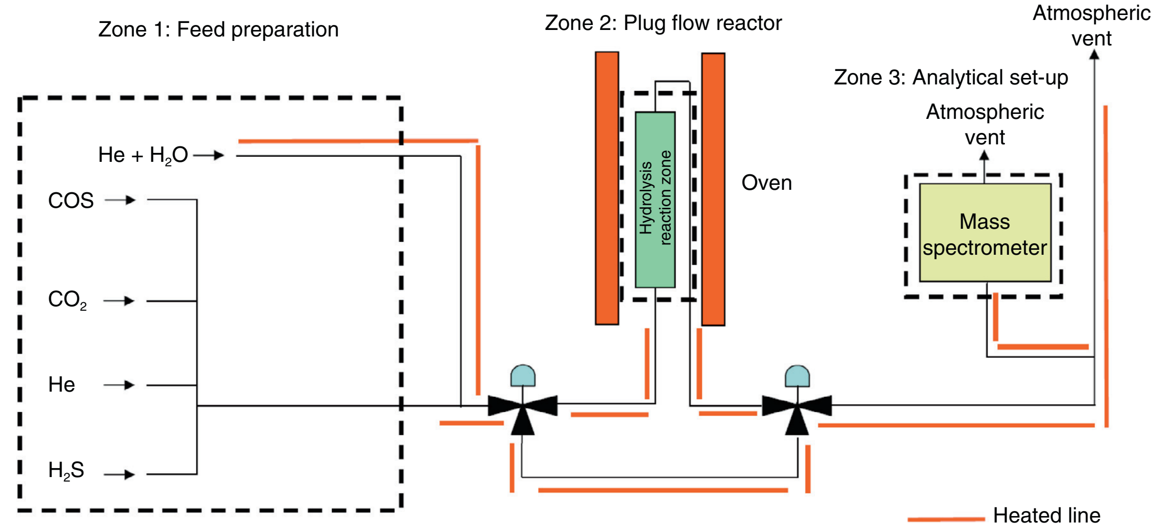

Figure 9

Experimental equipment for kinetic measurements.

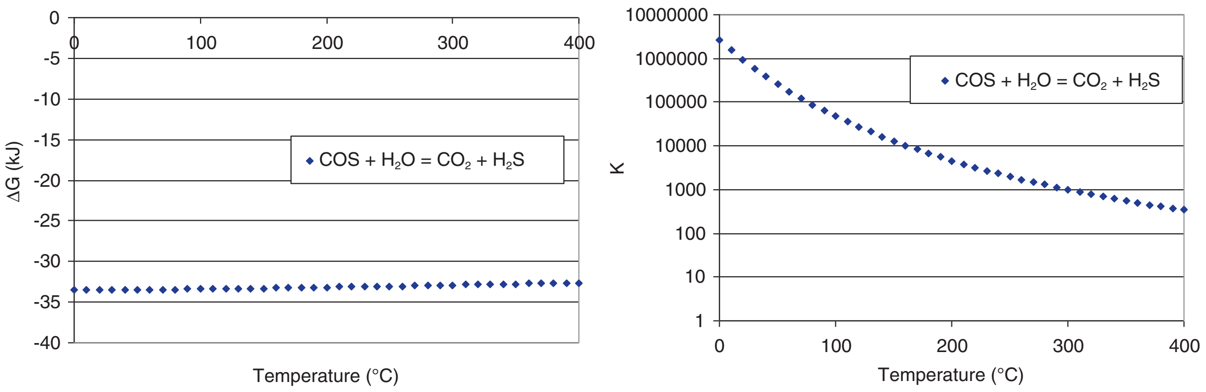

Figure 10

Free enthalpy and equilibrium constant of the COS hydrolysis reaction as a function of temperature (thermodynamic data obtained from HSC Chemistry v6.1 [10]).

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model of the COS hydrolysis reactor with the selected catalyst.

It was shown that the moderate presence of H_2S and CO_2 had no significant impact on the kinetics of the COS hydrolysis reaction in the operating range tested. At higher conversions, the presence of H_2S and CO_2 can decrease the conversion performances due to thermodynamic equilibrium.

The addition of water has a moderate impact on the conversion of COS, as water is already in large excess compared with the expected COS levels. It was verified that for industrial residence time ranges, the hydrolysis reaction of COS was not inhibited, and that the catalyst activity was not affected by the presence of water.

Experiments have also been performed on crushed and uncrushed catalyst particles to take into account potential macroporous diffusion limitations inside catalyst particles. Indeed, significant transport limitations have been highlighted from these experiments, due to the high reaction rate. In agreement with experimental observations, these transport limitations are also demonstrated by the modeling performed for both lab-scale experiments and industrial case study (Sect. 4).

