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**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY**
Office Of Research And Development
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**MEMORANDUM**

**SUBJECT:** Glycol Dehydrator Emissions Test Report and Emissions Estimation Methodology

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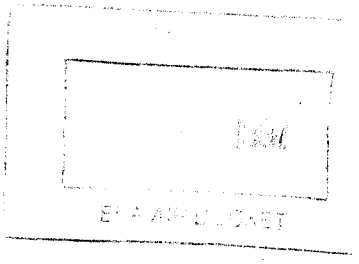

The Emissions and Modeling Branch (EMB) has completed a report titled ***Glycol Dehydrator BTEX and VOC Emissions Testing Results at Two Units in Texas and Louisiana.*** A copy of the report is enclosed for your reference. The primary objective of the project described in the report was to perform field tests at two glycol dehydrators to assess the effectiveness of the GRI-GLYCalc™ emissions model for estimating Hazardous Air Pollutant (HAP) and Volatile Organic Compound (VOC) emissions. GRI-GLYCalc is a personal computer based emissions model that has been developed by the Gas Research Institute (GRI) as a tool for gas industry use in estimating emissions from glycol dehydrators. Based on the results of our field test evaluations, and additional glycol dehydrator emissions tests sponsored by GRI and the American Petroleum Institute (API), we recommend that the GRI-GLYCalc model be included in EPA's guidance for state/local agency use for the development of emissions inventories to meet Clean Air Act requirements.

Background

Glycol dehydrators are used in the natural gas processing industry to remove water from natural gas. It has been estimated that as many as 40,000 dehydrators may be in use. Presently, AP-42 does not contain any emission factors for this process. The most common glycol dehydrator design uses an absorber, with triethylene glycol (TEG) used as the absorbent, to remove the water from natural gas. In the absorption step, aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX) that are present in the processed natural gas are also absorbed into the glycol. The BTEX compounds and other VOC species may be emitted to the atmosphere when, in a subsequent processing step, the glycol stream is distilled to recover the glycol for reuse. Emissions of BTEX and other VOCs occur from the reboiler still vent. For many dehydrators, emissions of BTEX and other HAPs are likely to exceed the "major source" HAP emissions

thresholds cited in Section 112 (a) of the 1990 Clean Air Act Amendments. The Emission Standards Division of OAQPS has in development proposed Maximum Achievable Control Technology (MACT) emissions standards for glycol dehydrators.

Use of GRI-GLYCalc

The GRI-GLYCalc emissions model runs on an IBM-compatible personal computer, with minimal system requirements. The model is currently available from the Radian Corporation of Austin, Texas (contractor to GRI) at no cost to academic institutions and government agencies. ($25 for others). The model employs fundamental engineering thermodynamics and experimental data to estimate emissions. Inputs to the model include natural gas composition data, natural gas flow rate, and dehydrator design parameters such as glycol circulation rate, dehydrator operating temperature and pressure, glycol pump type, and presence or absence of a flash tank. A user-friendly interface is provided for data input. With the exception of natural gas composition data, input data should normally be available from company operators. If necessary, default values may be assumed for some process input values. GRI-GLYCalc is a second generation model, succeeding the GRI-DEHY model previously developed by GRI. GRI-GLYCalc can output reports showing tons/year or pounds/hour emissions of BTEX, HAP, and VOC species. The model can estimate emissions for either triethylene glycol (TEG) or ethylene glycol (EG) based units. TEG units represent about 95% of the units in use. GRI-GLYCalc can also estimate the effects of condensation and incineration systems used as controls, and adjust emissions to take the use of stripping gas in the glycol regenerator into account.

Field Test Results

For the two sites where EMB sponsored emissions tests, the use of GRI-GLYCalc with measured natural gas composition data produced emissions estimates that agreed very closely with the test results for the most accurate test method. Emissions estimated by GRI-GLYCalc for both BTEX and VOC were within 10% of the measured emissions values for both sites. These test results are summarized in Tables 1 and 2. The most accurate test method is the "total capture technique" in which the entire still vent gas stream is captured, condensed, and analyzed. This method is used as a benchmark against which the results from other emissions testing and estimation methods may be compared. Other simpler test methods were also evaluated as part of this project. Test results for the atmospheric rich/lean method and the pressurized glycol cylinder method are also shown. These methods both involve the collection of glycol samples upstream and downstream of the reboiler. Emissions are calculated by material balance using glycol flow rate and glycol composition data based on laboratory analysis of glycol samples. For the EMB test sites, emissions measured with these simpler methods were generally consistent with each other and agreed well with the total capture results, except for the VOC emissions estimated for Site 1, where the simpler test methods underestimated the VOC emissions.

