Simulation of Glycol Processes for CO_2 Dehydration

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Abstract

Water must be removed from CO_2 prior to transport or storage to avoid corrosion and hydrate formation. Absorption into triethylene glycol (TEG) followed by desorption is the traditional gas dehydration method, and is expected to be the preferred method for large scale CO_2 dehydration. There is no agreement on the level of accepted water content after dehydration, and the specifications vary normally in the range between 5 and 500 ppm (parts per million by volume). In literature, it is claimed that use of solid adsorbents is necessary to reduce the water content to below 30 or 10 ppm. In this work, simulations in Aspen HYSYS demonstrate that it is possible to obtain below 1 ppm water using a traditional glycol dehydration process including an extra stripping column. The models Peng-Robinson (PR) and Twu-Sim-Tassone (TST) with updated parameters in Aspen HYSYS version 8.0 are used. A Drizo process using a stripping gas which is later condensed and recirculated is also simulated, and this process also achieves a water content below 1 ppm in dehydrated CO_2.

Keywords: CO_2, glycol, dehydration, Aspen HYSYS

1 Introduction

CO_2 removed from natural gas or from CO_2 capture should be dehydrated prior to transport or storage. Water may lead to problems like corrosion and hydrate formation. The need for water removal from CO_2 and possible specifications are discussed in several references (Cole et al., 2011; Uilhorn, 2013; Buit, 2011) and water specifications are normally in the range between 5 and 500 ppm (parts per million by volume). CO_2 for enhanced oil recovery normally requires the lowest water content.

There are several different gas dehydration methods available. The most used processes for dehydration are based on absorption, adsorption or 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 claimed to be necessary (Kohl and Nielsen, 1997; Kemper et al., 2014). There are however simulated reasonable processes for glycol dehydration of CO_2 down to water levels below 5 ppm (Øi and Fazlagic, 2014) using stripping gas and an extra stripping column. The Drizo process makes use of a condensable stripping gas which is recirculated and is able to reduce the water content down to 1 ppm (Prosernat, 2016).

A recent study (Kemper et al., 2014) has evaluated different commercial processes for CO_2 dehydration based partially on information from vendors of technology. Processes based on glycol and on solid adsorption were evaluated. It was claimed that use of solid adsorbents is necessary to reduce the water content to below 30 or 10 ppm.

The main purpose of this paper is to present updated simulations of flow-sheet models for CO_2 dehydration by absorption in triethylene glycol. The Peng-Robinson (PR) model and the Twu-Sim-Tassone (TST) model (the glycol package in Aspen HYSYS) are used. In version 8.0, the parameters in the TST model have been updated compared to version 7.2 which was used in earlier work with Aspen HYSYS (Øi and Fazlagic, 2014). Especially, it is an aim to simulate the alternative including an extra stripping column and a Drizo process achieving a water level down to 1 ppm. The simulation results in this work are mainly from a Master Thesis work (Rai, 2016).

2 Simulation Programs and Models for Glycol Dehydration

Commercial process simulation programs which have been 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 models for absorption and desorption columns are available.

Absorption and distillation columns are traditionally simulated as a sequence of equilibrium stages. The stages can also be specified with a Murphree efficiency. A Murphree efficiency can be defined as the change in mole fraction of a component (in this case water) from the stage below to a given stage, divided by the change if equilibrium was achieved on the given stage (Kohl and Nielsen).

Vapour/liquid equilibrium data in the TEG/water system has been discussed in several papers (Kohl and Nielsen, 1997; Øi and Fazlagic, 2014; Øi, 1999). The vapour/liquid equilibrium between CO_2 and water has also been evaluated (Cole et al., 2011; Austegard, 2006). This equilibrium must be included in a complete model of the TEG/water/CO_2 system. One special challenge for such a model, is to calculate the correct solubility of CO_2 in a TEG/water solution.

In Aspen HYSYS, the equilibrium models PR (Peng and Robinson, 1976) and TST (Twu et al., 2005) are available for glycol dehydration. The TST model is claimed in the Aspen HYSYS program documentation to be the most accurate. This is however based on the assumption of dehydration of natural gas, and it is uncertain whether the TST model is accurate when CO_2 is the dominating gas. The TST model parameters have been updated from earlier versions in the Aspen HYSYS version 8.0 used in this work. The PR model has only one adjustable parameter for each binary component pair while TST has 5 adjustable parameters for each binary pair. In Aspen Plus, PRO/II and ProMax there are also models available recommended for the TEG/water system (Øi and Fazlagic, 2014).

