

# **PREDICTION OF BTEX EMISSIONS AND WATER CONTENT IN TEG DEHYDRATION UNITS**

James L. Holoboff and Mohammad Khoshkbarchi  
Process Ecology Inc.  
Calgary, Alberta, Canada

## **ABSTRACT**

Glycol dehydration units are an integral part of many gas production and processing operations, with as many as 20,000 to 45,000 units in the United States alone. One of the main environmental issues with the operation of glycol units is the release of BTEX emissions, which are controlled by federal and/or local regulatory agencies.

The vast majority of dehydration units use Triethylene Glycol (TEG) to remove the water. Therefore, the ability of simulation tools to accurately predict BTEX emissions and dry gas water content in TEG dehydration units is of primary importance for both operators and regulatory agencies.

In North America, HYSYS and GRI-GLYCalc are the most common simulation tools used to predict benzene emissions from glycol dehydration units. For HYSYS, the Peng Robinson equation of state has been the recommended property package over the years. Recently a new Glycol property package has been developed with promising results for TEG and BTEX. In this study we compared the predictions of HYSYS and GLYCalc to experimental data and concluded that:

- HYSYS-Peng Robinson, HYSYS-Glycol and GLYCalc all had a reasonable match to the BTEX liquid-phase concentration data at contactor and flash tank conditions, with HYSYS-Glycol giving the best match.
- HYSYS-Peng Robinson and HYSYS-Glycol had reasonable matches to BTEX concentration data at regenerator conditions. We conclude that GLYCalc consistently overpredicts BTEX K-values in the regenerator.
- HYSYS-Glycol predicts dry gas water content more accurately than GLYCalc. We conclude that GLYCalc frequently predicts dry gas water contents 50% lower than expected values.

# Table of Contents

Table of Contents .....	1
Executive Summary .....	2
Introduction.....	4
Calculation Basis .....	5
GLYCalc.....	5
HYSYS .....	7
Data Comparison .....	8
GPA RR-131 – Contactor Conditions.....	8
GPA RR-131 – Flash Tank Conditions.....	12
GPA RR-131 – Regenerator Conditions .....	15
Water Removal vs. Circulation Rate graphs .....	17
Comparison to Plant Data .....	21
Recommendations for Further Review .....	22
References.....	22

## Executive Summary

GRI-GLYCalc and AspenTech's HYSYS are simulation tools frequently used to predict benzene emissions from glycol dehydration units. GLYCalc has been the software of choice for regulatory agencies in North America with respect to estimating benzene emissions from Glycol Dehydration units. There are some drawbacks in the implementation of the calculations in the GLYCalc software and in this study it is shown that it is possible to improve the accuracy and consistency of the emissions estimations by relying on more sophisticated simulation tools such as HYSYS.

The vast majority of dehydration units use Triethylene Glycol (TEG) to remove water from natural gas; the ability of these software tools to accurately predict benzene emissions in TEG dehydration units is therefore of primary importance for both operators and regulatory agencies and is the subject of this paper. In addition, since accurate prediction of dry gas water content is essential for the optimization of dehydration units and for the generation of Dehydrator Engineering and Operations Sheet graphs (as required by the Alberta Government), the calculation of dry gas water content was also reviewed. It is noted that a review of ethylene glycol (EG) systems will be made in a subsequent report.

Specifically, the predictions from GLYCalc and both the Peng Robinson and "Glycol" property packages in HYSYS were compared to:

- GPA Research Report 131 [3] equilibrium data at contactor, flash tank and regenerator conditions
- Water removal vs. glycol circulation relationships [1]

It was determined that:

- HYSYS-Peng Robinson, HYSYS-Glycol and GLYCalc all had a reasonable match to the BTEX liquid-phase concentration data from GPA RR-131 at contactor and flash tank conditions.
- HYSYS-Peng Robinson and HYSYS-Glycol had reasonable matches to BTEX concentration data at regenerator conditions. Given the empirical nature of the relationship used to model the regenerator in GLYCalc, it is difficult to make the comparison; however, we conclude that GLYCalc consistently overpredicts BTEX K-values in the regenerator.
- HYSYS predicted dry gas water content more accurately than GLYCalc. It is not uncommon for GLYCalc and HYSYS to give vastly different predictions; we conclude that GLYCalc frequently predicts dry gas water contents 50% lower than expected values. HYSYS-Glycol gave the best predictions here.
- It is further noted that property packages can be modified (most notably by modifying interaction parameters to better represent available experimental and plant data) and selectively applied in HYSYS providing an opportunity to improve on the available methods.

Another aspect of BTEX emissions calculations which cannot be ignored is the fact that poor data or faulty assumptions can result in greater inaccuracies than what is inherent in the calculations. As far as data is concerned, it is important to establish a methodology to ensure that accurate data can be obtained from the field and that errors in transferring data can be minimized. This is an advantage of HYSYS, which allows for data to be imported programmatically.

In terms of the assumptions used in the calculations, HYSYS features the flexibility to be extended to improve the accuracy and reduce reliance on assumptions; for example:

- The contactor temperature has a significant influence on BTEX emissions and dry gas water content – typically the user assumes it as constant while in reality it can also fluctuate with ambient temperature (e.g., the gas may be compressed/cooled before being routed to the contactor). HYSYS can automatically run a number of case studies to quickly determine the influence of contactor temperature and calculate emissions which take into account changes in contactor temperature. While GlyCalc could be used for this purpose, HYSYS can be automated to make the task much simpler.
- It is generally assumed that as the glycol circulation increases, the TEG purity will also remain constant. This is only true if the reboiler duty is adjusted to maintain a constant reboiler temperature. However, if there is a constant reboiler duty, then the TEG purity will decrease as the glycol circulation increases. HYSYS can be configured to use this option.
- The Alberta Government regulatory body (Energy Resources Conservation Board or ERCB) suggests that for the purposes of generating benzene emissions estimates, flaring reduces emissions by 90% while incineration reduces emissions by 95%. HYSYS can be used to rigorously model combustion reactions to obtain a better estimate of the emissions reduction.
- Simulation of other glycol regeneration configurations and technologies can be modeled in HYSYS, such as Drizo and Coldfinger [6].

