

Dehydration with Aspen HYSYS®: Validation of the CPA Property Package

Suphat Watanasiri, Senior Director, R&D, Aspen Technology, Inc.

Rainie Sachdev, Senior Software Quality Engineer, Quality, Aspen Technology, Inc.

Ya-Tang Chang, Product Management, Aspen Technology, Inc.

Jennifer Dymont, Product Marketing, Aspen Technology, Inc.



Introduction

In the operation of natural gas pipelines, a blockage or leak can cause expensive production losses, damaged equipment and safety hazards. When water is present, for instance, gas hydrates can form, creating an icy plug in natural gas mixtures, especially when at low temperatures and high pressures. With water, carbon dioxide and hydrogen sulfide present, acid gases form and cause corrosion in pipelines, which can lead to damaged downstream equipment. In order to create safer and more reliable operations, organizations need to remove free water from the natural gas.

With the risk of gas hydrate formation, corrosion in pipelines and damage to downstream equipment, removing free water from natural gas can allow for safer and more reliable operations^{1,2}. Many governments or agencies regulating shared pipelines maintain restrictions on the water content of sales gas or fungible product. Common specifications are 7 lb/MMscf in the southern U.S., 4 lb/MMScf in the northern U.S. and 2 to 4 lb/MMscf in Canada³.

While there are many options to remove excess water, dehydration by a glycol is most commonly used by gas processing facilities, with more than 36,000 glycol dehydration units in the U.S. Triethylene glycol (TEG) is most frequently used, but other glycols including diethylene glycol (DEG) and monoethylene glycol (MEG) are also utilized.

There are, however, still some issues with the dehydrator units, as they are often oversized, resulting in high capital or operating costs. According to a report by the U.S. Environmental Protection Agency (EPA), TEG is recirculated two or more times higher than necessary⁴. In order to ensure design options meet the necessary requirements of saving capital, solvent or energy costs, thermodynamic modeling and a holistic view of operations is needed.

This paper discusses the dehydration modeling technology available with Aspen HYSYS in V10 and above. Aspen HYSYS has historically employed the glycol property package for TEG. With the addition of the Cubic-Plus-Association (CPA) package in V10, Aspen HYSYS can be used to model dehydration with TEG, MEG and DEG.

First, we will describe the CPA Equation of State and development of the model parameters, then provide an overview of natural gas dehydration process and BTEX emission requirements, and discuss how dehydration is modeled in Aspen HYSYS. We will provide validation of the CPA property package developed in this work by comparing the calculation results to experimental phase equilibrium data of binary and multi component systems. Finally, the property package is used in the Aspen HYSYS dehydration model — focusing on two case studies.

CPA Equation of State: Thermodynamic Model for Describing the Dehydration Process

The CPA equation of state combines the Soave-Redlich-Kwong (SRK) equation⁵ with association terms to describe the polar/association effect.

The CPA equation of state, proposed by Kontogeorgis et al.^{6,7}, can be expressed as:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \left(\frac{RT}{V_m} \right) \left(1 + \frac{1}{V_m} \frac{\partial \ln g}{\partial (1/V_m)} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i})$$

where V_m is molar volume, x_i is mole fraction of component i , T is temperature, P is pressure, R is gas constant, b is co-volume parameter and $a(T)$ is the physical energy parameter of the classical SRK equation.

X_{A_i} represents the fraction of association sites that do not form bonds with other active sites:

$$X_{A_i} = \frac{1}{1 + \left(\frac{1}{V_m} \right) \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad \Delta^{A_i B_j} = g(V_m) \left[\exp \left(\frac{\epsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j}$$

where $\Delta^{A_i B_j}$ describes association strength between site A on molecule i and site B on molecule j . In the association strength $\Delta^{A_i B_j}$ term, $\epsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ represent cross-association energy and effective cross-association volume, respectively. $g(V_m)$ is the radial distribution function for the reference fluid defined as:

$$g(V_m) = 1 / (1 - 1.9\eta)$$

$$\eta = b / (4V_m)$$



Mixing and Combining Rules

For $a(T)$ and b , the conventional van der Waals one-fluid mixing rules and combining rules are used:

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad b = \sum_i x_i b_i$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}), \quad b_{ij} = \frac{b_i + b_j}{2}$$

where, for each pure component i :

