

# GLYCOL DEHYDRATION OF CAPTURED CARBON DIOXIDE USING ASPEN HYSYS SIMULATION

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## ABSTRACT

Water must be removed from carbon dioxide ( $\text{CO}_2$ ) after capture because of risk for corrosion and hydrate formation. The level of accepted water content after dehydration depends on the next step for the captured  $\text{CO}_2$ , and can be in the range between 5 and 500 parts per million (ppm) on a volume basis. A water specification of 50 ppm is a traditional specification for pipeline transport. Absorption into triethylene glycol (TEG) followed by desorption is a traditional gas dehydration method, and can also be used for  $\text{CO}_2$ . For very low water content, use of solid adsorbents is expected to be the preferred method. There are very few references in the open literature on simulation of  $\text{CO}_2$  dehydration. It is in this work demonstrated that it is possible to simulate both a traditional glycol dehydration process and more advanced  $\text{CO}_2$  dehydration processes using different equilibrium models in the process simulation program Aspen HYSYS. Depending on the water content specification for the captured  $\text{CO}_2$ , different processes modifications have been suggested. It is simulated reasonable process alternatives for  $\text{CO}_2$  dehydration down to water levels below 5 ppm.

**Keywords:**  $\text{CO}_2$ , glycol, dehydration, Aspen HYSYS, simulation

## INTRODUCTION

### Water specifications for $\text{CO}_2$ dehydration

$\text{CO}_2$  capture and storage has been extensively studied as a possible way to mitigate global warming. Removal of water (dehydration) from captured  $\text{CO}_2$  is necessary to avoid corrosion and hydrate formation under transport and storage. The need for water removal from  $\text{CO}_2$  and possible specifications are discussed in several references [1,2,3]. In some cases, a water level of 500 ppm (by volume) has been accepted. A specification of 50 ppm is a traditional specification for pipeline transport.  $\text{CO}_2$  for enhanced oil recovery normally requires a stricter water specification.

### Dehydration methods

There are several different gas dehydration methods available. The simplest dehydration method is by cooling, water condensing and gas/water separation. Other methods are dehydration by absorption, adsorption or by using membranes.

The most traditional method for large scale dehydration to moderate water levels is by absorption into triethylene glycol (TEG). For very low water levels, adsorption processes are necessary [4]. Membrane dehydration is economical only for low gas flow rates [5].

### Process simulation programs

Process simulation programs solve material and energy balances and calculate vapour/liquid equilibrium in different unit operations like tanks,

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heat exchangers, pumps and distillation columns. Most of the programs are sequential modular and solve the unit operations in the same sequence as in the real process. Commercial process simulation programs used for glycol dehydration are Aspen Plus, Aspen HYSYS, Pro/II and ProMax. Process simulation programs are useful for simulation of absorption processes because complex vapour/liquid equilibrium models are available in the programs, and because efficient stage to stage procedures are available.

Absorption and distillation columns are often simulated as a sequence of equilibrium stages. The stages can also be specified with a Murphree efficiency. Murphree efficiency can be defined as the change in concentration (in this case water content) from the stage below to a given stage, divided by the change if equilibrium was achieved on the given stage [4].

### Vapour/Liquid data and equilibrium models

Equilibrium values in the TEG/water system from the work of Herskowitz and Gottlieb [6] and activity coefficients at infinite dilution measured by Bestani [7] are regarded as the most reliable data for this system [8].

To represent this vapour/liquid equilibrium either an equation of state can be used for the vapour phase and an activity model for the liquid phase or an equation of state for both phases. To describe the gas phase by an equation of state, the liquid phase by an activity model and the total pressure dependence by a Poynting correction is recommended for the TEG-natural gas-water system at high pressure [8].

The vapour/liquid equilibrium between CO<sub>2</sub> and water is reviewed by Cole [1]. This equilibrium must be included in a complete model of the TEG/water/CO<sub>2</sub> system. One special task is to calculate the correct solubility of CO<sub>2</sub> in a TEG/water solution.