Thiele modulus calculations have been performed in order to have an estimation of the potential limitations

TABLE 6

Experimental range of acid gas partial pressures, temperature and space velocity. GHSV stands for Gas Hourly Space Velocity. NTP for Normal Temperature and Pressure

	Laboratory operating conditions range
Temperature	100-200°C
Total pressure	5-7 bar
GHSV (at NTP)	500-34000 h^{-1}
Pressure CO_2	1-2 bar
Pressure H_2O	0.05-0.25 bar
Pressure COS	0.005-0.025 bar
Pressure H_2S	0-0.01 bar

TABLE 7

Estimation of transport limitations from Thiele modulus calculations for some experimental conditions lab scale *versus* industrial scale

	Lab scale experiments conditions		Typical industrial operating conditions
Temperature	150°C	150°C	150°C
Pressure	5 bar	5 bar	70 bar
Mean particle size: Uncrushed: L_c = 3 mm Crushed: L_c = 0.75 mm	3 mm	0.75 mm	3 mm
Thiele modulus ϕ	7.7	1.9	29

encountered, which are function of the relative importance of reaction kinetic towards mass transport [11]. Thiele modulus ϕ is given by the following relation:

$$\phi = L_c\sqrt{\frac{k[\mathrm{COS}]^{n-1}}{D}}$$

with k the rate constant as calculated from the modeling (Sect. 4), [COS] the COS concentration, n the order of reaction (= 1 in the modeling), D the COS effective molecular diffusion coefficient (calculated from the Füller correlation, Eq. 11), L_c the particle diameter.

Thiele modulus calculations for some operating conditions for lab scale experiments as a function of particle size (crushed *versus* uncrushed particles), and for a typical industrial case are given in Table 7. This shows in every case the occurrence of mass transport limitations inside catalyst porosity, due to high catalyst activity (high kinetic rate). The extent of mass transport limitations are more pronounced with increasing particle size and/or pressure (the latter affecting molecular diffusivity). As a consequence, diffusion limitations are more pronounced at an industrial scale.

Collected kinetics data as a function of reactor size, gas residence time, temperature and reactant partial pressures were then used to develop a reactor modeling tool taking into account all of the relevant operating parameters that may affect reaction kinetics and process performances.

4 COSWEET$^{\mathrm{TM}}$ REACTOR MODEL AND SIMULATOR

An industrial reactor model is developed for scale-up purposes. This model is based on a kinetic model validated with experiments obtained in a lab scale fixed bed reactor. First of all, the lab scale reactor is described taking into account all the limitations (external mass transfer and intra particle diffusion) in order to catch the so-called intrinsic kinetic parameters for COS and CS_2 elimination reactions. Then, this kinetic model is implemented in a complete industrial reactor model taking into account potential limitations. Then, it is used for scale-up and optimisation purposes.

4.1 Industrial Reactor Configuration

The industrial reactor is a two-phase (gas-solid) fixed bed system. It works under isothermal conditions due to the low amount of impurities to be removed. The pressure drop along the reactor should be below 1 bar (industrial specification). Different catalyst shapes can be used (spheres or cylinders) with an average size ranging from 1 to 3 mm. Typical operating conditions are in the range of 30-100 bar for the pressure, and 100-200°C for the temperature.

4.2 Gas Composition and Impurities to Be Removed

This process is used for natural gas treatment. A typical gas composition is given in Table 8.

COS and CS_2 are the main impurities to be removed. The final concentration of both species should be lower than 1 ppm mol.

4.3 Reaction Scheme, Thermodynamics and Kinetics

As mentioned previously, COS and CS_2 can react with water in order to form H_2S, COS and CO_2 compounds according to the following reactions:

$$\mathrm{COS}_{(g)} + \mathrm{H_2O}_{(g)} \leftrightarrow \mathrm{CO_2}_{(g)} + \mathrm{H_2S}_{(g)}$$

Reaction 7

$$\mathrm{CS_2}_{(g)} + \mathrm{H_2O}_{(g)} \leftrightarrow \mathrm{COS}_{(g)} + \mathrm{H_2S}_{(g)}$$

Reaction 8

TABLE 8

Typical composition of natural gas

Feed composition	
Compounds	Vol.%
COS	0.0083
H_2S	0.0002
CO_2	2.0272
H_2O	0.1738
CS_2	0.0000
CH_4	97.790
Total	100.000

TABLE 9

Equilibrium constants

	a	b	Reference
Reaction 7	3796.1	−0.505	IFPEN data
Reaction 8	4163.9	1.063	Fact sage data http://www.crct.polymtl.ca/fact/

Both reactions are reversible. Thermodynamic equilibrium constants depend on the temperature as shown in Equation (1). Table 9 gives the corresponding thermodynamic parameters for the equilibrium constants:

$$\ln\left(\mathrm{K}_{eq,i}\right) = \frac{a_i}{T_{(K)}} + b_i \qquad i = \text{reaction number} = 7,\ 8 \tag{1}$$

For both reactions, an Eley-Rideal mechanism was used in order to take into account the inhibition effect of water. Kinetic rate expressions are given in Equation (2):

$$\begin{aligned} r_{7}{}_{(mol/s/kg\,cat)} &= \frac{b_7 \cdot k_7 \cdot \left(P_{\mathrm{COS}} \cdot P_{\mathrm{H_2O}} - \frac{1}{K_{eq,7}} \cdot P_{\mathrm{H_2S}} \cdot P_{\mathrm{CO_2}}\right)}{1 + b_1 \cdot P_{\mathrm{H_2O}}} \\ r_{8}{}_{(mol/s/kg\,cat)} &= \frac{b_8 \cdot k_8 \cdot \left(P_{\mathrm{CS_2}} \cdot P_{\mathrm{H_2O}} - \frac{1}{K_{eq,8}} \cdot P_{\mathrm{COS}} \cdot P_{\mathrm{H_2S}}\right)}{1 + b_8 \cdot P_{\mathrm{H_2O}}} \end{aligned} \tag{2}$$

Kinetic parameters for reaction 7 were estimated from lab scale experiments (Tab. 10). For reaction 8, kinetic parameters are taken from the literature [12].