$$a_i = a_{0i} [1 + m_i (1 - \sqrt{T_{ri}})]^2$$

$$a_{0i} = \Omega_a (RT_{ci})^2 / P_{ci}, \quad \Omega_a = 0.42784$$

$$b_i = \Omega_b RT_{ci} / P_{ci}, \quad \Omega_b = 0.08664$$

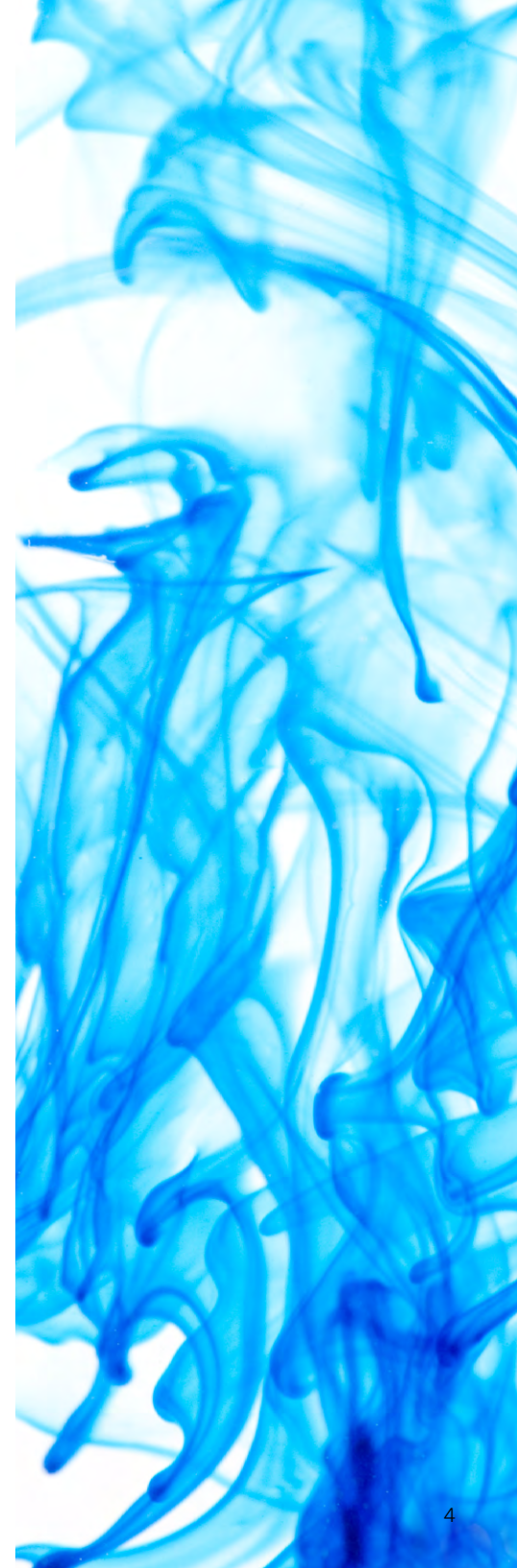
$$T_{ri} = T / T_{ci}$$

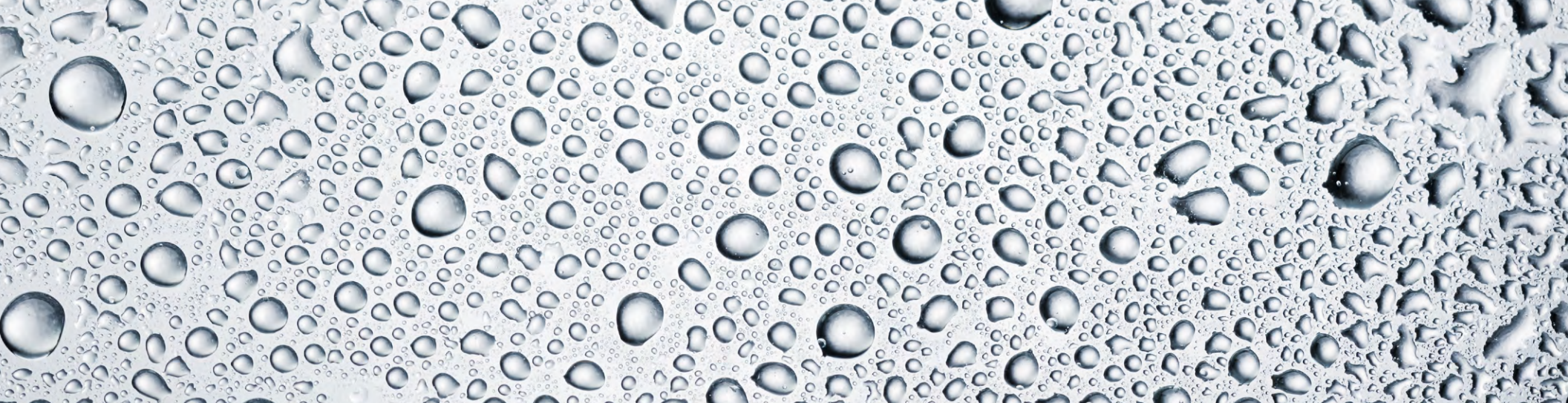
T_{ci} is the critical temperature of component i , P_{ci} is the critical pressure of component i , and m_i is a component specific parameter.

In this work, the CR-1 combining rule for the cross-association energy and volume parameters is used:

$$\epsilon^{A_i B_j} = \frac{\epsilon^{A_i B_i} + \epsilon^{A_j B_j}}{2}, \quad \beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}}$$

The 2B association type is used for alcohols (e.g., methanol) while the 4C association type is used for water and glycols.





Model Parameters

For non-associating compounds, three pure-component parameters are required: critical temperature (T_c), critical pressure (P_c) and m . For associating compounds, the effective association energy ($\epsilon^{A_i B_j}$) and association volume ($\beta^{A_i B_j}$) parameters are required. A maximum of three binary interaction parameters can be used: k_{ij} , $\epsilon^{A_i B_j}$ and $\beta^{A_i B_j}$. For most of the cases, regressing only one binary interaction parameter (k_{ij}) is sufficient to match experimental data; cross-association energy and volume are usually estimated from combining rule. However, for some systems, fitting the association volume parameter, $\beta^{A_i B_j}$ provides more satisfactory results⁸.

Pure component and binary interaction parameters for water, methanol, glycols (EG, DEG and TEG) and related components (C1-C10, benzene, toluene, ethyl-benzene, CO₂, H₂S, N₂ and m-, o- and p- xylenes) were obtained from the literature or determined by AspenTech using available experimental data collected from the literature and from NIST-TDE⁹. These parameters have been carefully reviewed, validated and stored in a databank that is built into Aspen HYSYS and are used automatically. Parameters for 149 pure components and 414 binary pairs are available. For components that are not in the databank, the required parameters are estimated or set to default.

Overview of the Natural Gas Dehydration Process

A typical glycol dehydration process can be divided into dehydration and regeneration units, as shown in Figure 1. For dehydration, first, wet gas enters the inlet scrubber to remove any free water from the gas. Then it passes through the contactor. The lean glycol enters from the top of the contactor and flows counter-current to the wet gas, absorbing water from the gas.

The water-rich glycol leaves the bottom of the contactor and enters the flash tank. Acidic gases and light hydrocarbons in the rich glycol stream is flashed off and can be used as a fuel for the regenerator reboiler or as a stripping gas. The rich glycol stream then goes to the lean/rich exchanger, and exchanges heat with the regenerator bottom stream before entering the regenerator.

For the regeneration unit, the rich glycol liquid stream from the flash tank is sent to the regenerator, which separates TEG from water. The rich glycol is preheated through a heat exchanger by the lean glycol from the reboiler before it enters the regenerator. A stripping gas such as methane and nitrogen (or the flash gas) can be injected into the reboiler to help further reduce the water contents and reboiler duty. Finally, the regenerated glycol from bottom of the regenerator recycles to the contactor^{10,11}.

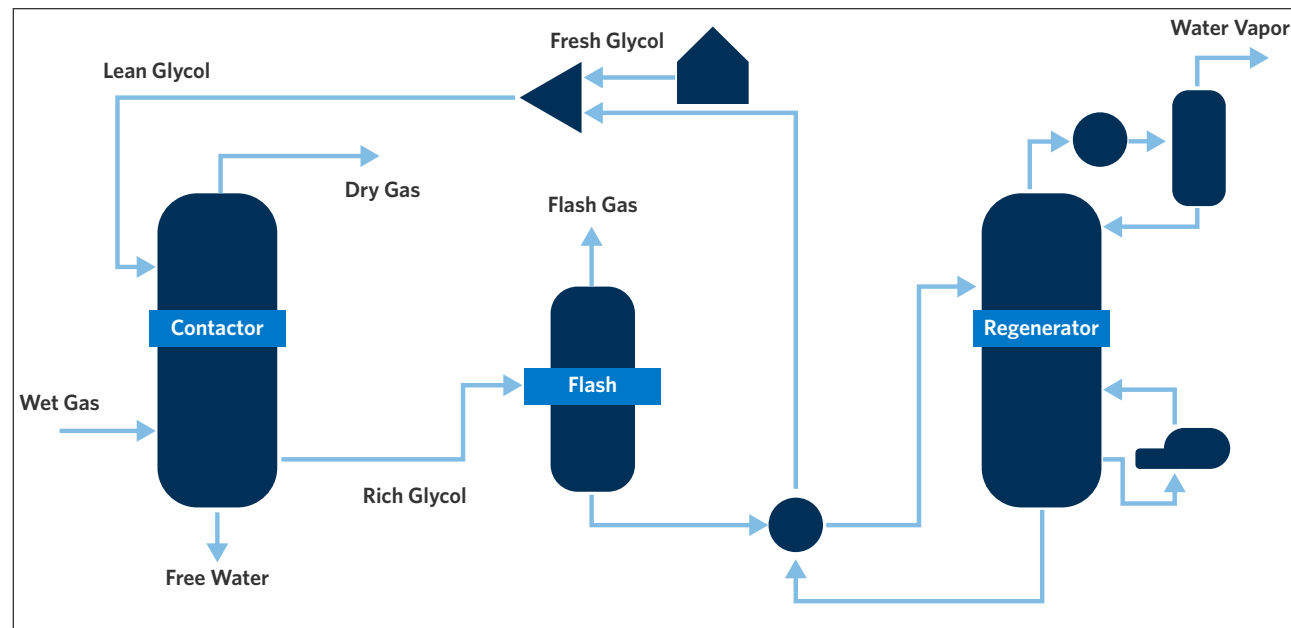


Figure 1: Typical glycol dehydration unit

Figure 2 shows typical operating ranges for the contactor, flash and regenerator in the dehydration system using TEG. The operating conditions of contactor are usually 50-100 bar and 20-40 degrees C. The flash gas obtained from the flash tank can be used as fuel for the reboiler or as stripping gas. Since hydrocarbon liquid can cause problems such as reducing the efficiency of reboiler, if the hydrocarbon liquid exists at the condition, a three-phase separation flash drum is required.

