

Use of Glycerol (Glycerin) to Dehydrate CO₂ Above the Critical Pressure at Denbury's Mississippi Facilities

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ABSTRACT

Denbury Onshore LLC (Denbury) is currently building the world's third glycerol dehydration unit for drying carbon dioxide (CO₂). There are two other known glycerol dehydration systems in the world; of which, one is still operating on a CO₂ production gas stream. The Denbury unit will be the first new glycerol dehydration system built in over 15 years. Fabrication of major vessels is underway as of July 2004, and startup is scheduled for early 2005.

Glycerol dehydration is a process that is used when high-pressures and non-idealities cause excessive vapor losses of glycol (example glycols: ethylene glycol, diethylene glycol, triethylene glycol), which makes normal glycol dehydration uneconomical. The use of glycerol (also known as glycerin) may be desirable in high-CO₂ dehydration applications, high pressure gas applications, and in acid gas compression and dehydration applications associated with natural gas production facilities. Such applications are growing in number within the CO₂-flood EOR community and the natural gas industry, especially in combination with deeper reservoirs and/or overseas.

This paper discusses differences between glycerol and glycol dehydration with supercritical, dense-phase CO₂ gas streams. This paper also discusses the design, and construction of Denbury's new glycerol dehydration system. Since commercial process simulators are not well suited for design of this type of system, Trimeric Corporation developed a means to rigorously predict phase equilibria in the absorber as part of the project. The simulator and other available data were used to design the Gluckstadt glycerol dehydration unit.

BACKGROUND

The decision to install the new glycerol dehydration at Denbury's Gluckstadt facility is based on a doubling of Denbury's CO₂ production over the next two years and the benefits of processing the gas at pipeline conditions. At planned pipeline conditions, CO₂ is in the supercritical phase, and glycerol can dehydrate the gas more effectively than glycols. (Critical pressure and temperature for pure CO₂ are 1070 psia and 87.8°F, respectively.) A significant amount of research was performed in the 1980's to understand the dynamics of dehydrating supercritical CO₂ with glycols and glycerol (1, 2, 3, 4). The existing glycerol process that is in operation at Jackson Dome was based on this research. The Jackson Dome process is reaching capacity and additional dehydration facilities are required.

In 2003, an expansion to the glycerol process at Jackson Dome increased the design capacity from 150 MMscfd to 300 MMscfd. Equipment changes consisted of an internal upgrade to the inlet separator, change-out of trays to structured packing in the contactor, and larger rod size on circulation pumps. The post-expansion performance of the process at Jackson Dome was valuable for the design of the new Gluckstadt facility. Performance data provided confirmation of the process simulation developed for the Gluckstadt design. Results from the rigorous process simulation were used with operational knowledge of process and design improvements that have occurred over the past 20 years to develop the design basis for the Gluckstadt fabrication.

The Gluckstadt glycerol process will be a central dehydration facility, located about 15 miles from Jackson Dome, near the well head production. As such, the process will operate at a higher pressure than Jackson Dome operations because the pipeline that serves the enhanced oil recovery (EOR) fields begins at Jackson Dome. General design parameters for Gluckstadt were:

- 100 MMscfd gas flow;
- 99.4% CO₂, 0.3% C₁, 0.3% N₂; and
- 1,500 psig and 115 °F

Because the Gluckstadt process would operate at conditions outside the experience range at Jackson Dome, efforts were made to best understand the effect on glycerol solubility, glycerol/water equilibrium, and other dehydration design parameters. A simulation was developed using this information to facilitate the design of the Gluckstadt unit.

GLYCEROL DEHYDRATION FOR SUPERCRITICAL CO₂

Supercritical CO₂ impacts the design of a dehydration system primarily in two main ways:

- Mutual solubilities of the desiccant and CO₂; and
- Saturated water content of CO₂ with temperature and pressure.