4.4 Reactor Modeling

Material balances are written for each compound at different scales: in the gas flow, in the external mass transfer film around the catalyst pellet, and inside the catalyst porous network. For the gas flow, a dispersed-plug flow model was used to take into account a potential back-mixing effect. Equation (3) gives the corresponding gas material balance:

$$\begin{aligned} \varepsilon_g \cdot \frac{\partial C_i^g}{\partial t} = D_{ax}^g \cdot \frac{\partial}{\partial z}\left(\varepsilon_g \cdot \frac{\partial C_i^g}{\partial z}\right) - \frac{\partial\left(v_{sg} \cdot C_i^g\right)}{\partial z} \\ - k_{gs} \cdot \frac{\varepsilon_s}{L} \cdot \left(C_i^g - C_i^s\right) \end{aligned} \tag{3}$$

Gas axial dispersion coefficient was estimated using the Gunn correlation [13] (Eq. 4):

$$D_{ax}^g = \frac{v_{sg}/\varepsilon_g \cdot d_p}{Pe_a}$$

with

$$\begin{aligned} \frac{1}{Pe_a} = X \cdot (1-\phi)^2 + X^2 \cdot \phi \cdot (1-\phi)^3 \\ \cdot \left[e^{\left(-\dfrac{1}{X \cdot \phi \cdot (1-\phi)}\right)} - 1\right] + \frac{\varepsilon_g}{\tau \cdot \mathrm{Re} \cdot Sc} \end{aligned} \tag{4}$$

and

$$X = \frac{\mathrm{Re} \cdot Sc}{21.13 \cdot \varepsilon_g}, \quad \mathrm{Re} = \frac{\rho_g \cdot v_{sg} \cdot d_p}{\mu_g}, \quad Sc = \frac{\mu_g}{\rho_g \cdot D_m}$$

$$\phi = 0.17 + 0.33 \cdot e^{-\frac{24}{\mathrm{Re}}}, \quad \tau = 1.4 \quad \text{for sphere}$$

$$\phi = 0.17 + 0.29 \cdot e^{-\frac{24}{\mathrm{Re}}}, \quad \tau = 1.93 \quad \text{for cylinder}$$

The material balance in the external film is given by Equation (5):

$$\delta \cdot \frac{\partial C_i^s}{\partial t} = k_{gs} \cdot \left(C_i^g - C_i^s\right) - D_{eff,i} \cdot \left.\frac{\partial C_i^p}{\partial r}\right|_{r=R_p} \tag{5}$$

with $\delta = \frac{D_m}{k_{gs}}$ (film thickness)

and $L = \frac{V_p}{A_p}$ (characteristic length of the catalyst)

The mass transfer coefficient is given by the Yoshida correlation [14] which takes into account the gas flow pattern around the particle (Eq. 6):

$$\begin{aligned} Sh = 0.983 \cdot \mathrm{Re}^{0.59} \cdot Sc^{1/3} \quad \text{if } \mathrm{Re} > 190 \\ Sh = 1.66 \cdot \mathrm{Re}^{0.49} \cdot Sc^{1/3} \quad \text{if } \mathrm{Re} < 190 \end{aligned} \tag{6}$$

with $\mathrm{S}h = \frac{k_{gs,i} \cdot d_p}{D_{m,i}}, \quad \mathrm{Re} = \frac{\rho_g \cdot v_{sg} \cdot d_p}{\mu_g}, \quad Sc = \frac{\mu_g}{\rho_g \cdot D_{m,i}}$

Gas material balances should respect the equation of state $\sum_i C_i^g = \frac{P_t}{R.T}$. Then, after summing all the gas equations and

TABLE 10

Kinetic parameters

	k_i (mol/kg/s/Pa)	E (J/mol)	b_i (Pa^{-1})	ΔH ads (J/mol)	Reference
Reaction 7	10.78	58393	2.07E-09	−67352	IFPEN experiments
Reaction 8	1.85	56735	6.69E-15	−91787	[12]

introducing the equation of state, we obtain the corresponding equation for the gas velocity:

$$\Rightarrow \frac{\partial\left(v_{sg} \cdot P_t\right)}{\partial z} = D_{ax}^{g} \cdot \frac{\partial}{\partial z}\left(\varepsilon_g \cdot \frac{\partial P_t}{\partial z}\right) - R \cdot T \cdot \sum_i k_{gs,i} \cdot \frac{\varepsilon_s}{L} \cdot \left(C_i^g - C_i^s\right) \tag{7}$$

Particle material balances (Eq. 8 and 9) are written for two particle shapes (cylinders and spheres):

$$\text{Spheres } \varepsilon_p \cdot \frac{\partial C_i^p}{\partial t} = \frac{D_{eff,i}}{r^2} \cdot \frac{\partial\left(r^2 \cdot \frac{\partial C_i^p}{\partial r}\right)}{\partial r} + \sum_j \mu_{i,j} \cdot r_j \cdot \rho_s \tag{8}$$

$$\text{Cylinders } \varepsilon_p \cdot \frac{\partial C_i^p}{\partial t} = \frac{D_{eff,i}}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial C_i^p}{\partial r}\right) + \sum_j \mu_{ij} \cdot r_j \cdot \rho_s \tag{9}$$

with $\varepsilon_p =$ particle porosity.