In Aspen HYSYS, the equilibrium models Peng-Robinson (PR) [9] and Twu-Sim-Tassone (TST) [10] are available for glycol dehydration. The PR model is a standard cubic equation for general use with only one adjustable parameter for each component pair in the system. The TST model is

a more advanced cubic equation of state with more adjustable parameters. The parameters are especially fitted for the glycol gas dehydration system. The TST model is recommended in the Aspen HYSYS program documentation as the most accurate. It is however not clear whether any of these models are especially suited for dehydration of CO<sub>2</sub>.

In the Aspen Plus simulation program the SR-POLAR model is recommended for TEG dehydration simulation [11]. SR-POLAR is a property method based on the Schwartzentruber and Renon cubic equation of state [12]. The process simulation programs PRO/II and ProMax also have models available recommended for the TEG/water system.

### Dehydration simulations in literature

Simulations of the natural gas dehydration process in Aspen HYSYS have been performed with emphasis on glycol regeneration by Øi and Selstø [13]. A traditional TEG dehydration process has been simulated using the Peng-Robinson equation of state [9]. A water content of 58 ppm was specified in the dehydrated gas. Different regeneration processes were simulated, e.g. addition of stripping gas to the reboiler, adding stripping gas to an extra stripping column and also some commercial processes. For the same inlet data, Emah [11] performed simulations of a natural gas dehydration process in Aspen HYSYS and Aspen Plus using different equilibrium models in order to investigate configurations suitable for achieving 37 ppm in the dehydrated gas.

Farhat [14] described TEG dehydration of a CO<sub>2</sub> stream with an additional stripping column below the reboiler for improving TEG regeneration. Dry CO<sub>2</sub> gas from the process was utilized as stripping gas. Bilsbak [15] used the simulation program Pro/II to simulate TEG dehydration of CO<sub>2</sub> using an equation of state.

Besides these references, there is very little information found in the open literature about simulation of CO<sub>2</sub> dehydration processes and particularly of CO<sub>2</sub> dehydration based on absorption in glycol.

## Purpose of the paper

The main purpose of the paper is to give an overview over process simulation flow-sheet models for CO<sub>2</sub> dehydration by absorption in triethylene glycol. Especially, it is an aim to simulate different alternatives dependent on the water level specifications in dehydration gas. The results in this work are mainly from simulations performed in the Master Thesis work of Mirela Fazlagic [16].

## PROCESS DESCRIPTION

### Traditional TEG dehydration process

A traditional dehydration process for natural gas or CO<sub>2</sub> is shown in Figure 1. Wet gas is absorbed by a TEG solution in an absorption column (contactor). The liquid (rich glycol) is then depressurized to flash off some of the natural gas. Then the liquid is heated and sent to a desorber (regenerator). In this distillation column, water is removed from the top and regenerated TEG is removed from the bottom. Heat is added in the reboiler below the desorber. The regenerated TEG (lean glycol) is pumped through two heat exchangers back to the absorber.

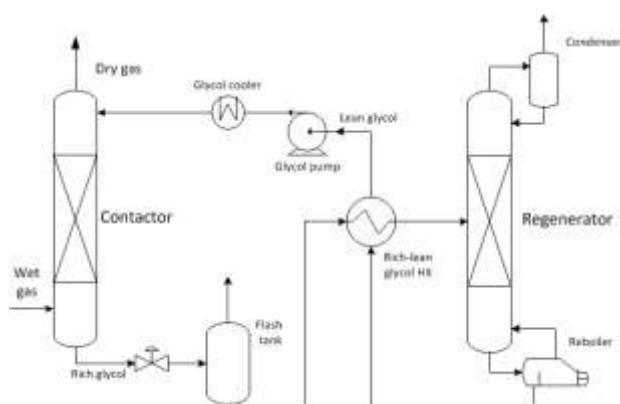


Figure 1: A traditional TEG dehydration process

### **Stripping gas to reboiler**

It is possible to improve the removal of water in the regeneration by adding stripping gas to the reboiler or the bottom of the desorber column. The main effect of adding stripping gas is that the partial pressure of water in the gas phase is reduced so that more water will evaporate and then reduce the water content in the glycol. The stripping gas can come from the flash gas or from the dehydrated gas as indicated in Figure 2.

