A NEW CRYOGENIC DISTILLATION TECHNOLOGY FOR NATURAL GAS SWEETENING

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ABSTRACT

The paper introduces a new distillation process for natural gas purification from acid gas, namely CO_2 and/or H_2S.
The "traditional" chemical absorption of CO_2 and H_2S by means of alkanolamines is not competitive when the amount of acid gas is high, because the energy required for the solvent regeneration is proportional to the quantity of acid gas to be removed.
On the other hand, the cryogenic distillation technologies can be usefully applied to process natural gas with any amount of acid components, since the costs are incrementally reduced, the higher the acid gas content in the stream.
In the "traditional" separation methods CO_2 and H_2S are recovered at low pressures (nominally 1-2 bar) and need then to be compressed for re-injection into underground storage; on the contrary the distillation technology discharges the CO_2 and H_2S mixture as a high pressure liquid, with a commercial advantage when this stream is re-injected for storage into depleted reservoirs or for EOR purposes.
A "dual-pressure" distillation unit is proposed with its two sections (the high-pressure column for the CO_2 bulk removal and the low-pressure column for the methane recovery) working across the critical pressure of methane and the SVL locus of the binary CO_2-CH_4 mixture. This allows a complete separation of CO_2 and H_2S from methane, while avoiding the CO_2 freezing; the presence of H_2S helps in avoiding dry ice formation, since it increases CO_2 solubility.
A dynamic simulation study has been developed in order to validate the process architecture and to define the unit start-up procedure, while a laboratory experimental campaign is starting.

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1. INTRODUCTION

Technical studies by the International Energy Agency (IEA) and major Oil & Gas global players show that, over the next decades, natural gas demand will continue to experience a significant growth, outperforming other fossil fuels [1, 2, 3, 4]. According to the forecasts, by 2025 natural gas will become the second largest supply source behind crude oil [3]. One of the main drivers of this growth will be the higher need for power generation, where natural gas is expected to gradually replace coal due to its abundance and to its lower CO_2 emissions. In some regions a new promising market is also foreseen, since natural gas will become an alternative fuel for heavy-duty transportation, mainly due to its lower price and to the lower carbon footprint [3].

This higher demand will likely turn into the need to take into account new conventional and unconventional gas reserves, many of which are lying unexploited because of the high concentrations of carbon dioxide and hydrogen sulfide. Figure 1 shows that such sour and acid gas fields can be found in Europe, Africa, and South America, while Middle East, Central Asia, Far East and North America hold the largest volumes [5, 6].

