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Task 2 Deliverable

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ADVANCED ENERGY SYSTEMS

GTI REPORT

Natural Gas Liquefier Gas Clean Up System

GTI Project Number 20285

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Natural Gas Liquefaction System Controls

INTRODUCTION

SMALL-SCALE LIQUEFACTION TECHNOLOGY DESCRIPTION

GTI's small-scale natural gas liquefier is designed to enable conversion of natural gas into a liquid at much smaller scale than normally seen in commercial practice. Figure 1 shows a picture of skid-mounted liquefier, including the gas clean-up system (shown in the background).

Figure 1: GTI Skid-Mounted Liquefier

Natural Gas Sulfur, Water and Carbon Dioxide Removal

The removal of compounds such as hydrogen sulfide, odorants, carbon dioxide, and water are a necessary requirement in liquefaction because these compounds will turn to solids at cryogenic temperature conditions. One of the cost challenges on small-scale liquefaction is ensuring the cost and performance of this equipment is acceptable and reliable.

Natural gas can be made to convert from a gas to a liquid at temperatures ranging from –220°F to –260°F (depending on gas composition and pressure). Natural gas is not pure methane. The composition of natural gas is predominantly methane, with a number of decreasing heavy hydrocarbons and trace non-hydrocarbon species including nitrogen, carbon dioxide, and water. Some of these components will be partially or wholly soluble or insoluble in liquid at cryogenic conditions, resulting in a possible three-phase situation involving gaseous, liquid, and solid compounds (Figure 2).

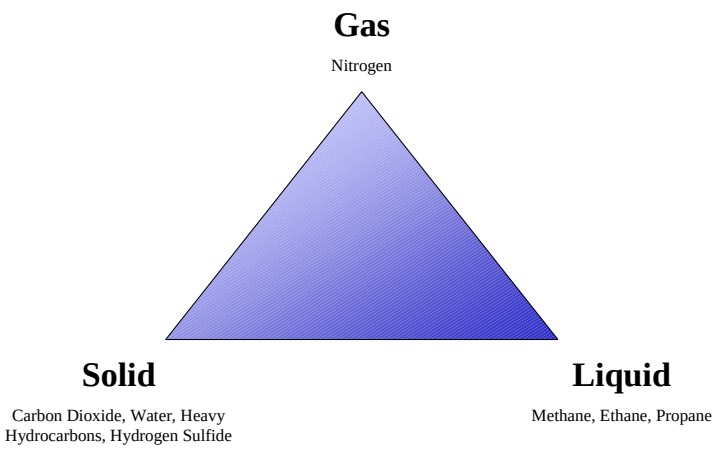

Figure 2: Natural Gas Phase Considerations

Insoluble compounds may remain as a gas (e.g., nitrogen) or may condense as solids (e.g., carbon dioxide, water, heavy hydrocarbons). To address these concerns, natural gas cleanup systems are needed to nearly completely remove certain key actors such as carbon dioxide, water, and hydrogen sulfide.

Table 1 provides a summary of typical pipeline natural gas compositions seen in the U.S.

Table 1: Typical Pipeline Natural Gas Composition.

Component	Mole %
Nitrogen	1.68%
Methane	93.81%
Ethane	3.5%
Propane	0.67%
i-butane	0.1%
n-butane	0.12%
i-pentane	0.04%
n-pentane	0.02%
n-hexane	0.06%
Aromatics (benzene, toluene etc.)	~1 ppm

Table 2 shows the nominal design basis for sizing of the desulfurization and TSA system for these key components.

Table 2: Key Contaminants in Design Basis

Contaminant	Level
CO_2 content: design level	1 mol %; maximum(*) = 2 mol%
Water content	4 -7 lb/MMscf = 140-200 ppmv
Typical sulfur	8 ppm including mercaptan odorant

(*) reduced product flow

There are several methods that can be used to address these minor or trace constituents. The approach used in this system is a two-step process. The first addresses sulfur removal, followed by combined removal of carbon dioxide and water. Both of these employ the use of solid adsorbents, a proven approach in the area of natural gas liquefaction.

The GTI small-scale liquefier system relies on temperature swing adsorption (TSA) to remove carbon dioxide and water. In the tri-tower TSA scheme, three individual vessels are packed with adsorbent materials that selectively remove certain species. This is complemented by a separate sulfur removal column to trap hydrogen sulfide and odorants.

Natural Gas Desulfurization System and Materials

Typically, desulfurization can be accomplished by using either activated promoted carbon or zinc oxide. Previously, GTI used a product called NUSORB FC-3, an activated carbon impregnated with metal oxides. These were charged into three different columns during prior testing at GTI. Overall, this material provided suitable removal of sulfur compounds, achieving purity levels below detectable limits with instruments used at the time (below 30 ppb).

