The route to recovery

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Introduction

As CO_2 emission is becoming an increasing issue in the oil and gas industry and alternative fuels are being investigated, CO_2 capture and H_2 production technologies are being developed and improved continuously. One of the sources of CO_2 emission is the flue gas from sulphur recovery units (SRUs), especially in gas plants where substantial amounts of CO_2 are present in the feed gas to the SRU. This paper studies the options that are available to recover this CO_2 from the SRU and in parallel recover hydrogen, a carbon-free fuel.

To capture CO_2 and recover H_2 form the SRU, modifications have to be made to the SRU to maximize the potential for CO_2 capture and H_2 recovery. This paper presents a case study highlighting these modifications and subsequently evaluates the available technologies for optimized CO_2 capture and H_2 recovery both from a technical and a commercial perspective.

Plant line-up

The line-up considered in this study is a commonly applied line-up in a natural gas plant, consisting of an amine base acid gas removal unit (AGRU) removing the acid gas components from the main gas stream, resulting in an acid gas feed to the sulphur plant consisting of typically more than 60% H_2S and approximately 30% CO_2, with the remainder being some hydrocarbons and water vapor.

The sulphur recovery unit considered is a standard modified Claus unit, consisting of a thermal stage followed by two catalytic stages. The tail gas of the Claus unit is routed to a tail gas treating unit (TGTU), in which the remainder of the sulphur species is converted to H_2S, absorbed and recycled to the Claus section. The overall recovery of the SRU and TGTU is more than 99.9%, which ensure the flue gas from the incinerator section contains less than 500 mg/Nm^3 SO_2, which is considered to be state-of-the-art.

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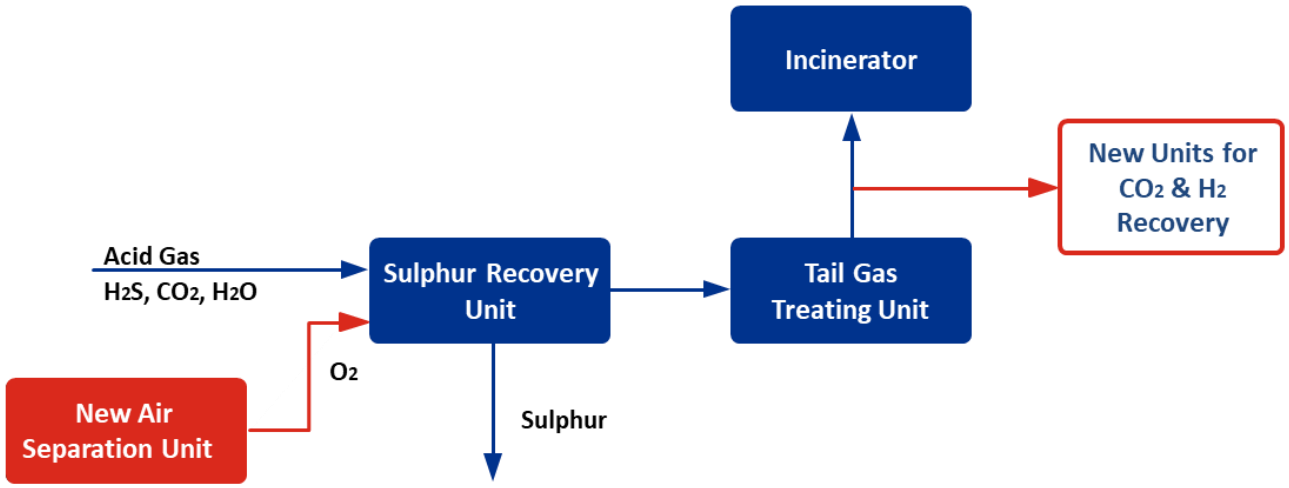
Location for CO_2 capture

The potential locations that were identified for CO_2 capture were the following:

- Front-end capture in the acid gas
- Pre-combustion capture in the TGTU off-gas
- Post-combustion capture in the flue gas from the incinerator.

Previous studies showed that the optimum/preferred location for CO_2 capture is in the off gas from the TGTU absorber, since front-end capture will require substantial modification to the AGRU, whereas post-combustion capture has to deal with strongly diluted CO_2 streams and requires flue gas pre-treatment before the gas can be handled in the CO_2 capture system. Also, both front end capture and post-combustion technology will not be able to produce H_2, since no H_2 is present in the AGRU gas, whereas for post-combustion the H_2 is burned in the incinerator.