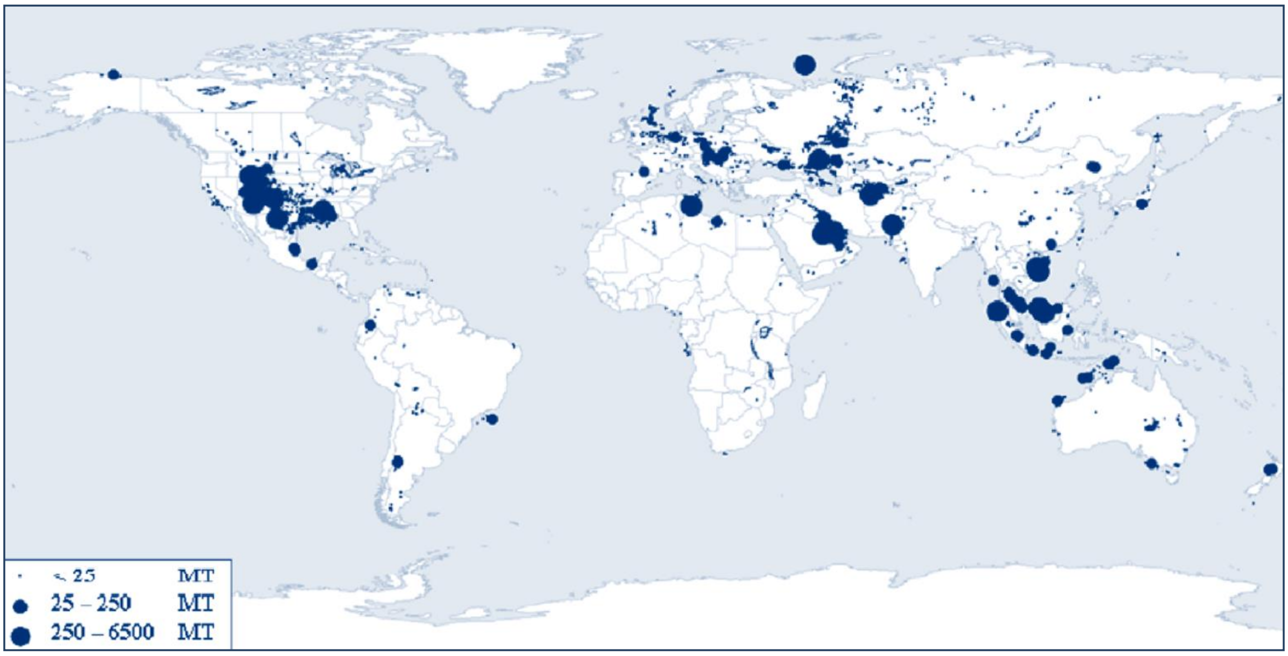


Figure 1. World distribution of the largest sour and acid gas reserves [6].

In particular, over the next years, Middle East Countries will experience a major increase in natural gas demand: this fossil fuel will be necessary in order to cope with the growing demand for electricity and for water desalination plants as well [3]. Many GCC Countries, after being natural gas exporters over the last decades, are today facing shortage problems, hence becoming net importers due to an imbalance between production and domestic gas demand [7]: this is why, in the last years, projects involving sour gas processing have been developed across the Region. For instance, in UAE, the sour gas field of Shah as well as the super-sour giant field of Bab are under development. Moreover, Middle East is also extremely rich of oil fields, hence fostering research interests in the application of Enhanced Oil Recovery (EOR) techniques by means of re-injection of the separated acid components. The use of acid gas components instead of raw natural gas for re-injection allows boosting oil production while unlocking additional gas supply [7, 8].

In the South East and in the Far East many countries have significant resources of highly acid and sour gases. China, Thailand, Vietnam and Pakistan are, presently, net importers of gas, the main reason being the excessive cost for extraction and treatment of the locally available natural gas reserves [9]. However, from a strategic perspective, in the next years one of the key points in the Energy field will be the security of supply, thus leading to the possible need of developing these domestic, highly acid, resources [1, 2, 3].

For the exploitation of acid and sour gas fields, either with existing and new technologies, the key economic driver is the cost to separate and recover the acid components (e.g. CO_2, H_2S). International and local environmental regulations push towards an increasing limitation of the CO_2 emissions to the atmosphere [8, 10], while H_2S recovery and conversion to sulfur can become limited by economical reasons. As a final result, in the exploitation of highly sour gas fields, an interesting option seems to be the separation of acid gas components alongside with their re-injection into the well.

While several process options to remove acid components exist, nearly all of them reject H_2S and CO_2 as a low pressure gaseous stream [11], therefore leading to high recompression costs for the subsequent re-injection.

The new acid and sour gas sweetening process, based on an innovative cryogenic distillation scheme [12], allows the separation of acid components as high pressure liquid while still being able to meet the required specifications on the sweet gas. In principle, it can represent a promising solution for the unlocking and exploitation of acid and sour gas fields.

2. CRYOGENIC DISTILLATION TECHNOLOGY: ADVANTAGES AND ISSUES

Cryogenic distillation for the sweetening of natural gas has been a topic of discussion for many years, but without significant applications. In recent years, International and National Oil Companies and O&G Technology Providers have intensified their efforts for the application of this technology on an industrial scale.

For the treatment of highly acid and sour natural gas, cryogenic distillation offers competitive advantages over other techniques nowadays widely used, such as chemical absorption with aqueous solutions of alkanolamines [13]. In fact, the proportionality coefficient between the energy consumption and the CO_2 content in the feed stream is much lower for distillation than for chemical absorption. Furthermore, with cryogenic distillation, the stream composed of the separated acid components is liquid at high pressure, therefore more suitable for re-injection and EOR.

At a first sight, distillation is an attractive process for gas sweetening, due the strong volatility difference between methane and the acid components; however, when trying to produce methane with the purity required by commercial applications, CO_2 will precipitate into a solid phase (Figure 2).