Glycol circulation rate (at a given glycol concentration) determines the water content in the dry gas and the amount of volatile organic components (VOCs)* emission from regenerator as well. The higher the glycol rate, the lower the water content and the higher the venting emission. Therefore, it is important to optimize the circulation rate of glycol to tradeoff between the two. The recommended design circulation rate is 2 to 5 gallons of glycol per pound of water, with lean glycol weight percent ranging from 98 to 99.9.

The composition of the rich glycol is usually 93 to 97 percent glycol by weight, depending on the operating conditions and process requirements. Also, the lean glycol stream is desired to be 5-15 degrees C higher than the temperature of the gas stream to prevent hydrocarbon condensation in the absorber and foaming effect. Reboiler temperature should not be higher than 205 degrees C to prevent glycol decomposition and minimize glycol losses. Usually, the reboiler operates at 175-205 degrees C to separate glycol from water and regenerate it to high concentration^{12,13}.

*VOCs encompass all volatile hydrocarbon compounds, including BTEX, except methane.

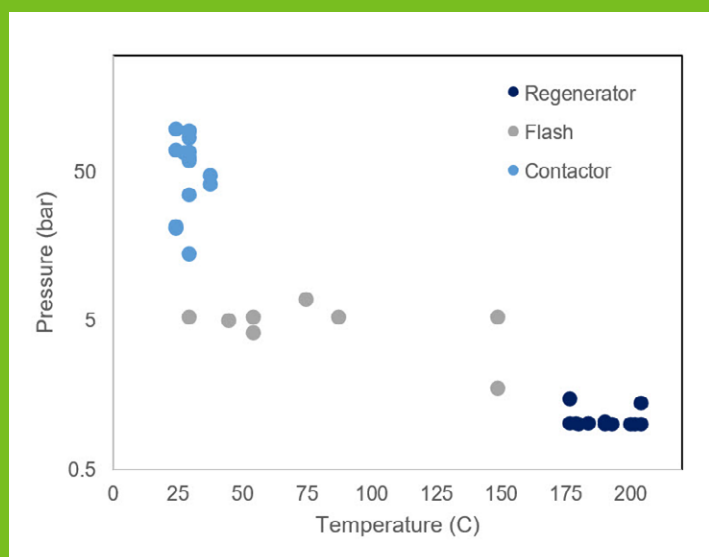


Figure 2: Operating conditions for TEG glycol dehydration process ^{14,15,16,17,18}

BTEX Emission

Glycol absorbs not only water but also methane, other hydrocarbons, and BTEX (benzene, toluene, ethyl-benzene, xylene), which are eventually emitted into the atmosphere from the glycol regenerator. BTEX compounds are considered hazard air pollutants (HAPs). The BTEX concentration from the top of the regenerator can be hundreds of times higher than that in the raw natural gas by concentrating effect of the absorption process. Therefore, although the main purpose of glycol dehydration process is to decrease water content of natural gas, control of HAPs emission is also an integral part of the process design.

Also, some light hydrocarbons may not be completely separated from rich glycol in the flash tank, but remain in the glycol liquid and are therefore vented through the regenerator. These compounds can be considered VOCs with BTEX. According to the Abu Dhabi National Oil Company guidelines, BTEX and VOC emission should not exceed 22 metric tons per year and 227 metric tons per year, respectively².

Modeling the Dehydration Process in Aspen HYSYS

There are a number of variables affecting gas dehydration performance. Lean glycol concentration, glycol recirculation and stripping gas flow rates, temperature, pressure and number of equilibrium stages of the contactor and regenerator are examples of process conditions that have major impacts on the results.

Aspen HYSYS V10 was utilized in this work to simulate natural gas dehydration process to match plant data and to optimize process conditions. A simplified Aspen HYSYS process flow diagram for natural gas dehydration is shown in Figure 3. In earlier versions of Aspen HYSYS, the Glycol property package is the recommended thermodynamic model for simulation of TEG dehydration process. Good results have been reported in prediction of BTEX emission and water content in TEG dehydration units³¹. However, some deficiencies have been reported, such as when methanol is present. The Glycol property package is also limited to TEG only; EG and DEG are not supported.



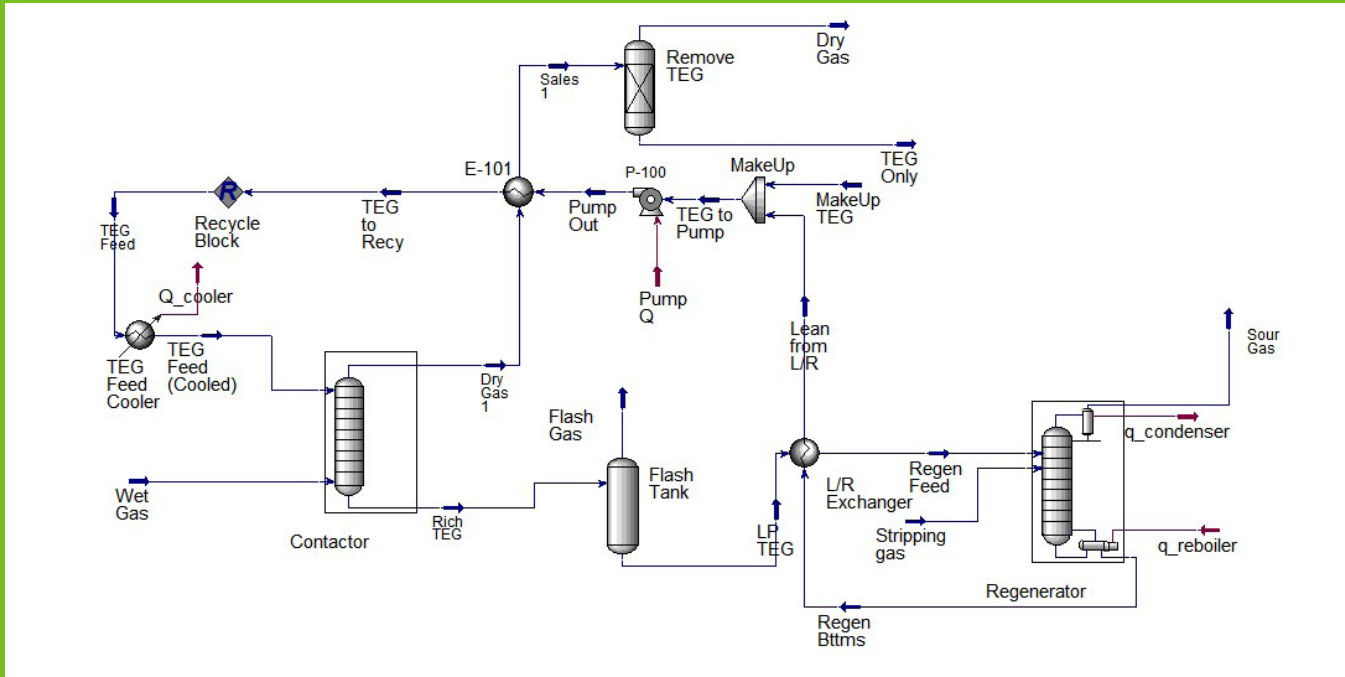


Figure 3: Natural gas dehydration flowsheet in Aspen HYSYS simulation

In Aspen HYSYS V10, it was decided to build on earlier work using the CPA property package to model methanol-related systems and extend it to fully support EG, DEG and TEG. The CPA equation of state is widely used in the industry and has been widely studied with many published parameters^{1,6,7,8}. Therefore, it is a good model to adopt for modeling glycol dehydration processes. It can also be readily extended to model additional components and processes in the future.