The supercritical CO₂ acts very much like a solvent in the way that it holds on to these compounds. Much work was performed by Wallace (1) and Kobayashi (2, 3, 4) to document the solubility of glycerol and glycols in supercritical CO₂ in the early 1980's. Data taken both in a laboratory setting and also from field tests concluded that glycerol had a much lower solubility in supercritical CO₂ than ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG). For example, over a pressure range of 1200 to 2000 psig, TEG was 10 to 200 times more soluble than glycerol in CO₂. This means that TEG would have excessive vapor losses and makeup requirements, which makes normal glycol 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.

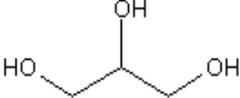
It was also shown that, unlike the glycols, glycerol solubility in the CO₂ did not increase as significantly with lower CO₂ temperatures. However, because of the high glycerol viscosity and rapidly increasing supercritical CO₂ density as the temperature decreases, glycerol dehydration would probably not be used to dehydrate CO₂ below 100°F. In addition, the solubility of CO₂ in glycerol was also determined to be only a tenth of the volume absorbed by the glycols. This results in lower flashing losses.

Water solubility in CO₂ is well documented in several sources, e.g., the GPSA handbook (5). Generally speaking, at a fixed temperature the water content decreases with increasing pressure up to near the critical pressure (subcritical). As the pressure increases beyond the critical pressure (1070 psia), the water content increases. This dual effect makes a V-type curve for a water content curve at a given temperature. As an example – the water content for a pure CO₂ stream at 100 °F is 428 lb/MMCF for 100 psig, 93 lb/MMCF for 800 psig, and 192 lb/MMCF for 1500 psig. Knowing the correct moisture content of the supercritical CO₂ are required to ensure that the absorber and regeneration equipment are not undersized for an application.

Other parameters that are important to review in the design are the density of CO₂ and also the viscosity of glycerol. Many property sets do not provide good density values for supercritical CO₂ when small amounts of inert gases are present. This can be a very significant issue that should not be overlooked since relatively trace amounts of contaminants (e.g., N₂ and hydrocarbons) can greatly change the density, water content, and other properties of supercritical CO₂ (4). It is important to use measured data when possible.

The viscosity of glycerol is also much different than the glycols. It is important to heat trace lines to account for the higher viscosity and freezing point. Table 1 compares the properties of glycerol to TEG because most in industry are more familiar with TEG.

Table 1. Physical Properties of Glycerol and Triethylene Glycol

Property	Triethylene Glycol	Glycerol
Molecular structure		
Molecular formula	C ₆ H ₁₄ O ₄	C ₃ H ₈ O ₃
Molecular weight	150.17	92.09
Specific gravity, 20°/20°C	1.125	1.261
Boiling point, °C and 1 atm	285	290
Vapor pressure, mm Hg at 20°C	< 0.01	<0.01
Freezing point, °C	-7.2	17
Solubility in water, % by weight at 20°C	Miscible	Miscible
Absolute viscosity, cps at 20°C	47.8	1490
Heat of vaporization, Btu/lb at 1 atm	227	401
Specific heat at 30°C, Btu/lb/°F	0.525	0.574

Sources: NIST website, Chemfinder website, Material Safety Data Sheets

OTHER POTENTIAL APPLICATIONS OF GLYCEROL DEHYDRATION

Although the use of glycerol was developed specifically for dehydrating supercritical CO₂, there are other potential applications of the technology. For example, acid gas compression and injection systems typically involve high CO₂ as well as high H₂S concentrations. Glycerol may be a good solvent to dehydrate these streams if dehydration at high pressure is needed. Similarly, natural gas streams can also have large CO₂ contents. Glycerol may be a very good agent to dehydrate such gas at the production facility to reduce its corrosivity so that it can be transported via pipeline to an end user or to additional processing facilities.

GLUCKSTADT DESIGN DEVELOPMENT

The existing glycerol process at Jackson Dome is one of three plants to have been built for the dehydration of supercritical CO₂-rich streams. It is believed to be the only one still in operation. Denbury's first-hand operating experience with this process was very valuable in the design of the Gluckstadt unit.