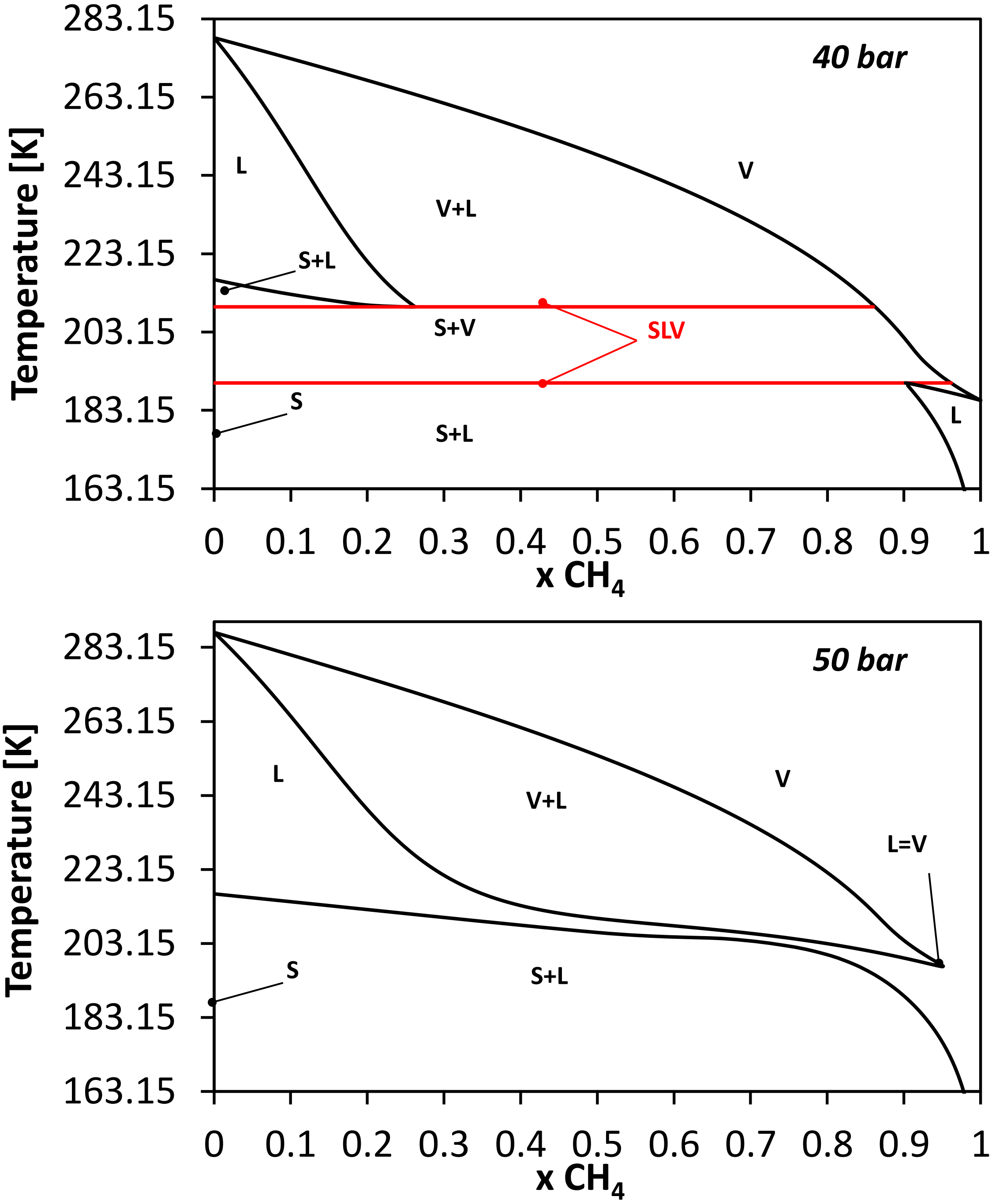


Figure 2. Isobaric phase diagrams for the CH_4-CO_2 binary system at 40 and 50 bar(a).

The distillation operation occurs in the vapor-liquid area of the phase diagrams. When performing a direct distillation of the inlet gas feed, CO_2 freezing can be avoided by operating the distillation at pressures higher than the one corresponding to the maximum of the solid-liquid-vapor locus of the binary CH_4-CO_2 mixture.

Considering the isobar at 50 bar(a), it is possible to observe that the VLE and the SLE areas are completely separated, hence no dry ice can be formed during distillation since it is not possible to have a solid phase in the presence of both liquid and vapor phases at this pressure. However, since the critical pressure of methane is below 50 bar(a), the gas cannot be purified to commercial grade, and the limit is given by the mixture critical point.

