



14th International Conference on Greenhouse Gas Control Technologies, GHGT-14

21st -25th October 2018, Melbourne, Australia

Study of different configurations for CO₂ removal in SMR plant for hydrogen production

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Abstract

The production of hydrogen by steam methane reforming (SMR) requires a step for purification of the product-rich stream from carbon dioxide, which, after the water gas shift reaction, is the component (other than H₂) present in the highest amount.

This work focuses on the evaluation of different configurations for the MDEA scrubbing system with the aim of defining a scheme that allows for energy saving. This is fundamental for this type of processes, in order to make the CCS technology being operated with low economic impacts, also in fields which are not directly related to the power production.

Simulations of the CO₂ removal system have been carried out in ASPEN Plus[®], customized for the description of the thermodynamically non-ideal system, and the best configuration has been defined.

Results show that modifications of the operating conditions and addition of units as flash vessel or splitter for the rich amine solvent can help in reducing the energy requirement.

Keywords: CO₂ removal, shifted syngas, hydrogen production, energy saving.

1. Introduction

Hydrogen is used extensively for a wide range of applications, being a key raw material to other energy intensive industries, mainly employed for the production of chemicals such as ammonia and methanol, and in oil refining for hydrotreating. It has been estimated that the amount of hydrogen required for these applications is about 90% of the one globally produced [1].

H₂ can be produced by steam methane reforming at high temperature, to obtain a gaseous mixture whose main components are carbon monoxide and hydrogen, with residual methane and little amount of CO₂. This gaseous stream, exiting the reformer, is then processed in shift reactors, where carbon monoxide reacts with steam to produce a mixture rich in carbon dioxide and poor of CO. The carbon dioxide is removed from the shifted gas in order to obtain a stream rich in hydrogen, with high purity units, though also other technologies may be employed.

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The tail gas from this equipment is used for the burners of the Steam Methane Reformer (SMR), from which a stream rich in carbon dioxide exits.

In this type of process, then, streams with CO₂ content can be found in three different parts of the plant:

- in the reformer and in the water-gas shift reactor;
- in the PSA tail gas;
- in the flue gases from the burner of the SMR,

and CCS technologies may be applied for its removal. While for post-combustion removal from flue gases usually traditional MonoEthanolAmine (MEA) solvent is used, for removal of CO₂ from the shifted syngas and from the PSA tail gas the chemical absorption technology by aqueous MethylDiEthanolAmine (MDEA) scrubbing can be employed.

MDEA presents some advantages if compared to MEA, as lower heat of absorption and lower corrosion rates. However, the operation of a purification plant is expensive also with this type of amine, in particular because of the heat requirement in the regeneration section, so the usually employed baseline scheme for purification from CO₂ could be improved for allowing energy savings, as recently stated in a report by IEAGHG [1].

Several modifications to amine scrubbing systems are reported in the literature [2-5]. The focus is mainly on studies for application to post-combustion CO₂ capture from flue gases of power plants [2-4], often by employing an aqueous solution of MEA at near atmospheric pressure. However, a previous work on an analysis related to pre-combustion CO₂ removal sections of IGCC plants by MDEA scrubbing has shown that configurations alternative to the one considering only the typical absorber and desorber can allow energy saving [5].

This work focuses on the study of the purification section in a steam methane reforming plant for production of hydrogen, located downstream the reformer and the water-gas shift reactor, and aims at comparing different schemes for removing carbon dioxide from the shifted syngas.

2. Considered schemes

The gas to be treated is available at 35°C and 26 bar, with a flowrate of about 19.4 kg/s. Its composition (detailed in Table 1) is rich in hydrogen (about 76%) and carbon dioxide (about 16%), which must be removed in order to let only 4 mol/s of carbon dioxide in the purified gaseous stream, with a percentage of CO₂ removal equal to 98.65%.

Table 1. Characteristics of the shifted syngas stream to be purified [1].