While GLYCalc has been successfully used in industry to calculate benzene emissions in TEG units, there are limitations. A customizable simulation platform such as HYSYS can be used to improve thermodynamic calculations as well as improve on data transfer and modeling aspects.

## Introduction

The objective of this paper is to evaluate the accuracy of GRI GLYCalc (GLYCalc) and AspenTech HYSYS (HYSYS) in calculating BTEX emissions in dehydration units. GLYCalc and HYSYS are tools frequently used to predict benzene emissions from dehydration units. These simulation tools are recognized by:

- The ERCB (Alberta Energy Resources Conservation Board), in Directive 39 - Revised Program to Reduce Benzene Emissions from Glycol Dehydrators), *and*
- CAPP (Canadian Association of Petroleum Producers), in “Best Management Practices – Control of Benzene Emissions from Glycol Dehydrators”

The ERCB also recognizes BR&E Prosim as a suitable simulation tool. There are other simulation platforms which could also be used for this application (and for which work has been done to optimize parameters for benzene emissions in dehydration units), including Virtual Materials Group VMGSim, SimSci ProII and proprietary tools.

This report specifically reviews GLYCalc and HYSYS as the most common simulation tools used for this purpose.

Triethylene Glycol (TEG) is used in the vast majority of glycol units, and prediction of BTEX emissions in TEG dehydration units is the focus of the report. Ethylene Glycol (EG), and Diethylene Glycol (DEG) are also used to a lesser extent, as are glycol mixtures.

It is also important to review the accuracy of dry gas water content predictions. The Dehydrator Engineering and Operations Sheet (DEOS) graph required by the ERCB plots dry gas water content as a function of glycol circulation rate. The objective is to review how low the circulation rate can be set while still achieving dry gas water content specification. If recommendations are to be made regarding optimizing the circulation rate, then accurate prediction of the dry gas water content is critical.

This report reviews the calculation basis for GLYCalc and HYSYS, then compares predictions of these simulation tools vs. available experimental data.

## Calculation Basis

### *GLYCalc*

GLYCalc has been available since the early 1990's and in North America is the most commonly used tool used to calculate benzene emissions from dehydration units. It is easy to use and is known to estimate benzene emissions in TEG dehydrators with reasonable accuracy. One of the drawbacks of GLYCalc is that it is not possible to adjust thermodynamic parameters and as it is currently not supported it is unlikely that further improvements will be made.

The thermodynamic calculations in GLYCalc are described in detail as part of the documentation provided with the GRI GLYCalc software. For TEG, the most important flash calculations occur in the contactor (absorber), flash tank, still and condenser. This report focuses on the contactor, flash tank and still, as experimental data was readily available for conditions at each of these locations.

In the contactor and flash tank, the models used are shown in Figure 1[2]:

Parameter	Model
$P_i^{sat}$	Antoine's Equation
$\Phi_i$	Peng-Robinson Equation of State
$\Phi_i^{sat}$	Peng-Robinson Equation of State
$\eta_i$	Assume partial molar volume equals pure component molar volume
$\gamma_i$	Universal Quasi-Chemical Activity Coefficient (UNIQUAC)

**Figure 1** – Models used in GLYCalc (From GLYCalc manual)

For supercritical components (i.e., methane, ethane, carbon dioxide, hydrogen sulfide, and nitrogen), GRI-GLYCalc uses a Henry's law expression to calculate the liquid-phase fugacity [2].

The following data sources were used to fit interaction parameters [2]:

Parameter	Interacting Compounds	Data Source
UNIQUAC Binary Interaction Parameters	TEG - BTEX	<i>The Solubility of Selected Aromatic Hydrocarbons in TEG</i> . GPA Report RR-131. DB Robinson Research, 1991.
	TEG - Aliphatic Hydrocarbon	Preliminary GRI experimental work.
	BTEX - Water	<i>Mutual Solubilities of Hydrocarbons and Water at 0 and 25 deg C</i> . Polak and Yu, 1973; review of existing literature.
	TEG - Water	<i>Water Equilibrium in the Dehydration of Natural Gas with Triethylene Glycol</i> . Rosman, 1973.
Henry's Law Constants	Acid Gas - TEG; Methane-TEG	<i>Vapor-Liquid Equilibria for Acid Gases and Lower Alkanes in Triethylene Glycol</i> . Jou, Mather, et. al., 1987.
UNIQUAC Binary Interaction Parameters	DEG - BTEX	Various literature sources (see Sources of Additional Information).
	DEG - Aliphatic Hydrocarbon	Hutton, P.G. and J. H. Jones. <i>J. Chem. Eng. Data</i> . 8 (1963) 617. (DEG/n-hexane).
	DEG - Water	Formulated Glycol Additives Study. GRI Contract 5091-221-2366.
Henry's Law Constants	Methane - DEG	D.B. Robinson Research, Ltd. <i>Equilibrium Phase Compositions for Systems Containing Methane, Benzene, and Water in DEG</i> . GRI Contract 5093-260-2578.
UNIQUAC Binary Interaction Parameters	EG - BTEX	<i>The Solubility of Selected Aromatic Hydrocarbons in Ethylene Glycol</i> . GPA Report. DB Robinson Research, 1993.
	EG - Aliphatic Hydrocarbon	Preliminary GRI experimental work.
	EG - Water	Data of Trimble (1935) and Sokolov (1967) from DECHEMA compilation; <i>DOW Gas Conditioning Fact Book</i> , 1958.
Henry's Law Constants	Acid Gas - EG	<i>Vapor-Liquid Equilibria of H<sub>2</sub>S and CO<sub>2</sub> and Ethylene Glycol at Elevated Pressures</i> . Jou, Mather, et. al., 1990.
	Methane - EG	<i>The Solubility of Selected Aromatic Hydrocarbons in Ethylene Glycol</i> . GPA Report. DB Robinson Research, 1993.