The effective diffusion coefficient is a function of the molecular diffusion coefficient of each compound, the porosity and the tortuosity of the catalyst (as shown in Eq. 10):

$$D_{eff,i} = \frac{D_{m,i} \cdot \varepsilon_p}{\tau} \tag{10}$$

Molecular diffusion coefficients are estimated using the Füller correlation [15] (Eq. 11):

$$D_{iB} = \frac{1.43 \cdot 10^{-3} \cdot T^{1.75}}{P_t \cdot M_{iB}^{1/2} \cdot \left[(\Sigma_v)_i^{1/3} + (\Sigma_v)_B^{1/3}\right]^2} \quad \text{with} \quad M_{iB} = \frac{2}{\frac{1}{M_i} + \frac{1}{M_B}} \tag{11}$$

The effects of pressure and temperature were taken into account for the molecular diffusion coefficient.

Reactor pressure drop is calculated using the Ergun equation or the Handley equation according to the gas flow regime (Eq. 12):

Ergun:

$$\frac{dP}{dz} = \frac{150}{d_p^2} \cdot \frac{\varepsilon_s^2}{(1-\varepsilon_s)^3} \cdot \mu_g \cdot v_{sg} + \frac{1.75}{d_p} \cdot \frac{\varepsilon_s}{(1-\varepsilon_s)^3} \cdot \rho_g \cdot v_{sg}^2 \quad 0 < \mathrm{Re}/\varepsilon_s < 1000$$

Handley *et al.*: (12)

$$\frac{dP}{dz} = \frac{368}{d_p^2} \cdot \frac{\varepsilon_s^2}{(1-\varepsilon_s)^3} \cdot \mu_g \cdot v_{sg} + \frac{1.24}{d_p} \cdot \frac{\varepsilon_s}{(1-\varepsilon_s)^3} \cdot \rho_g \cdot v_{sg}^2 \quad 1000 < \mathrm{Re}/\varepsilon_s < 5000$$

4.5 Numerical Aspects

A spatial discretisation of the partial derivative equations was done using an upwind finite differences scheme for the convection terms and a centered finite differences scheme for the diffusion or dispersion terms. For time integration, the Lsode solver was used based on a predictor-corrector algorithm [16]. An excel interface coupled with Matlab (for 3D visualisation) was developed.

4.6 COSWEET$^{\text{TM}}$ Simulator

Figure 11 shows the model interface. For one simulation, the reactor geometry, operating conditions, the catalyst geometry and the gas composition can be changed.

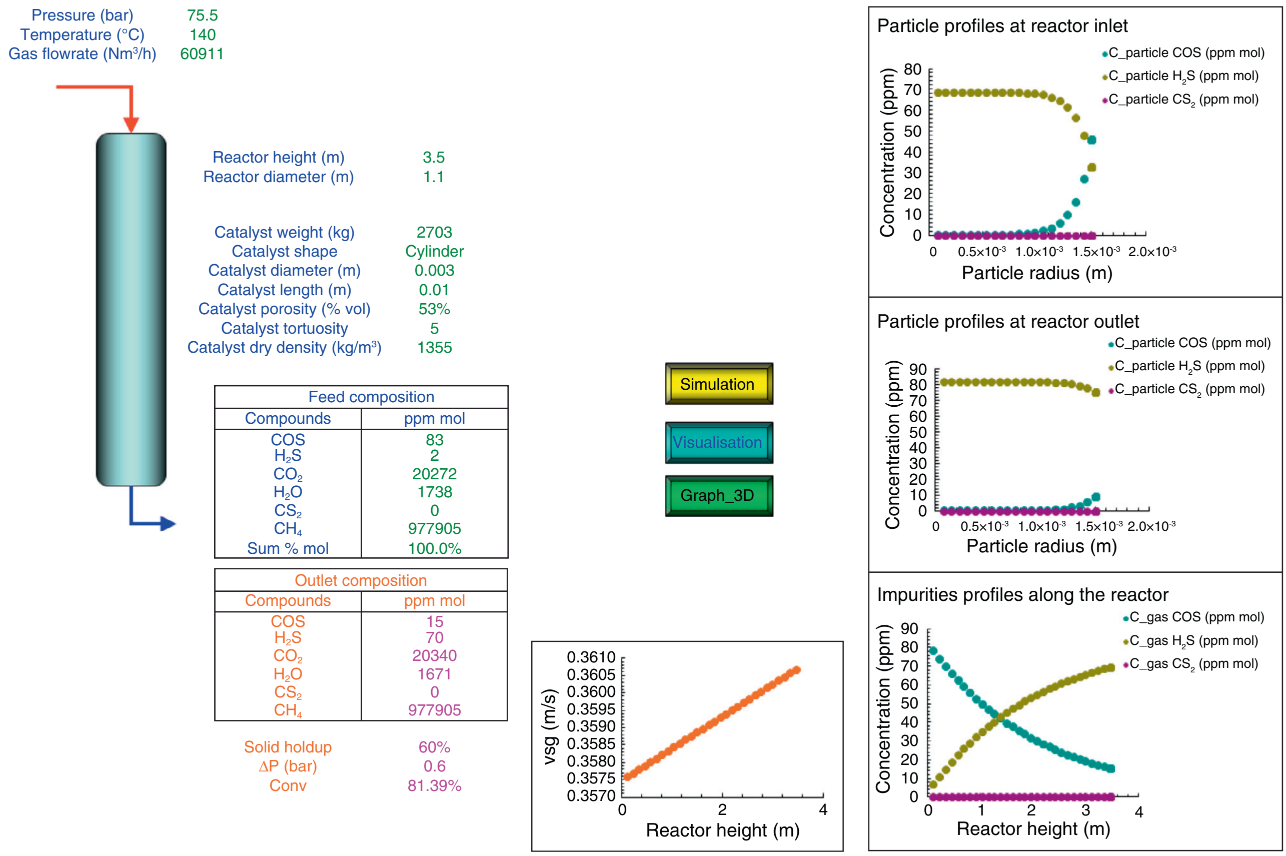
Figure 12 shows the COS intra-particle concentration profile at different reactor elevations.