The formation of solid CO_2 during distillation can be avoided also by operating the process at pressures under the maximum of the SLV locus of the mixture: considering the isobar at 40 bar(a), the VLE area intersects the SLV locus in two points. When operating the distillation in these conditions, the limit is given by the gas composition corresponding to the one of the first triple point at high temperature, but, also in this case, the commercial specification cannot be fulfilled using only one distillation step.

The general conclusion is that, when operating with a single standard distillation column, the product, regardless of the operating pressure, has a high residual content of CO_2 that does not meet the required purity specifications for pipeline and LNG applications (CO_2 content respectively 2%v, and 50 ppmv).

In order to overcome the issue of CO_2 freezing, different processes have been proposed in the past.

One process is based on an extractive distillation with the addition to the acid natural gas of simple alkanes or other non-polar liquids, with the objective to significantly increase the solubility of solid CO_2 into the liquid phase [14]. This process has the drawback of requiring a further separation in order to recover the additive.

A different approach is based on the use of an *ad hoc* designed distillation column, with a special section in which carbon dioxide solidification occurs [15]. The dry ice formed in this section is then melted onto a special tray, with the resulting liquid flowing to the lower part of the distillation column.

Other multistep processes based on the coupling of cryogenic distillation and other techniques (e.g. amine washing, membrane separation) have also been developed [16, 17]. These processes make use of cryogenic distillation as a first step for acid gas bulk removal, with a single column operating at pressures around 30-40 bar(a). The residual CO_2 content in the overhead product is around 15-20% so to avoid solid formation; hence this stream is further processed with amines or membranes in order to meet the required specifications.

3. THE NEW CRYOGENIC DISTILLATION TECHNOLOGY

The proposed cryogenic distillation is a patented solution [12] jointly developed by Stamicarbon and Tecnimont (Maire Tecnimont Group) with Politecnico di Milano. The process manages the critical issue posed by CO_2 solidification in a different way from the techniques already known in literature: the distillation is carried out by means of two standard columns operating at different pressure levels. Figure 3 shows a base scheme and one of the developed alternative solutions, improved as to energy consumption, of the proposed new process.