Simulation Development

Trimeric Corporation developed a simulation tailored specifically for supercritical dehydration of CO₂ with glycerol. Supercritical CO₂ is very non-ideal and requires careful review of thermodynamic properties and relationships to accurately predict process performance. Most commercial process simulators are not well suited for design of this type of system because the standard thermodynamic packages perform poorly when modeling fluid properties and phase equilibria at near-critical conditions. Using a publicly available simulator "as is", without checking the results and modifying the appropriate physical property or thermodynamic variables as needed, can lead to faulty equipment design and poor performance in the field. For example, the solubility of TEG in supercritical CO₂ is 975 times greater than what would be predicted using Raoult's law at 115 °F and 1200 psig. Similarly, industry work-horse equations-of-state such as the Peng-Robinson become very inaccurate when predicting the water content of CO₂ at conditions near the critical point. Some of the key aspects in the model development are discussed in the subsections below.

Absorber K-Values – One of the important aspects of designing glycerol dehydration systems for supercritical CO₂ is to have a good estimate of the K-value (i.e., phase equilibrium distribution coefficient) for water at the conditions in the absorber. Inadequate CO₂-water equilibrium data can produce erroneous results in the absorber that adversely affect the prediction of operations in downstream vessels as well. Trimeric uses WINSIM's Design II process simulation software to do the absorber calculations with K-values for water that are rigorously calculated from the following thermodynamic relationship:

$$K = \gamma P^{\text{sat}} \Phi^{\text{sat}} \eta / \Phi P \quad [1]$$

where

K = K-value, defines as y/x

y = Mole fraction water in the dense CO₂ phase

x = Mole fraction water in the liquid phase

γ = Activity coefficient for water

P^{sat} = Vapor pressure of pure water at the system temperature

Φ^{sat} = Fugacity coefficient for pure water vapor at the system temperature and P^{sat}

η = Poynting correction factor for water

Φ = Fugacity coefficient of water for the vapor phase

P = System pressure.

Most of the parameters in Equation 1 are readily known or accessible from the literature. For example, the system operating pressure is known and the vapor pressure for pure water can be obtained from steam tables. The fugacity coefficient for pure water vapor at the system temperature, Φ^{sat} , can be assumed to be unity. The calculation of the Poynting factor is relatively straightforward based on the partial molar volumes of the components. The activity coefficients can be found from available vapor-liquid equilibrium data (see discussion in the subsection below). However, it is the calculation of the vapor-phase fugacity of water in dense-phase CO₂ 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 2 shows the water contents of the treated gas and then the equilibrium water content that would be predicted for the lean glycerol solution at the absorber conditions. The absorber outlet is in very close approach to equilibrium under these operating conditions. The approach is within a few lb/MMscf or 5 to 17% of the measured data. These results show that the method discussed above is reliable for predicting K-values and dehydrator outlet water contents under various conditions.

Table 2. 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 of water in glycerol is important because it is used in the prediction of the K-values in the absorber as discussed above (activity coefficient of water). It is also used to determine the water content in the lean glycerol from the reboiler and Stahl column. The lean glycerol water content is in turn important in modeling the absorber.

The Wilson activity coefficient model is used in the simulation to predict activity coefficients for water and glycerol. Vapor-liquid equilibrium data for water and glycerol were obtained from the public literature and used to regress the adjustable parameters in the Wilson equation. Of particular interest were data in the concentration and temperature ranges in the absorber and reboiler.

CO₂ Solubility in Glycerol – It is important to know the solubility of CO₂ in glycerol for several reasons. First, it provides a means of determining how much CO₂ is picked up in the absorber and how much will evolve in the flash tank. The flash gas flow rate is one of the key variables used to size the flash tank. Second, the solubility of CO₂ in glycerol

is important in predicting two-phase flow through the heat exchangers in the process as the temperatures and pressures of the streams vary. Two-phase flow needs to be considered because the properties of the liquid and vapor in these streams can greatly affect the velocities through the exchangers and this impacts the size of the equipment. Available equilibrium data were used with the Wilson activity coefficient model to predict CO₂ solubility in glycerol.