As discussed in Section 3, transport limitations are indeed highlighted by the modeling performed for both lab-scale experiments and industrial case study. Significant transport limitations are observed at the bed inlet due to the high reaction rate. At the reactor outlet, there are less limitations due to lower COS gas content.

In both industrial and lab-scale, heat transfers have been neglected (isothermal conditions), as COS concentrations in every cases remain very low (<< 1%v).

4.7 Model Validation

The model was validated with experiments carried out in a lab scale fixed bed reactor for non-crushed and crushed catalysts.



Pressure (bar)	75.5
Temperature (°C)	140
Gas flowrate (Nm^3/h)	60911

Reactor height (m)	3.5
Reactor diameter (m)	1.1

Catalyst weight (kg)	2703
Catalyst shape	Cylinder
Catalyst diameter (m)	0.003
Catalyst length (m)	0.01
Catalyst porosity (% vol)	53%
Catalyst tortuosity	5
Catalyst dry density (kg/m^3)	1355

Feed composition

Compounds	ppm mol
COS	83
H_2S	2
CO_2	20272
H_2O	1738
CS_2	0
CH_4	977905
Sum % mol	100.0%

Outlet composition

Compounds	ppm mol
COS	15
H_2S	70
CO_2	20340
H_2O	1671
CS_2	0
CH_4	977905

Solid holdup	60%
ΔP (bar)	0.6
Conv	81.39%

Figure 11

Model interface.

Figure 13 shows a comparison between experimental and modeling data for COS conversion. A good agreement was obtained.

5 TECHNO-ECONOMIC EVALUATION

5.1 Case Study 1: Deep COS Removal with Bulk CO_2 Removal

The following example presents a CO_2 bulk removal application. The solvent used for acid gas removal is a formulated MDEA which is effective in absorbing H_2S and CO_2 and some of the COS. The COSWEET^{TM} process allows the removal of COS down to very low levels. The treated gas has to meet typical pipeline gas specifications: less than 4 ppm vol. H_2S and less than 2.0 vol.% CO_2. The COS specification is less than 0.5 ppm vol. The feed gas composition and conditions are given in Table 11.

The process scheme is as described in Figure 14. The absorber operates at relatively high temperature (85-90°C) because there is constant and intensive reaction of CO_2 with amine occurring on every stage of the column. The need for heating the extracted gas prior to entering the hydrolysis reactor is minimised, and no gas/gas exchanger is necessary, reducing the overall pressure drop.

If a traditional formulated MDEA process can easily reach the CO_2 and H_2S specifications, it does not allow complete removal of COS, even if the initial content is very low. Destruction of the COS by hydrolysis in a COSWEET^{TM} catalytic section allows slipping of the required amount of CO_2 with the treated gas, substantially reducing the size and the energy consumption of the amine section that would be traditionally designed with formulated MDEA. Table 12 presents the main sizing data of the COSWEET^{TM} process which guarantees the three required specifications to be met.

