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United States
Environmental Protection
Agency

Office of Air Quality
Planning And Standards
Research Triangle Park, NC 27711

EPA-454/R-98-011
June 1998

AIR

EPA

LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF BENZENE

6.2 GLYCOL DEHYDRATION UNITS

Glycol dehydrators used in the petroleum and natural gas industries have only recently been discovered to be an important source of volatile organic compound (VOC) emissions, including benzene, toluene, ethylbenzene, and xylene (BTEX). Natural gas is typically dehydrated in glycol dehydration units. The removal of water from natural gas may take place in field production, treatment facilities, and in gas processing plants. Glycol dehydration units in field production service have smaller gas throughputs compared with units in gas processing service. It has been estimated that between 30,000 and 40,000 glycol dehydrating units are in operation in the United States.[122] In a survey conducted by the Louisiana Department of Environmental Quality, triethylene glycol (TEG) dehydration units accounted for approximately 95 percent of the total in the United States, with ethylene glycol (EG) and diethylene glycol (DEG) dehydration units accounting for approximately 5 percent.[123]

Data on the population and characteristics of glycol dehydration units nationwide is limited. Demographic data has been collected by Louisiana Department of Environmental Quality, Texas Mid-Continent Oil and Gas Association and Gas Processors Association, Air Quality Service of the Oklahoma Department of Health (assisted by the Oklahoma Mid-Continent Oil and Gas Association), and Air Quality Division of the Wyoming Department of Environmental Quality.[124] Table 6-2 presents population data and characteristics of glycol dehydration units currently available.[124]

6.2.1 Process Description for Glycol Dehydration Units

The two basic unit operations occurring in a glycol dehydration unit are absorption and distillation. Figure 6-1 presents a general flow diagram for a glycol dehydration unit.[125] The "wet" natural gas (Stream 1) enters the glycol dehydrator through an inlet separator that removes produced water and liquid hydrocarbons. The gas flows into the bottom of an absorber (Stream 2), where it comes in contact with the "lean" glycol (usually triethylene glycol [TEG]). The water and some hydrocarbons in the gas are absorbed by the glycol. The "dry" gas passes overhead from the absorber through a gas/glycol exchanger (Stream 3), where it cools the incoming lean glycol. The gas may enter a knock-out drum (Stream 4), where any residual glycol is removed. From there, the dry natural gas goes downstream for further processing or enters the pipeline.

After absorbing water from the gas in the absorber, the "rich" glycol (Stream 5) is preheated, usually in the still, and the pressure of the glycol is dropped before it enters a three-phase separator (Stream 6). The reduction in pressure produces a flash gas stream from the three-phase separator. Upon exiting the separator (Stream 7), the glycol is filtered to remove particles. This particular configuration of preheat, flash, and filter steps may vary from unit to unit. The rich glycol (Stream 8) then passes through a glycol/glycol exchanger for further preheating before it enters the reboiler still.

TABLE 6-2. GLYCOL DEHYDRATION UNIT POPULATION DATA

Survey	Service	No. of Units		
		Total	Capacity ≤ 10 MMscfd	Capacity > 10 MMscfd
Texas Mid-Continent Oil and Gas Association (TMOGA) and Gas Processors Association (GPA) Survey[a]	Production	618	556	62
	Gas Processing	206	103	103
	Pipeline	192	144	48
	Total	1016	803	213
Louisiana Department of Environmental Quality (LDEQ) Survey[b]	Ethylene Glycol	12	0	12
	Triethylene Glycol	191	96	95
	Total	203	96	107
Oklahoma Mid-Continent Oil and Gas Association (OKMOGA) Survey[c]	Total	1,333	NR	NR
Wyoming Department of Environmental Survey[d]	Total	1,221	1,185	36

Source: Reference 124.

[a] The survey only covers some companies; therefore it should not be considered a complete listing of units in Texas.
[b] The survey was only directed to units > 5 MMscfd; therefore it should not be considered a complete listing of units in Louisiana.
[c] The survey only covers dehydrator units for eight companies; therefore it should not be considered a complete listing of units in Oklahoma.
[d] The survey covered 50 companies owning and/or operating glycol units in Wyoming.

NR = Not reported.