Viscosity – The viscosity of glycerol mixtures is calculated using the Ln Average method in WINSIM. This method calculates the natural log of the mixture viscosity from the summation of the mole fraction for each component in the liquid stream times the natural log of the pure component viscosity. Pure component viscosity data are available in the simulator for glycerol, water, and many other more minor components of interest.

The Ln Average method was selected because the predicted viscosities closely matched those found in the literature. Accurate viscosity data are needed to calculate pressure drop through the equipment in the dehydration system and to model the hydraulics in the absorber.

Thermal Conductivity – The Li method is used to calculate the thermal conductivity of glycerol mixtures in the system (6). This method accurately predicts the thermal conductivity for both 50-50 glycerol-water mixtures and high purity glycerol streams.

Density – The densities of the inlet and outlet CO₂ streams from the absorber were calculated using the Peng-Robinson equation of state. The fluid densities calculated with the Peng-Robinson equation of state and binary parameters in WINSIM compared reasonably well to those obtained from other sources.

Solubility of Glycerol in Dense-Phase CO₂ – The solubility of glycerol in dense-phase CO₂ has been reported (1) and is used to estimate glycerol losses from the absorber.

DESIGN PARAMETERS OF THE GLUCKSTADT DEHYDRATION UNIT

The Gluckstadt dehydration unit will treat 100 MMscfd of gas at 115 °F and 1500 psig. The gas will contain approximately 99.4 mole% carbon dioxide, 0.3 mole% methane, and 0.3 mole% nitrogen on a dry basis. (Gas from the wellhead is actually at 145 °F but will be cooled to 115 °F and the condensed water removed prior to entering the dehydration unit.) The gas is saturated with water at the inlet temperature and pressure (approximately 200 lb/MMscf). The treated gas will have a design specification of 30 lb/MMscf water content maximum; however, the Gluckstadt dehydration unit will be conservatively sized for 20 lb/MMscf outlet water content.

Trimeric worked cooperatively with Dickson & Tryer (D&T) to provide a package dehydration system to meet the gas specifications at Gluckstadt. Trimeric developed the design basis and equipment sizes and D&T performed the detailed engineering and fabrication of vessels and process modules.

