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Use of Glycerol to Dehydrate High-Pressure, High-CO_2 Streams
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Introduction

Twenty years after the first two glycerol dehydration units were built for supercritical CO_2 use, Denbury Resources Inc. (Denbury) began building new units to process the increasing amount of CO_2 production from the Jackson Dome area in Mississippi. Denbury has now completed and started up five new glycerol-based dehydration facilities in the last five years with other units under construction. Glycerol is used to dehydrate CO_2 when high-pressures and non-idealities cause excessive vapor losses of glycol (examples: ethylene, diethylene, or trietheylene glycol), which makes normal glycol-based dehydration uneconomical in comparison with glycerol-based dehydration. Denbury uses the supercritical CO_2 primarily for enhanced oil recovery (EOR).

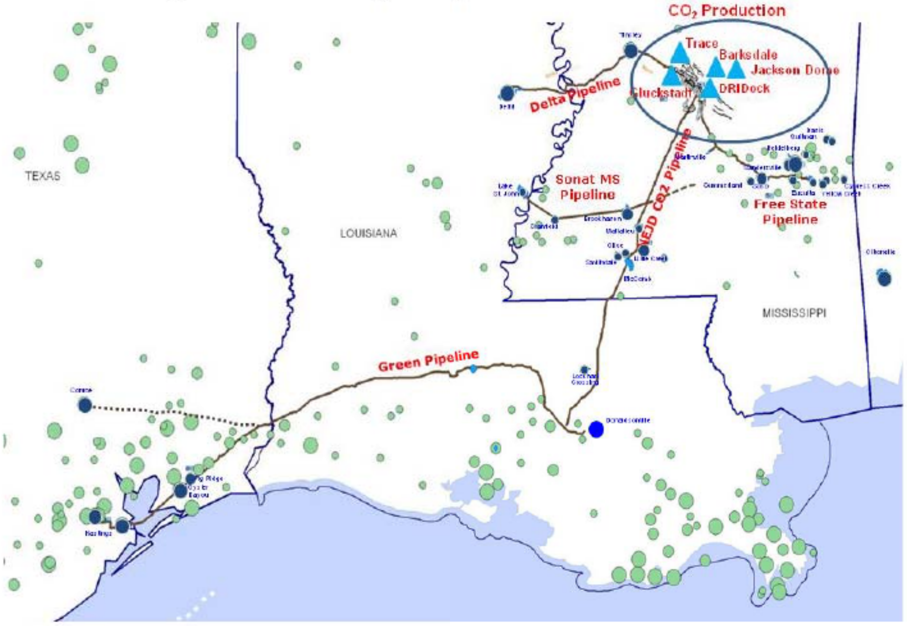
This paper presents the reasons for the recent surge in glycerol unit construction as well as the types of other applications to which glycerol dehydration may well be suited. Differences between using glycerol and glycol for dehydration with supercritical, dense-phase CO_2 gas streams are also discussed. Since commercial process simulators are not well suited for design of this type of system, a model was developed to rigorously predict phase equilibria in the absorber and simulate other portions of the process. The simulator and other data used to build the new glycerol dehydration units are reviewed. Key design features of the dehydration plants are presented as well.

Denbury's New and Existing CO_2 Dehydration Facilities

Denbury is a growing independent oil and natural gas company. The company is the largest oil and natural gas operator in Mississippi, owns the largest reserves of CO_2 used for tertiary oil recovery east of the Mississippi River, and holds significant operating acreage in Louisiana, Alabama, Texas, Montana, North Dakota, and Wyoming.

Denbury's CO_2 source field, Jackson Dome, located near Jackson, Mississippi was discovered during the 1970s while being explored for hydrocarbons (see Figure 1). This significant source of CO_2 is the only known one of its kind in the United States east of the Mississippi River. Mississippi's first EOR project began in the mid 1980s in the Little Creek Field following the installation of Shell Oil Company's Choctaw CO_2 pipeline. The 183-mile Choctaw Pipeline (now referred to as the NEJD Pipeline) transported CO_2 produced from Jackson Dome to the Little Creek Field. While the CO_2 flood proved successful in recovering significant amounts of oil, commodity prices at that time made the project unattractive and Shell later sold their oil fields in this area, as well as the CO_2 source wells and pipelines.