Simulations of the natural gas dehydration process in Aspen HYSYS have been performed with emphasis on glycol regeneration by Øi and Selstø (2002). A traditional TEG dehydration process was simulated using the PR equation of state. 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 and adding stripping gas to an extra stripping column. Bilsbak (2009) used the simulation program Pro/II to simulate TEG dehydration of CO_2 using an equation of state.

Besides the references mentioned in this work, there is very little information found in the open literature about simulation of CO_2 dehydration processes and particularly of CO_2 dehydration based on absorption in glycol.

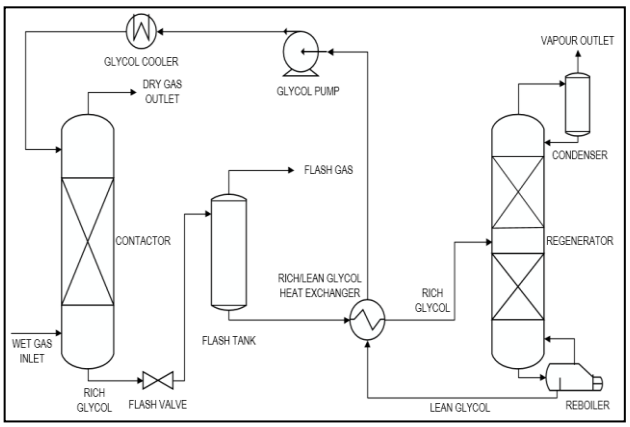

Figure 1. A traditional TEG dehydration process

3 Process Description

A traditional glycol dehydration process is shown in Figure 1. Water is absorbed from a gas into a glycol solution in an absorption column (contactor). The liquid (rich glycol) is then depressurized to a flash tank to evaporate some of the absorbed CO_2. Then the liquid is heated by regenerated glycol in a heat exchanger and sent to a desorber (regenerator). In this column, water is removed from the top and regenerated TEG is removed from the bottom. Heat is added in the reboiler. The regenerated TEG (lean glycol) is pumped through the heat exchanger and a cooler back to the absorber. More detailed process descriptions can be found in e.g. (Kohl and Nielsen, 1997; Øi and Fazlagic, 2014). It is possible to reduce the water content in the glycol by adding stripping gas to the reboiler. The reduction in water content in the glycol will make it possible to improve the dehydration of the CO_2 in the treated gas. The stripping gas can come from the flash gas or from the dehydrated gas. The water content in the glycol can be reduced further by adding an extra stripping column below the reboiler. This is shown in Figure 2.

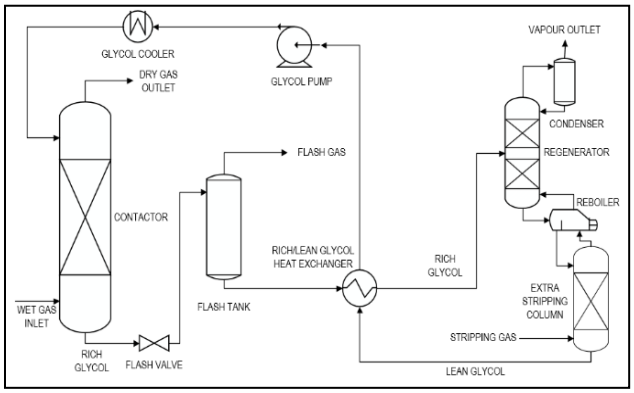

Figure 2. A TEG dehydration process with extra stripping column

There are also different special glycol dehydration processes. One example is the Drizo process (Prosernat, 2016) where the added stripping gas is a condensable component which is condensed after the stripping column and recirculated to the bottom of the stripping column. In earlier work (Øi and Fazlagic, 2014) the possible water content achievable from these processes was calculated using Aspen HYSYS. A traditional process could achieve below 200 ppm. Using stripping gas, less than 50 ppm could be achieved. Adding an extra stripping column below the reboiler could reduce the water content to below 5 ppm.

To achieve very low water content, the height of the absorption column has to be increased compared to a traditional process. The absorption column will contain plates or packing. An expected plate efficiency is order

of magnitude 50 %, and an expected packing efficiency of a packing height of 0.5 meter is also order of magnitude 50 % (Øi, 2003). An increase of the packing height from 10 to 20 stages or order of magnitude from 5 to 10 meters will increase the cost significantly. The extra stripping column will add complexity to the process. The cost for extra height in this column is however small because the diameter is very low.