**Figure 2 – Data sources used to fit interaction parameters (From GLYCalc manual)**

From the GRI GLYCalc Manual – “This ‘tuning’ of the fugacity models with selected experimental data ensures that K-values calculated with GRI-GLYCalc will be as accurate as possible at glycol unit conditions.”

The contactor is not modeled using a rigorous stage-by-stage flash calculation; it is noted that “The K-values are used with the vapor and liquid flow rates to calculate absorption factors for each component. The absorption factors are used with the Kremser-Brown approximation to calculate the moles of natural gas components absorbed in the dehydrator by the glycol.”

As for the regenerator (still), the manual [2] notes that “to avoid the complex heat and material balances that would be needed if the regenerator were rigorously modeled, a simple empirical calculation is used.”

## ***HYSYS***

HYSYS is a general-purpose process simulator which has been widely used in the oil and gas industry since its first inception when it was introduced as HYSIM in the early 1980's. However, it wasn't until the "Glycol" property package was introduced in version 2004.1 that AspenTech focused specifically on BTEX emissions in TEG units. It is noted that in later versions (2006, 2006.5), successive improvements were made in the interaction parameters. The differences in calculations between these versions are very significant and the basis for this report was version 2006.5, which introduced many additional fitted binary parameters. Some comparisons were made for version 2006, and have been included in this report. It is also noted that the Peng Robinson (PR) property package can also be used for these calculations (and is very likely the most common property method used by HYSYS users for this purpose). Therefore, both the PR and Glycol package results are reviewed in this report.

The Glycol package is based on the "TST" equation of state which has the following characteristics [5]:

"The TST cubic equation of state improves the representation of the pure component vapour pressures by the introduction of a three parameter alpha function. TST uses Cubic Equation of State/Excess Helmholtz energy (CEoS/AE) mixing rules [4, 5] that permit a smooth transition of the mixing rules [*author addition*: from  $A^E$  models] to the conventional van der Waals one-fluid mixing rules. It also uses an excess Gibbs Energy (GE) model, which when combined with the CEoS/AE mixing rules allows both a van der Waals fluid and highly non-ideal mixtures to be described over a broad range of temperatures and pressures in a consistent and unified framework."

Wassenhove et al. regressed interaction parameters to improve the performance of HYSYS in predicting BTEX emissions in TEG dehydrators. It is believed that these interaction parameters (along with additional interaction parameters regressed from NIST data) made their way into the Glycol package in version 2006.5 as default interaction parameters.

It is finally noted that the column models in HYSYS utilize rigorous stage-by-stage mass and energy balances (not using shortcut methods as in GLYCalc).



## Data Comparison

One of the most important data sources for BTEX solubility in TEG systems is the Gas Processors Association Research Report RR-131 – “The Solubility of Selected Aromatic Hydrocarbons in Triethylene Glycol”. It is important from the perspective that a great deal of data is available at conditions expected in the contactor, flash tank and regenerator of a typical TEG unit.

Therefore the bulk of the comparison will be in the context of RR-131. There are other sources of data available but these have not been reviewed in this report. Additionally, it is useful to compare to plant data – and this is discussed later in the report.

In addition to reviewing the calculations of BTEX emissions, the prediction of dry gas water content is also addressed later in the report.

### *GPA RR-131 – Contactor Conditions*

Perhaps the most critical calculation in terms of BTEX emissions occurs at the contactor. The lean glycol absorbs not only water but also small amounts of BTEX and other hydrocarbons. These components ultimately make their way out of the system at the flash tank and still vent. It is important to accurately calculate the amount of benzene absorbed into the rich glycol stream.

GPA Research Report 131 (“The Solubility of Selected Aromatic Hydrocarbons in Triethylene Glycol”) [3] contains a significant amount of equilibrium phase composition data for multicomponent mixtures of methane, benzene, toluene, ethylbenzene, o-xylene, water and TEG at various contactor, flash tank and regenerator conditions.

The following tables compare the predictions of HYSYS and GLYCalc to the GPA-131 data for four sets of data at contactor conditions. Each table shows the molar composition (on a percent basis) in the equilibrium liquid phase, based on the feed composition provided in GPA-131. GLYCalc does not allow for direct input of this feed composition but it can be closely approximated by properly setting the wet gas composition/rate and lean glycol rate and water content.