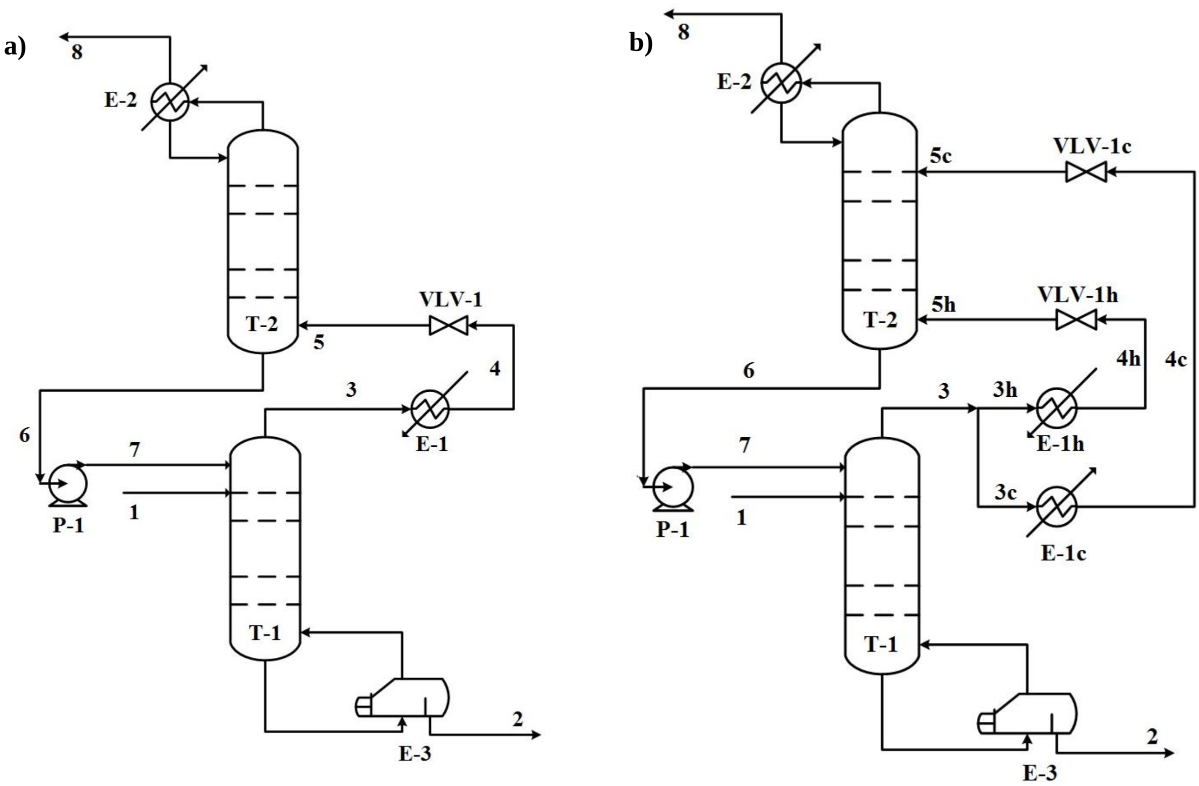


Figure 3. a) Base scheme of the proposed new process and b) optimized process layout.

The acid or sour natural gas to be treated is fed into a high pressure (or hot) column, working typically around 50 bar(a), where solid carbon dioxide solubility is such that no precipitation can occur. The bottom product is a high pressure liquid stream, containing all the components having a lower volatility than methane (e.g. CO_2, H_2S). The overhead product, a gaseous stream enriched in the lightest natural gas components, is fed to a low pressure (or cold) column, working typically around 40 bar(a). In order to avoid solid CO_2 formation, this gaseous stream (or part of it as in Figure 3.b) is heated above its dew point at the working pressure of the low-pressure column and then, before entering the column, the pressure of the stream is reduced while avoiding the occurrence of solid deposition. In the optimized scheme the stream 3c is cooled down and, after expansion, enters the low-pressure column as a liquid.

The final purification is carried out in the low-pressure column. The overhead product meets the required purity specifications for pipeline or LNG applications; the bottom product (enriched in CO_2) is pumped back as a liquid reflux to the high-pressure column. The CO_2 concentration in this bottom product is controlled in order to avoid solid deposition.

Figure 4 qualitatively describes the system behavior. The first column works at 50 bar(a), out of the freezing zone and in such a way that the product has a residual content of CO_2 that is beyond the boundary of the freezing zone (point A). The product is then fed to the second column (point B), working at a lower pressure, thus allowing to obtain a product meeting the required purity specification.