4 Process Simulation, Results and Discussion

4.1 Simulation of Standard Process

A traditional TEG dehydration process as in Figure 1 has been simulated in the simulation program Aspen HYSYS version 8.0 using the PR equation of state and TST model (the glycol property package). The Aspen HYSYS flow-sheet model for the base case simulation is presented in Figure 4. The specifications for the base case process calculation are given in Table 1. These are similar to the specifications in earlier simulations (Øi and Fazlagic, 2014). The enthalpy setting in Aspen HYSYS was changed to the Cavett model instead of the default property package EOS (equation of state) to avoid unrealistic low temperatures.

Table 1. Specifications for base case simulation

Parameter	Value
Inlet gas temperature	30 °C
Inlet gas pressure	3000 kPa
Inlet gas molar flow rate	501.1 kmol/h
Water in inlet gas	0.23 mol-%
TEG to contactor temperature	35 °C
TEG to contactor pressure	3000 kPa
TEG to contactor, flow (in first iteration)	3.583 kmol/h
Water in lean TEG (in first iteration)	1.04 mass-%
Number of stages in absorber	10
Murphree efficiency in absorber stages	0.5
Pressure after depressurization valve	110 kPa
Temperature in TEG to regeneration	153 °C
Number of stages in desorber	4
Murphree efficiency in desorber stages	1.0
Reflux ratio in desorber	0.5
Reboiler temperature	200 °C
Desorber pressure	101 kPa
Pressure after TEG pump	3000 kPa

Recommendations for a traditional process can be found also in Kohl and Nielsen (1997). The absorption column was simulated with 10 stages and with Murphree efficiency 0.5 on each stage, which is assumed to be equivalent to approximately 10 actual plates or 5 meter of structured packing (Shresta, 2015).

The calculation sequence of the process in the Aspen HYSYS flow-sheet is mostly following the real flow direction. The gas feed stream to the absorber is saturated with water. The liquid feed to the absorber has to be estimated in the first iteration. 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 based on a specified temperature on the stream to the desorber.

Using the base case specifications in Table 1, the water content in dehydrated gas was calculated to 153 ppm with the PR model and 133 ppm with the glycol package using the TST model. Compared to earlier simulations, the results from the PR model were identical. The results using the TST model were lower in water content compared to the earlier results (Øi and Fazlagic, 2014). The differences are expected to be due to updated TST parameters. The deviations between calculated water content from PR and TST are lower in this work. The process was simulated also at other absorption pressures. The results are shown in Figure 3.

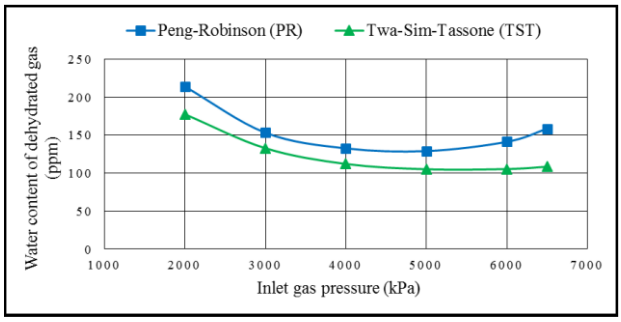

Figure 3. Water content in dehydrated gas as a function of absorption pressure

Both models gave a minimum water content and maximum dehydration efficiency at 5000 kPa. Minimum water content was 129 ppm at 5000 kPa using the PR model and 105 ppm using the TST model. In earlier work Øi and Fazlagic (2014) the TST model gave a minimum water content at 3000 kPa.

The dehydration can be improved by increasing the TEG circulating rate and by increasing the number of absorption stages in the standard process. However, these changes gave only minor improvements in achieved water content in the dehydrated gas.