### **Stripping gas to extra stripping column**

The regeneration of TEG can be improved further by adding an extra stripping column below the reboiler. This is shown in Figure 2. The extra stripping column results in more efficient water removal and reduced amount of stripping gas to achieve a specified TEG concentration [21].

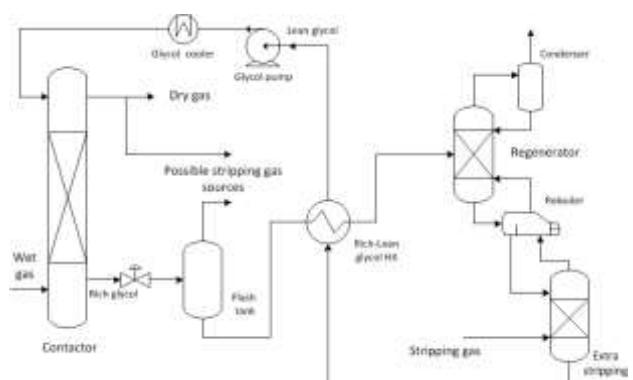


Figure 2: A TEG dehydration process with extra stripping column

PROCESS SIMULATION

### Simulation of standard process

A traditional TEG dehydration process as in Figure 1 has been simulated in the simulation program Aspen HYSYS version 7.2 using the Peng-Robinson equation of state and the glycol property package (using the TST equilibrium model).

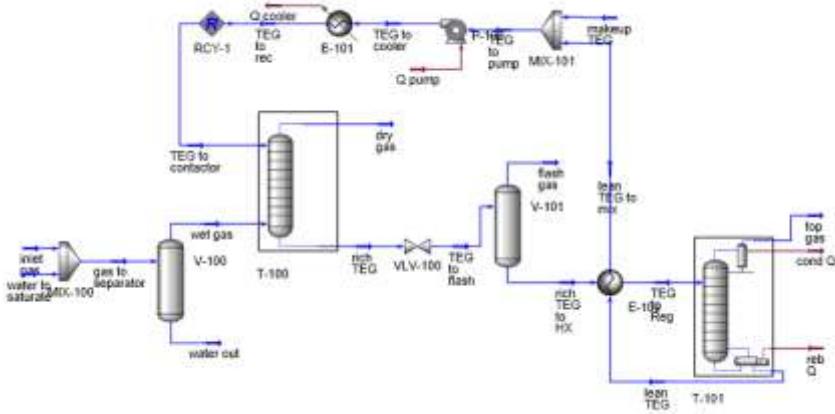


Figure 3: Aspen HYSYS flow-sheet model for traditional TEG dehydration process

|   |       |
|---|-------|
| Inlet gas temperature [°C]                          | 30    |
| Inlet gas pressure [kPa]                            | 3000  |
| Inlet gas flow [kmol/h]                             | 501.1 |
| Water in inlet gas [mol-%]                          | 0.23  |
| Lean TEG temperature [°C]                           | 35    |
| Lean TEG pressure [kPa]                             | 3000  |
| Lean TEG rate [kmol/h] (in first iteration)         | 3.583 |
| Water in lean TEG [mass-%] (in first iteration)     | 1.04  |
| Number of stages in absorber                        | 10    |
| Murphree efficiency in absorber                     | 0.5   |
| Pressure after the depressurization valve [kPa]     | 110   |
| Heated rich TEG temperature [°C]                    | 153   |
| Number of stages in stripper (+ condenser/reboiler) | 4     |
| Murphree efficiency in stripper                     | 1.0   |
| Reflux ratio in stripper                            | 0.5   |
| Reboiler temperature [°C]                           | 200   |
| Pressure in stripper [kPa]                          | 101   |
| Lean TEG pump pressure [kPa]                        | 3000  |

Table 1: Base-case specifications

The Aspen HYSYS flow-sheet model for the base case simulation is presented in Figure 3. The specifications for the base case process calculation are given in Table 1. The absorption column was simulated with 10 stages and with Murphree efficiency 0.5, which is assumed to be equivalent to approximately 10 actual plates or 5 meters of structured packing [17].

