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Project Summary

Glycol Dehydrator BTEX and VOC Emission Testing Results at Two Units in Texas and Louisiana

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Glycol dehydrators are used in the natural gas industry to remove water from natural gas and, in the process, may also remove and emit significant quantities of benzene, toluene, ethylbenzene, and xylenes (BTEX). The objective of this project was to collect emissions test data at two triethylene glycol (TEG) units to provide data for comparison to GRI-GLYCalc[™], a computer program developed to estimate emissions from glycol dehydrators. Three analytical techniques were used to determine emissions: total capture condensation, pressurized glycol cylinders, and atmospheric rich/lean glycol sampling.

Site 1 test results, using the various techniques, yielded BTEX emission estimates that agreed reasonably well. Total volatile organic compound (VOC) emissions from the two glycol methods did not match well with the total capture benchmark results; this is consistent with previous results for systems without flash tanks. Site 2 atmospheric rich/lean glycol and pressurized glycol emission results agreed closely with the total capture results for both BTEX and total VOCs. GRI-GLYCalc predictions using natural gas samples taken before the glycol absorber agreed well with the total capture results for total BTEX emissions.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the

same title (see Project Report ordering information at back).

Overview

The Emissions and Modeling Branch (EMB) of EPA's Air and Energy Engineering Research Laboratory was established to develop new and improved emissions inventory methodologies for use by states. New improved methods are reviewed by the Emission Factor and Inventory Group of EPA's Office of Air Quality Planning and Standards (OAQPS). New methods approved by OAQPS are incorporated into EPA guidance documents for state use in preparing emissions inventories required by the Clean Air Act.

Emissions estimation procedures for glycol dehydrators are not available in current EPA emissions estimation guidance. EMB held discussions with the Gas Research Institute (GRI) and the American Petroleum Institute (API) and determined that they were actively involved in the development of process models for estimation of emissions from glycol dehydrators. An industry working group, chaired by GRI, had begun a program to develop field testing methods and to collect emissions test data. The testing program and associated emissions model development were of immediate interest to EMB as a potential tool for estimating emissions from glycol dehydrators. EPA, GRI, and API agreed that it would be appropriate for EMB to supplement the industry program with an independent EPA testing program to assess the acceptability of the process emissions model as an approved method for inclusion in EPA emissions estimation

guidance. This report describes two emissions tests conducted by EMB to assess the current GRI glycol dehydrator emissions model GRI-GLYCalc[™]. Additional tests, not discussed in this report, have been performed by GRI and API at eight other sites. These data will also be reviewed prior to making a recommendation on including GRI-GLYCalc in EPA emissions inventory guidance documents.

Glycol dehydrators are used to remove water from natural gas and, in the process of removing the water, may also remove and emit significant quantities of benzene, toluene, ethylbenzene, and xylenes (BTEX). The most common glycol dehydrator design employs an absorber, with triethylene glycol (TEG) used as the absorbent, to remove water from natural gas. In the absorption step, aromatic hydrocarbons such as BTEX are also absorbed into the glycol stream. Following the absorption step, the glycol, rich with water and BTEX compounds, is distilled to strip water from the glycol. Recovered lean (dry) glycol is recycled for use in the absorber. Emissions of BTEX and other volatile organic compounds (VOCs) occur from the glycol reboiler still vent. As a result of the 1990 Clean Air Act Amendments, hazardous air pollutant emissions (primarily BTEX) from the reboiler still vent stream of glycol dehydrators have become a concern for the natural gas industry.

Site 1, a gas plant in west Texas, was processing 3.6 million standard cubic feet per day (MMSCFD)* of gas without a flash tank and using a gas-driven pump. Site 2, in southwest Louisiana, was processing 4.9 MMSCFD of gas with a flash tank and using a gas-driven pump. Testing was conducted over a 2-day period at each site. Three emissions measurement techniques were used at each site: total capture condensation (the most accurate method) and two lower cost methods (pressurized glycol cylinders and atmospheric rich/lean glycol). The lower cost methods were included in the test protocol to evaluate their applicability as emissions screening tools where use of the total capture method

may not be technically feasible or economically justifiable.