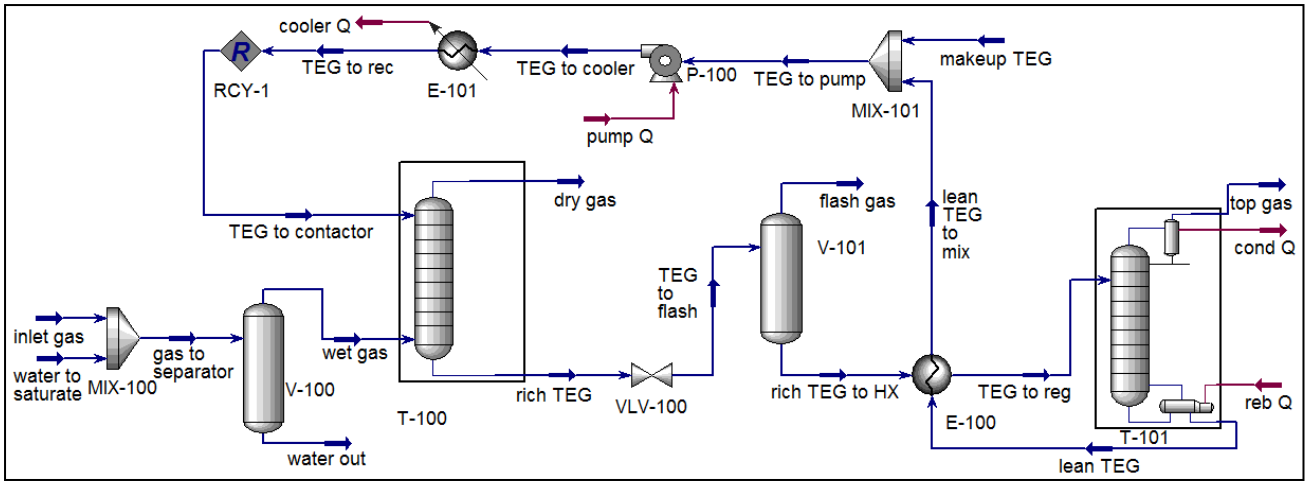

Figure 4. Aspen HYSYS flow-sheet model for traditional TEG dehydration process

4.2 Simulation of Stripping Gas to Reboiler

A process with stripping gas added to the reboiler was simulated. The stripping gas was specified with temperature 190 °C, pressure 101 kPa, 99.17 % CO_2 and 0.83 % water (Øi and Fazlagic, 2014). The composition was similar to the flash gas composition from depressurization after the absorption column in the base case calculation. Figure 5 shows the results from the Aspen HYSYS simulations using the TST model.

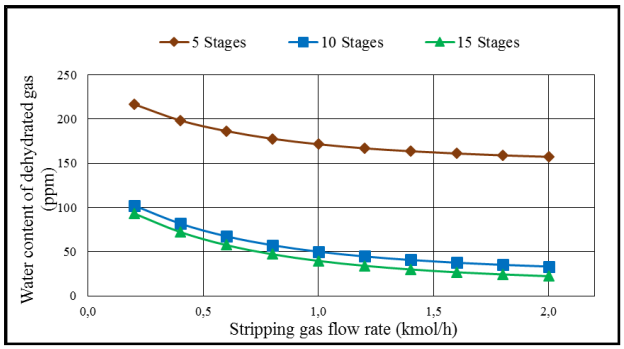

Figure 5. Water content as a function of stripping gas and number of absorber stages with stripping gas to reboiler using the TST model

Calculations comparable to the base case simulations were performed with varying the stripping gas flow and number of stages in the absorption column. Using the TST model, less than 50 ppm was achieved using 10 absorption stages and 1 kmole/h stripping gas. Using 15 stages, it was necessary to use 0.6 kmole/h to achieve less than 50 ppm in the dehydrated gas.

There is some difference in calculated flash gas amount for the two models, 0.89 kmole/h for the PR model and 0.63 kmole/h for the TST model. This indicates that the two models calculate the CO_2 solubility in the TEG/water solution differently. When using the PR model, the water amount for a given stripping gas amount is slightly higher than using the TST model. But because the PR model calculates a higher flash gas amount, the PR model also calculates about 50 ppm when the amount of stripping gas is set to the amount of available flash gas.

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 the TST model.

4.3 Simulation of Stripping Gas to Extra Column

A simulation of the process in Figure 2 was performed. In earlier work (Øi and Fazlagic, 2014) this process has been simulated using two strategies. The first strategy was to simulate the process with two columns. The second strategy was to simplify the flow-sheet model by simulating the desorption column and the extra stripping column as one column with heating at an intermediate stage as shown in Figure 6. Similar numerical results have been achieved using these two strategies (Øi and Fazlagic, 2014; Øi and Selstø, 2002). The strategy with only one column was chosen in this work because these simulations are easier to converge.

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. The number of stages above and below the feed in the desorber and in the extra stripping column have been varied in earlier work (Shresta, 2015). The results showed that increasing the number of stages in the sections above 3 (as specified in this work) did not improve the dehydration efficiency significantly.