To maximize the production of H_2 and to minimize the dilution of the CO_2 it is considered to convert the SRU from standard air operation to high level oxygen enrichment, such that the flow of inerts (mainly nitrogen) through the SRU is minimized. In the sketch below the proposed line-up with the optimum CO_2 and H_2 recovery unit is represented:



SRU modification

For the plant that was studied, the actual sulphur processing capacity was considered to be adequate and capacity increase was not required. The proposed modifications to the SRU/TGTU equipment were minimal since less gas needed to be processed. Retrofitting the SRU/TGTU for high level oxygen enrichment only required modification of the burner to introduce the oxygen. The thermal reactor temperature was still within acceptable operating limits since the acid gas was relatively lean. The single stage combustion in the thermal reactor could be retained.

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The SRU is provided with a degassing system to remove dissolved H_2S from the liquid sulphur, such that a premium sulphur quality is produced with less than 10 ppmwt H_2S. This degassing system gives a vent air stream which is routed to the incinerator, where any sulphur species are converted to SO_2. In air operation this results in a marginal increase of SO_2 in the flue gas, but since the gas flow from the SRU is strongly reduced when there is no nitrogen in the TGTU off gas, the SO_2 resulting from the vent air is not diluted, resulting in increased SO_2 concentrations in the small flue gas stream, even though the absolute emission in kg/h is reduced. For this reason, it is advised to align the emission values with the industry standard and use the EPA formula to correct for the actual oxygen content in the combustion medium to the thermal stage, which ultimately results in this reduced flue gas dilution.

With the above conversion to oxygen blown SRU, the gas from the TGTU absorber contains about 65% CO_2, 16% H_2, 6% N_2 and traces of CO, H_2S and COS. The absorber off-gas is saturated with water vapor.

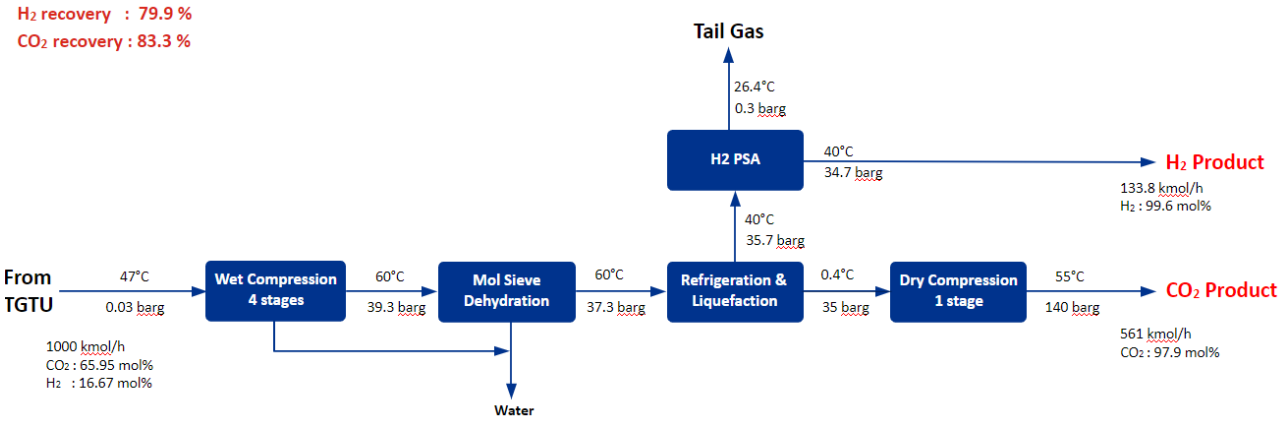
Selection of CO_2 capture options

The options considered for CO_2 recovery were the following:

- Chemical (amine-based) absorption
- Cold flash
- Adsorption
- Physical Solvent Absorption
- Membrane technology
- Cryogenic Separation