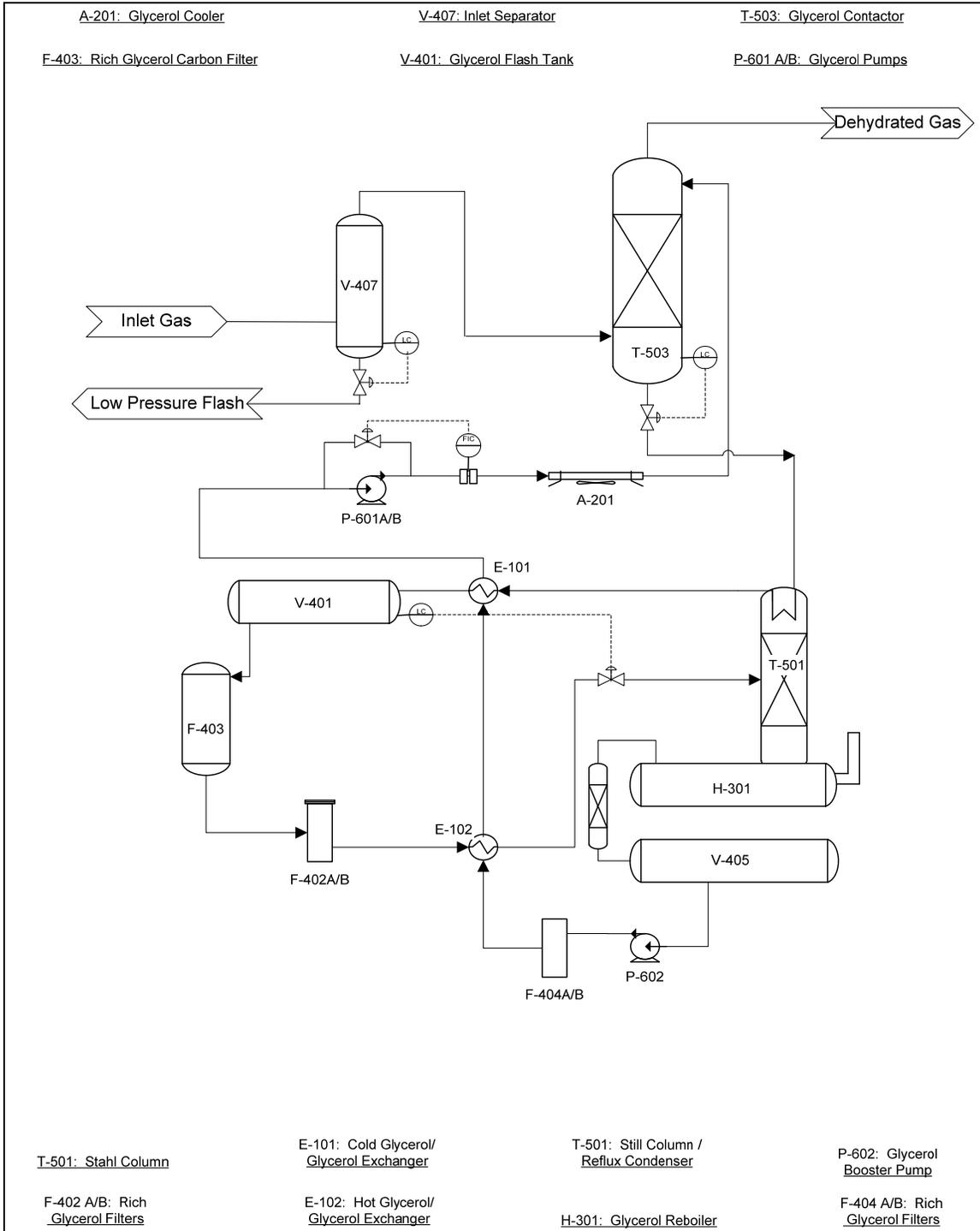
Process Description

Figure 1 shows the process flow diagram of the glycerol dehydration unit for the Gluckstadt facility. Wet feed gas passes through the inlet separator (V-407) to remove free and entrained liquids. The gas then enters the bottom of the glycerol contactor (T-503) and is contacted countercurrently with lean glycerol to remove water from the CO₂ stream. The dry CO₂ exits the top of the absorber and is routed into a dry line for delivery. The contactor is equipped with a high efficiency horizontal flow mist eliminator to recover residual glycerol. The rich glycerol from the absorber bottoms is at high pressure (1500 psig) and flows through a pressure control valve where the pressure is reduced to 90 psig. This pressure reduction causes the flow to be two-phase.

The rich glycerol from the pressure control valve then flows through the reflux condenser section of the still column (T-501) to provide the necessary reflux. The rich glycerol from the reflux condenser then flows to E-101, the glycerol heat exchanger, where it is preheated. The heated glycerol from E-101 flows to the flash tank V-401. V-401 is a horizontal two-phase separator where glycerol is separated from CO₂. The glycerol from V-401 flows to E-102 where it is heated again by cross-exchange with the hot, lean glycerol from the surge tank. This temperature increase causes the flow from E-102 to be two-phase. The rich glycerol then flows across a pressure control valve where the pressure is reduced to near atmospheric prior to entering the regeneration portion of the process.