Parameter	Value
Temperature [K]	308.15
Pressure [bar]	26
Molar Flow [kmol/sec]	1.833
Mass Flow [kg/sec]	19.37
Component	Value
CO ₂	0.1627
H ₂ O	0.0024
CH ₄	0.0305
CO	0.0463
H ₂	0.7561
N ₂	0.0020

The amount of carbon dioxide is high, therefore a high flowrate of circulating MDEA solvent is needed in the plant. This increases the energy consumption, in particular in the regeneration section of the plant, where steam is employed to run the reboiler. In this unit, indeed, heat is provided to:

- reverse the chemical reactions occurring in the absorber;
- heat the liquid mixture up to the operating temperature of the reboiler;
- generate a vapor flowrate used for stripping along the column.

Alternative configurations are usually considered with the aim of reducing one or more of these contributions, and therefore to decrease the total heat requirements. In this paper, the addition of a flash vessel and the split of the rich stream into two parts have been considered for alternative schemes. The flash vessel makes part of carbon dioxide leave the rich solvent before entering the distillation column, while the rich split option allows to decrease the amount of heat needed to bring the liquid mixture to the operating temperature of the reboiler and to modify the vapor flowrate flowing along the column, so as to reduce the vapors generated in the reboiler.

Table 2. Operating conditions of the units for the considered schemes.

	Configuration 1 (reference case)	Configuration 2	Configuration 3	Configuration 4
Case	1 Flash 6 bar	2 Flash 6-3 bar	2 Flash 6-1 bar	2 Flash 6-1 bar, rich split 10%
Absorption column				
Operating pressure [bar]	26	26	26	26
Temperature of the feed gas [K]	308	308	308	308
Temperature of the solvent [K]	313	313	313	313
High Pressure Flash Vessel				
Operating pressure [bar]	6	6	6	6
Operating temperature [K]	344	344	344	344
Low Pressure Flash Vessel				
Operating pressure [bar]	-	3	1	1
Operating temperature [K]	-	353	353	353
Lean-Rich Heat Exchanger				
Pressure Drop [bar]	0.1	0.1	0.1	0.1
$\Delta T_{\text{approach}}$ [K]	10	10	10	10
Approach on side	cold	cold	cold	cold
Splitter				
% split cold rich stream	-	-	-	10%
Distillation column				
Operating pressure [bar]	2.9	2.9	2.9	2.9
Temperature of the rich solvent [K]	383	383	387	390
Feed height of hot rich split stream [m]	-	-	-	7.5
Condenser temperature [K]	322	322	322	322
Reboiler temperature [K]	401	401	401	401

Table 2 reports the operating conditions of the main units of the considered schemes, which are described in the following.