- Data – The first column is the experimental data from GPA-131
- PR – Results based on the Peng Robinson property package in HYSYS, with the default interaction parameters
- 2006 – Results from the Glycol property package in HYSYS 2006, with modified interaction parameters as recommended by Aspentech
- 2006.5 – Results from the Glycol property package in HYSYS 2006.5, with the default interaction parameters
- GLYCalc – Results from GLYCalc Version 4.0

Component	X-Data	X-PR	X-2006	X-2006.5	X-GLYCalc
CH4	0.9595	0.7681	0.4754	0.7703	0.9227
BZ	0.3405	0.3394	0.3404	0.3394	0.3382
TOL	0.2865	0.2864	0.2873	0.2866	0.2852
Et-BZ	0.0256	0.0258	0.0258	0.0258	0.0255
O-XYL	0.2563	0.2566	0.2574	0.2567	0.2553
H2O	7.6824	7.6963	7.7190	7.6962	7.6525
TEG	90.4492	90.6273	90.8947	90.6250	90.5206

**Table 1** - 300 psia, 77 F, containing 1 wt% H2O

Component	X-Data	X-PR	X-2006	X-2006.5	X-GLYCalc
CH4	0.9488	1.0066	0.5366	0.7706	0.9139
BZ	0.3405	0.3366	0.3386	0.3376	0.3346
TOL	0.2865	0.2852	0.2869	0.2862	0.2852
Et-BZ	0.0260	0.0254	0.0255	0.0255	0.0253
O-XYL	0.2564	0.2552	0.2565	0.2560	0.2552
H2O	7.6832	7.6748	7.7116	7.6938	7.6747
TEG	90.4590	90.4163	90.8442	90.6303	90.5110

**Table 2** - 300 psia, 122 F, containing 1 wt% H2O

Component	X-Data	X-PR	X-2006	X-2006.5	X-GLYCalc
CH4	2.8985	2.1153	1.3787	2.2229	2.8634
BZ	0.3338	0.3321	0.3349	0.3316	0.3305
TOL	0.2809	0.2807	0.2832	0.2809	0.2787
Et-BZ	0.0251	0.0258	0.0261	0.0259	0.0255
O-XYL	0.2513	0.2518	0.2539	0.2518	0.2495
H2O	7.5320	7.5914	7.6482	7.5833	7.5030
TEG	88.6784	89.4028	90.0750	89.3036	88.7494

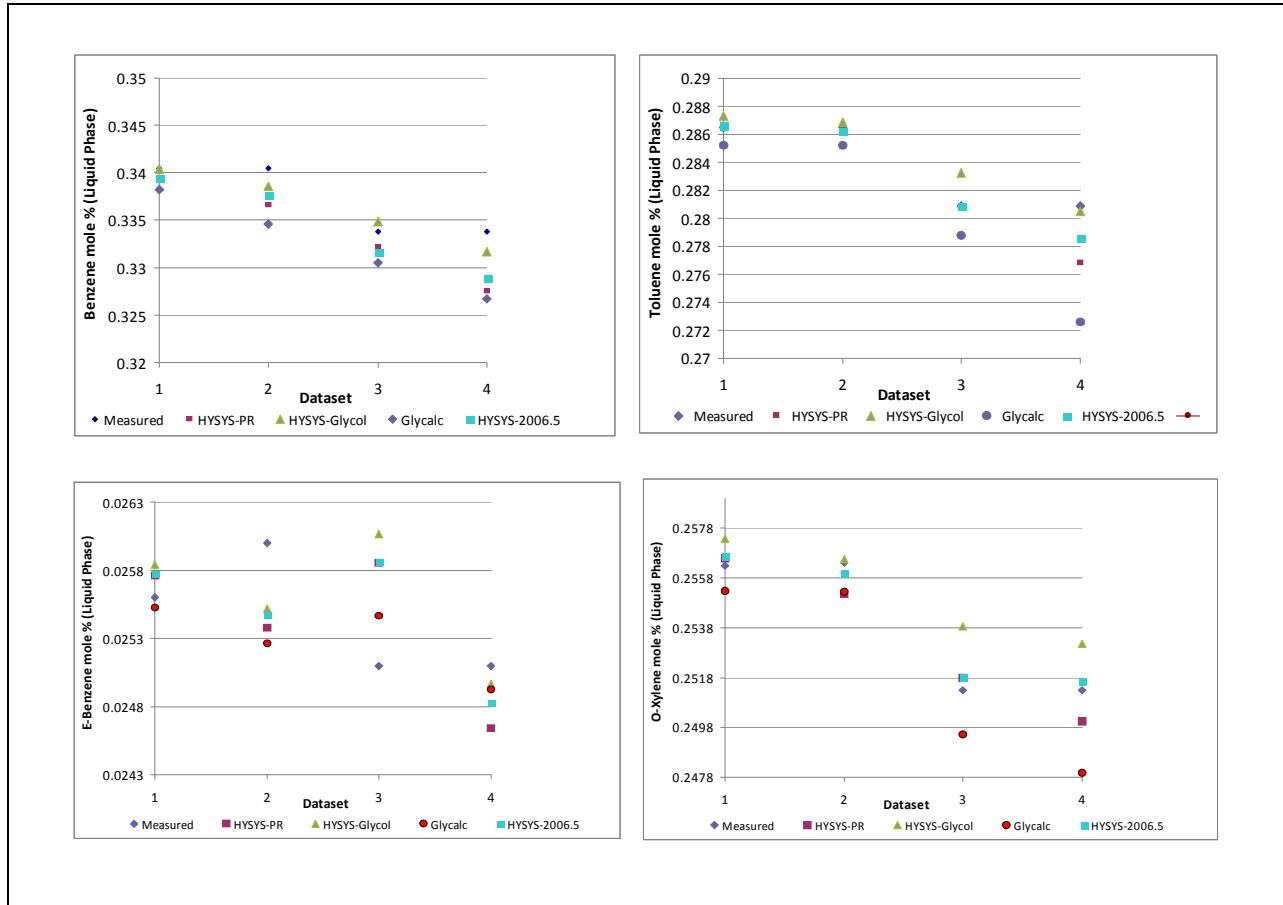
**Table 3** - 1000 psia, 77 F, containing 1 wt% H2O