Additional glycol dehydrator emissions tests have been sponsored by GRI and API at 8 other test sites. These results are summarized in Tables 3 and 4. The EMB test sites appear as Sites 9 and 10 in these tables. For many of the GRI/API sites GRI-GLYCalc tended to overestimate

Table 1. EMB Glycol Dehydrator Site 1 Test Results
(tons/year)

| Pollutant | Emissions Measurement Method | | | | Difference from TCC Benchmark (tons/year) | | |
|---|---|---|---|---|---|---|---|
| | Total Capture Condensation | Pressurized Rich/Lean Glycol | Atmospheric Rich/Lean Glycol | Calculated using GRI-GLYCalc | Pressurized Rich/Lean Glycol | Atmospheric Rich/Lean Glycol | Calculated using GRI-GLYCalc |
| Total BTEX | 3.58 | 3.71 | 3.79 | 3.88 | 0.13 | 0.21 | 0.3 |
| Total VOC | 19.8 | 10.7 | 11.4 | 21.8 | -9.1 | -8.4 | 2 |

Site Characteristics: Processing 3.6 MMSCFD natural gas
Gas-fired pump
No flash tank

Table 2. EMB Glycol Dehydrator Site 2 Test Results
(tons/year)

| Pollutant | Emissions Measurement Method | | | | Difference from TCC Benchmark (tons/year) | | |
|---|---|---|---|---|---|---|---|
| | Total Capture Condensation | Pressurized Rich/Lean Glycol | Atmospheric Rich/Lean Glycol | Calculated using GRI-GLYCalc | Pressurized Rich/Lean Glycol | Atmospheric Rich/Lean Glycol | Calculated using GRI-GLYCalc |
| Total BTEX | 22.9 | 25.9 | 21.4 | 22.3 | 3 | -1.5 | -0.6 |
| Total VOC | 36.9 | 37.9 | 30.8 | 36.1 | 1 | -6.1 | -0.8 |

Site Characteristics: Processing 4.9 MMSCFD natural gas
Gas-fired pump
Flash tank in operation

Table 3. Comparison of BTEX Measured and Modeled Emissions for All Test Sites (tons/year)

| Site | Emissions Measurement Method | | | Calculated using GRI-GlyCalc | Difference from TCC Benchmark | | | % Difference | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total Capture Condensation | Pressurized Rich\Lean Glycol | Atmospheric Rich\Lean Glycol | | Pressurized | Atmospheric | GRI-GlyCalc | Pressurized | Atmospheric | GRI-GlyCalc |
| Site 1 | 0.34 | 0.43 | 0.5 | 0.4 | 0.09 | 0.16 | 0.06 | 26.5 | 47.1 | 17.6 |
| Site 2 | 4.92 | 5.48 | 5.39 | 9.76 | 0.56 | 0.47 | 4.84 | 11.4 | 9.6 | 98.4 |
| Site 3 | 89.6 | 98.6 | 98.1 | 85.4 | 9 | 8.5 | -4.2 | 10.0 | 9.5 | -4.7 |
| Site 4 | 9.89 | 9.88 | 9.87 | 20.6 | -0.01 | -0.02 | 10.71 | -0.1 | -0.2 | 108.3 |
| Site 5 | 29.1 | 26.8 | 26.8 | 45.7 | -2.3 | -2.3 | 16.6 | -7.9 | -7.9 | 57.0 |
| Site 6 | 8.56 | 10.1 | 8.55 | 13.5 | 1.54 | -0.01 | 4.94 | 18.0 | -0.1 | 57.7 |
| Site 7 | 17.7 | 20.6 | 19.3 | 30.1 | 2.9 | 1.6 | 12.4 | 16.4 | 9.0 | 70.1 |
| Site 8 | 2.61 | 2.71 | 3 | 4.25 | 0.1 | 0.39 | 1.64 | 3.8 | 14.9 | 62.8 |
| Site 9 | 3.58 | 3.71 | 3.79 | 3.88 | 0.13 | 0.21 | 0.3 | 3.6 | 5.9 | 8.4 |
| Site 10 | 22.9 | 25.9 | 21.4 | 22.3 | 3 | -1.5 | -0.6 | 13.1 | -6.6 | -2.6 |