Physical Properties Validation

Validation of Binary Systems

Various relevant glycol dehydration binary systems have been validated using experimental data from a broad range of pressures and temperatures. The following systems — methane-TEG, water-TEG and toluene-TEG — are selected for illustrative purpose. These are some of the key binaries in the TEG dehydration process. Because methane is the main component in natural gas, water-TEG absorption and separation are important to achieving dry gas and lean glycol specifications, and aromatic emission is important in meeting HAPs emission standard.

Experimental Data Used in This Work

Experimental data for binary system validation is listed in Tables 1-3. Also, the ranges of temperature, pressure and mole fraction of liquid phase are presented.

Data Type	T, K	P, Pa	X_TEG	Points	Reference
VLE	298	1e5-1e7	0.936-0.999	10	Jou ¹⁹
VLE	323	1e5-2e7	0.928-0.999	10	Jou ¹⁹
VLE	348	1e5-1e7	0.925-0.999	11	Jou ¹⁹
VLE	373	1e5-1e7	0.921-0.999	10	Jou ¹⁹
VLE	398	1e5-1e7	0.916-0.999	10	Jou ¹⁹
VLE	298	3e6-1e7	0.940-0.983	9	Wilson ²⁰
VLE	273	3e6-1e7	0.946-0.984	7	Wilson ²⁰

Table 1: CH4-TEG experimental data used in the validation

Data Type	T, K	P, Pa	X_TEG	Points	Reference
VLE	400-560	1e5	0.6-1	14	-
GAMMA	297	-	0.013-0.339	24	Herskowitz ²¹
GAMMA	332	-	0.002-0.197	16	Herskowitz ²¹
GAMMA	298	-	0.002-0.354	17	Tsuji ²²
GAMMA	300-378	-	-	18	Parrish ²³
GAMMA	373-433	-	-	6	Rafflenbeul ²⁴
GAMMA	323-393	-	-	13	Bestani ²⁵
GAMMA	322-358	-	-	5	Ikari ²⁶

Table 2: H2O-TEG Experimental data used in the validation

Data Type	T, K	P, Pa	X1_TEG	X2_TEG	Points	Reference
LLE	279-345	1e5	0.515-0.691	0.0107-0.0866	8	Folas ²⁷
VLE	385-442	1e5	0.064-0.918	-	10	Gupta ²⁸
LLE	298-320	1e5	0.620-0.652	0.0126-0.0311	9	Hughes ²⁹

Table 3: Toluene-TEG Experimental data used in the validation

Comparison of Calculation Results Using CPA and Experimental Data

The CPA calculation results of the three binary systems are compared to experimental data in Figures 4-8. The results show that the CPA property package can accurately reproduce the phase behavior of these systems.

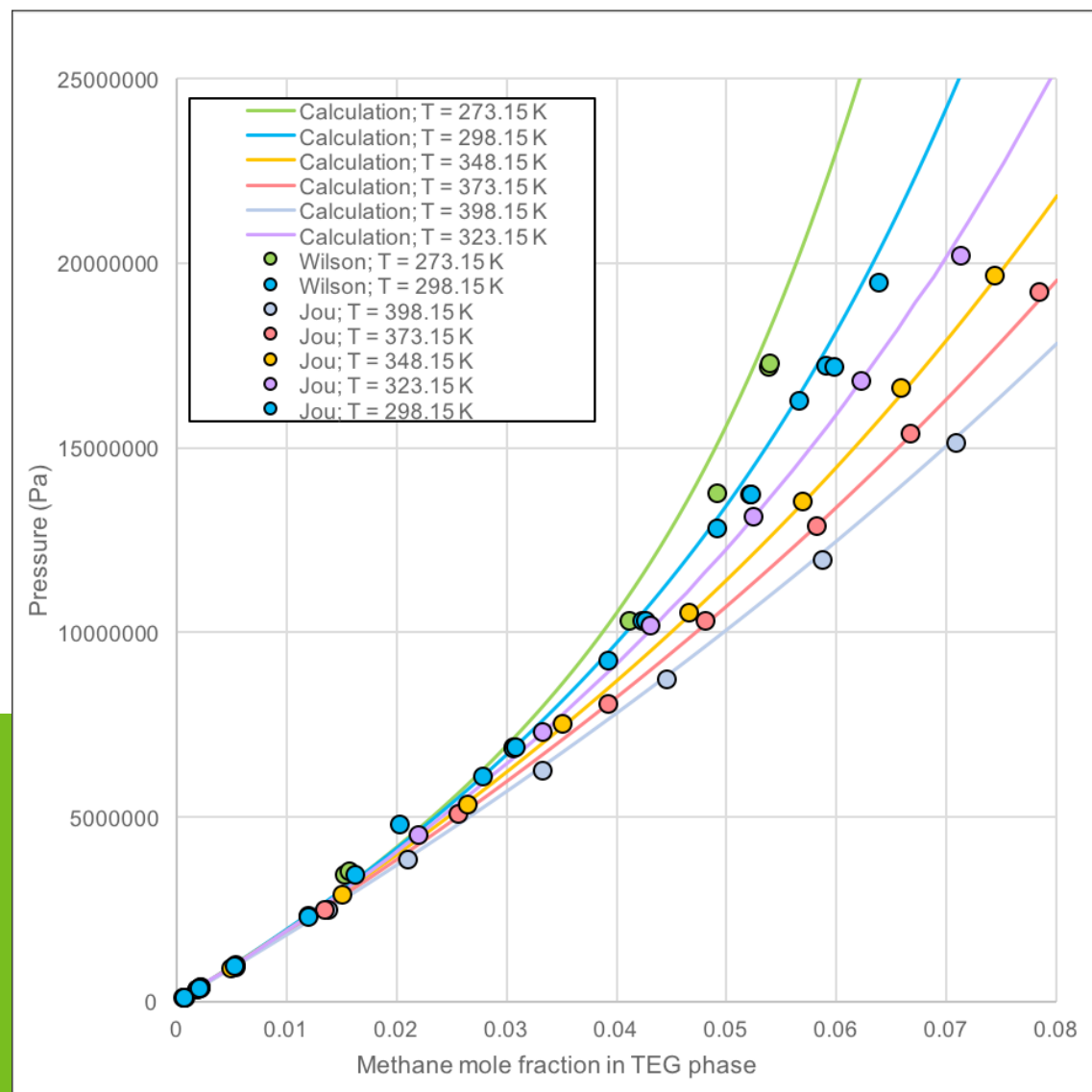


Figure 4:

Solubility of methane in TEG phase. The circles represent the experimental data from Jou¹⁹ and Wilson²⁰. The curves represent the calculation results using the CPA property package.