Component	X-Data	X-PR	X-2006	X-2006.5	X-GLYCalc
CH4	2.9009	2.6394	1.5981	2.2834	2.9366
BZ	0.3338	0.3275	0.3317	0.3288	0.3267
TOL	0.2809	0.2768	0.2805	0.2786	0.2725
Et-BZ	0.0251	0.0246	0.0250	0.0248	0.0249
O-XYL	0.2513	0.2500	0.2532	0.2517	0.2480
H2O	7.5318	7.5483	7.6281	7.5766	7.5330
TEG	88.6763	88.9333	89.8836	89.2561	88.6583

**Table 4** - 1000 psia, 122 F, containing 1 wt% H2O

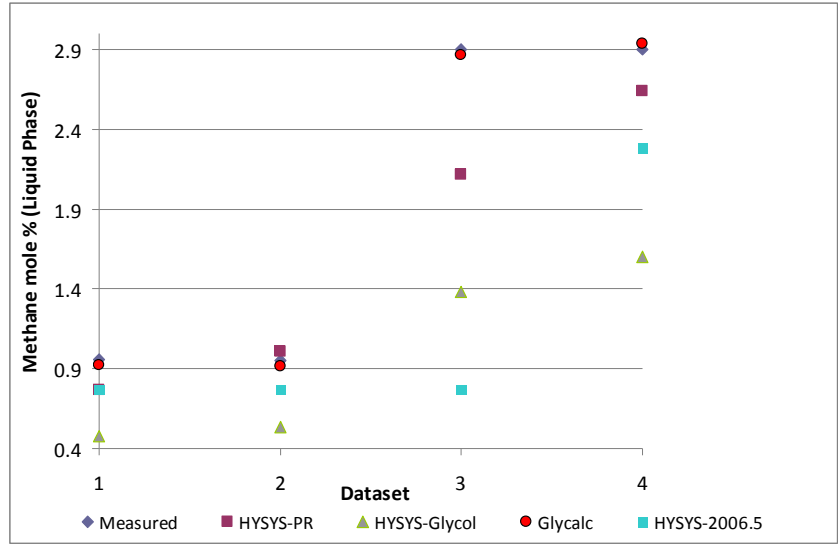
Based on data from these four tables, the following figures plots the measured vs. calculated BTEX liquid phase mole percent for each of the four datasets:

- Dataset 1 - 300 psia, 77 F, containing 1 wt% H2O
- Dataset 2 - 300 psia, 122 F, containing 1 wt% H2O
- Dataset 3 - 1000 psia, 77 F, containing 1 wt% H2O
- Dataset 4 - 1000 psia, 122 F, containing 1 wt% H2O



**Figure 3 - GPA-131 Comparison for BTEX (Contactor Conditions)**

All of the methods compare quite well to the GPA-131 data, perhaps not surprisingly since GLYCalc and the Glycol package used the GPA-131 data to fit parameters. It is not known whether the HYSYS-Peng Robinson parameters were fitted to GPA-131. It is noted that in these cases Glycalc provides better predictions for methane in the liquid phase (Figure 4) – this is an area for improvement in HYSYS as it becomes more important to predict methane emissions in glycol dehydration units.



**Figure 4** - Methane comparison at contactor conditions

### ***GPA RR-131 – Flash Tank Conditions***

The following tables compare the predictions of HYSYS and GLYCalc relative to the GPA-131 data for two sets of data at flash tank conditions. Each table shows the molar composition (on a percent basis) in the equilibrium liquid phase, based on the feed composition provided in GPA-131. Again, GLYCalc does not allow for direct input of this feed composition but it can be approximated by manipulating case parameters. In this case it was much more difficult to exactly match the flash tank inlet gas to the experimental feed composition. Because of this, we have compared the K-values for each of the components, since our feed composition in GLYCalc did not exactly match but was close enough to provide a reasonable basis for comparing K-values.

- Data – The first column is the experimental data from GPA-131
- PR – Results based on the Peng Robinson property package in HYSYS 2006, with the default interaction parameters
- Glycol – Results from the Glycol property package in HYSYS 2006.5, with the default interaction parameters
- GLYCalc – Results from GLYCalc Version 4.0

<b>Component</b>	<b>K-Data</b>	<b>K-PR</b>	<b>K-Glycol</b>	<b>K-GLYCalc</b>
CH4	422	297	1084	379
BZ	0.820	0.806	0.996	0.666
TOL	0.527	0.546	0.515	0.460
Et-BZ	0.355	0.400	0.205	0.288
O-XYL	0.241	0.289	0.155	0.198
H2O	---	0.05	0.04	0.021
TEG	2.18E-04	3.65E-05	1.15E-05	---

**Table 5 – K-values @ 100 psia, 167 F, containing 5 wt% H2O**

<b>Component</b>	<b>K-Data</b>	<b>K-PR</b>	<b>K-Glycol</b>	<b>K-GLYCalc</b>
CH4	429	208	895	375
BZ	2.527	2.421	3.281	2.363
TOL	1.772	1.732	2.287	1.940
Et-BZ	1.311	1.495	1.109	1.416
O-XYL	0.941	1.101	0.890	1.035
H2O	---	0.33	0.27	0.14
TEG	2.18E-04	0.001	0.000	---

**Table 6 – K-values @ 100 psia, 257 F, containing 5 wt% H2O**

Comparisons of X (liquid phase) and Y (vapour phase) data are also shown here; however, it is again noted that for GLYCalc we were not able to exactly match the inlet composition to the flash tank. Nevertheless, X and Y calculations for GLYCalc compared favorably.