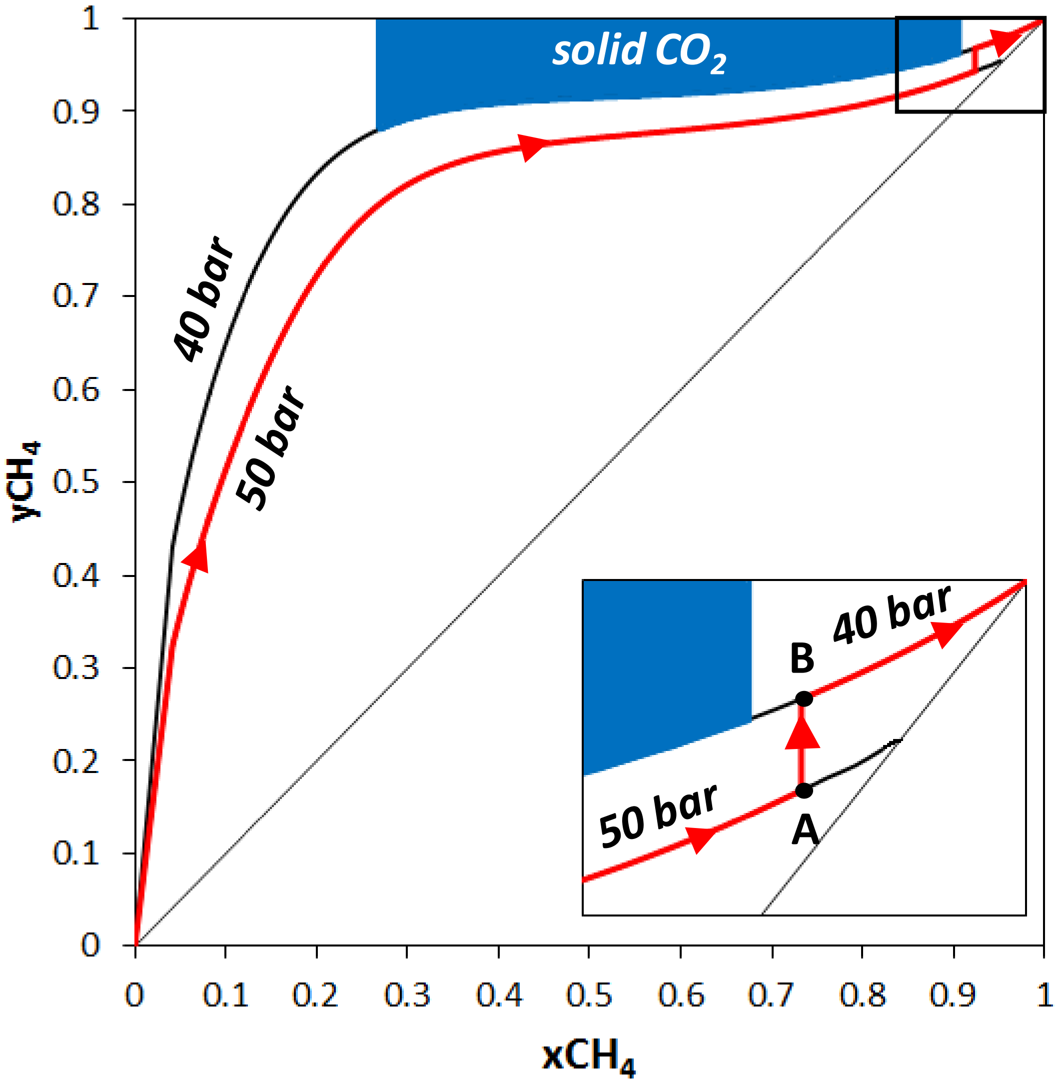


Figure 4. y-x diagram with the distillation path of the new proposed cryogenic distillation process.

Since the only equipment required by this process are standard distillation columns, heat exchangers and pumps available in every commercial simulator library, the entire system has been successfully modeled with Aspen HYSYS® [18]. In order to define the optimal operating conditions, and, in particular, to verify that no CO_2 freezing occurs, an *ad hoc* routine has been developed [19, 20].

The new process has been modeled for a wide range of different feed gas compositions (with a CO_2 content ranging from 5 to 75%v) and for conditions and compositions of actual gas fields as well: results show that, though meeting the required purity specification, the sweet gas can be obtained without incurring in carbon dioxide freezing. The presence of H_2S into the raw feed does not represent a limitation to this process. The required H_2S specification in the sweet gas is also met, and, since this component has a lower volatility than CO_2, it is almost completely recovered in the acid gas bottom stream.

This process enables, by means of cryogenic distillation only, an almost complete methane recovery while meeting the required purity specification for the sweet gas. The basic process configuration can be tailored to specific gas field characteristics and to Customer needs; the process byproduct is a high pressure liquid stream that can be conveniently re-injected for storage/sequestration or EOR purposes.

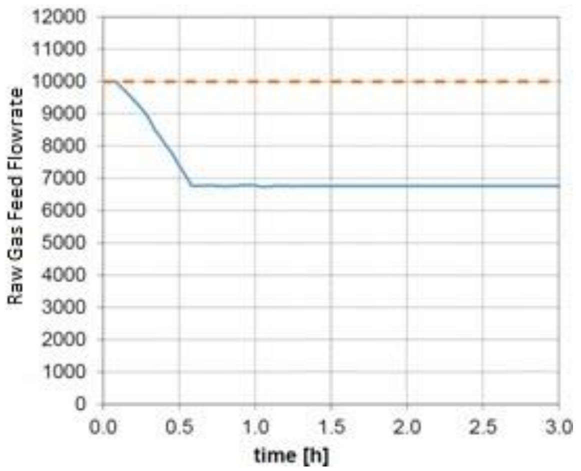
4. PROCESS OPERABILITY AND STABILITY TESTS: DYNAMIC SIMULATION STUDY

In order to assess the operability and the stability of this new process, a dynamic simulation study has been performed by means of commercial software (Aspen HYSYS Dynamics® [21]). The process control architecture, practically the same of traditional distillation systems, has been successfully modeled.