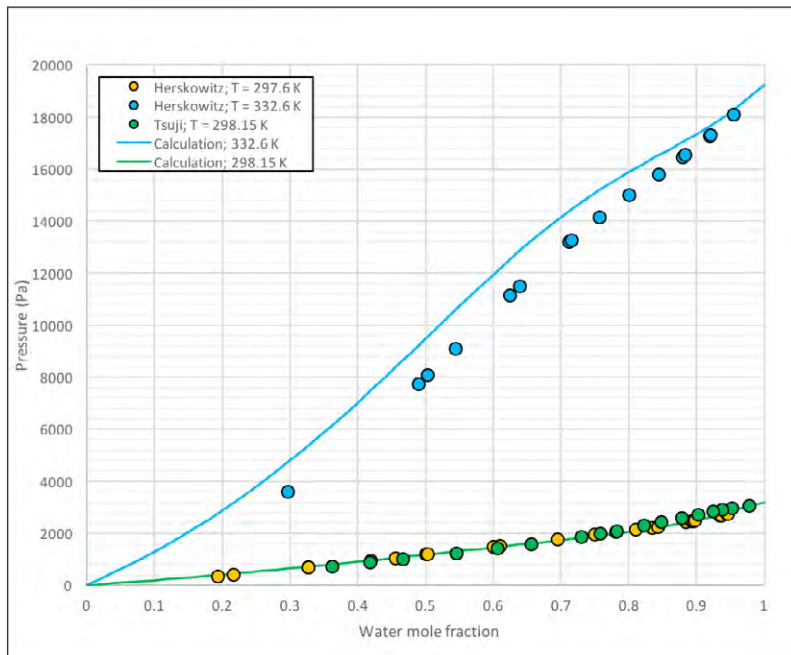


Figure 5:
Mixture pressure calculated from activity coefficient at different amount of water in TEG. The circles represent the experimental data from Herskowitz²¹ and Tsuji²². The curves represent the calculation results using the CPA property package.

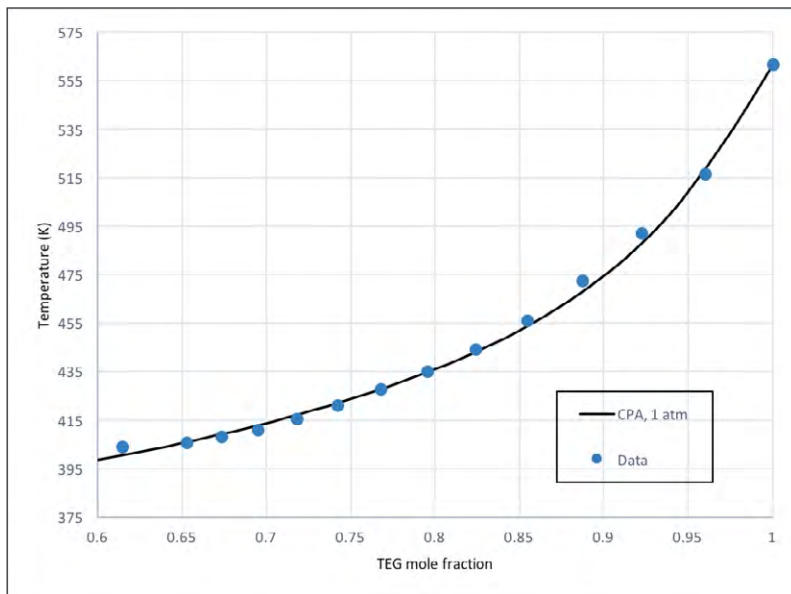


Figure 6:
T-x diagram in the high TEG concentration region relevant to the TEG regenerator. The curve represents the calculation results using the CPA property package.

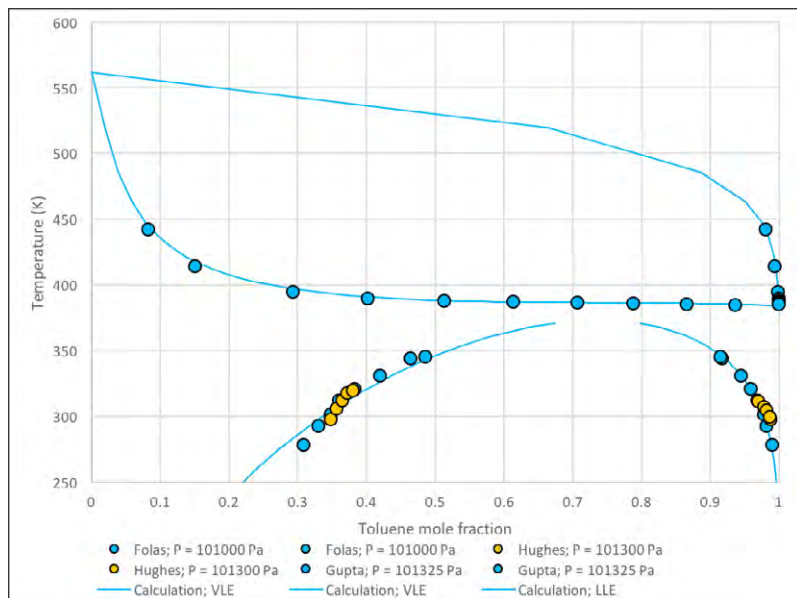


Figure 7:
Infinite dilution activity coefficient of water in TEG. The circles represent the experimental data from Parrish²³, Rafflenbeul²⁴, Bestani²⁵ and Ikari²⁶. The curve represents the calculation results using the CPA property package.

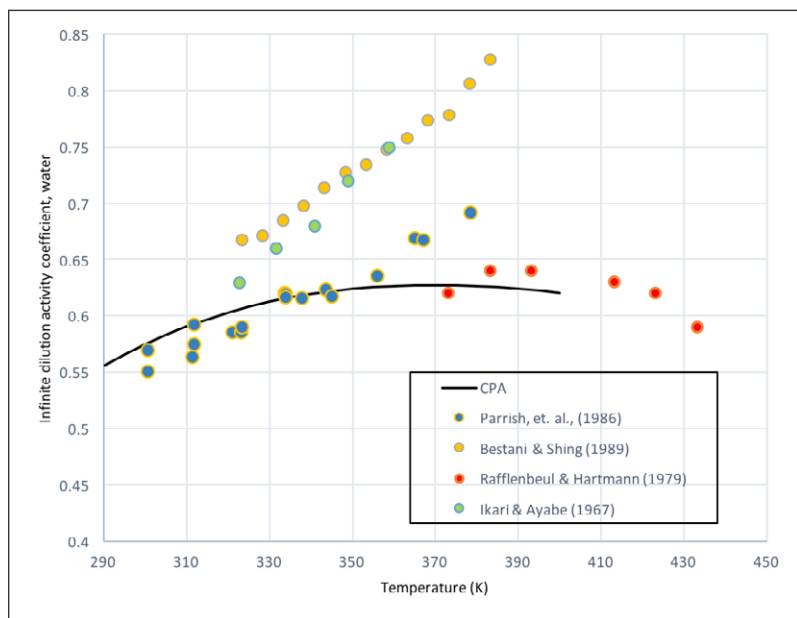


Figure 8:
VLE and LLE of Toluene-TEG system at 1 atm. The circles represent the experimental data from Folas²⁷, Gupta²⁸ and Hughes²⁹. The curves represent the calculation results using the CPA property package.

In addition to the above systems, many other relevant glycol dehydration binary systems have been regressed and validated, including glycols (TEG, DEG, EG) and hydrocarbons (C1-C10), aromatic compounds (BTEX), water, methanol and light gases (H_2S , CO_2 , N_2).