Component	X-Data	X-PR	X-2006.5	X-GLYCalc
CH4	0.2363	0.3295	0.0907	0.2612
BZ	0.2468	0.2381	0.2360	0.2492
TOL	0.2077	0.2021	0.2026	0.2088
Et-BZ	0.0185	0.0185	0.0187	0.0181
O-XYL	0.1858	0.1828	0.1843	0.1781
H2O	30.3296	30.2759	30.3583	29.9008
TEG	68.7752	68.7530	68.9093	69.1837

**Table 7** – X-values @ 100 psia, 167 F, containing 5 wt% H2O

Component	Y-Data	Y-PR	Y-2006.5	Y-GLYCalc
CH4	99.6359	97.9826	98.3253	99.1000
BZ	0.2024	0.1920	0.2352	0.1660
TOL	0.1094	0.1103	0.1043	0.0961
Et-BZ	0.0066	0.0074	0.0038	0.0052
O-XYL	0.0447	0.0528	0.0286	0.0352
H2O	---	1.6524	1.3019	0.6220
TEG	0.0010	0.0025	0.0008	0.0000

**Table 8** – Y-values @ 100 psia, 167 F, containing 5 wt% H2O

Component	X-Data	X-PR	X-2006.5	X-GLYCalc
CH4	0.2305	0.4274	0.1010	0.2522
BZ	0.2307	0.2237	0.2150	0.2442
TOL	0.1985	0.1940	0.1891	0.2082
Et-BZ	0.0180	0.0176	0.0179	0.0188
O-XYL	0.1820	0.1772	0.1789	0.1817
H2O	29.8151	30.0081	30.1438	30.1163
TEG	69.3252	68.9519	69.1543	68.9785

**Table 9** – X-values @ 100 psia, 257 F, containing 5 wt% H2O

Component	Y-Data	Y-PR	Y-2006.5	Y-GLYCalc
CH4	98.8554	88.9461	90.3954	94.7000
BZ	0.5830	0.5415	0.7055	0.5770
TOL	0.3517	0.3360	0.4325	0.4040
Et-BZ	0.0236	0.0264	0.0199	0.0266
O-XYL	0.1712	0.1952	0.1592	0.1880
H2O	---	9.9031	8.2619	4.1000
TEG	0.0151	0.0518	0.0256	0.0000

**Table 10** – Y-values @ 100 psia, 257 F, containing 5 wt% H2O

We found that there was a greater discrepancy in the match at flash tank conditions vs. contactor conditions. Our major conclusions here are:

- Liquid-phase BTEX compositions match very well for all methods.
- The comparison was not as good for methane; GLYCalc appears to provide the best prediction here; For HYSYS, PR is better than the Glycol package in predicting methane equilibrium.

## ***GPA RR-131 – Regenerator Conditions***

The results for the regenerator conditions are shown in the next two tables. As before, GLYCalc does not allow for direct input of this feed composition but it can be approximated by manipulating case parameters.

- Data – The first column is the experimental data from GPA-131
- PR – Results based on the Peng Robinson property package in HYSYS, with the default interaction parameters
- Glycol – Results from the Glycol property package in HYSYS 2006.5, with the default interaction parameters
- GLYCalc – Results from GLYCalc Version 4.0. It is noted that empirical relationships are used in the regenerator and a direct comparison cannot be made given that these relationships likely do not assume a single stage of separation. Nevertheless, the results are shown in the table for reference.

<b>Component</b>	<b>K-Data</b>	<b>K-PR</b>	<b>K-Glycol</b>	<b>K-GLYCalc*</b>
CH4	1132	600	1298	1.44E+18
BZ	15.9	17.9	13.1	919.8
TOL	11.5	12.5	9.6	563.3
Et-BZ	9.26	11.6	6.1	412.6
O-XYL	6.92	8.7	5.2	322.6
H2O	4.08	4.87	4.73	3.0
TEG	0.019	0.032	0.020	

**Table 11 – K-values @ 21.8 psia, 350 F, Containing 1 wt% H2O**

\* Glycalc regenerator model is empirical and likely does not assume a single equilibrium separation stage

<b>Component</b>	<b>K-Data</b>	<b>K-PR</b>	<b>K-Glycol</b>	<b>K-GLYCalc*</b>
CH4	784	476	1066	7.14E+17
BZ	20.8	23.6	16.9	457.9
TOL	15.3	16.6	13.0	280.2
Et-BZ	11.7	16.2	8.8	206.7
O-XYL	9.14	12.4	7.7	161.7
H2O	6.57	7.66	8.00	10.95
TEG	0.058	0.078	0.055	---

**Table 12 – K-values @ 23.5 psia, 400 F, Containing 1 wt% H2O**

\* Glycalc regenerator model is empirical and likely does not assume a single equilibrium separation stage

The HYSYS-PR and HYSYS-Glycol compare favorably to the data. It is difficult to make a direct comparison of the GLYCalc results to the data given the empirical nature of the GLYCalc regenerator model. One would expect that the K-values calculated by GLYCalc would be greater than the experimental K-values based on a typical assumption of 2 equilibrium stages above the reboiler; however



a check in HYSYS indicates that the K-values there do not increase by this magnitude. It is also clear that the methane K-value in GLYCalc is far too large.

A question that could be asked is, if the match is very good at the contactor but possibly poor at the regenerator, what will be the overall impact on BTEX emissions? Based on our experience, the match is usually reasonable – as both HYSYS and Glycalc predict that *most* of the BTEX at the inlet of the regenerator goes to the vent; it is more critical to ensure that there is a good match at the contactor to ensure prediction of BTEX concentration in the rich glycol phase.

However, the empirical model of the regenerator in Glycalc is restrictive in that a reboiler duty cannot be estimated nor can a duty be specified. The impact of different configurations or technologies in the regenerator which might reduce benzene emissions cannot be properly reviewed. This is where a process simulator such as HYSYS provides a significant advantage.