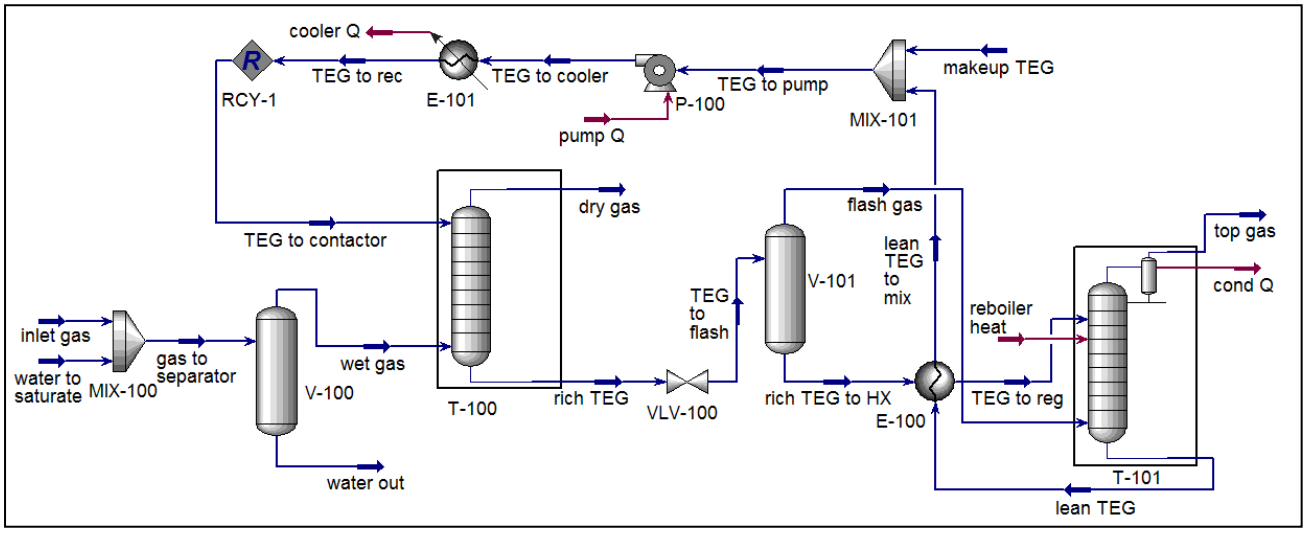

Figure 6. HYSYS flow-sheet of dehydration process with extra stripping column

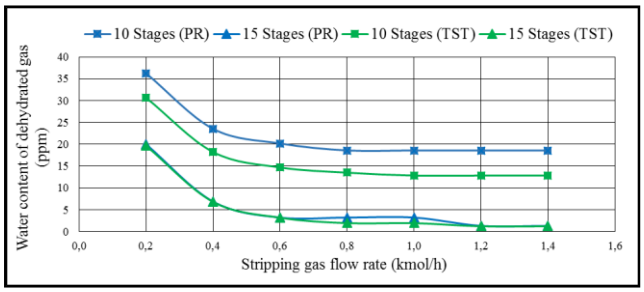

Figure 7. Water content as a function of stripping gas and number of absorber stages with extra stripping column

Figure 7 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 10 absorber stages reduces the water content down to about 20 ppm using the PR model and down to about 15 ppm using the TST model. The water content is not reduced further by adding more stripping gas with 10 absorber stages. With 15 stages or more, less than 5 ppm was achieved using the available flash gas, and less than 2 ppm was achieved by adding more stripping gas. Using more than 15 absorber stages did not improve the dehydration efficiency significantly.

In earlier work (Øi and Fazlagic, 2014) similar results were obtained using 20 absorber stages for the same conditions. With more than 1.2 kmole/h, less than 5 ppm was achieved with both the PR model and the TST model.

At very low water content (below 2 to 5 ppm) the water amount in the stripping gas is a limiting factor. Less than 1 ppm water in dehydrated gas has been calculated when pure (dehydrated) CO_2 was used as stripping gas. This was calculated using 15 absorber stages and a high stripping gas amount with both the PR and the TST model.

4.4 Simulation of a Drizo process

A Drizo process with n-heptane as stripping gas was simulated. The flow-sheet is shown in Figure 8. The condensing of the stripping gas is performed in a three phase separator, and the organic phase is pumped back and evaporated in a heater before it is added to the bottom of the extra stripping column. It was checked that the amount of recirculated n-heptane was approximately equal to the n-heptane added to the desorber in the simulation.