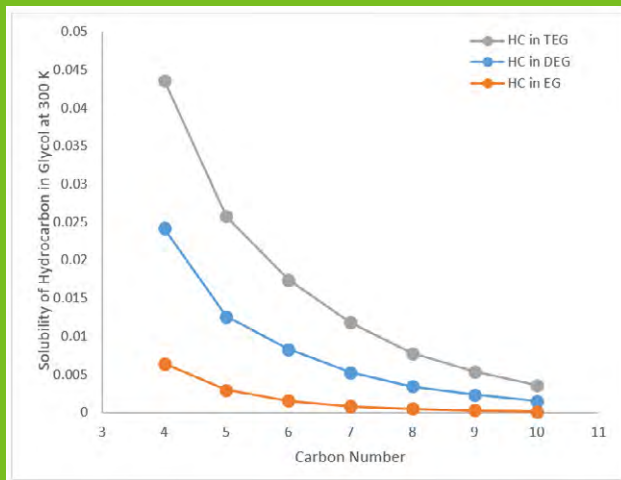


Figure 9: Solubility trend of hydrocarbon in glycol phase at 300 K

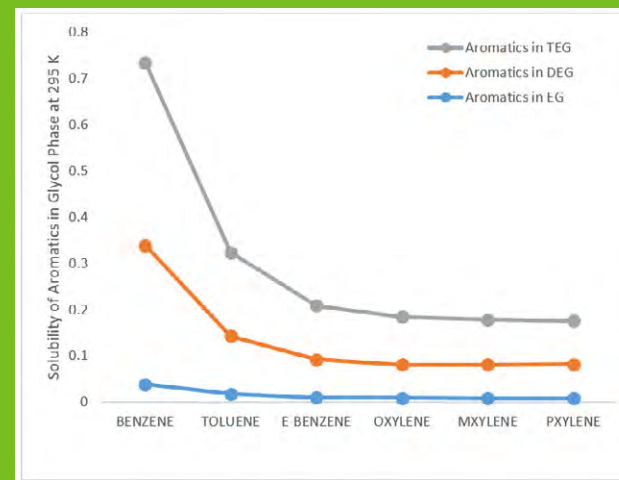


Figure 10: Solubility trend of benzene, toluene, ethylbenzene, xylenes in glycol phase at 295 K

Validation of Physical Properties Patterns

In addition to validation against data of a given binary system, we also compared the calculated relative physical properties of similar systems to confirm that the obtained parameters are reasonable. Systems in a homologous series should follow an orderly pattern. Also, we used the patterns to estimate parameters for a system which has missing or scarce data by interpolation.

Many family systems were studied, but the systems glycol-hydrocarbons and glycol-aromatic compounds are shown here in Figures 9 and 10 because hydrocarbon and BTEX adsorption in glycol is directly related to VOCs and HAPs emission from regenerator and are of importance, as discussed previously. Figure 9 shows the calculated solubility of various hydrocarbons in EG, DEG and TEG using the CPA property package developed in this work. The hydrocarbons studied are n-paraffins with carbon number ranging from 4 to 10. The solubility of hydrocarbon in each glycol decreases as the carbon number increases. This is expected because the hydrocarbon becomes more hydrophobic when its chain length increases. The figure also shows increase in solubility for each hydrocarbon in the three glycols: EG < DEG < TEG due to the increase in polarity (TEG > DEG > EG). Similar behavior is observed in Figure 10 for BTEX components.

Solubility in a given glycol is expected to decrease with increasing carbon number and substitute group of benzene, while the solubility in different glycols is expected to increase with increasing polarity of the glycol. The results in Figures 9 and 10 show that the CPA property package can predict the correct patterns of homologous series.



Multi-Component System Validation

Next, we check the applicability of the CPA property package to multi-component systems. Figure 11 shows results for a ternary system containing methane, toluene and TEG. The parity plots compare experimental and calculated liquid mole fractions for methane and toluene at two conditions.

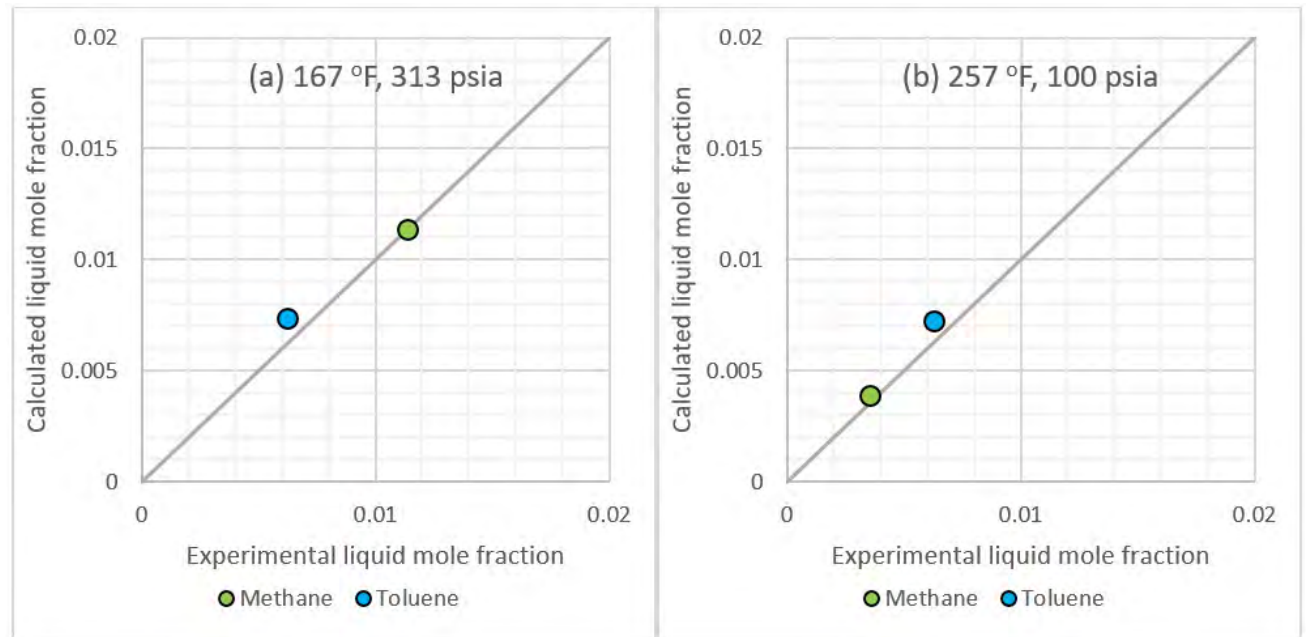


Figure 11: Liquid mole fraction of CH₄-Toluene-TEG system. (a) 167 °F, 313 psia, (b) 257 °F, 100 psia. The parity plot shows calculated values using CPA and experimental values³⁰.

Figure 12 and Table 4 show results for multi-component system of methane, water, TEG and BTEX with conditions that are representative of the operating conditions for flash tank, contactor and regenerator in a typical TEG dehydration process. In Figure 12, the K-value of each component is normalized (with data = 1) for easy comparison. Table 4 compares the experimental and calculated equilibrium phase compositions and K-values of all the components at typical contactor, regenerator and flash conditions. These results demonstrate that the CPA property model developed in this work can match experimental data for multi-component systems relevant to glycol dehydration process using TEG.