2.1. Configuration 1 (reference case)

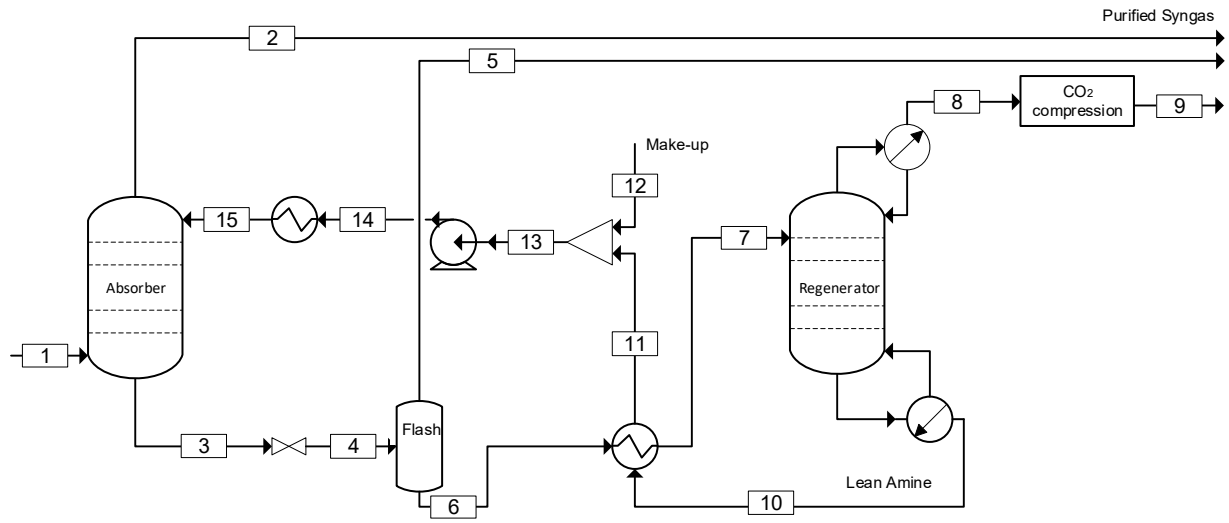


Fig. 1. Scheme of the reference case.

The base scheme (Fig. 1), taken as reference case in this work, is composed of one absorption column, one flash vessel and one regeneration column. The two columns are packed units with height equal to 20 m and diameter of 3.4 m for the absorber and 4.9 m for the desorber.

The raw syngas is fed to the absorber, where it is counter currently contacted with 452.29 kg/s of lean amine solution (lean loading = 0.025) flowing downwards, thus exiting purified from the top. The MDEA solution, rich in carbon dioxide, is sent to a flash vessel operated at 6 bar for the recovery of the co-absorbed hydrocarbons which are then sent to the furnace, and warmed in a process-process lean-rich heat exchanger by the hot lean solvent coming from the bottom of the regeneration column. It is then fed to the top of the stripper for removal of carbon dioxide (exiting from the top), and recycled back to the absorption column after pumping and cooling.

2.2. Configuration 2

Fig. 2 reports a scheme composed of two flash vessels. The configuration is similar to the one of the reference case, but with the addition of a further separation unit at a pressure lower than the pressure of the first unit. In this way, it may allow to pre-remove additional CO_2 from the rich solvent, which is fed to the distillation column with a lower amount of acid gas to be separated.

The pressure of this flash vessel has been chosen in accordance with the one of the distillation column, and considering the pressure drop in the lean-rich heat exchanger. The stream exiting from the low pressure flash is mixed with the one from the top of the distillation column and sent to compression.

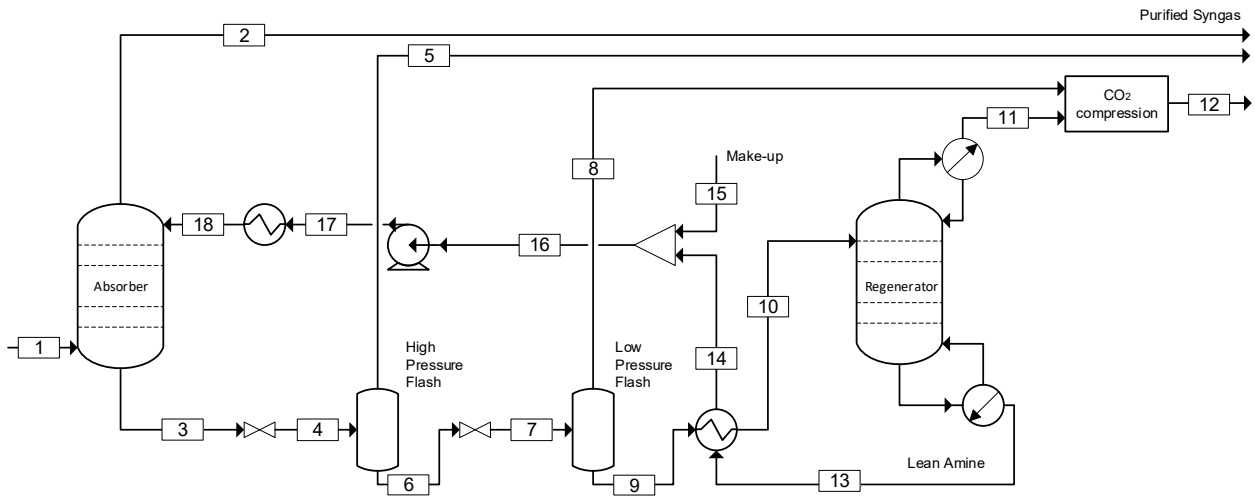


Fig. 2. Scheme with two flash vessels.