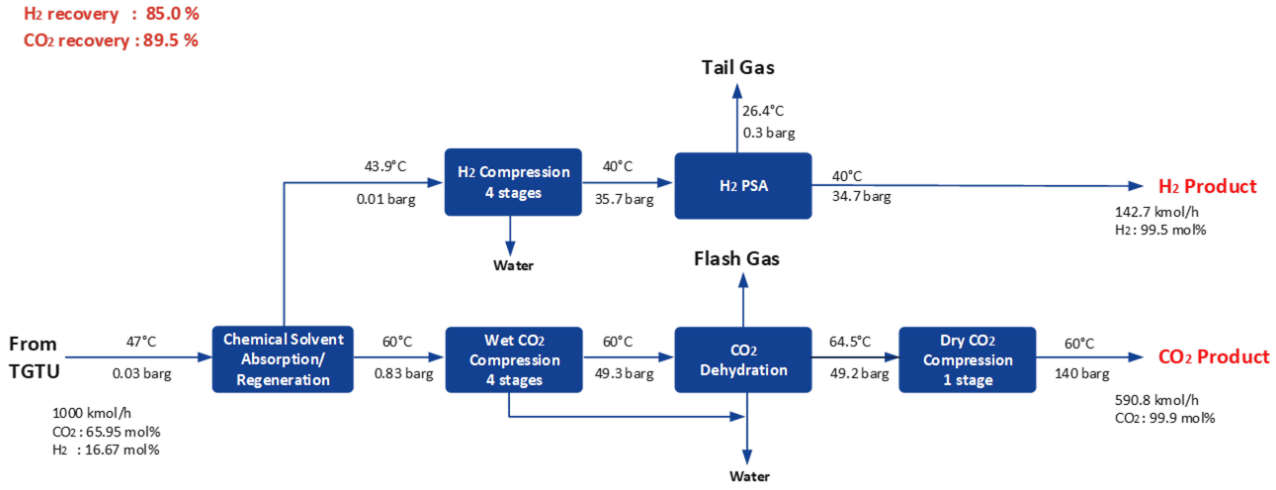
From these options, a first screening showed that chemical absorption and cold flash were the most viable options, and these options were further evaluated in this study. For the H_2 recovery, pressure swing adsorption was considered.

A simplified block flow diagram for the cold flash option is provided below:



The gas from the TGTU absorber is compressed to approx. 40 bar and dried in a mol sieve unit. The dry gas is then cooled and partly liquefied by cooling against propane. In this step the liquid CO_2 is separated from the gas in a flash vessel. After the separation, the CO_2 is evaporated again and routed to a dry CO_2 compression stage where it is boosted to 140 barg, which is the preferred pressure for the CO_2 injection facilities. The non-condensed gas, which mainly consists of H_2, is routed to the PSA unit, where the H_2 is separated with a purity of more than 99.5%. The remainder of the gas (mainly N_2 with traces of CO, H_2S and COS) is routed to the incinerator before emitting the gas to atmosphere. The overall H_2 recovery form the TGTU tail gas is around 80%, whereas the CO_2 recovery is nearly 85%.

A simplified block flow diagram for the chemical absorption option is provided below:



The gas from the TGTU absorber is routed to another absorber, which operates at near atmospheric pressure. In the absorber the bulk of the CO_2 is absorbed, and that loaded solvent is stripped in a regenerator. From the regenerator the CO_2 is routed to a compressor and dehydrated. Ultimately the CO_2 is delivered to the injection facilities at 140 barg and a very high purity of 99.9%. The off gas from the CO_2 absorber, which mainly consists of H_2, is compressed to nearly 40 barg. During compression, condensed water is separated, and the gas is routed to the PSA unit, where the H_2 is separated with a purity of more than 99.5%. Similar to the cold flash option, the remainder of the gas (mainly N_2 with traces of CO, H_2S and COS) is routed to the incinerator before emitting the gas to atmosphere. The overall H_2 recovery form the TGTU tail gas is around 85%, whereas the CO_2 recovery is nearly 90%. With that, the performance of the chemical absorption is marginally better than for the cold flash option, but that can be tweaked at a later stage. Note that for the above two block flow diagrams a "normalized" tail gas flow of 1000 kmol/h from the TGTU absorber has been assumed.

Assessment of the selected technologies

A qualitative first assessment of the cold flash and chemical solvent option is provided in the table below:

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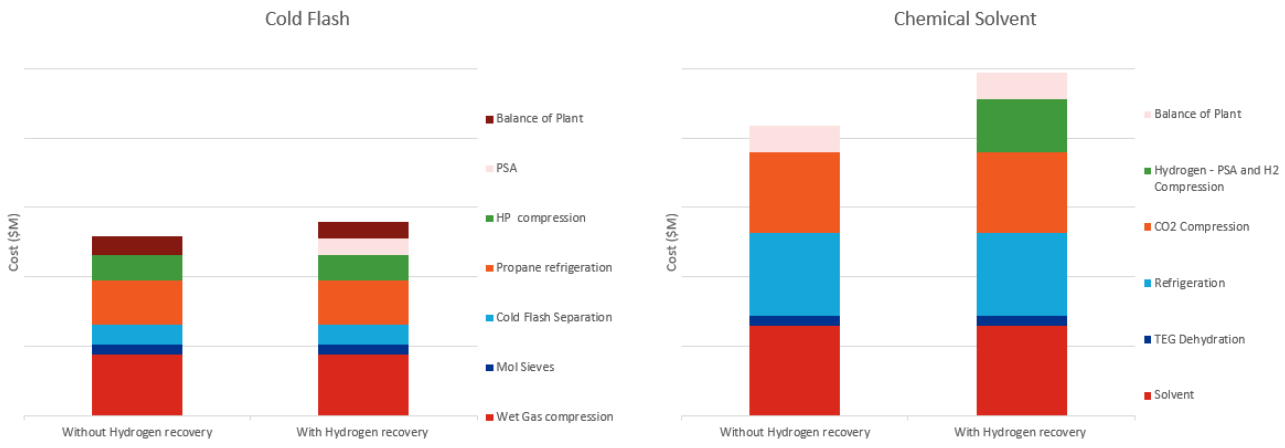
	Cold Flash	Chemical Solvent
Pros	• Simplicity of the process • Low equipment count • No proprietary solvent - no license fee • Lower utility consumption • Inherent safety	• Technology readiness & maturity • Proven technology • High CO_2 & H_2 recovery • Product Quality
Cons	• Limited known applications for CO_2 removal • Lower CO_2 & H_2 recovery • COS specification is not met	• High equipment count • More plot space required • Construction logistics are more challenging due to higher equipment count & larger diameters • COS hydrolysis uncertainty limits H_2S content allowable in the TGTU off-gas

As in other comparison studies, a first step is to make a sized equipment list and a high-level capital cost estimate. For the cold flash option and for the chemical absorption option, this results in the following graph:



From this graph it can be seen that the simple cold flash option without H_2 recovery has lowest investment cost, partly because it has the lowest number of equipment and high refrigeration cost for the chemical solvent option. Especially the fact that in the cold flash option only one compressor is required to compress the gas from the TGTU absorber to 40 barg is determining the lower investment cost. The addition of H_2 recovery adds additional cost but this will be paid out rapidly when the additional value of the recovered H_2 is considered.

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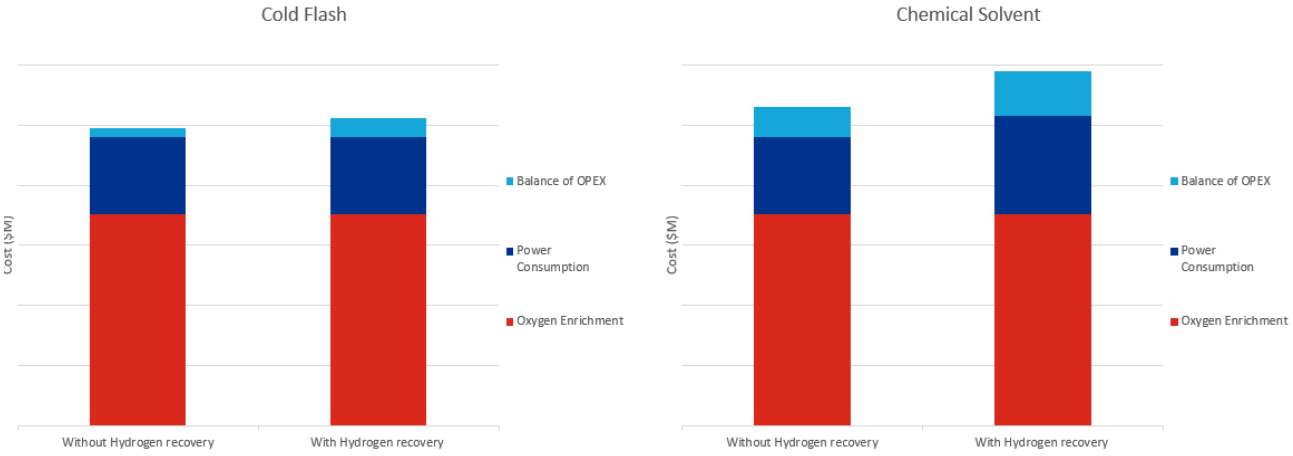
In a similar way, the operational cost can be estimated, resulting in the below graph.



In this graph a similar trend as for the investment cost can be seen, with cold flash without H_2 recovery giving the lowest operational cost, and chemical absorption with H_2 recovery giving the highest operational cost.

The capital cost and operating cost were subsequently used to develop the so-called Unit Technical Cost (UTC), which gives the cost per unit of product produced (in this case CO_2 and H_2) taking into account the required investment cost and 20 years of operating cost. This UTC is normalized against the UTC for chemical absorption without H_2 recovery, and is summarized in the table below:

	Without H_2 recovery	With H_2 recovery (hydrogen @$1.0/kg)	With H_2 recovery (hydrogen @$1.5/kg)
Cold Flash	90	75	65
Chemical solvent	100	94	84

From this table it can be seen that the cold flash option with hydrogen recovery gives the lowest UTC. Despite the higher investment cost and the higher operating cost, the revenue from the recovered H_2 gives a substantial improvement in the cash flow position, resulting in the lowest UTC for that option.