Table 4. Comparison of Total VOC Measured and Modeled Emissions for All Test Sites (tons/year)

| Site | Emissions Measurement Method | | | Calculated using GRI-GlyCalc | Difference from TCC Benchmark | | | % Difference | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Total Capture Condensation | Pressurized Rich\Lean Glycol | Atmospheric Rich\Lean Glycol | | Pressurized | Atmospheric | GRI-GlyCalc | Pressurized | Atmospheric | GRI-GlyCalc |
| Site 1 | 3.48 | 5.42 | 2.41 | 4.68 | 1.94 | -1.07 | 1.2 | 55.7 | -30.7 | 34.5 |
| Site 2 | 8.37 | 8.39 | 7.87 | 13.4 | 0.02 | -0.5 | 5.03 | 0.2 | -6.0 | 60.1 |
| Site 3 | 166 | 176 | 168 | 203 | 10 | 2 | 37 | 6.0 | 1.2 | 22.3 |
| Site 4 | 155 | 61.1 | 42.5 | 183 | -93.9 | -112.5 | 28 | -60.6 | -72.6 | 18.1 |
| Site 5 | 66.7 | 46 | 42.7 | 81.3 | -20.7 | -24 | 14.6 | -31.0 | -36.0 | 21.9 |
| Site 6 | 48.2 | 40.4 | 24.2 | 66.1 | -7.8 | -24 | 17.9 | -16.2 | -49.8 | 37.1 |
| Site 7 | 49.3 | 57 | 48.3 | 65.8 | 7.7 | -1 | 16.5 | 15.6 | -2.0 | 33.5 |
| Site 8 | 45.6 | 28.4 | 26.5 | 44.9 | -17.2 | -19.1 | -0.7 | -37.7 | -41.9 | -1.5 |
| Site 9 | 19.8 | 10.7 | 11.4 | 21.8 | -9.1 | -8.4 | 2 | -46.0 | -42.4 | 10.1 |
| Site 10 | 36.9 | 37.9 | 30.8 | 36.1 | 1 | -6.1 | -0.8 | 2.7 | -16.5 | -2.2 |

Notes:

Sites 1-8 are GRI/API test sites, sites 9 & 10 are EMB test sites (Tables 1 and 2).
Sites 1 & 2 are early field evaluation sites, sites 3-10 are field validatin sites.
Sites 2, 3, 8, and 10 have operating flash tanks, the other sites have no flash tank.

emissions, compared to the total capture benchmark, by as much as 50 to 100% for BTEX emissions. For the GRI/API test sites, the pressurized glycol and atmospheric rich/lean glycol tests compared reasonably well to the total capture results for BTEX, but tended to underestimate VOC emissions at some sites.

A second objective of the EMB project was to assess different sampling techniques for the collection of natural gas samples for laboratory analysis. As noted previously, GRI-GLYCalc requires gas composition data as an input. The model is sensitive to BTEX concentrations in the wet gas stream, so therefore accurate gas composition data are essential for accurate prediction of emissions by GRI-GLYCalc. Five different gas collection methods were assessed. For the EMB test sites, the modified EPA Compendium Method TO-14 with Gas Processors Association (GPA) sampling manifold, with the gas sample collected before the absorber, gave the best results when used with GRI-GLYCalc. The other collection methods tested were GPA Standard 2166 with sampling manifold before and after the absorber, and GPA Standard 2166 without sampling manifold before and after the absorber. GPA Standard 2166 is the industry-accepted method for natural gas sampling. These methods differ primarily in the apparatus used for sample collection, as described on pages 27 to 30 of the project report.

Discussion

Existing EPA stack testing methods are unsuitable for use with glycol dehydrators due to the typically low, fluctuating flow rate of the still gas vent stream and high water vapor levels in this stream. Accurate measurement of organic compound concentrations in a gas stream that may be 90+% water is problematic. The total capture technique overcomes the flow problem by capturing the entire still vent gas stream. A total capture test run lasted for 60 minutes, which is adequate time to account for flow variations and reboiler on/off firing cycles. All condensable hydrocarbons and water from the still vent stream were collected during a test run. The volume of noncondensable gas was measured with a dry gas meter. Grab samples of the noncondensable gas were collected for laboratory analysis. The total capture technique provides the most accurate estimate of emissions, but is more hazardous, expensive, and difficult to perform, and is unsuitable for use with large dehydration units processing over 10 million standard cubic feet per day of natural gas.

The alternative test methods, pressurized glycol and atmospheric rich/lean glycol, are simpler and cheaper to perform. The test results from pressurized glycol and atmospheric rich/lean glycol sampling were usually very similar. While both methods compared favorably to the total capture benchmark for BTEX (Table 3), both alternative test methods tended to underestimate VOC emissions. This is most likely due to the difficulty in obtaining a representative sample of the glycol stream for units with a high noncondensable gas component in the glycol stream. The function of the flash tank is to remove entrained or absorbed gas from the glycol stream. For units without flash tanks, a high noncondensable gas flow, possibly as two-phase gas/liquid flow, is likely. Therefore, a glycol stream sample that accurately includes the noncondensable gas component may not have been collected. Note that in Table 4, sites 2, 3, 8, and 10 had flash tanks in operation. For sites 2, 3, and 10, agreement between atmospheric/rich lean results and total capture results for VOC emissions is better than for most of the other sites, where no flash tank

was present. Site 8 had added stripping gas, which may explain why VOC emissions for this site were underestimated.