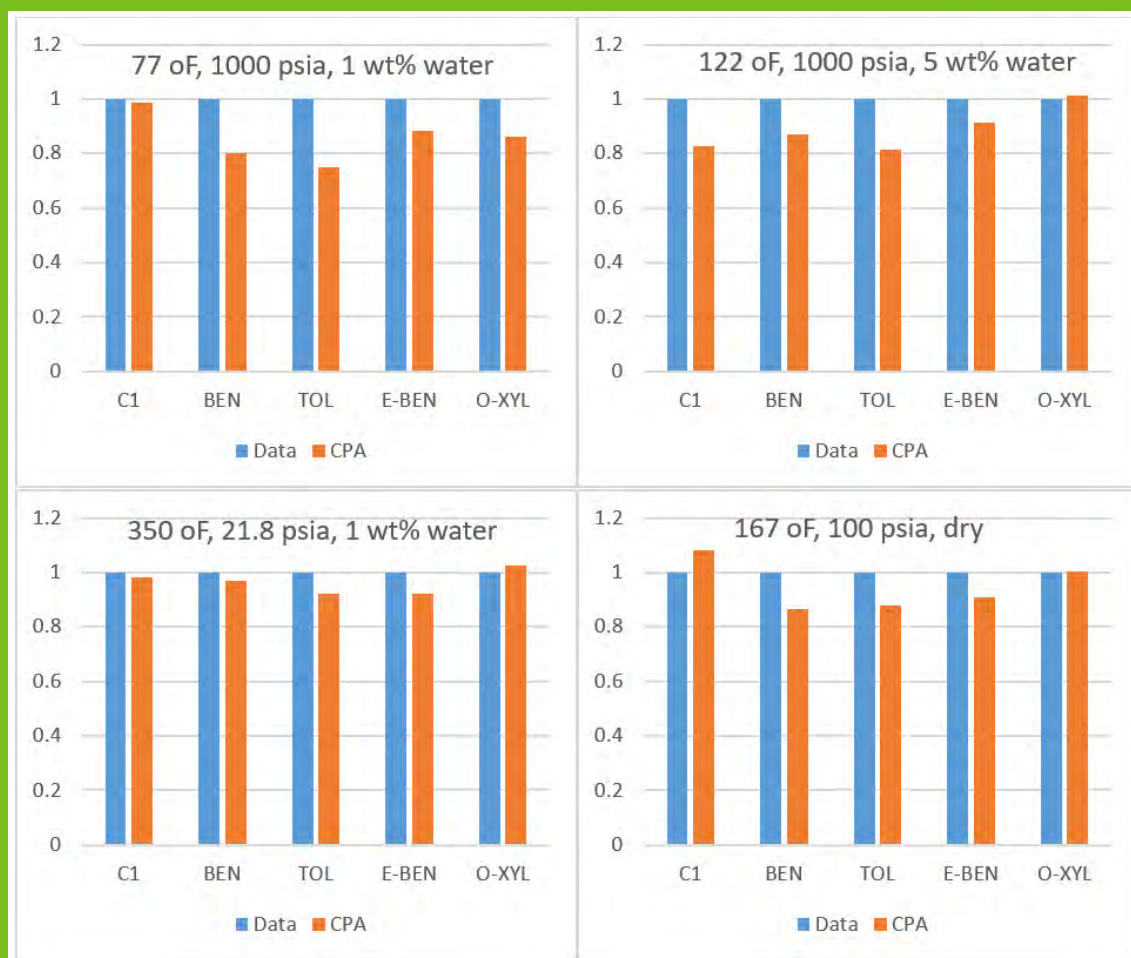


Figure 12: Equilibrium $K(y/x)$ value analysis for methane and BTEX components at different conditions and water composition. Each calculation K-value normalized to the data³⁰. (a) Normalized K-value of methane and BTEX at 77°F and 1000 psia with 1 wt% water, (b) Normalized K-value of methane and BTEX at 122°F and 1000 psia with 5 wt% water, (c) Normalized K-value of methane and BTEX at 350°F and 21.8 psia with 1 wt% water, (d) Normalized K-value of methane and BTEX at 167°F and 100 psia without water.

	Contactor Condition				Regenerator Condition		Flash Condition	
Temperature	77°F		122°F		350°F		167°F	
Pressure	1000 psia		1000 psia		21.8 psia		100 psia	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Y (C1)	1.00E+00	1.00E+00	1.00E+00	9.99E-01	5.14E-01	5.06E-01	9.97E-01	9.97E-01
Y (BEN)	1.03E-04	8.33E-05	2.34E-04	1.94E-04	5.37E-02	4.67E-02	1.63E-03	1.66E-03
Y (TOL)	5.79E-05	4.31E-05	1.39E-04	1.09E-04	3.45E-02	2.80E-02	8.23E-04	8.56E-04
Y (E-BEN)	3.50E-06	3.15E-06	9.50E-06	8.63E-06	2.53E-03	2.01E-03	4.70E-05	5.07E-05
Y(O-XYL)	2.34E-05	2.00E-05	6.46E-05	6.37E-05	1.96E-02	1.73E-02	2.98E-04	3.58E-04
Y (H2O)	-	2.59E-05	-	4.99E-04	-	3.82E-01	-	-
Y (TEG)	2.50E-06	6.28E-08	2.90E-06	4.23E-07	1.74E-02	1.84E-02	4.60E-05	1.24E-05
X (C1)	2.90E-02	2.94E-02	2.02E-02	2.45E-02	4.54E-04	4.54E-04	4.05E-03	3.76E-03
X (BEN)	3.34E-03	3.30E-03	2.42E-03	2.31E-03	3.39E-03	3.04E-03	3.75E-03	4.42E-03
X (TOL)	2.81E-03	2.79E-03	2.04E-03	1.97E-03	3.00E-03	2.64E-03	3.17E-03	3.75E-03
X (E-BEN)	2.51E-04	2.57E-04	1.82E-04	1.81E-04	2.73E-04	2.36E-04	2.81E-04	3.34E-04
X (O-XYL)	2.51E-03	2.50E-03	1.82E-03	1.78E-03	2.83E-03	2.43E-03	2.81E-03	3.36E-03
X (H2O)	7.53E-02	7.53E-02	2.98E-01	2.97E-01	8.78E-02	8.48E-02	-	-
X (TEG)	8.87E-01	8.86E-01	6.75E-01	6.73E-01	9.02E-01	9.06E-01	9.56E-01	9.84E-01
K (C1)	3.45E+01	3.40E+01	4.94E+01	4.08E+01	1.13E+03	1.11E+03	2.46E+02	2.66E+02
K (BEN)	3.10E-02	2.52E-02	9.66E-02	8.40E-02	1.59E+01	1.54E+01	4.34E-01	3.76E-01
K (TOL)	2.06E-02	1.55E-02	6.82E-02	5.54E-02	1.15E+01	1.06E+01	2.60E-01	2.28E-01
K (E-BEN)	1.39E-02	1.23E-02	5.22E-02	4.77E-02	9.26E+00	8.53E+00	1.67E-01	1.52E-01
K (O-XYL)	9.30E-03	8.02E-03	3.54E-02	3.59E-02	6.92E+00	7.10E+00	1.06E-01	1.07E-01
K (H2O)	-	3.45E-04	-	1.68E-03	-	4.50E+00	-	-
K (TEG)	2.80E-06	7.09E-08	4.20E-06	6.29E-07	1.90E-02	2.03E-02	4.70E-05	1.26E-05

Table 4: Comparison between experimental³⁰ and calculated (CPA) values of equilibrium phase compositions and K-values in multi-component mixtures of methane (C1), benzene (BEN), toluene (TOL), ethyl-benzene (E-BEN), o-xylene (O-XYL), water (H2O) and TEG (TEG) at different operating conditions. Y = vapor mole fraction, X = liquid mole fraction, K = K-value.