In total capture condensation, the entire still vent stream was passed through a 50-ft length of 1-in. diameter copper tubing coiled inside a 55-gal barrel and submerged in an ice/water mixture. Condensed hydrocarbons, condensed water, and noncondensable gas were measured and sampled. Results from total capture condensation were used as the benchmark against which other methods were compared.

The atmospheric rich/lean glycol method used samples of glycol from both upstream (rich) and downstream (lean) of the reboiler collected at atmospheric pressure in volatile organic analysis vials. Emissions were calculated using the difference in analyte concentrations in the rich and lean samples and the glycol circulation rate. Based on sampling experience in the GRI project, the glycol methods may not produce a representative sample for total VOC determination, particularly on systems without a flash tank.

The pressurized glycol cylinder method used samples of glycol (rich) collected at line pressure upstream of the reboiler in stainless steel cylinders. Emissions were calculated using the difference between the analyte concentrations in the glycol cylinder and a lean glycol sample downstream of the reboiler and the glycol circulation rate.

GRI-GLYCalc is a computer program developed by GRI as an alternative screening tool to estimate emissions from glycol dehydrators using process operating data and the composition of natural gas for the unit of interest. To evaluate the use of GRI-GLYCalc and alternative natural gas sampling methods, five types of natural gas samples were collected and analyzed:

- Sub-atmospheric pressure canisters upstream of the absorber using a sampling manifold;
- High-pressure cylinders upstream of the absorber with and without a sampling manifold; and
- High-pressure cylinders downstream of the absorber with and without a sampling manifold.

Results

The results of Site 1 testing, presented in tons per year plus or minus 1 standard deviation, are listed in Table 1. BTEX emission estimates using the various techniques agreed reasonably well. Prediction by GRI-GLYCalc of total BTEX emissions was close to the total capture results for some of the gas sample types. Quality control data, however, indicate that the natural gas BTEX concentrations for the cylinders may have been biased high, which caused the high prediction by GRI-GLYCalc. Total VOC emissions from the two glycol methods did not match well with the total capture benchmark results; this is consistent with previous results for systems without flash tanks.

Results of Site 2 sampling are listed in Table 2. Atmospheric rich/lean glycol and pressurized glycol emission results agreed closely with the total capture results for both BTEX and total VOC. Removal of volatile components in a flash tank upstream of the glycol sample point eliminates two-phase gas/liquid flow in glycol lines, thus allowing a more representative glycol sample. GRI-GLYCalc predictions using natural gas samples taken before the glycol absorber agreed well with the total capture results for total BTEX emissions.

For these two test sites, the GRI-GLYCalc model, using natural gas sampled with evacuated canisters, agreed very well with measured emissions as measured by the most accurate test method (total capture condensation) for each site. As shown in Tables 1 and 2, the GRI-GLYCalc estimated emissions of BTEX and total VOC are within 10% or less of the measured emissions.

Metric Equivalents

The following conversion factors are provided for use by readers more familiar with the metric system.

<u>Nonmetric</u> °F	Multiplied by 5/9(°F - 32)	<u>Yields metric</u> °C
ft	`0.305 <i>´</i>	m
ft ³	28.3	L
gal	3.79	L
in	2.54	cm
psig ton	6.89	kPa
ton	0.907	tonne

^{*} Conversion factors for nonmetric units are listed at the end of this Summary.