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

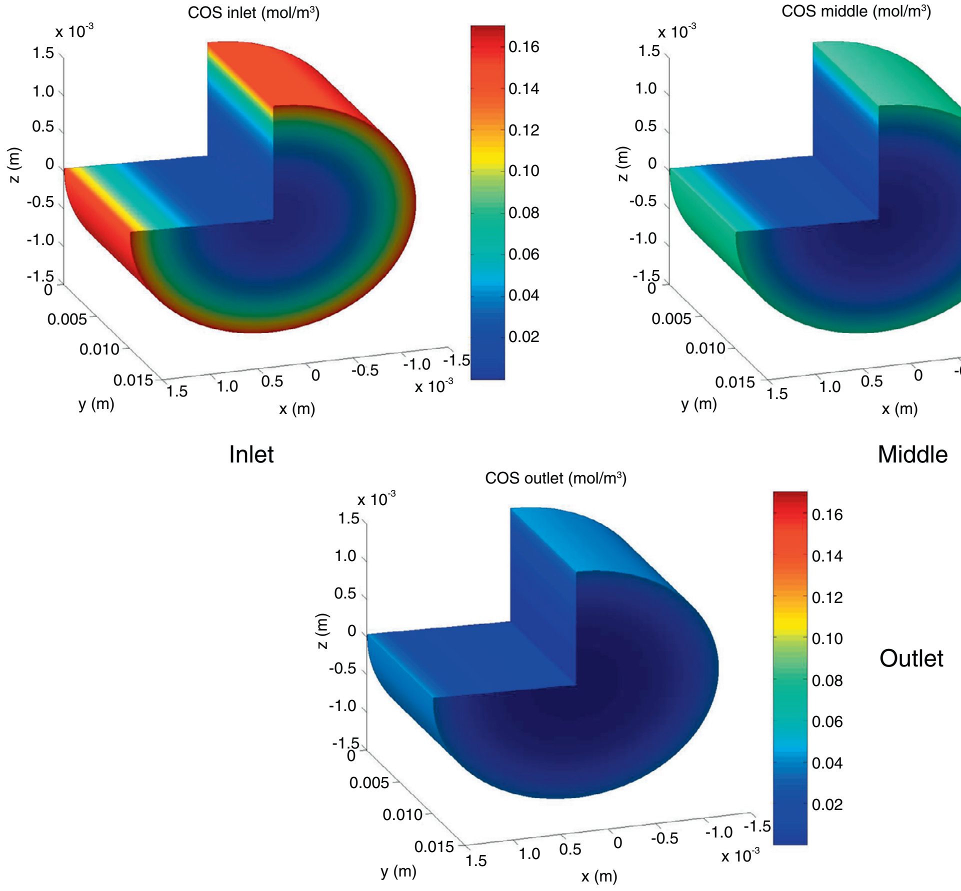


Figure 12

Particle COS concentration profiles at different axial positions in the reactor.

TABLE 11

Feed gas description

Component	Vol.%
CO_2	6.8
H_2S	0.0002
COS	0.0005
C_1	84.2
C_2	6.7
C_3	1.44
i+nC_4	0.4
i+nC_5	0.12
C_6^+	0.1
H_2O	0.24
Dry gas flow rate (MMm^3/d @ 1 atm. 15°C)	4.0
Pressure (bar g.)	93

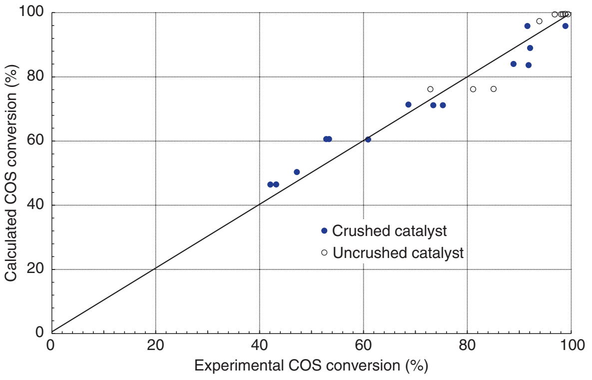


Figure 13

Parity plot for COS conversion with crushed and non-crushed catalyst.

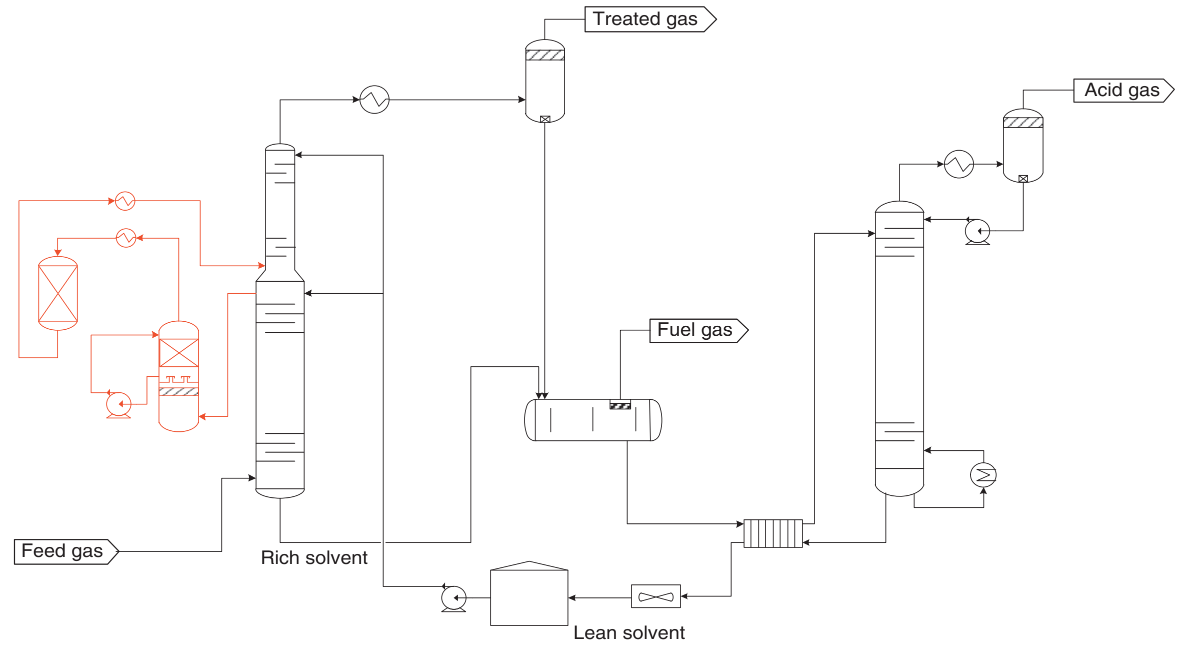


Figure 14

Process scheme.