## ***Water Removal vs. Circulation Rate graphs***

Various sources contain Water Removal vs. TEG Circulation Rate graphs, including:

- Gas Conditioning and Processing Vol 2. The Equipment Modules (J.M. Campbell & Company)
- Gas Processors Suppliers Association (GPSA) Engineering Data Book
- Surface Production Operations Vol. 2 (Ken Arnold and Maurice Stewart)

These graphs display the fraction of water removed  $(W_{in} - W_{out})/W_{in}$  as a function of the TEG Rate (gal/lb water removed), for various lean glycol concentrations and number of equilibrium trays.

While these graphs are an approximate representation, they provide a useful guide in determining the expected dry gas water content at different conditions. Additionally, since GLYCalc and HYSYS are so far different in their respective predictions of dry gas water content, these graphs can help to determine which calculations are more in line with expectations.

Only the graphs from Surface Production Operations [1] display absorber conditions (1000 psia and 100 F), so these graphs were used as the basis of the comparison. It is further noted that the composition of the gas does not have a significant impact on the results (we tested a few “typical” gas compositions).

The results are displayed for the following eight conditions:

- 99.5% Lean Glycol; One equilibrium tray; 1000 psia; 100 F
- 99.0% Lean Glycol; One equilibrium tray; 1000 psia; 100 F
- 98.5% Lean Glycol; One equilibrium tray; 1000 psia; 100 F
- 98.0% Lean Glycol; One equilibrium tray; 1000 psia; 100 F
- 99.5% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F
- 99.0% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F
- 98.5% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F
- 98.0% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F

	<b>Fraction of Water Removed (Win-Wout)/Win</b>			
<b>TEG Rate (Gal/lb H2O Removed)</b>	<b>Data</b>	<b>PR</b>	<b>Glycol</b>	<b>GLYCalc</b>
1	0.60	0.50	0.61	0.78
1.5	0.68	0.62	0.70	0.84
2	0.74	0.69	0.75	0.87
2.5	0.78	0.74	0.79	0.90
3	0.80	0.77	0.82	0.91
3.5	0.82	0.80	0.83	0.92
4	0.83	0.82	0.85	0.93
4.5	0.85	0.83	0.86	0.94

**Table 13** – 99.5% Lean Glycol; One equilibrium tray; 1000 psia; 100 F

	<b>Fraction of Water Removed (Win-Wout)/Win</b>			
<b>TEG Rate (Gal/lb H2O Removed)</b>	<b>Data</b>	<b>PR</b>	<b>Glycol</b>	<b>GLYCalc</b>
1	0.59	0.48	0.60	0.77
1.5	0.67	0.60	0.68	0.83
2	0.73	0.67	0.74	0.86
2.5	0.76	0.71	0.77	0.88
3	0.78	0.75	0.80	0.90
3.5	0.80	0.77	0.82	0.91
4	0.82	0.79	0.83	0.92
4.5	0.83	0.81	0.84	0.92

**Table 14** – 99% Lean Glycol; One equilibrium tray; 1000 psia; 100 F

	<b>Fraction of Water Removed (Win-Wout)/Win</b>			
<b>TEG Rate (Gal/lb H2O Removed)</b>	<b>Data</b>	<b>PR</b>	<b>Glycol</b>	<b>GLYCalc</b>
1	0.58	0.46	0.59	0.77
1.5	0.66	0.58	0.67	0.82
2	0.71	0.65	0.72	0.85
2.5	0.74	0.69	0.75	0.87
3	0.76	0.72	0.78	0.89
3.5	0.78	0.75	0.80	0.90
4	0.80	0.76	0.81	0.91
4.5	0.82	0.78	0.82	0.91

**Table 15** – 98.5% Lean Glycol; One equilibrium tray; 1000 psia; 100 F

	<b>Fraction of Water Removed (Win-Wout)/Win</b>			
<b>TEG Rate (Gal/lb H2O Removed)</b>	<b>Data</b>	<b>PR</b>	<b>Glycol</b>	<b>GLYCalc</b>
1	0.57	0.44	0.57	0.75
1.5	0.64	0.56	0.66	0.81
2	0.69	0.62	0.70	0.84
2.5	0.72	0.67	0.74	0.86
3	0.74	0.70	0.76	0.88
3.5	0.76	0.72	0.78	0.89
4	0.78	0.74	0.79	0.90
4.5	0.78	0.75	0.80	0.90

**Table 16** – 98.0% Lean Glycol; One equilibrium tray; 1000 psia; 100 F

	<b>Fraction of Water Removed (Win-Wout)/Win</b>			
<b>TEG Rate (Gal/lb H2O Removed)</b>	<b>Data</b>	<b>PR</b>	<b>Glycol</b>	<b>GLYCalc</b>
1	0.83	0.76	0.84	0.94
1.5	0.88	0.85	0.90	0.96
2	0.92	0.89	0.92	0.97
2.5	0.94	0.92	0.94	0.98
3	0.95	0.93	0.95	0.98
3.5	0.95	0.94	0.95	0.98
4	0.96	0.95	0.96	0.99
4.5	0.96	0.95	0.96	0.99
5	0.9625	0.95	0.96	0.99

**Table 17** – 99.5% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F

	<b>Fraction of Water Removed (Win-Wout)/Win</b>			
<b>TEG Rate (Gal/lb H2O Removed)</b>	<b>Data</b>	<b>PR</b>	<b>Glycol</b>	<b>GLYCalc</b>
1	0.81	0.74	0.82	0.93
1.5	0.86	0.83	0.88	0.95
2	0.89	0.87	0.90	0.96
2.5	0.91	0.89	0.91	0.97
3	0.92	0.90	0.92	0.97
3.5	0.92	0.91	0.93	0.97
4	0.93	0.91	0.93	0.97
4.5	0.93	0.92	0.93	0.98
5	0.93	0.92	0.94	0.98