Figure 1. Denbury Dehydration Facility Map



Currently more than 1.0 Bscf/d of CO_2 is produced from Jackson Dome Area operations. The pipeline network has been expanded from the single NEJD pipeline to include the Free State pipeline to East Mississippi, the Delta pipeline that goes into northeast Louisiana, and the recent completion of the Green Pipeline that delivers CO_2 across the Gulf Coast Region from the end of the NEJD Pipeline to South of Houston. Source well operating pressures range from 800 to 4000 psig. Jackson Dome is generally referred to as the source of the CO_2, but is also the name of the original central dehydration facility that uses a glycerol process to dehydrate supercritical CO_2-rich streams. The Jackson Dome dehydration unit was built by Shell and based on research performed in the 1980s to understand the dynamics of dehydrating supercritical CO_2 with glycols and glycerols[1,2,3,4,5]. The research showed that glycerol can dehydrate supercritical CO_2 more effectively than glycols. (Critical pressure and temperature for pure CO_2 are 1070 psia and 87.8°F, respectively.) It should be noted that the other glycerol unit[6] built ~20 years ago and operated by a different company is believed to be no longer operational.

In 2003, an expansion to the Jackson Dome dehydration plant was completed, adding internals to the inlet separator and contactor to almost double the capacity. Since then, Denbury has built several new glycerol-based CO_2 dehydration units to keep pace with the increase in Denbury's CO_2 production. Because Denbury continues to find high pressure source wells, it is advantageous to dehydrate the CO_2 with glycerol at pipeline conditions without compression. The new dehydration units are described briefly in Table 1 below. The gas composition is generally 99.4% CO_2, 0.3% N_2, and 0.3% C_1.

The post-expansion performance of the process at Jackson Dome was used to validate modeling results. Improvements were also made to the new dehydration plants based on Denbury's Jackson Dome experience and advancements with process technology.

Table 1. New Denbury Glycerol-Based CO_2 Dehydration Units

Plant	Gluckstadt	Barksdale North	Barksdale South	Trace	Gluckstadt	DRI Dock
Operation Date	2006	2007	2008	2010	2010	2011
Flow, MMScfd	100	300	300	150	300	300
Operating Pressure, psig	1550	1500	1500	1500	1550	TBD
Operating Temperature, F	120	110	110	110	115	TBD
Water content In, lb/MMscf	201	201	201	201	201	201
Water content Out, lb/MMscf	20	20	20	20	20	20
Reboiler Duty, MMBtu/hr	2.05	6	6	2.75	6	6

Dehydration of Supercritical CO_2 Streams with Glycerol

The properties of supercritical CO_2 impact the design of a dehydration system primarily in two main ways: 1) mutual solubilities of the desiccant and CO_2 and 2) saturated water content of CO_2 with temperature and pressure.

Data taken both in a laboratory setting and also from field tests concluded that glycerol had a much lower solubility in supercritical CO_2 than do ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG). Table 2 shows that TEG is 10-200 times more soluble than glycerol in CO_2 over a pressure range of 1200-2000 psig. This means that TEG would have excessive vapor losses and makeup requirements, making normal glycol-based dehydration uneconomical. Operational data from Jackson Dome support the glycerol solubility data from these sources. A gross material balance of the glycerol added to the system indicates 4-5 ppmv of glycerol is soluble at 1300 psig and 115 °F.