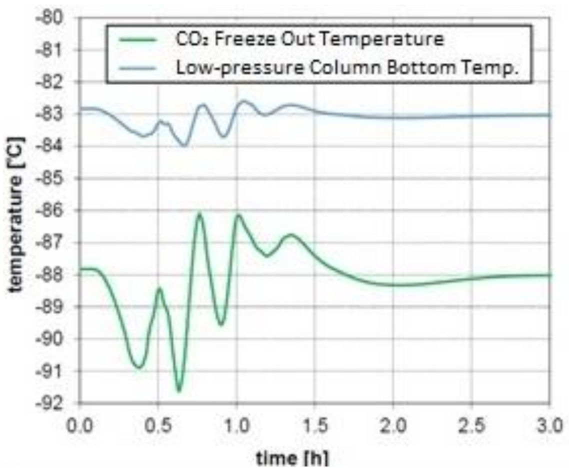
To study the dynamic response and the robustness of the entire system, different upsets leading to new operating conditions have been studied, in particular:

- a rapid decrease of the raw gas feed flow rate (Figure 5);
- a change in the raw gas composition with a ramp increase of the CO_2 content (Figure 6).

The results of the simulations show the process robustness, i.e. the system responds to disturbances by reaching new, stable operating conditions with a safe margin on the CO_2 solidification region even during the transient.



a)



b)

Figure 5. Response of the system to a rapid decrease of raw gas feed flow rate.

a) b)

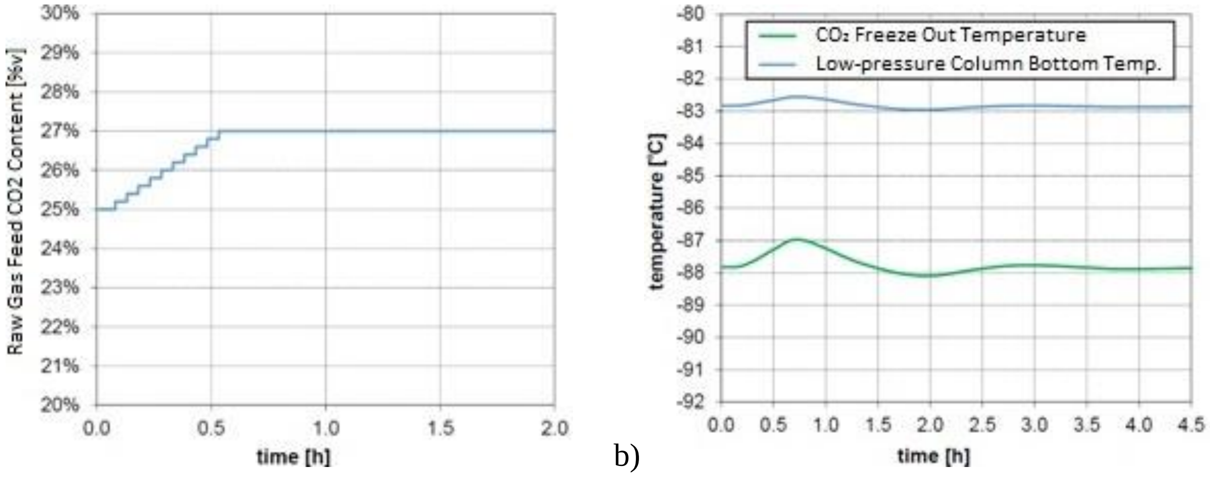


Figure 6. Response of the system to a change in the raw gas composition.

Major upsets, e.g. low-pressure column reflux pump failure and high-pressure column reflux pump failure, have also been studied.

Results confirm that, in case of major upsets, enough time is guaranteed for the successful intervention of plant operators (start-up of spare equipment), before the occurrence of CO_2 freezing.

5. FUTURE DEVELOPMENTS

A laboratory scale pilot plant, complete with all the ancillaries required for the distillation of acid gas mixtures at high pressure and low temperature, is at present under construction in Piacenza, Italy. The plant will allow testing the cryogenic distillation of different acid gas mixtures (total acid content in the range of 5-75%v) either in normal (start-up, steady state, shutdown) and upset conditions. The first experimental campaign is scheduled to start before the end of the current year 2015.

Studies aiming to prove the technical feasibility of the process on industrial scale are under way. The basic design package of a semi-industrial scale demonstration plant with a nominal capacity of 10 MMSCFD has been already completed. The main features of the items and components have been defined, and a preliminary 3D model of the plant (Figure 7) has been developed. Future engineering developments will include the detailed design of a skid mounted small scale process plant for offshore applications and the detailed design of an onshore large capacity process plant.