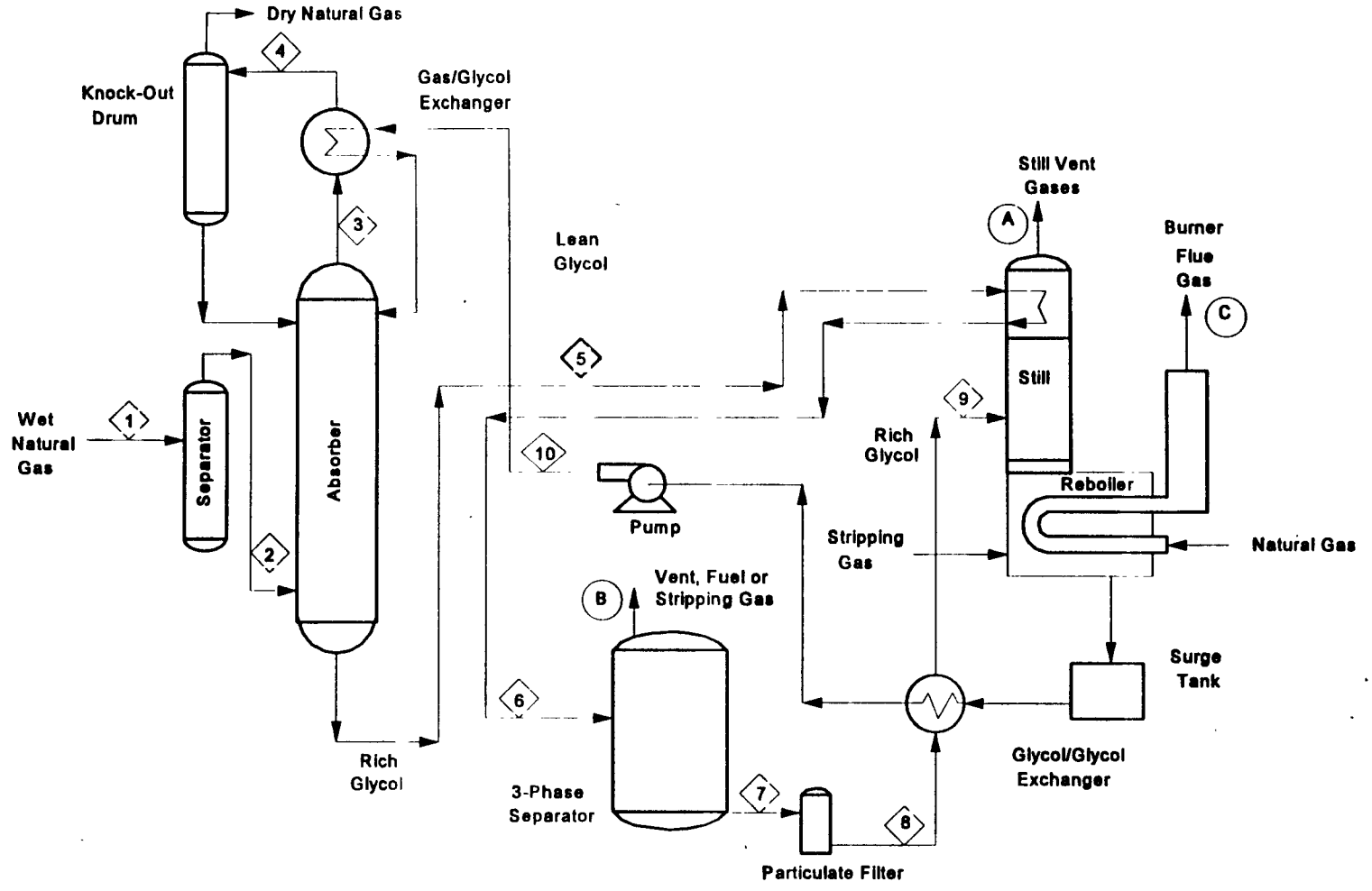

Figure 6-1. Flow Diagram for Glycol Dehydration Unit

Source: Reference 125.

Then, the rich glycol enters the reboiler still (Stream 9) (operating at atmospheric pressure), where the water and hydrocarbons are distilled (stripped) from the glycol making it lean. The lean glycol is pumped back to absorber pressure and sent to the gas/glycol exchanger (Stream 10) before entering the absorber to complete the loop.

6.2.2 Benzene Emissions from Glycol Dehydration Units

The primary source of VOC emissions, including BTEX, from glycol dehydration units is the reboiler still vent stack (Vent A).

Because the boiling points of BTEX range from 176°F to 284°F (80 to 140°C), they are not lost to any large extent in the flash tank but are separated from the glycol in the still. These separations in the still result in VOC emissions that contain significant quantities of BTEX.[126]

Secondary sources of emissions from glycol dehydration units are the phase separator vent (Vent B) and the reboiler burner exhaust stack (Vent C).

Most glycol units have a phase separator between the absorber and the still to remove dissolved gases from the warm rich glycol and reduce VOC emissions from the still. The gas produced from the phase separator can provide the fuel and/or stripping gas required for the reboiler.