2.3. Configuration 3

This scheme is very similar to “*Configuration 2*”, with the flash operated at 1 atm in order to enhance the carbon dioxide release in this unit. Being the pressure lower than the one of the regeneration column, a pump is needed to bring the pressure of the rich stream exiting the flash and entering the lean-rich heat exchanger up to 3 bar. The CO₂-rich stream exiting from this unit is at lower pressure than the one exiting from the distillation column, therefore an additional compression is needed before mixing the two streams.

This configuration needs additional units for pumping and compression, for which additional work is required, however the operation of the flash at lower pressure than the one in “*Configuration 2*” allows to recover more carbon dioxide in the gaseous stream exiting from the separation vessel, thus reducing the heat needed at the reboiler and the employed steam.

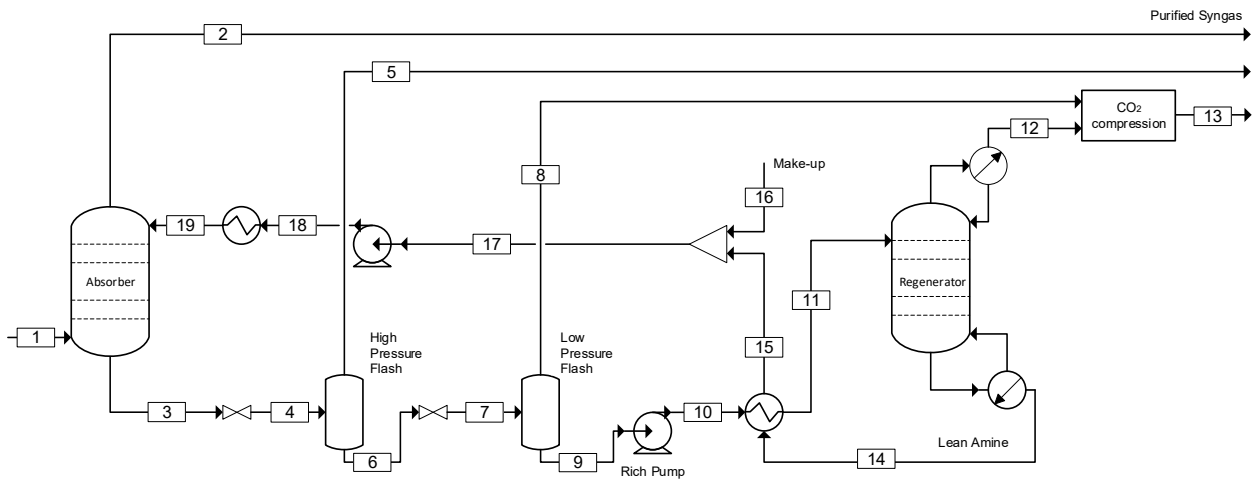


Fig. 3. Scheme with two flash vessels and the pump for the rich solvent.

2.4. Configuration 4

A modification of “*Configuration 3*” in order to achieve a higher saving in reboiler consumptions is shown in Fig. 4.

By the addition of a splitter, the rich stream exiting from the pump can be split into two streams. One stream is fed to the lean-rich heat exchanger for the recovery of the heat content of the lean stream exiting the distillation column, while the second stream is directly fed to the regenerator, without being pre-heated. This modification was firstly proposed by Eisenberg and Johnson [6] and later applied by Cousins et al. [2] to the post-combustion CO₂ removal plant by MEA aqueous solution, resulting in a saving of energy of about 10%. In this work it has been applied to a different system (MDEA scrubbing for purification of H₂-rich stream), already provided with two flash vessels, to evaluate whether a similar reduction of energy requirement for the purification plant can be obtained.