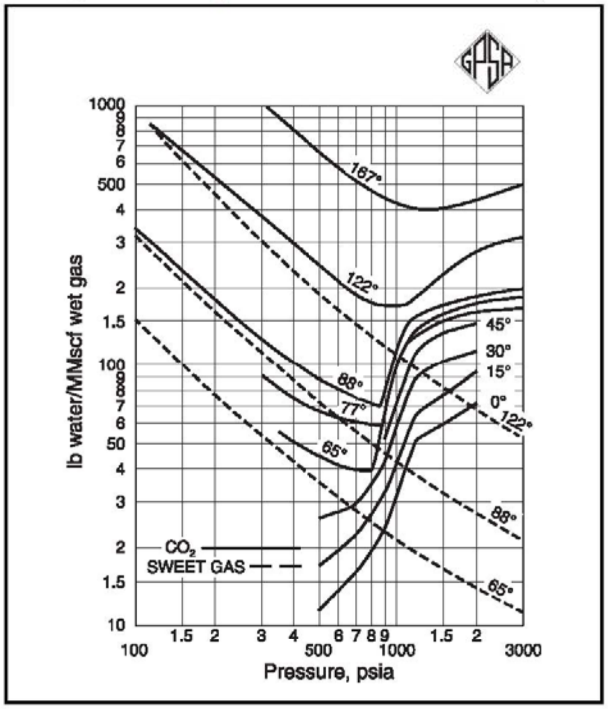
Table 2. Glycol and Glycerol Solubility in CO_2 (ppmv)[1]

	1200 psi		**2000 psi**	
	TEG	**Glycerol**	**TEG**	**Glycerol**
73 °F	1800	12.3	2800	30
95 °F	390	8.2		37
115 °F	30	3.3	1900	42

Table 2 also shows that, unlike the glycols, glycerol solubility in the CO_2 did not increase as significantly with lower CO_2 temperatures. However, because of the high glycerol viscosity and rapidly increasing supercritical CO_2 density as the temperature decreases, glycerol would probably not be used to dehydrate CO_2 below 100°F. In addition, the solubility of CO_2 in glycerol was also determined to be only a tenth of the solubility in glycols. This results in lower flashing losses.

Water solubility in pure CO_2 is well documented in several sources, e.g., the GPSA handbook[7]. Figure 2 shows the maximum amount of water that can be dissolved into a homogeneous CO_2 phase, which, for the purposes of this paper, is called the "solubility limit" for water in CO_2. As shown in the figure, at a fixed temperature the solubility limit for water decreases with increasing pressure up to near the critical pressure. As the pressure increases beyond the critical pressure (1070 psia), the solubility limit for water increases. However, small concentrations of other gases can significantly impact the water holding capacity of CO_2[4]. Knowing the correct moisture content of the supercritical CO_2 ensures that the absorber and regeneration equipment are not undersized.

Figure 2. Solubility Limit for Water in Pure CO_2[7]
(used with permission from GPSA)



Other parameters that are important are the density of CO_2, which can also change greatly in the presence of small amounts of inert gases and hydrocarbons[4], and the viscosity of glycerol, which is significantly different than glycol (1490 and 47.8 cps, respectively at 20°C).

Other Potential Applications of Glycerol Dehydration

Although glycerol dehydration was originally developed for essentially pure supercritical CO_2, streams that contain high CO_2 content and also need to be dehydrated at high pressure are also candidates for use of the technology. An example is the stream dehydrated using glycerol in Hungary[6]. The Hungarian stream had about 81% CO_2 with the bulk of the remainder consisting of methane, and it was dehydrated at a pressure of near 2000 psi. Other potential applications of the glycerol technology may also exist where a combination of high CO_2 content and a need to dehydrate at high pressure create the operating conditions and compositions where glycerol may have lower solubility losses than glycols and better overall economics.

Glycerol Dehydration Simulation Development

A simulation was developed specifically for supercritical dehydration of CO_2 with glycerol. This is because the standard property sets in most process simulators perform poorly when modeling fluid properties and phase equilibrium at near-critical conditions. Careful review of the thermodynamic parameters in the process simulator is required with adjustments made to match reliable data. Key modeling aspects are discussed below.