To improve overall performance and ensure capture of a wide spectrum of odorants that can be found in natural gas, a new desulfurizer material system is being used. This is based on two newer sulfur adsorbent products from Sud-Chemie. A new single-tower unit was built by GTI with a 1' diameter by 8' high column.

The Sűd-Chemie (SCI) ambient temperature desulfurization agents being used are designated FCDS-GS12 and FCDS-GS13. SCI recommends using a sequential bed configuration of GS12 on the inlet followed by GS13. DMS (dimethyl sulfide) and TBM (tertiary butyl mercaptan) are the main odorants present in the natural gas supply at GTI, while THT (thiopane), COS and H2S appear at varying but significantly lower levels. FCDS-GS12 is a zeolite-based adsorbent and demonstrates a higher capacity for DMS compared to activated carbon and other commercially available zeolitic adsorbents and it also has a good capacity for THT. Studies have shown DMS to be the most difficult odorant to remove from natural gas. FCDS-GS13 is a base metal type adsorbent and has shown good capacities for TBM and H2S. Although COS is even more difficult to remove than DMS, as it is typically present in lower concentrations than the odorants, it should be removed by the GS13.

Tri-Tower Adsorbent System and Materials

The tri-tower selective gas adsorption process is desirable for this application because it permits continuous round-the-clock operation and is capable of achieving very high selectivity and removal performance for potential compounds that could form solids.

Figure 3 shows the basic logic for this type of system. In this graphic, the three towers are depicted over time, with the logic for the first time interval shown. In this design, the first interval is approximately 4 hours and the total cycle time is 12 hours. Note that the natural gas that ultimately goes to the natural gas prime mover is carrying a higher concentration of water and carbon dioxide and is consumed as fuel gas in the system. The logic for the subsequent two time sequences is similar, but shifted to begin with tower 2 and tower 3, respectively.

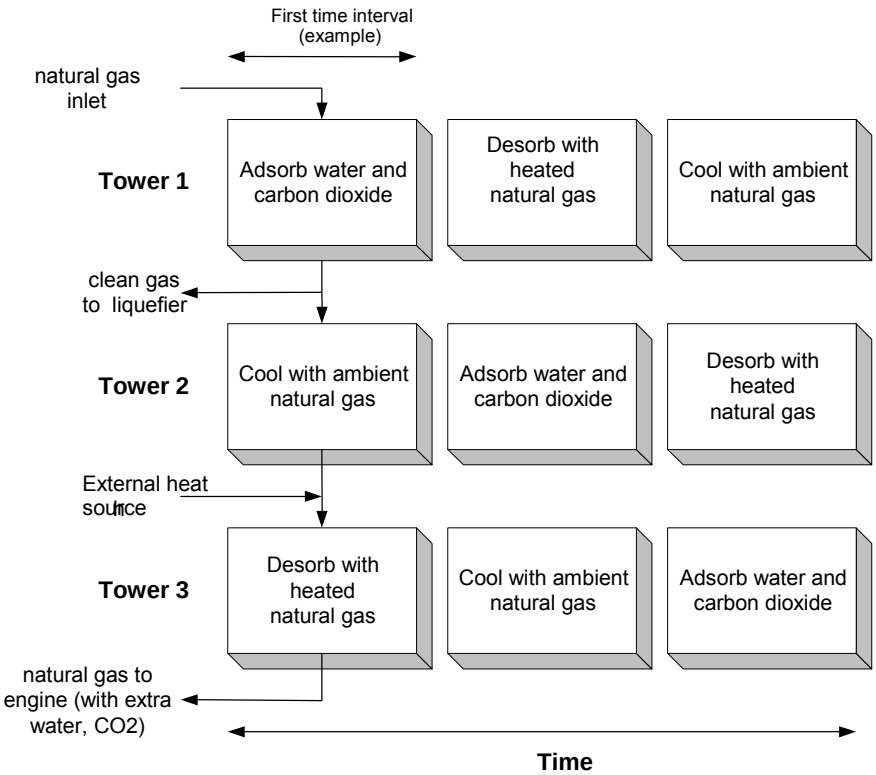

Figure 3: Operational Logic for Tri-Tower System

The specific process flow and gas volumes for the TSA system designed for the 1000 gallon per day liquefier is shown in Figure 4. The feed gas volume of 78 scfm passes through the first tower (labeled A for adsorbing). The clean product gas from this tower is split, with 55 scfm of clean product gas going to the liquefier. The balance, 23 scfm, goes to the tower C (for cool down) and then to tower H (which is being heated to desorb trapped carbon dioxide and water). This gas then is cycled to the natural gas prime mover.