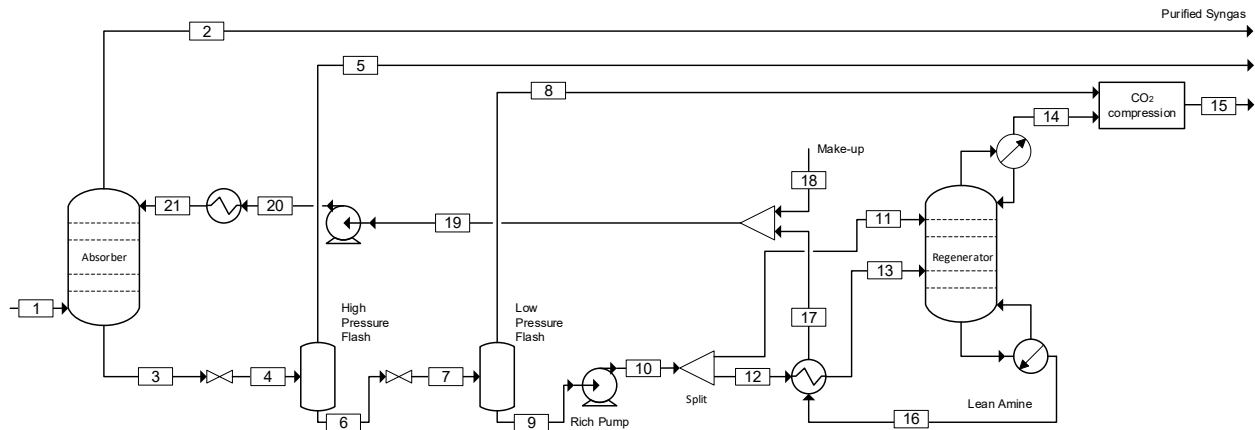


Fig. 4. Scheme with two flash vessels, the pump for the rich solvent and the rich split.

3. Results and discussion

Simulations have been carried out for the configurations described in Section 2. The commercial software ASPEN Plus[®], previously customized for thermodynamics [7,8] and mass transfer [9], has been employed for simulations of the MDEA scrubbing plant.

CO₂ compression system consists in a multistage intercooled compression process, calculated with ASPEN Plus[®] with assumptions consistent with the ones in a previous work [5]. The number of intercoolers has been defined in order to avoid stream temperatures exceeding 100°C at the outlet of each compressor.

The study has been performed by maintaining the same column dimensions and the same amount of CO₂ to be absorbed of the reference case, while the operating conditions and the solvent flowrates to single units may have been modified in order to run the plant with low operating costs.

Table 3. Obtained results for the considered schemes.

	Configuration 1 (reference)	Configuration 2	Configuration 3	Configuration 4
Case	1 Flash 6 bar	2 Flash 6-3 bar	2 Flash 6-1 bar	2 Flash 6-1 bar, rich split 10%
Lean pump power [MW]	1.27	1.27	1.27	1.27
Rich pump power [MW]	-	-	0.10	0.10
Temperature of the rich solvent [K]	383	383	387	390
Reboiler duty [MW]	40.42	40.42	31.40	27.86
Reboiler duty [MJ/kg _{CO2abs}]	3.122	3.122	2.425	2.152
Compression power for stream exiting from distillation column [MW]	3.124	3.124	1.636	1.647
Compression power for stream exiting from distillation column [MJ/kg _{CO2}]	0.242	0.242	0.242	0.242
Compression power for stream exiting from Low Pressure Flash [MW]	-	0.008	1.950	1.950
Compression power for stream exiting from Low Pressure Flash [MJ/kg _{CO2}]	-	0.283	0.316	0.316

For all the configurations, the main operating expense of the plant is related to the reboiler duty, as usually occurs in amine scrubbing systems [10]. The power required for pumping the lean amine solvent is the same for all the considered cases, since the flowrate and the composition of the lean solution is the same. For schemes that need pumping of the rich solvent (because the pressure of the distillation column is higher than the one of the low pressure flash) the additional needed power is low while the saving in the heat requirement is high.