The calculation sequence of the process in the Aspen HYSYS flow-sheet is in practice following the real flow direction. The gas feed stream to the

absorber is saturated with water and is calculated first. The liquid feed to the absorber is then guessed. Then the absorption column and the rest of the process is calculated step by step. The cold side of the main heat exchanger is calculated first based on a specified temperature on the stream to the desorber. The recycle block compares the stream returned from the TEG cooler with the guessed stream. Some iterations may be necessary to achieve convergence. In some simulations, Aspen HYSYS calculated unrealistic low temperatures. This indicates that it is something wrong with the enthalpy calculations. It is a traditional recommendation to be careful with calculations of enthalpies from an equation of state and rather replace the enthalpy calculation with a simpler and often more accurate method. This problem was solved by changing the enthalpy setting to the Cavett model instead of the default property package EOS (equation of state). Using the base case specifications in Table 1, the water content in dehydrated gas was calculated to 153 ppm with the PR model and 206 ppm with the glycol package using the TST model.

Because the glycol package using the TST model is probably the most accurate model, it is assumed that the optimum is between 3000 and 4000 kPa.

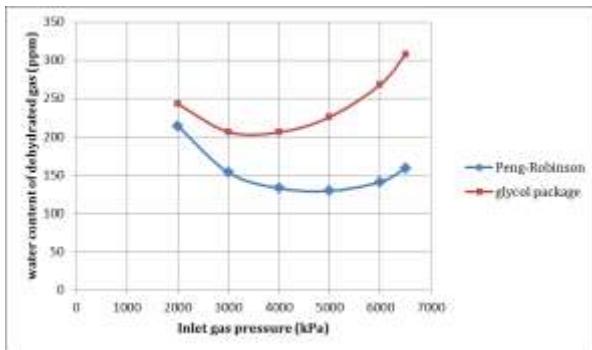


Figure 4: Water content in dehydrated gas as a function of absorption pressure

It was tried to improve the dehydration by increasing the TEG circulating rate and by increasing the number of absorption stages. This gave only minor improvements in achieved water content in the dehydrated gas.

### Simulation of stripping gas to reboiler

A process with stripping gas added to the reboiler was simulated. Figure 5 shows the regeneration part of the flow-sheet of the Aspen HYSYS simulation.

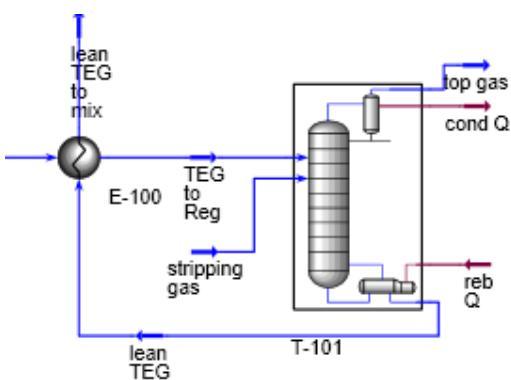


Figure 5: Aspen HYSYS flow-sheet of process with stripping gas to desorber

The stripping gas was specified with temperature 190 °C, pressure 101 kPa, 99.17 % CO<sub>2</sub> and 0.83 % water. The composition was similar to the flash gas composition from depressurization after the absorption column in the base-case calculation.

Calculations comparable to the base case simulations were performed with varying stripping gas flow and number of stages in the absorption column. Using the Peng-Robinson model, less than 50 ppm was achieved using 10 absorption stages and 1.8 kmole/h stripping gas. Using the glycol package, slightly more than 10 absorption stages was necessary. Using 20 stages, it was necessary to use 1.2 kmole/h to achieve less than 50 ppm in the dehydrated gas. Results from the calculations using the TST model is shown in Figure 6. It is seen that an increase to 30 absorber stages did not increase the efficiency significantly.