Absorber K-Values – One of the important aspects of designing glycerol-based dehydration systems for supercritical CO_2 is to have a good estimate of the K-value (i.e., phase equilibrium distribution coefficient) for water at the conditions in the absorber. Unreliable CO_2-water equilibrium data can produce erroneous results in the absorber that adversely affect the prediction of operations in downstream vessels. Absorber K-values for water were calculated using the thermodynamic relationship:

$$K = y/x = \gamma P^{sat} \Phi^{sat} \eta / \Phi P \qquad [1]$$

where

K = K-value, phase equilibrium distribution coefficient
y = Mole fraction water in the dense CO_2 phase
x = Mole fraction water in the liquid phase
γ = Activity coefficient for water (from vapor-liquid equilibrium data discussed in subsection below)
P^{sat} = Vapor pressure of pure water at the system temperature (from steam tables)
Φ^{sat} = Fugacity coefficient for pure water vapor at the system temperature and P^{sat} (assumed to be unity)
η = Poynting correction factor for water (from the component partial molar volumes)
Φ = Fugacity coefficient of water for the vapor phase
P = System operating pressure (known).

Most of the parameters in Equation 1 are readily known or accessible from the literature as indicated above. However, it is the calculation of the vapor-phase fugacity of water in dense-phase CO_2 near the critical conditions that is more difficult.

Field data were used to validate the accuracy of the simulation in predicting K-values and resulting water contents over a range of actual operating conditions. Table 3 shows that the treated gas water contents are in very close agreement with the predicted equilibrium water content for the lean glycerol solution at the absorber conditions (i.e., within 5 to 17% of the measured data). This indicates that the method discussed above is reliable for predicting K-values and dehydrator outlet water contents.

Table 3. Comparison to Known Field Data

Treated Gas Measured, lb/MMscf	Predicted Equilibrium Limit, lb/MMscf	% Difference
7.0	6.7	-4.3
9.1	7.9	-13.2

7.2	7.8	8.3
9.8	10.9	11.2
13.2	15.5	17.4
21.4	25.1	17.3

Water –Glycerol Phase Behavior – The vapor-liquid equilibrium (VLE) of water in glycerol is important because it is used 1) in the prediction of the K-values in the absorber (activity coefficient of water) and 2) in the determination of the lean glycerol water content from the reboiler and Stahl column. VLE data for water and glycerol (in the concentration and temperature ranges in the absorber and reboiler) were obtained and used to regress the adjustable parameters in the Wilson activity coefficient model.

CO_2 Solubility in Glycerol – It is important to know the solubility of CO_2 in glycerol for several reasons. First, it provides a means of determining how much CO_2 is picked up in the absorber and will evolve in the flash tank. Second, the solubility of CO_2 in glycerol is important in predicting the potential for two-phase flow through the heat exchangers in the process as the temperatures and pressures of the streams vary. Equilibrium data were used with the Wilson activity coefficient model to predict CO_2 solubility in glycerol.

Viscosity – The viscosity estimation method in the process simulator that most closely predicted viscosities found in the literature was selected. Viscosity data were used to calculate equipment pressure drop and model absorber hydraulics.

Thermal Conductivity – A method that accurately predicted the thermal conductivity for both 50-50 glycerol-water mixtures and high purity glycerol streams was selected.

Density – The densities of the inlet and outlet CO_2 streams from the absorber were calculated using the Peng-Robinson equation of state. The calculated densities compared reasonably well to those obtained from other sources.

Solubility of Glycerol in Dense-Phase CO_2 – The solubility of glycerol in dense-phase CO_2 has been reported in the literature[1] and was used to estimate glycerol losses from the absorber.