TABLE 12

Main sizing data - COSWEET^{TM}

Bulk removal section (bottom)	
Amine solution flow rate (m^3/h)	150
Packing height (mm)	4000
COSWEET^{TM} catalytic section	
Mass of catalyst (tons)	16.3
Gas heater duty (MW)	1.0
Gas cooler duty (MW)	−2.9
"On-spec" section (top)	
Amine solution flow rate (m^3/h)	65
Packing height (mm)	3000
Amine reboiler duty (MW)	12.2

5.2 Case Study 2: Deep COS Removal with Selective Sweetening

The main purpose of the COSWEET^{TM} process is the removal of COS with the use of selective gas sweetening schemes using amine solvent that can produce a rich acid gas to the SRU, achieving at the same time a severe COS specification on the sweetened gas. The purpose of this case study is to explore the benefits of selective sweetening schemes, in addition to the removal of COS in high pressure AGRU.

The raw gas is first sent to the Acid Gas Removal Unit (amine based AGRU) and the separated acid gases are sent to a claus SRU followed by a selective amine Tail Gas Treatment Unit (TGTU). The overall sulfur recovery (in term of H_2S conversion) must be higher than 99.9%. The case study, based on different AGRU schemes that remove COS (COSWEET^{TM} or formulated MDEA) focuses on the impact of the different AGRU designs on the design of the sulfur recovery chain.

The design bases are presented hereafter. The feed gas composition on a wet basis along with conditions is given in Table 13.

The treated gas has to meet typical pipeline gas specifications for H_2S and CO_2: less than 4 ppm vol. H_2S and less than 2.0 vol.% CO_2. The COS specification is less than 1 ppm vol. The incinerator effluent specifications impose

TABLE 13

Feed gas composition and conditions

Component	Vol.%
CO_2	4.4000
H_2S	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_1SH	0.0075
C_2SH	0.0050
H_2O	0.0030
Dry gas flow rate (MMm^3/d @ 1 atm. 15°C)	12.98
Pressure (bar g.)	67.75
Temperature (°C)	25.0

TABLE 14

Treated gas and incinerator effluent specifications

Treated gas specifications	H_2S (ppm vol.)	4
	CO_2 (vol.%)	2
	COS (ppm vol.)	1
Incinerator effluent specifications	H_2S (mg/Nm^3)	15
	Total reduced S (CS_2, COS, H_2S) (mg/Nm^3)	50
	Unburnt hydrocarbons (mg/Nm^3)	20
	SO_2 (mg/Nm^3)	500

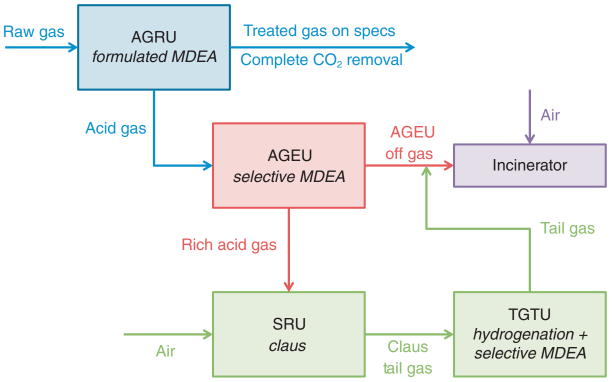


Figure 15

Base treatment case: formulated MDEA and AGEU.

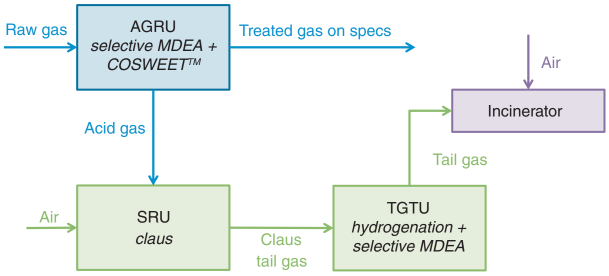


Figure 16

Selective AGRU + COSWEET^{TM}.

an effective destruction of all hydrocarbons, a reduced amount of sulfur compounds, and low sulfur emissions. Treated gas and incinerator effluent specifications are summarised in Table 14.