Table 1. Summary of Site 1 Emission Results^a

Emissions (tons per year)								
Method	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX	Total VOC		
Total Capture Condensation	1.25 ± 0.32	1.68 ± 0.29	0.08 ± 0.02	0.56 ± 0.15	3.58 ± 0.61	19.8 ± 4.0		
Pressurized Glycol Cylinders	1.22 ± 0.16	1.81 ± 0.25	$\textbf{0.08} \pm \textbf{0.01}$	0.61 ± 0.09	3.71 ± 0.51	10.7 ± 1.9		
Atmospheric Rich/Lean Glycol	1.24 ± 0.20	1.85 ± 0.28	$\textbf{0.08} \pm \textbf{0.01}$	0.62 ± 0.10	3.79 ± 0.59	11.4 ± 1.8		
GRI-GLYCalc with Canister Gas Samples	1.31	1.87	0.06	0.64	3.88	21.8		
GRI-GLYCalc with Cylinder Gas Samples Before Absorber, with Manifold	2.50	3.68	0.24	1.44	7.86	28.2		
GRI-GLYCalc with Cylinder Gas Samples Before Absorber, without Manifold	2.25	3.40	0.18	1.36	7.18	28.3		
GRI-GLYCalc with Cylinder Gas Samples After Absorber, with Manifold	1.68	2.29	0.06	1.68	5.71	25.5		
GRI-GLYCalc with Cylinder Gas Samples After Absorber, without Manifold	1.68	2.26	0.06	0.80	4.80	23.7		

^aSite 1 was a TEG dehydrator treating 3.6 MMSCFD of gas at 86°F and 659 psig; glycol circulation rate was 48.6 gal/hr.

Table 2. Summary of Site 2 Emission Results^a

Emissions (tons per year)									
Method	Benzene	Toluene	Ethylbenzene	Xylenes	Total BTEX	Total VOC			
Total Capture Condensation	6.02 ± 1.04	9.87 ± 1.50	0.84 ± 0.16	6.14±0.74	22.9 ± 3.2	36.9 ± 3.1			
Pressurized Glycol Cylinders	6.71 ± 0.98	11.1 ± 1.6	0.98 ± 0.18	7.05 ± 0.82	25.9 ± 3.2	37.9 ± 4.9			
Atmospheric Rich/Lean Glycol	5.62 ± 0.76	<i>9.25 ± 0.93</i>	0.80 ± 0.12	5.74 ± 0.40	21.4 ± 2.0	<i>30.8</i> ± <i>3.4</i>			
GRI-GLYCalc with Canister Gas Samples	5.22	8.63	0.89	7.58	22.3	36.1			
GRI-GLYCalc with Cylinder Gas Samples Before Absorber, with Manifold	5.55	8.94	0.89	6.13	21.5	32.7			
GRI-GLYCalc with Cylinder Gas Samples Before Absorber, without Manifold	5.62	8.51	0.82	5.33	20.3	31.1			
GRI-GLYCalc with Cylinder Gas Samples After Absorber, with Manifold	3.93	5.69	0.41	2.87	12.9	23.3			
GRI-GLYCalc with Cylinder Gas Samples After Absorber, without Manifold	4.35	6.32	0.49	3.48	14.6	25.3			

^aSite 2 was a TEG dehydrator treating 4.9 MMSCFD of gas at 111°F and 1063 psig; glycol circulation rate was 204 gal/hr, and flash tank conditions were 205°F and 46 psig.

C. Rueter, D. Reif, and D. Myers are with Radian Corp., Austin, TX 78720-1088. Charles O. Mann is the EPA Project Officer (see below). The complete report consists of two volumes, entitled "Glycol Dehydrator BTEX and VOC Emissions Testing Results at Two Units in Texas and Louisiana" "Volume I - Technical Report" (Order No. PB95-194130; Cost: \$27.00, subject to change) "Volume II - Appendices" (Order No. PB95-194148; Cost: 36.50, subject to change) Both volumes of this report will be available only from: National Technical Information Service 5285 Port Royal Road *Springfield, VA 22161 Telephone: 703-487-4650* The EPA Project Officer can be contacted at: Air and Energy Engineering Research Laboratory U.S. Environmental Protection Agency Research Triangle Park, NC 27711

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