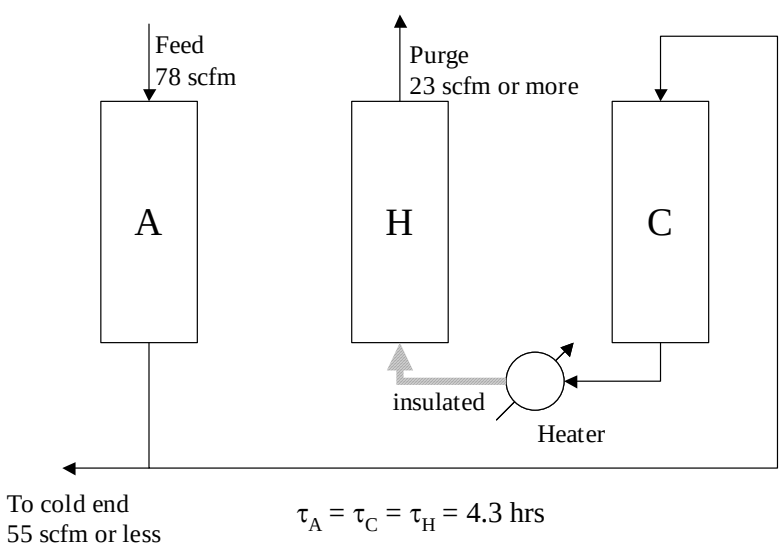

Figure 4: Series Cool-Heat Regeneration Scheme

Each of these towers is charged with an adsorbent product developed by UOP for natural gas liquefaction or LNG service. The material is a molecular sieve material designated as 5A-50. This binderless molecular sieve material is expected to demonstrate higher carbon dioxide removal effectiveness compared to a standard 4A product often used for LNG.

Major upgrades were made to enable the tri-tower temperature swing adsorption system to function in an automated fashion. This effort began by building a manifold assembly to enable the sequenced valve operation required to allow tri-tower operation. Figure 5 shows a picture of the tri-tower TSA system with the installed manifold of air-actuated control valves. There are a total of 18 air-actuated valves that provide the time sequenced switching required for this system.

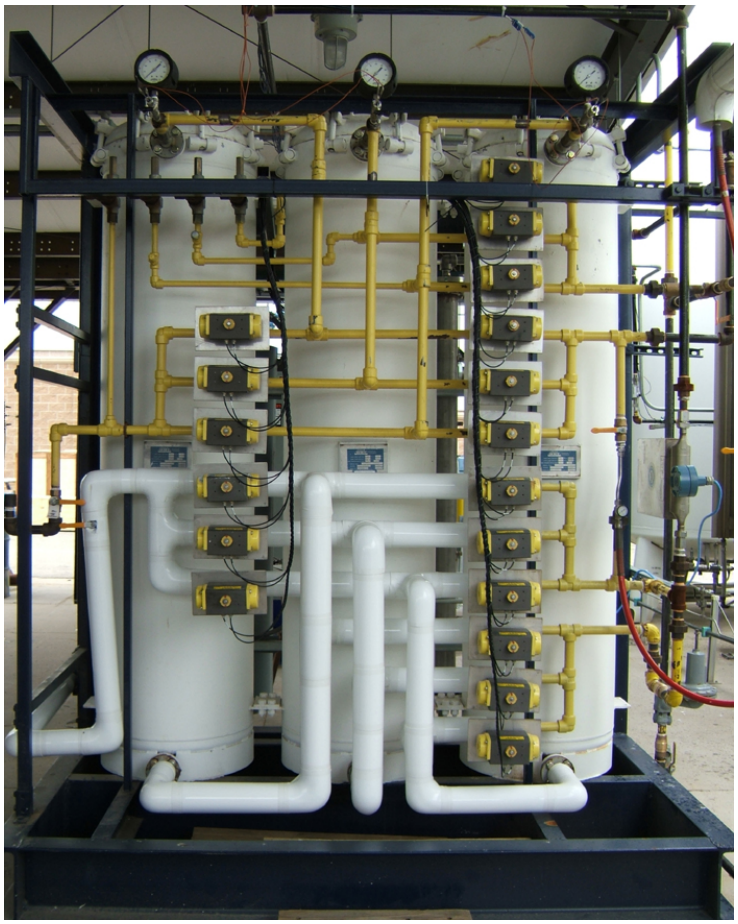

Figure 5: TSA System and Air-Actuated Control Valves

A feature of the TSA control system is an electric heater used to ensure adequate temperature is obtained to effect the TSA desorption cycle that results in removal of trapped carbon dioxide and water. Figure 6 shows a picture of the TSA heater and controller. The heater is required to achieve gas temperatures in excess of 400°F to provide an effective removal of captured carbon dioxide and water – this is typically referred to as regeneration of the adsorbent materials.

Figure 6: TSA Regeneration Heater and Controller