Two treatment options are considered:

- in base treatment case (Fig. 15), sweetening of the gas is achieved with formulated MDEA. This unit is designed to achieve the COS specification: the solvent flow rate and number of stages in the absorber are increased to enhance COS removal. This results in an almost complete co-absorption of CO_2 from the gas. As a consequence the H_2S content of the acid gas feeding the Claus unit is low, and the required overall sulfur recovery cannot be achieved. An Acid Gas Enrichment Unit (AGEU), using selective MDEA (MDEAmax process), is installed prior to the sulfur recovery chain to produce an acid gas of adequate quality to achieve the targeted sulfur recovery efficiency;
- in the second treatment option (Fig. 16), sweetening of the gas is done with a COSWEET^{TM} process combined with the use of MDEA as amine solvent. This process achieves

TABLE 15

AGRU - sizing data and performances

Option	Base case	COSWEET^{TM}
Bulk AG removal section		
Solvent flow (% of base)	100	61
ID (mm)	4000	3800
Height (*T*/*T*) water wash section included (mm)	30500	19500
COSWEET^{TM} reactor		
ID (mm)	-	3700
Polishing section		
ID (mm)	-	3100
Height (*T*/*T*) gas scrubber and water wash section included (mm)	-	19500
Treated gas quality		
H_2S (ppm vol.)	4	4
CO_2 (ppm vol.)	< 20	20000
COS (ppm vol.)	1	1
RSH (ppm vol.)	51	82

TABLE 16

Sulfur recovery - sizing data and performances

Option	Base case	COSWEET^{TM}
AG from AGRU (kmol/h)	2290	1860
H_2S content		
AG from AGRU (vol.% wet basis)	46.6	55.5
AG to SRU (vol.% wet basis)	58	47.8
BTX content		
AG from AGRU (ppm vol.)	550	300
Solvent flow AGEU/TGTU (% of base)	100	45
Overall sulfur recovery (%)	99.9	99.9
Overall sulfur production (tons/d)	809	809

TABLE 17

CAPEX comparison

Option	Base case	COSWEET^{TM}
CAPEX (arbitrary unit)		
AGRU	137	143
AGEU	69	-
SRU + incinerator	94	103
TGT	-	31
Total	300	277

TABLE 18

OPEX comparison

Option	Base case	COSWEET^{TM}
OPEX (Arbitrary unit)		
Steam	13.7	4.1
Power	2.6	1.5
Total	16.3	5.6

the severe COS specification and a sufficient CO_2 slippage with the treated gas to eliminate the need for an AGEU prior to sulfur recovery.

Units design and performances are presented in Tables 14 to 17. Significant sizing data and performances of the AGRU for the 2 options are summarised in Table 15.

Main performance data of the sulfur recovery facilities are presented in Table 16.

The capital costs of the treatment units for the 2 options are given in Table 17.

Table 18 indicates the yearly cost of steam and power, in the same arbitrary unit as used in Table 17.

These results demonstrate that COSWEET^{TM} offers an attractive solution for deep COS removal when selective H_2S removal would be desired. It reduces the necessary amine solution circulation rate and simplifies the sulfur recovery facilities. CAPEX and OPEX savings of the COSWEET^{TM}/selective amine integrated scheme compared to the usual formulated MDEA scheme are quite substantial (more than 7% for the CAPEX and more than 65% for the OPEX). This is due to the high efficiency of the hydrolysis catalyst at low temperature and the fact that while amine circulation rate in the AGRU is maintained at a low level, the H_2S selectivity is increased without the need of an AGEU. This low temperature catalyst allows a good heat integration of the COS removal section minimising energy consumption.

CONCLUSION

The COSWEET^{TM} process development is an example of the result of teamwork that benefits from the skill set of IFPEN, combined with an industrial approach integrating industrial constraints.

After a complete analysis of the gas treatment market, the gas treatment chain, existing processes and new challenges regarding raw acid gas compositions – with increasing amounts of acid gas contents like H_2S and CO_2 but also COS which contribute to the total sulfided compounds – an important challenge has been identified: what solution can be developed for COS removal while keeping a certain amount of CO_2 to meet gas pipe specifications?

A complete internal review of existing technical solutions for removal of COS, combined with other technical and industrial constraints such as hydrocarbon solubility, has been performed in order to select the catalytic solution to achieve deep COS specification. The best catalyst has been selected regarding its performance at low temperatures in order to optimise the integration in an industrial gas treatment chain.

Then different process schemes have been identified and short-cut models have been developed in order to check the technical capability of these different process schemes, taking into account gas compositions and thermodynamic constraints, but also the economic evaluation of each scheme, in order to check the economic viability of each solution. Based on this study, the COSWEET^{TM} scheme has been identified, a reactor model has been developed integrating thermodynamic and kinetic models, and kinetic measurements have been performed in order to collect all required data to estimate the model parameters.

COSWEET^{TM} is a process developed for the treatment of natural gases containing COS. 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^{TM} 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 hydrolysed gas back to amine absorber temperature.

The COSWEET^{TM} process can be combined with any amine, such as MDEA or formulated MDEA. This allows removal of COS down to very low specifications while maintaining some CO_2 in the treated gas. When sulfur recovery is associated with the gas sweetening, using COSWEET^{TM} to convert COS allows maintenance of a high H_2S/CO_2 ratio in the acid gas, which is required to optimise the gas treatment chain, including SRU. COSWEET^{TM} removes COS in the gas phase, meeting strict COS specification without an increase in amine solvent flow rate and reboiler duty. Evaluations have been performed on CAPEX and OPEX and they show that COSWEET^{TM} allows a reduction in the investment cost as well as the operating cost when compared to a formulated MDEA unit sized to reach the same COS specification.

When selectivity is required on a gas treatment, COSWEET^{TM} provides 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 H_2S content and low levels of hydrocarbons contaminants, without needing a dedicated acid gas enrichment unit.

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