Although the economic criteria are a large factor in deciding which technology to select, other factor come into play as well.

The criteria considered are given below, each with their weight factor in the total evaluation.

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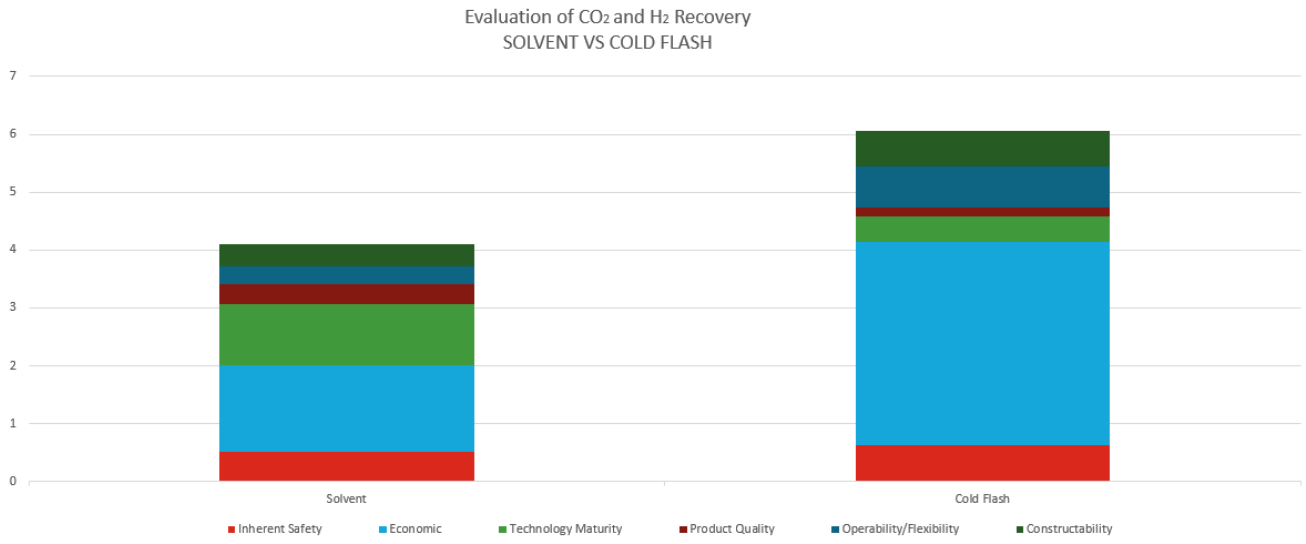
Selection criteria

- Inherent Safety – 10%
- Economic (UTC) – 50%
- Technology Maturity – 15%
- Product Quality – 5%
- Operability/flexibility – 10%
- Constructability – 10%

The above criteria are each ranked with a figure between 1 and 10 and combined with the above weightage, this results in the graph below:



From this graph it can be concluded that the cold flash technology with PSA is the preferred technology for CO_2 and H_2 recovery.

Conclusion

From this study it is concluded that 100% oxygen enrichment is the preferred route for processing the acid gas in the SRU when CO_2 and H_2 capture is to be considered, since it will result in the most concentrated/ less diluted gas stream for the CO_2 and H_2 recovery and with that will minimize the investment cost and operating cost for the CO_2 and H_2 recovery. On top of that, 100% oxygen enrichment will result in the highest H_2 formation in the thermal reactor, making H_2 recovery an economical option. Considering the

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relative ease at which the H_2 can be recovered as a product, this additional processing step is highly recommended.

For the CO_2 capture, the cold flash option seems to be the most promising one, since it results in the lowest (relative) UTC for the produced CO_2 and because of the simplicity of the process. Also, the operability, flexibility and constructability are considered more positive for the cold flash technology when compared to the chemical absorption technology.

It should be noted that this study was performed at a high level, and optimizations have not yet been addressed and with no specific CO_2 recovery target. In a next phase the reduction of the cooling/ refrigeration duty could be further evaluated, as well as potential reduction in equipment count. This might change the individual contributions for these criteria somewhat, but it is expected that it will not change the final conclusion that oxygen operation with cold flash and PSA is the preferred option for CO_2 and H_2 recovery downstream an SRU/TGTU complex.

Interested or have any questions? We're ready to help.

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