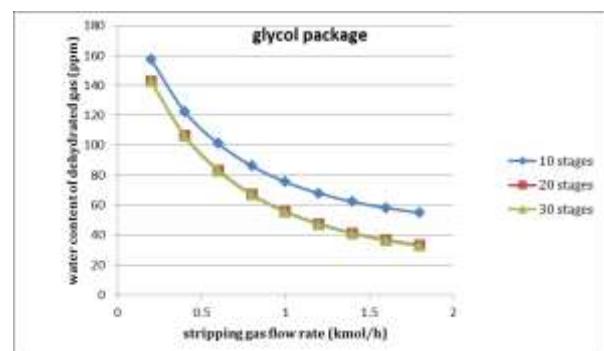


Figure 6: Water content as a function of stripping gas to reboiler and number of absorber stages

When the amount of stripping gas was limited to the amount of flash gas after the absorption column, the PR model calculated 42 ppm and the TST model 103 ppm. This large difference is mainly due to the large difference in calculated flash gas in the two cases, 0.9 kmole/h for PR and 0.4 for TST.

Increasing the number of stages and the amount of stripping gas made it possible to improve the dehydration down to about 30 ppm. This was achieved with both the PR and TST models.

## Simulation of stripping gas to extra column

A simulation of the process in Figure 2 was performed with an extra stripping column. First, the process was simulated with two columns as in Figure 7. The calculation sequence is more complex than in the base case. To calculate the desorber, it is necessary to guess the stream from the extra stripping column. After that the extra stripper can be calculated, and the recycle stream from the extra stripping column is compared with the guessed stream in a second recycle block.

This process simulation approach is difficult to converge. The recycle blocks are normally solved using iteration by replacement. The water concentration in each recycle stream is normally the critical parameter. With only one recycle loop, the water content in the recycle stream normally stabilizes and the simulation converges. In case of more than one recycle loops, the water concentration in the recycle loops tend to be less stable, and the simulation does not converge.

Because of these problems it was tried to simplify the simulation flow-sheet model, and the desorption column and the extra stripping column were simulated as one column in Aspen HYSYS with heating at an intermediate stage. The resulting flow-sheet in Aspen HYSYS is shown in Figure 8. The same numerical results were achieved when using these two approaches.

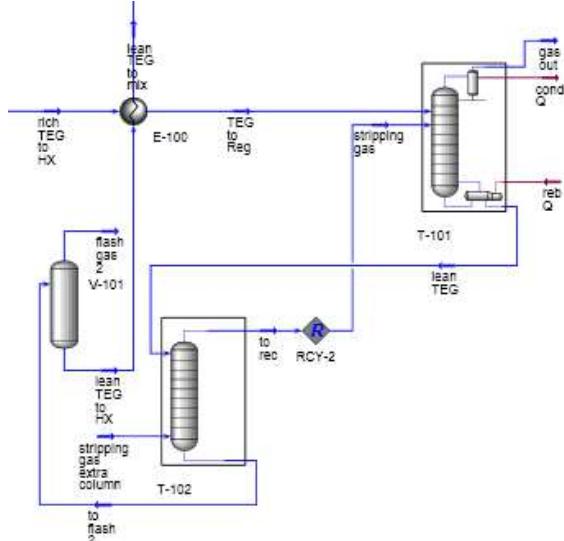


Figure 7: Aspen HYSYS flow-sheet of desorber with extra stripping column

The extra stripping column was specified with 3 equilibrium stages. In the case of the extra stripping gas and the desorber simulated as one column, it was 3 stages between the stripping gas feed to the bottom and the reboiler heat addition.

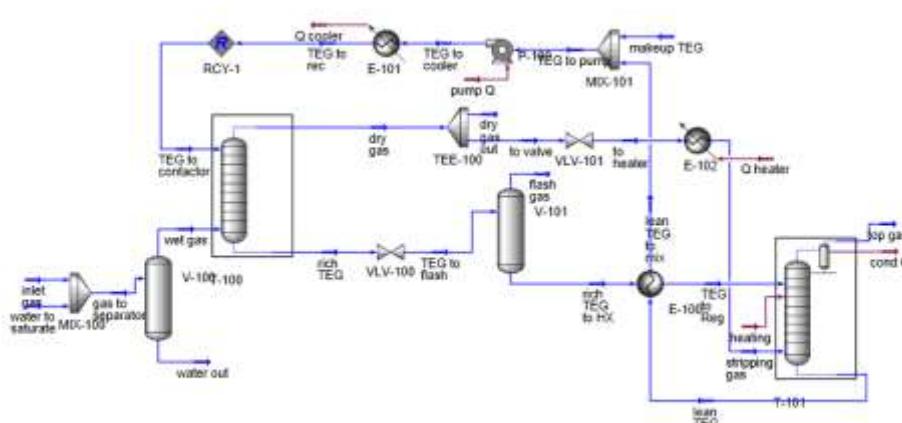


Figure 8: Aspen HYSYS simplified flow-sheet of process with extra stripping column