For the best application of GRI-GLYCalc, the most significant concern is for the collection of accurate input data. As with any emissions model, accurate estimates of emissions cannot be expected if the input data to the model are not accurate. For GRI-GLYCalc, the most critical data inputs are natural gas composition and glycol circulation rate. An estimate of the dry gas water content, or a specified number of equilibrium stages in the absorber, is needed to run GRI-GLYCalc. At most glycol dehydrator sites, the dry gas water content is not routinely measured. Dry gas water content or the number of equilibrium stages in the absorber may be specified from design values. For site 10 (Tables 3 and 4), continuous measurements of dry gas water content were available. For site 10, GRI-GLYCalc-predicted BTEX and VOC emissions are within 3% of the total capture benchmark, a much better result than for the other sites. Thus, it appears that the uncertainty of emissions estimated by GRI-GLYCalc may be significantly reduced if actual dry gas water contents are input to the model.

For BTEX emissions estimation, GRI-GLYCalc is sensitive to BTEX concentrations in the inlet gas stream. BTEX concentrations in natural gas must be determined by collection and analysis of a natural gas sample. The EMB project evaluated different approaches for sample collection, as discussed previously. While the modified EPA Compendium Method TO-14 measurement approach gave the best results for the EMB sites, the GPA Standard 2166 approaches with samples collected before the absorber produced very similar GRI-GLYCalc results for site 10. For other GRI/API locations where the different gas sample collection methods were tested, their experience was similar. The different sampling approaches sometimes agreed closely, and sometimes differed. The GPA 2166 method may be more susceptible to bias caused by collection of condensed liquids in the gas cylinders. Use of a manifold may be effective in removing entrained aerosols and liquids from the collected samples, but the manifold needs to be maintained at a temperature above the natural gas temperature to prevent condensation of BTEX compounds on the manifold walls.

The GRI-GLYCalc model is relatively sensitive to the glycol circulation rate. Ideally, glycol circulation rate would be a measured value. However, measurements of glycol circulation rate may not be available or practical for some sites. If the glycol flow rate is not known, it may be estimated by counting glycol pump strokes per minute and using pump manufacturer's specifications for volume of glycol per pump stroke. Alternatively, a design rule-of-thumb for the ratio between volume of glycol and weight of water to be removed (recirculation ratio) may be used. The reference manual for GRI-GLYCalc suggests a typical value for the recirculation ratio, as well as default values for selected other process variables where specific measurements may not be available.

Conclusions and Recommendations

Use of GRI-GLYCalc with natural gas composition data is recommended as the preferred method for estimating HAP and VOC emissions for glycol dehydrators for emissions inventories. Previously, states have not used a standard technique for estimating emissions from glycol

dehydrators. The GRI-GLYCalc model provides such a standard technique. In order to use GRI-GLYCalc, site-specific input data are required. In particular, natural gas composition data are needed to estimate BTEX emissions. Various techniques may be used to collect a gas sample for laboratory analysis. Comparison of the results from the different sample collection methods has indicated that the methods can give equivalent results, but that use of the modified EPA TO-14 Compendium method appears to be less likely to introduce errors from the sampling technique.

For the sites where source tests have been conducted, the experience has been that GRI-GLYCalc either estimates emissions accurately or overestimates emissions. The likelihood of overestimating emissions may be reduced by obtaining accurate measurements of process variables for as many model inputs as is possible. Since the use of default values for model inputs will be necessary in many cases, some overestimation of emissions is unavoidable. While this may be acceptable for emissions inventory purposes, for determination of the applicability of regulatory standards or compliance determinations, it may still be necessary to conduct source emissions tests to more accurately quantify emissions.

The atmospheric rich/lean sampling method would be the most reasonable approach if measurement of emissions is necessary. The atmospheric rich/lean method was found to give reasonably accurate measures of BTEX emissions when compared to the total capture benchmark results. For VOC emissions, use of the atmospheric rich/lean method gave good results for units with flash tanks and no injection of stripping gas in the reboiler. For units without flash tanks or where stripping gas is used, the application of correction factors to compensate for the method's tendency to underestimate VOC emissions is recommended.

Any technical questions about the enclosed report, or requests for additional copies, may be directed to Chuck Mann of my staff, at 541-4593.

Enclosures

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