The rich glycerol flows from E-102 to the Still column (T-501) where water is stripped from the wet glycerol by steam generated in the reboiler. The reflux condenser in the Still column condenses trace amounts of glycerol leaving the stripper and returns it to the system. The partially stripped glycerol flows from the stripper to the reboiler where it is further heated. Additional water can be removed by the introduction of stripping gas into the bottom of the Stahl column. The water stripped from the glycerol is vented from the Still column to the atmosphere.

Figure 1. Process Flow Diagram for Gluckstadt Glycerol Dehydration Unit



The hot lean glycerol from the surge tank flows to booster pumps (P-602A/B), is pumped through the lean glycerol filter (F-304A/B), and then through E-102 and E-101 where it is cooled. The glycerol then flows to the circulation pump (P-601) where it is pumped to the air cooler (A-201) at 1500 psig. High pressure glycerol from P-601 flows through A-201 where it is cooled to the absorber operating temperature. The glycerol then flows back to the contactor (T-503).

Process Design Criteria

Trimeric modeled the Gluckstadt dehydration unit using the WINSIM simulator, as previously described. The simulation results provided the basis for the process operating conditions needed to perform detailed equipment design. The equipment design criteria are summarized in Table 3.

Table 3. Gluckstadt Dehydration Unit Design Criteria

Tag No.	Description	Specification
V-407	Inlet Separator	100 MMscfd capacity at 115°F, 1500 psig, 31 lb/ft ³ density, 15 gpm condensed water, 316L SS.
T-503	Glycerol contactor	Column diameter and packing height from Jackson Dome data (see discussion below), 316L SS/CS.
P-601 A	Glycerol pumps	Lean glycerol circulation rate of several gallons/lb of water removed, small amount of gas in stream.
P-602 A/B	Glycerol booster pumps	Lean glycerol boost pressure to 60 psig, high temperature service (370 °F)
V-401	Rich glycerol flash tank	Horizontal vessel for two-phase separation. 50 psig and elevated temperature. CO ₂ flash gas rate based on 1.1 scf/gal glycerol from simulation.
T-501	Glycerol still/reflux condenser	Random packing; size for 2 scf/gal stripping gas; 20% reflux ratio; ambient pressure. Two-phase flow through tube side of reflux condenser.
E-101 A/B	Cold glycerol heat exchanger	20 psi drop on tube side and 5 psi drop on shell side; two-phase flow on tube side; 316L SS on rich side.
E-102 A/B	Hot glycerol heat exchanger	20 psi drop on tube side and 5 psi drop on shell side; two-phase flow on tube-side (exit only); 316L SS on rich side.
H-301	Glycerol reboiler	Operating temperature to avoid thermal degradation; firetube flux maximum 6000 Btu/hr/ft ² .
V-405	Surge Tank	Capacity determined from main circulation rate and desired residence time.
A-201	Lean glycerol cooler	Aerial cooler to cool lean glycerol to contactor to 115°F. Carbon steel.
F-402 A/B	Rich glycerol filter	Main circulation flow rate, 10 psi drop, carbon steel.
F-403	Rich glycerol filter (carbon)	Main circulation flow rate, 10 psi drop, carbon steel.
F-404 A/B	Lean glycerol filter	Main circulation flow rate, 10 psi drop, carbon steel.

The physical design and sizing of the glycerol contactor was of particular importance for this project. Data from the Jackson Dome dehydration unit were critical in sizing the contactor for the Gluckstadt facility. The Gluckstadt glycerol dehydrator will use the same packing, have approximately the same gas and liquid composition, and operate at the same temperature but at a somewhat higher pressure. Operating data from the existing unit at Jackson Dome were used to scale the column diameter and packing height of the new contactor at Gluckstadt.

Process Design Decisions

Operational experience at Jackson Dome and advancements in process technology influenced the Gluckstadt process design. The main areas that will be discussed are with material and equipment choices. Photos of the Gluckstadt unit currently being built are shown in Figure 2.