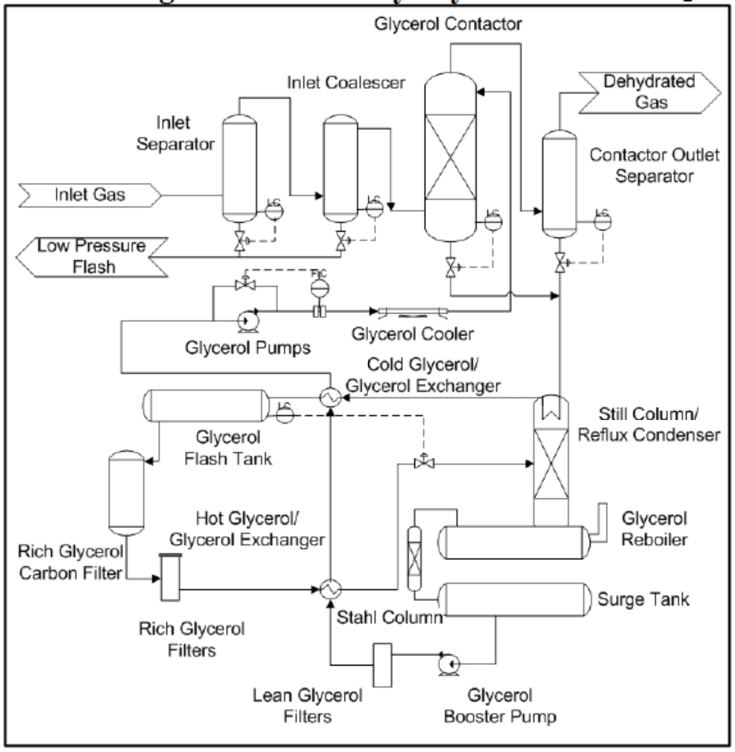
Denbury Glycerol-Based Dehydration Design Features and Research

Figure 3 shows a typical process flow diagram of the glycerol-based CO_2 dehydration units for the new Denbury facilities. The glycerol process operates much in the same manner as a TEG unit so a detailed process description is not provided[7].

Operational experience at Jackson Dome and advancements in process technology influenced the new glycerol process designs. Construction material for all process piping and vessels at the original Jackson Dome facility is 316/316L SS. In general, many of the same material choices used for glycol are appropriate for glycerol. The following materials choices were different in the new units compared to the original Jackson Dome plant.

- The contactor was built with 316L SS in the lower section and a carbon steel shell above the bottom 2-feet of packing. This is because the gas is sub-saturated as it moves counter-current to the glycerol through the packed section and this concept was proven successfully elsewhere.
- Carbon steel was used for all glycerol piping except for downstream of the glycerol flash tank; in this area, 316L SS was used instead to provide low temperature integrity if CO_2 vented through the control valve if liquid level control in the flash absorber was lost.
- Carbon steel was used for the rich/lean exchanger shells, the glycerol air cooler, reboiler shell, and filter vessels.

Figure 3. Process Flow Diagram for Denbury Glycerol-Based CO_2 Dehydration Unit



Design elements of note from the Jackson Dome process that were incorporated into the new glycerol units are described next. Isolation valves for the hot and cold glycerol exchangers were included for periodic cleaning / maintenance due to fouling from upset conditions or high skin temperatures. Due to high glycerol viscosity, glycerol booster pumps were used to ensure continuous flow from the reboiler through the hot and cold glycerol exchangers. An Inconel fire tube liner was included in the reboiler to moderate the skin temperature in contact with the glycerol, thus reducing the degradation rate. The glycerol flash tank and still were constructed of 316L SS due to the wet CO_2 in those areas.

Other key design aspects include the use of low maintenance and low cost horizontal submersible pumps or gear pumps for glycerol circulation, incorporation of a Stahl column for enhanced water removal, and a provision for a filter coalescer upstream of the glycerol contactors for removal of water with high salt and chloride content as the well declines. Jackson Dome data were also used to size the absorbers in the new units.