The reboiler duty needed in “*Configuration 1*” is equal to 40.42 MW, but can be decreased if modifications are applied. Adding a second flash (“*Configuration 2*”) operated at 3 bar, close to the pressure of the distillation column, does not allow to obtain energy saving for this system because of the low vapor flowrate generated in this unit. In case the added separator is run at 1 atm (“*Configuration 3*”) power for pumping the rich solvent and additional power for compressing the CO₂-rich stream exiting from the low pressure flash are required, but, on the other hand, the decrease in steam consumption at the reboiler is relevant.

With no split, the total rich solvent stream is fed to the top of the desorber. In the rich split scheme (“*Configuration 4*”), only the cold rich stream is fed to the top of the unit, while the hot rich stream can be fed at a different height.

The split percentage has been varied in order to minimize the reboiler duty. Indeed, the vapour formed by heating the rich solvent enhances the performances of the regeneration column: by feeding the solvent at lower heights, the vapour released flows upwards the column and can pre-strip the cold rich solvent entering the top of the column, allowing further release of carbon dioxide in the top stages of the unit. However, additional energy must be provided by the reboiler for heating the cold split stream up to the operating temperature of the unit. Therefore, there is a trade-off between the advantage obtained by vapours formed by heating the rich solvent and the disadvantage of further heating of the cold split stream. Table 4 reports the results obtained for different split percentages, showing that a split of 10% is better than a split of 5% or 15%. This result is strongly related also to the temperatures in the lean-rich heat exchanger. By lowering the amount of rich solvent fed to this unit, a higher temperature can be obtained, up to the maximum temperature approach (10°C). When the $\Delta T_{\text{approach}}$ occurs on the hot side of the heat exchanger, no additional heat recovery can be obtained in this unit and increasing the split percentage only causes an increase in the reboiler duty because of the need of heating a higher cold split flowrate entering the top of the

column. A comparison (Table 3) between “*Configuration 3*” and “*Configuration 4*” shows that the reduction obtained with the rich split modification (11%) is in the range of the one already found for other amine systems [2].

Introducing also a splitter for feeding two streams at different heights and different heat contents to the distillation column allows further advantages with respect to “*Configuration 3*”, and the lowest heat requirement is obtained.

Table 4. Influence of the split percentage on the operation of the plant for “*Configuration 4*”.

Case	2 Flash 6-1 bar, rich split 5%	2 Flash 6-1 bar, rich split 10%	2 Flash 6-1 bar, rich split 15%
Lean-Rich Heat Exchanger			
Pressure Drop [bar]	0.1	0.1	0.1
$\Delta T_{\text{Approach}}$ [K]	10	10	10
Approach on side	cold	cold	hot
Splitter			
% split (cold rich stream)	5	10	15
Distillation column			
Temperature of the rich solvent [K]	389	390	391
Reboiler duty [MW]	29.27	27.86	28.45
Reboiler duty [MJ/kg _{CO2abs}]	2.261	2.152	2.197
Compression power for stream exiting from distillation column [MW]	1.647	1.647	1.647
Compression power for stream exiting from distillation column [MJ/kg _{CO2}]	0.242	0.242	0.242
Compression power for stream exiting from Low Pressure Flash [MW]	1.950	1.950	1.950
Compression power for stream exiting from Low Pressure Flash [MJ/kg _{CO2}]	0.316	0.316	0.316

4. Conclusions

This paper deals with the study of an alternative configuration for the section of removal of carbon dioxide from the shifted syngas generated by steam methane reforming in a hydrogen production plant. Several schemes have been considered, including two flash units, operated at different pressures, a pump for the rich amine solvent and the rich split, which allows to split the rich solvent before feeding the two split streams at different temperatures and different heights of the regeneration column.

Results show that taking advantage of the benefits of all the above mentioned units allows a reduction of the energy requirement and thus of the operating costs while requiring small changes to the plant.

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