**Table 18** – 99.0% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F

TEG Rate (Gal/lb H <sub>2</sub> O Removed)	Fraction of Water Removed (Win-Wout)/Win			
	Data	PR	Glycol	GLYCalc
1	0.79	0.71	0.81	0.92
1.5	0.84	0.80	0.86	0.94
2	0.87	0.84	0.88	0.95
2.5	0.88	0.86	0.89	0.96
3	0.89	0.87	0.90	0.96
3.5	0.90	0.88	0.91	0.96
4	0.91	0.89	0.91	0.96
4.5	0.91	0.89	0.91	0.96
5	0.92	0.89	0.91	0.96

**Table 19** – 98.5% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F

TEG Rate (Gal/lb H <sub>2</sub> O Removed)	Fraction of Water Removed (Win-Wout)/Win			
	Data	PR	Glycol	GLYCalc
1	0.78	0.69	0.79	0.90
1.5	0.82	0.77	0.84	0.93
2	0.85	0.81	0.86	0.94
2.5	0.86	0.83	0.87	0.95
3	0.87	0.84	0.88	0.95
3.5	0.87	0.85	0.88	0.95
4	0.88	0.86	0.89	0.95
4.5	0.88	0.86	0.89	0.95
5	0.88	0.86	0.89	0.95

**Table 20** – 98.0% Lean Glycol; Two equilibrium trays; 1000 psia; 100 F

It is not unexpected that HYSYS-PR predicted significantly higher dry gas water contents (characterized by lower  $(W_{in}-W_{out})/W_{in}$ ) than GLYCalc. This feature has consistently been observed from the author's experience in doing various calculations for dehydration units.

Three consistent trends could be observed:

- HYSYS-PR tended to underpredict water removal (which results in higher dry gas water contents).
- GLYCalc tended to significantly overpredict water removal (which results in lower dry gas water contents – typically half of what should be expected).
- HYSYS-Glycol consistently gave a reasonable match to water removal (and dry gas water content).

### ***Comparison to Plant Data***

The GLYCalc manual provides comparisons of emissions calculated in GLYCalc to measured emissions. According to the GLYCalc manual, “During pre-release testing of GRI-GLYCalc, extensive comparisons of measured emissions data and program estimates were made for TEG units ... The results demonstrate that estimates produced by GRI-GLYCalc compare reasonably well with experimental data for a wide range of operating conditions. On average, the program-predicted emissions tend to be higher than those measured using sampling data.”

Location	Emissions (tons/yr)	
	GRI-GLYCalc	Measured
Site 1	9.0	4.9
Site 2	80.5	89.6
Site 3	18.9	9.9
Site 4	42.2	29.0
Site 5	7.4	8.6
Site 6	28.7	17.7
Site 7	4.0	2.6
Site 8	3.7	3.6
Site 9	22.5	22.9

**Figure 5** – Comparison of Total BTEX Emission Estimates (From GLYCalc manual)

Based on the limited amount of data available it is difficult to determine why GLYCalc emissions tend to be higher than those measured using sampling data. One possibility, as discussed earlier, could be that the empirical models in the regenerator over-predict the amount of BTEX going to the vent.

It is noted that other sources which compare Glycalc to plant data are available – for example the U.S. Environmental Protection Agency released a memo comparing glycol dehydrator BTEX and VOC emissions at two units [4]. According to this report, “the GRI-GLYCalc estimated emissions of BTEX and total VOC are within 10% or less of the measured emissions.”

## Recommendations for Further Review

While significant effort has been made to review and improve on calculations, there is further work to be done. Some areas to focus on are:

- Prediction of benzene emissions in ethylene glycol (EG) units – this is a critical area to review since both GLYCalc and HYSYS have serious difficulties calculating the amount of benzene going to the ethylene glycol / water phase at the low temperature separator.
- Effect of Stripping Gas on lean glycol purity – some further study of the effect of stripping gas on lean glycol purity and the accuracy of the simulators to correctly predict it would be useful.
- Efficiency of condensers in removal of benzene – the ability of the simulators to properly account for the presence of condensers and other equipment such as above-ground or underground tanks would be useful. Methodologies for performing the calculation (e.g., accounting for ambient temperature fluctuation) would be reviewed. It is noted that GLYCalc does have some capability here.

## References

1. Arnold, K., Stewart, M. Surface Production Operations – Design of Gas-Handling Systems and Facilities, Volume 2, Second Edition, 1999.
2. GRI-GLYCalc User's Manual (Gas Research Institute).
3. H.-J. Ng, C.-J. Chen, D.B. Robinson, GPA Research Report RR-131, The Solubility of Selected Aromatic Hydrocarbons in Triethylene Glycol, December 1991.
4. Reuter, C.O., Reif, D.L., and Myers, D.B.. Glycol Dehydrator BTEX and VOC Emission Testing Results at Two Units in Texas and Louisiana. EPA Project Summary, May 1995.
5. Wassenhove, V.W., Twu, C., and Feliu, J.A. Using a More Thermodynamically Adapted Model Improves Modelling of TEG Dehydration Units - Allows Better Operation and Efficiency. Presented at May 2006 GPA Conference (Antwerp, Belgium).
6. Øi, Lars Erik and Selstø, Elisabeth Tyvand. Process Simulation of Glycol Regeneration. Presented at May 2002 GPA Conference (Bergen).