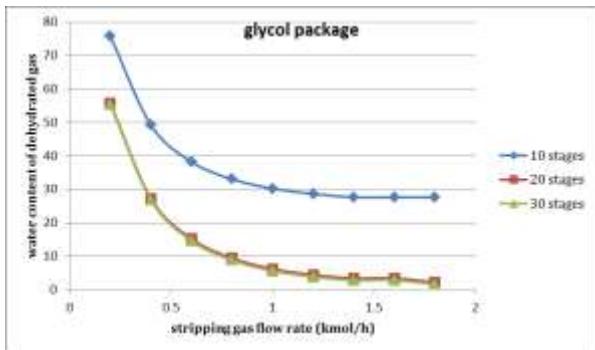


Figure 9: Water content as a function of stripping gas and number of absorber stages with extra stripping column

Figure 9 shows results from these calculations as a function of stripping gas and number of absorber stages for the process with an extra stripping column. Using 20 absorber stages and more than 1.2 kmole/h stripping gas gives less than 5 ppm in the dehydrated gas. These results were achieved using the TST model. Using the PR equilibrium model gave even better dehydration results. As in earlier simulations, increasing to 30 absorber stages did not improve the dehydration efficiency significantly.

### Influence of water content in stripping gas

The simulations were performed with different water levels in the stripping gas. For moderate water levels (50 ppm) there were no differences in the calculated results for different water levels of the stripping gas. To obtain very low levels (below 5 ppm) it is necessary to use almost pure stripping gas. Then it is reasonable to use stripping gas from the dehydrated CO<sub>2</sub>.

## DISCUSSION

### Comparison of equilibrium models

Dehydration of CO<sub>2</sub> gas by absorption in TEG has been simulated in Aspen HYSYS using two

different vapor/liquid equilibrium models. Both the PR and TST models give similar results for most of the simulated alternatives.

The calculated flash gas flow rate was significantly different between the two models. This indicates that the two models calculate the CO<sub>2</sub> solubility in TEG solution differently.

The glycol package in Aspen HYSYS using the TST model has been developed especially for TEG dehydration and is regarded as more accurate than the simpler PR model. The TST model gives slightly more conservative results than the PR model, and this is also an argument to recommend the glycol package using the TST model. It is assumed that the recommended equilibrium models in other process simulator programs also have satisfactory accuracy.

### Optimum dehydration pressure

The calculated water content for different absorption pressures indicates that a maximum dehydration efficiency is achieved at a pressure between 3000 and 5000 kPa. According to the calculations using the model assumed most accurate, the optimum was between 3000 and 4000 kPa. Because captured CO<sub>2</sub> will normally be compressed to a higher pressure than 5000 kPa for further processing, it is reasonable to perform dehydration at an intermediate pressure between 3000 and 4000 kPa.

### Process dependence on water specification

Water content requirement for dehydrated CO<sub>2</sub> influences the choice of dehydration process. From calculations performed in Aspen HYSYS it can be concluded that a traditional TEG dehydration process is satisfactory to achieve a water content of about 200 ppm in dehydrated gas. Using stripping gas, a water specification of less than 50 ppm can be achieved. In a process including an extra stripping column and a high absorption column, it is possible to achieve less than 5 ppm. In that case, it is necessary to use dehydrated CO<sub>2</sub> gas as stripping gas.

## CONCLUSION

It is demonstrated that it is possible to simulate both a traditional glycol dehydration process and more advanced CO<sub>2</sub> dehydration processes using Aspen HYSYS. Depending on the water content specification for the captured CO<sub>2</sub>, different processes modifications have been suggested. It has been simulated reasonable process alternatives for CO<sub>2</sub> dehydration down to water levels below 5 ppm.

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