Material of construction on all process piping and vessels at Jackson Dome is 316L SS clad. In general, many of the same material choices used for glycol are appropriate for glycerol. In contrast to Jackson Dome, the material changes for the Gluckstadt project include:

- Contactor with 316L SS lower section and carbon steel shell above 2-ft of packing;
- Carbon steel for all glycerol piping except downstream of glycerol flash tank;
- Carbon steel shell on rich/rich and lean/lean exchangers;
- Carbon steel glycerol air cooler;
- Carbon steel reboiler shell; and
- Carbon steel filter vessels.

Wet CO₂ is a corrosive environment and experience has shown 316L SS provides long-term integrity. For the contactor, the inlet gas is saturated with water below the packed section, but becomes sub-saturated as the gas moves counter-current with glycerol through the packed section. The use of carbon steel in the packed section of glycol contactors in CO₂ service has been demonstrated successfully in several applications. For Gluckstadt, the transition from 316L SS to carbon steel was after the first two feet of packing.

Circulating glycerol in the regeneration system will contain less than 10 wt% water. In this regard, the piping and vessels associated with the regeneration of glycerol could be carbon steel. However, in the case of the glycerol flash tank and the glycerol still, wet CO₂ is present and the vessels are 316L SS. The rich glycerol piping downstream of the glycerol flash tank was also made 316L SS. This decision was not from a corrosion concern, but to provide low temperature integrity if raw CO₂ vented through the control valve if liquid level was lost.



Figure 2 – Process Modules for Glycerol Dehydration in Fabrication

- reboiler / stahl column
- flash vessel and filters
- hot / cold exchangers



Design elements of note from the Jackson Dome process that were incorporated into the Gluckstadt project were:

- Isolation valves for the hot and cold glycerol heat exchangers;
- Glycerol booster pumps; and
- Inconel fire tube liner.

Isolation valves to the hot and cold glycerol heat exchangers were added to the regeneration design to enable periodic cleaning of the exchangers and other maintenance while in operation. Glycol heat exchangers have a tendency to foul over time for various reasons (possibly as a result of upset conditions, high skin temperature, etc.) and glycerol systems are no different. The Gluckstadt regeneration system was designed to operate at a temperature believed to be below the degradation temperature of glycerol.

An inconel fire tube liner was part of the Jackson Dome design and is critical to moderating the skin temperature in contact with the glycerol. The presence of a liner and good burner control is expected to minimize any glycerol degradation that may occur.

The glycerol booster pumps are used to ensure and maintain continuous flow from the reboiler through the hot and cold glycerol exchangers. Glycerol has a much higher viscosity than glycols, and complicates the common approach of just using gravity to flow through the exchangers. The use of booster pumps also allows for a more compact exchanger design because a larger pressure drop can be tolerated.

Other design aspects of note include the use of horizontal submersible pumps for glycerol circulation, incorporation of a Stahl column with the reboiler/surge tank, and a provision for a filter coalescer. A submersible pump was specified for the circulation pump because of the low maintenance requirement and cost experienced by Denbury. The Stahl column provides a mechanism to remove more water in the reboiler, but is not required to meet the design water content specification. Piping will be in place for the addition of a filter coalescer upstream of the glycerol contactor at a later date. As wells decline, formation water will contain more salt, and chlorides will accumulate in the circulating glycerol. A filter coalescer will provide a means to more effectively remove this water from the process.

PROJECT REVIEW

The rigorous review of thermodynamic properties associated with the dehydration of supercritical CO₂ with glycerol was paramount in the development of a reliable process simulation tool for the Gluckstadt process design. Detailed engineering has been completed and vessels and process modules will be fabricated by January 2005. First production from Gluckstadt is expected in the second quarter of 2005.

The tools and knowledge utilized in the Gluckstadt design are also being applied to several other glycerol dehydration projects. Jackson Dome operational data is periodically reviewed to identify future capacity restrictions. Also, the simulation was used to develop design criteria for a well head dehydration application; that is, available package glycol units were reviewed and a system chosen that could also function with glycerol as a desiccant.

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