As work with supercritical CO_2 has continued, there have been a couple of areas of research and innovation. A series of tests were conducted to quantify the performance of liquid and solid H_2S scavengers at process conditions when 50-100 ppm H_2S was detected in one of the source wells. The test results indicated a reduced efficiency of these scavenging products for H_2S removal compared to the typical performance on natural gas[8]. Another area of study was glycerol solubility in CO_2. Although the solubility is much less than glycols, the price of glycerol was over $1/lb in 2008 when oil prices were at their peak. Additives were identified to further reduce the solubility of glycerol in CO_2 (patent pending) and a full-scale test is planned. Figure 4 shows a new glycerol unit.

Figure 4. New Denbury Glycerol Unit

Conclusions

The rigorous review of thermodynamic properties associated with the dehydration of supercritical CO_2 with glycerol was required for the development of a reliable process simulation tool to design new glycerol processes. Denbury's operational experience at Jackson Dome was important in constructing high performing glycerol-based units for dehydration of supercritical CO_2. The use of glycerol dehydrators allows Denbury to process more CO_2 for increased hydrocarbon recovery. The information provided here can be applied for the design of other high-CO_2, high-pressure applications as well, even if the stream is not essentially pure CO_2.

References

1. Wallace, C., "Dehydration of Supercritical CO_2", 1985 Gas Conditioning Conference.

2. Song, Kyoo Y., and Kobayashi, Riki. "The Water Content of CO_2-rich Fluids in Equilibrium with Liquid Water or Hydrate", GPA Research Report 80, May 1984.

3. Takahashi, Shinji and Kobayashi, Riki. “The Water Content and the Solubility of CO_2 in Equilibrium with DEG-Water and TEG-Water Solutions at Feasible Absorption Conditions”, GPA Technical Publication 9, December 1982.

4. Song, Kyoo Y., and Kobayahsi, Riki. “H_2O Content Values of a CO_2-5.31 Mol Percent Methane Mixture”, GPA Research Report 120, January 1989.

5. Diaz, Zaida and Miller, James H., “Drying Substantially Supercritical CO_2 with Glycerol”, U.S. Patent No. 4,478,612, October 1984.

6. Udvardi, G., L. Gerecs, Y. Ouchi, F. Nagakura, E.A. Thoes, C.B. Wallace, “Processing Facilities for Enhanced Oil Recovery in Hungary”, Proceedings of 69th Annual GPA convention, Phoenix, AZ, 12-13 March 1990. (Note – 69th proceedings books mis-marked as 68th in headings of papers.)

7. Gas Processors Suppliers Association (GPSA) Engineering Databook, FPS Volume II, Twelfth Edition, Chapter 20, pages 20-7 and 20-30, 2004.

8. McIntush, K., Beitler, C., Swadener, M., and C. Wallace, “Screening Processes for Removal of H_2S from Enhanced Oil Recovery CO_2 Streams”, Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, 2010.

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Joe Lundeen is a principal engineer at Trimeric Corp. in Buda, Texas. He has 21 years of experience in process engineering, process troubleshooting, and facility installation for oil and gas production and CO_2 processing clients. His recent experience has been focused on dehydration, contaminant removal, and transport of super-critical CO_2. He holds BS and MS degrees in Chemical Engineering from the University of Missouri-Rolla and Texas A&M-College Station, respectively.

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Kevin Fisher is a principal engineer at Trimeric Corp. in Buda, Texas. He has over 20 years of experience in process engineering, research and development, and troubleshooting for oil and gas production and oil refining clients, as well as for private and government-sponsored research programs. Mr. Fisher specializes in the areas of acid-gas removal, CO_2 capture, gas processing and gas dehydration. He holds an MS degree in chemical engineering from the University of Texas at Austin, and BS degrees in chemical engineering and chemistry from Texas A&M-College Station and Sam Houston State University, respectively.

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Carrie Beitler is a senior engineer at Trimeric Corp. in Buda, Texas. She has over 15 years of experience in process engineering, process modeling and optimization of unit operating in the natural gas, petroleum refining and CO_2 processing areas. She also specializes in the development of process design packages for the fabrication of open-art technology such as caustic scrubbers, acid-gas injection units, glycol dehydrators and amine treaters. She has a BS degree in chemical engineering from Purdue University.