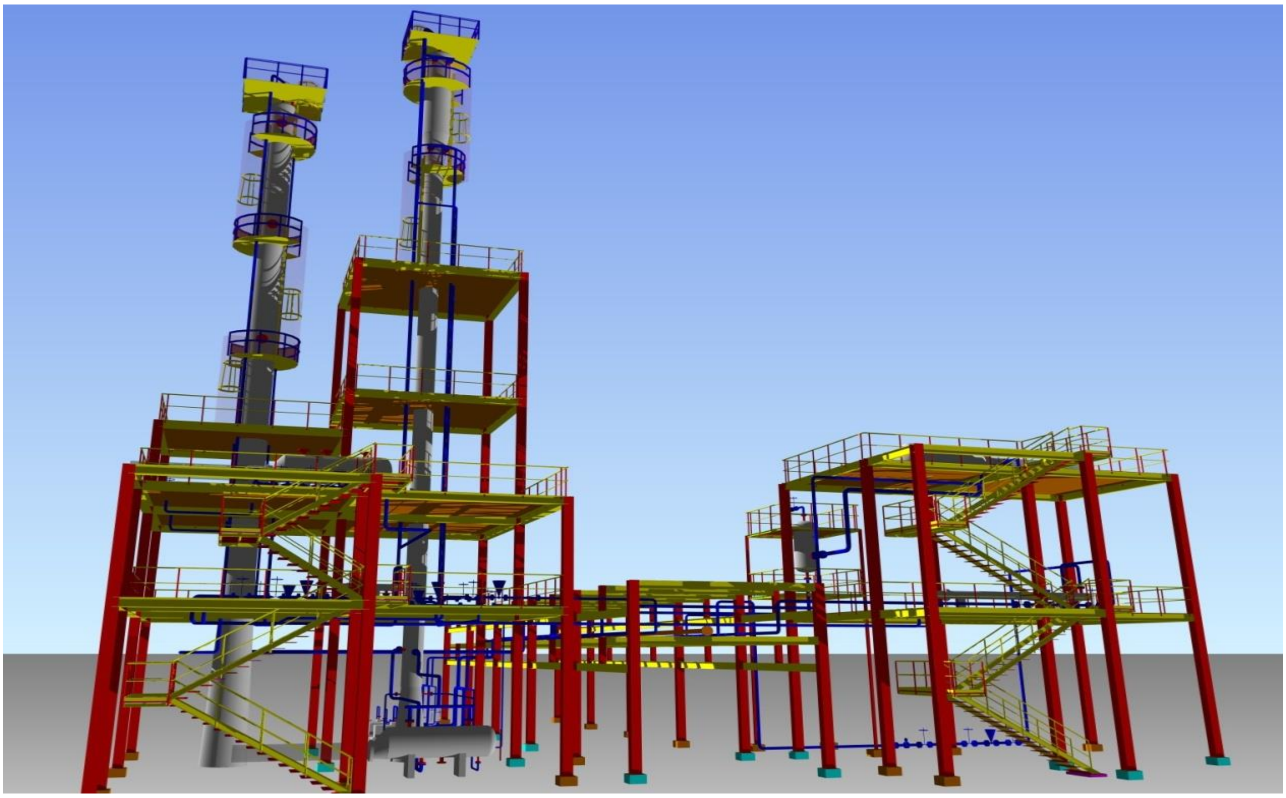


Figure 7. 3D snapshot of the engineered, semi-industrial scale, demonstration plant.

6. CONCLUSIONS

An innovative process for the cryogenic distillation of acid and sour gas mixtures has been developed and patented. The process is based on a dual-pressure distillation unit, operated always outside of the CO_2 freezing zone. The typical drawbacks of distillation at cryogenic temperature (i.e. solid CO_2 build-up) are therefore avoided. For this reason, the use of specially designed equipment, or the use of additional components is not needed.

Since it is based on standard equipment (distillation columns, heat exchangers and pumps), the process has been easily modeled with commercial process simulators. In particular, a dynamic simulation study has been performed (Aspen HYSYS Dynamics®) showing that the process is robust and flexible even with major upsets.

On the basis of the growing natural gas demand, very acid and sour gas fields are becoming a more and more valuable resource. Due to its features, this process is competitive in comparison to the most used purification technologies, for high contents of acid components in the gas stream to be sweetened.

Moreover, the acid components are recovered as a high pressure liquid, which represents a remarkable advantage in case of re-injection.

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