A similar process has been simulated earlier (Øi and Selstø, 2002). An argument for not closing the loop in the simulation of the recirculation of the stripping gas, is that a small fraction of the added stripping gas will be dissolved in the solvent and lost e.g. in the flash gas. This is of minor interest for the evaluation of the process.

The results for n-heptane as a stripping gas using the TST model are presented in Figure 9. Similar results were obtained using the PR model. Similar simulations were also performed with the components benzene and toluene as stripping gas. When using benzene and toluene, more of the stripping gas was dissolved in the glycol, so that the deviation between added stripping gas and recirculated stripping gas became larger.

Similar levels of water were achieved as in the simulations with flash gas or CO_2 as stripping gas. Less than 20 ppm was obtained using 10 absorption stages in the absorber and available flash gas. Less than 5 ppm was obtained with 15 stages and stripping gas amounts similar to the available flash gas and less than 1 ppm when the amount of stripping gas was increased.

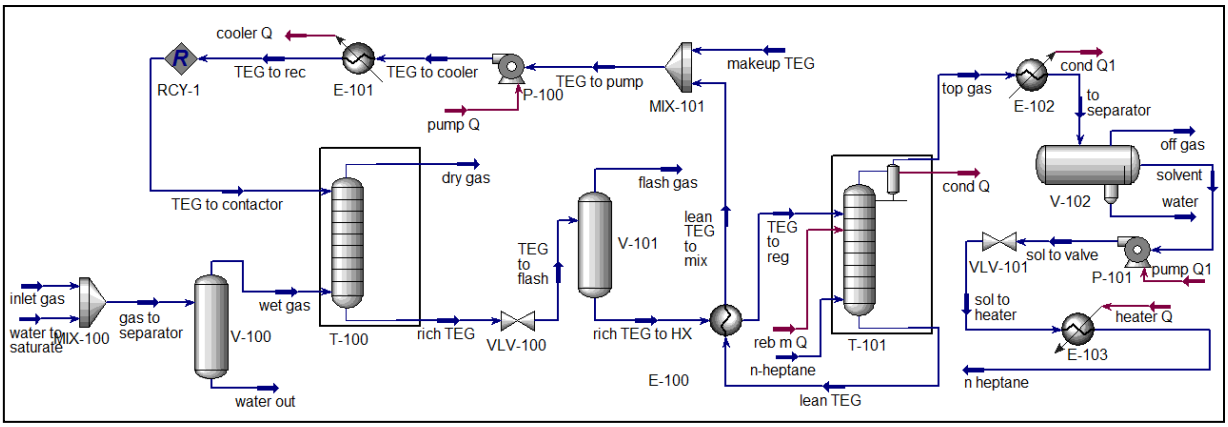

Figure 8. Aspen HYSYS flow-sheet of Drizo process using n-heptane as stripping gas

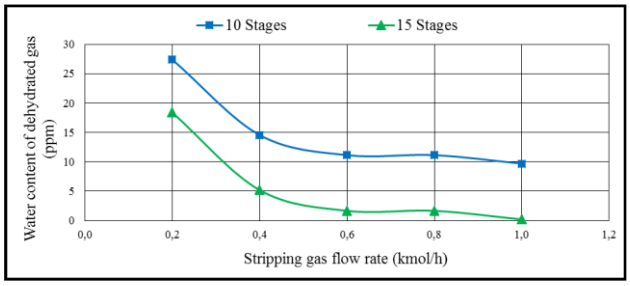

Figure 9. Water content in Drizo process with n-heptane as a function of stripping gas and number of absorber stages using the TST equilibrium model

5 Conclusions

It is demonstrated that it is possible to simulate both a traditional glycol dehydration process and more advanced CO_2 dehydration processes like the Drizo process using the process simulation program Aspen HYSYS. The PR and TST models give similar results for all the simulated alternatives. The calculated water content for different absorption pressures shows that a maximum dehydration efficiency is achieved at a pressure of about 5000 kPa.

A traditional TEG dehydration process is satisfactory to achieve a water content below 150 ppm in dehydrated CO_2. Using stripping gas, a water specification of less than 50 ppm can be achieved. In a Drizo process or a process including an extra stripping column and a high absorption column, it is possible to achieve less than 1 ppm water in dehydrated CO_2.

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