A large number of small glycol dehydration units use a gas-fired burner as the heat source for the reboiler. The emissions from the burner exhaust stack are considered minimal and are typical of natural gas combustion sources.

Reboiler still vent data have been collected by the Louisiana Department of Environmental Quality,[123] and the Ventura County (California) Air Pollution Control District.[127] Table 6-3 presents emission factors for both triethylene glycol (TEG) units and

TABLE 6-3. REACTIVE ORGANIC COMPOUNDS (ROCs)[a] AND BTEX EMISSION FACTORS FOR GLYCOL DEHYDRATION UNITS

SCC Number	SCC and Description	Emissions Source	Control Device	Emission Factor	Emission Factor Rating
3-10-003-01	Glycol dehydration units TEG units	Reboiler Still Vent	None	34×10^2 lb/yr of ROC/MMscfd[b] (54.46×10^3 kg/yr of ROC/MMscmd)	U
			None	18.6×10^2 lb/yr of BTEX/MMscfd[b] (29.79×10^3 kg/yr of BTEX/MMscmd)	U
			None	32.4×10^2 lb/yr of ROC/MMscfd[c] (51.90×10^3 kg/yr of ROC/MMscmd)	U
3-10-003-XX	Glycol dehydration units EG units	Reboiler Still Vent	None	54.0×10^1 lb/yr of ROC/MMscfd[b] (8.65×10^3 kg/yr of ROC/MMscmd)	U
			None	24×10^1 lb/yr of BTEX/MMscfd[b] (3.84×10^3 kg/yr of BTEX/MMscmd)	U
			None	74.0×10^1 lb/yr of ROC/MMscfd[c] (11.85×10^3 kg/yr of ROC/MMscmd)	U

[a] ROC are defined as total non-methane and ethane hydrocarbons.
[b] Louisiana DEQ emission factor from glycol dehydration unit survey.
[c] Ventura County (California) Air Pollution Control District emission factor from one source test.

MMscfd = Million standard cubic feet per day.
MMscmd = Million standard cubic meter per day.

ethylene glycol (EG) units based on the natural gas throughput of the gas treated. The emission factors developed from the LDEQ study were based on responses from 41 companies and 208 glycol dehydration units. The Ventura County, California, factors include testing results at two locations (one for TEG and one for EG). The amount of produced gas treated is thought to be the most important because it largely determines the size of the glycol system.[127] However, the data base does not show a strong correlation because other variables with countervailing influences were not constant.[127] VOC and BTEX emissions from glycol units vary depending upon the inlet feed composition (gas composition and water content) as well as the configuration, size, and operating conditions of the glycol unit (i.e., glycol type, pump type and circulation rate, gas and contactor temperatures, reboiler fire-cycles, and inlet scrubber flash tank efficiencies).[129]

The speciation of Total BTEX for TEG units reported by the LDEQ in their study indicated the following composition (% weight): benzene (35); toluene (36); ethylbenzene (5); and xylene (24). For EG units, the following compositions were reported: benzene (48); toluene (30); ethylbenzene (4); and xylene (17). Note that the BTEX composition of natural gas may vary according to geographic areas. Limited information/data on the BTEX composition is available.

Four methods for estimating emissions have been reported for glycol dehydration units: (1) rich/lean glycol mass balance, (2) inlet/outlet gas mass balance, (3) unconventional stack measurements (total-capture condensation, and partial stack condensation/flow measurement), and (4) direct stack measurements (conventional stack measurements, and novel stack composition/flow measurement).[129]

Sampling of the rich/lean glycol then estimating emissions using mass balance has been the selected method for measuring emissions to date. The Louisiana Department of Environmental Quality requested emission estimates using reboiler mass balances on the rich/lean glycol samples.

Based upon a set of studies conducted by Oryx Energy Co as part of a task force for the Oklahoma-Kansas Midcontinent Oil & Gas Association, rich/lean glycol mass balance is a highly convenient, cost effective method for estimating air emissions from glycol dehydration units.[129] The following conclusions were addressed in reference 129 regarding this method: (a) good estimates of BTEX can be obtained from rich/lean glycol mass balance, (b) the rich/lean glycol mass balance BTEX estimates are in excellent agreement with total capture condensation method, and (c) rich/lean glycol mass balance is a more reproducible method for emission estimations than nonconventional stack methods. Note that conventional stack methods cannot be used on the stacks of glycol dehydration units because they are too narrow in diameter and have low flow rates.

An industry working group consisting of representatives from the American Petroleum Institute, Gas Processors Association, Texas-Midcontinent Oil & Gas Association, Louisiana Mid-Continent Oil and Gas Association, and GRI is conducting field evaluation experiments to determine appropriate and accurate sampling and analytical methods to calculate glycol dehydration unit emissions.[125] GRI has developed a computer tool, entitled GRI-GLYCalc, for estimating emissions from glycol dehydrators. The U.S. EPA has performed their own field study of GRI-GLYCalc and has recommended that it be included in EPA guidance for State/local agency use for development of emission inventories.[130]

Atmospheric rich/lean glycol sampling is being evaluated as a screening technique in the above working group program. The goal is to compare these results to the stack and other rich/lean results and determine if a correction factor can be applied to this approach.[125]

A second screening technique under study is natural gas sampling and analysis combined with the software program GRI-GLYCalc© to predict emissions. Table 6-4 shows the inputs required of the user and also shows the outputs returned by GRI-GLYCalc©.[132]

TABLE 6-4. GLYCOL DEHYDRATION EMISSION PROGRAM INPUTS AND OUTPUTS

Inputs	Units
Gas Flow Rate	MMscfd
Gas Composition	Volume percent for C_1-C_6 hydrocarbons and BTEX compounds
Gas Pressure	psig
Gas Temperature	°F
Dry Gas Water Content[a]	lbs/MMscf
Number of Equilibrium Stages[a]	Dimensionless
Lean Glycol Circulation	gpm
Lean Glycol Composition	Weight % H_2O
Flash Temperature[c]	°F
Flash Pressure[c]	psig
Gas-Driven Pump Volume Ratio[c]	acfm gas/gpm glycol

Outputs	Units
BTEX Mass Emissions	lbs/hr or lb-moles/hr, lbs/day, tpy, vol%
Other VOC Emissions	lbs/hr or lb-moles/hr, lbs/day, tpy, vol%
Flash Gas Composition	lbs/hr or lb-moles/hr, lbs/day, tpy, vol%
Dry Gas Water Content[b]	lbs/MMscf
Number of Equilibrium Stages[b]	Dimensionless

Source: Reference 132.

[a] Specify one of these inputs.
[b] Dry Gas Water Content is an output if the Number of Equilibrium Stages is specified and vice versa.
[c] Optional

6.2.3 Controls and Regulatory Analysis

Controls applicable to glycol dehydrator reboiler still vents include hydrocarbon skimmers, condensation, flaring, and incineration. Hydrocarbon skimmers use a three-phase separator to recover gas and hydrocarbons from the liquid glycol prior to its injection into the reboiler. Condensation recovers hydrocarbons from the still vent emissions, whereas flaring and incineration destroy the hydrocarbons present in the still vent emissions.

For glycol dehydrators it has been determined by the Air Quality Service, Oklahoma State Department of Health that the Best Available Control Technology (BACT) could include one or more of the following: (1) substitution of glycol, (2) definition of specific operational parameters, such as the glycol circulation rate, reduction of contactor tower temperature, or increasing temperature in the three-phase separator, (3) flaring/incineration, (4) product/vapor recovery, (5) pressurized tanks, (6) carbon adsorption, or (7) change of desiccant system.[128]

The Air Quality Division, Wyoming Department of Environmental Quality has stated that facilities will more than likely be required to control emissions from glycol dehydration units. The Division has determined and will accept the use of condensers in conjunction with a vapor recovery system, incinerator, or a flare as representing BACT.[133]

Most gas processors have begun to modify existing glycol reboiler equipment to reduce or eliminate VOC emissions. Some strategies and experiences from one natural gas company are presented in Reference 124. For other control technologies refer to Reference 134.

Glycol dehydration units are subject to the NSPS for VOC emissions from equipment leaks for onshore natural gas processing plants promulgated in June 1985.[135] The NSPS provides requirements for repair schedules, recordkeeping, and reporting of equipment leaks.

The Clean Air Act Amendments (CAAA) of 1990 resulted in regulation of glycol dehydration units. Title III of the CAAA regulates the emissions of 188 hazardous air pollutants (HAPs) from major sources and area sources. Title III has potentially wide-ranging effects for glycol units. The BTEX compounds are included in the list of 188 HAPs and may be emitted at levels that would cause many glycol units to be defined as major sources and subject to Maximum Achievable Control Technology (MACT).[125]

Currently, the MACT standard for the oil and natural gas production source category, which includes glycol dehydration units, is being developed under authority of Section 112(d) of the 1990 CAAA and is scheduled for promulgation in May, 1999.

In addition to the federal regulations, many states have regulations affecting glycol dehydration units. The State of Louisiana has already regulated still vents on large glycol units, and its air toxics rule may affect many small units. Texas, Oklahoma, Wyoming, and California are considering regulation of BTEX and other VOC emissions from dehydration units.[125]

6.3 PETROLEUM REFINERY PROCESSES