Flowsheet Validation

The flowsheet model validation also has been conducted to validate the parameters with published plant data.

Case Study 1: Water Removal Fraction at the Contactor

The amount of water that can be removed from the wet gas stream is a function of lean glycol concentration and glycol circulation rate, among other factors. In this case study, a two-equilibrium tray contactor that operates at 100 degrees F and 1000 psia was used³¹. Case studies were created in Aspen HYSYS to study the effect of TEG circulation rate (gal/lb water) at different lean glycol concentration on the fraction of water removed.

Results using CPA property package are compared with plant data³¹ in Figure 13 and Table 5. Figure 13 shows comparison between data³¹ and CPA at four TEG concentrations of 98.0, 98.5, 99.0 and 99.5 percent by weight at a TEG rate that varies from 0 to 6 (gal/lb water). For clarity, the results are also shown in Table 5.

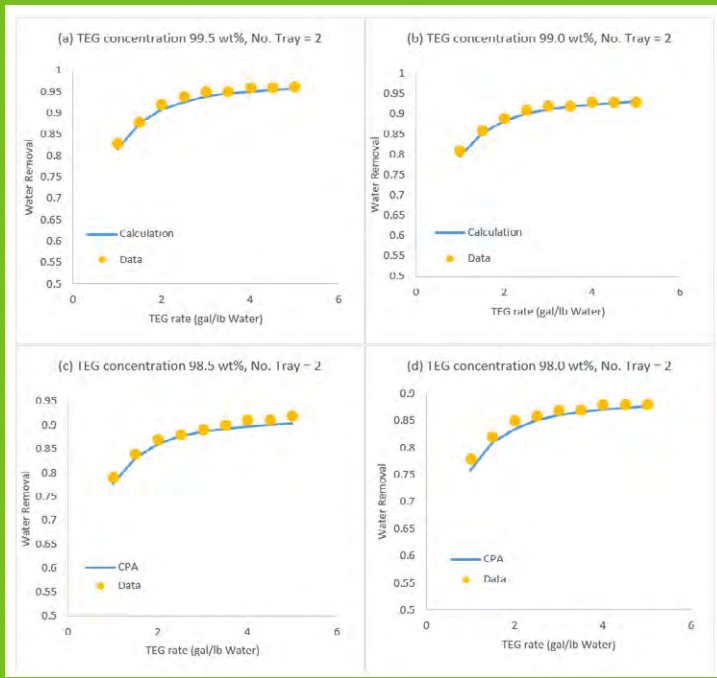


Figure 13: Water removal fraction at 1000 psia, 100 oF contactor condition with different lean glycol concentration and TEG rates (gal/lb water). Contactor used has two equilibrium stages. Experimental data are from³¹. (a) 99.5 wt% lean glycol, (b) 99.0 wt% lean glycol, (c) 98.5 wt% lean glycol, (d) 98.0 wt% lean glycol.

Table 5: Comparison of CPA-predicted water removal fraction from contactor against data³¹ with different lean glycol concentration and TEG circulation rate (100°F, 1000 psia). Contactor used has two equilibrium stages.

TEG rate (Gal TEG/ lb H ₂ O)	99.5 wt% glycol		99.0 wt% glycol		98.5 wt% glycol		98.0 wt% glycol	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
1	0.83	0.810	0.81	0.790	0.79	0.770	0.78	0.751
1.5	0.88	0.871	0.86	0.848	0.84	0.825	0.82	0.802
2	0.92	0.904	0.89	0.879	0.87	0.854	0.85	0.829
2.5	0.94	0.923	0.91	0.896	0.88	0.871	0.86	0.845
3	0.95	0.935	0.92	0.908	0.89	0.881	0.87	0.855
3.5	0.95	0.943	0.92	0.915	0.9	0.888	0.87	0.861
4	0.96	0.948	0.93	0.921	0.91	0.893	0.88	0.866
4.5	0.96	0.953	0.93	0.924	0.91	0.897	0.88	0.869
5	0.9625	0.956	0.93	0.927	0.92	0.899	0.88	0.872

Case Study 2: Water Contents in Dry Gas and BTEX Emission Rate

There are several methods to reduce the amount of VOCs emission¹⁴. One of the methods is to add a BTEX stripper to remove BTEX from the rich glycol using stripping gas, as shown in Figure 14. The three ideal stages for the contactor were applied to match the plant data. In a real system, roughly four stages match with one ideal stage. Although they precisely provide the plant data, there are still other remaining variables which can affect the results. For example, natural gas composition, initial water contents, stripping gas composition and flowrate could change the performance of the flowsheet.

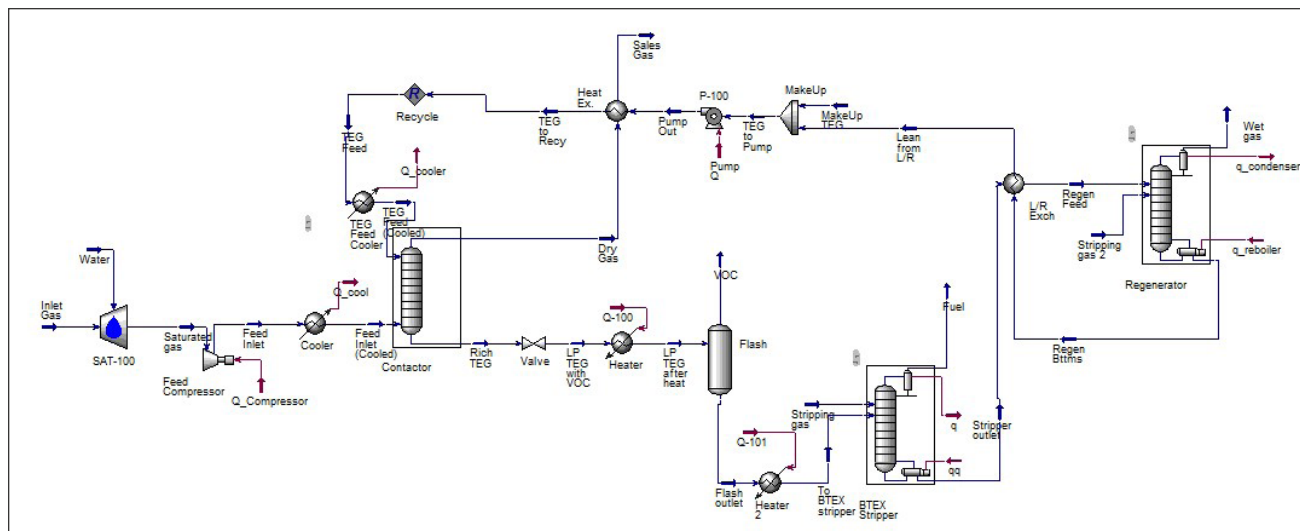


Figure 14: Glycol dehydration process with BTEX stripper

Compound	Mole %
Benzene	0.0005
Toluene	0.0007
Ethylbenzene*	< 0.0001
Xylenes*	< 0.0001

Table 6: BTEX composition of the inlet gas

*0.0001 was used as feed composition in the HYSYS simulation

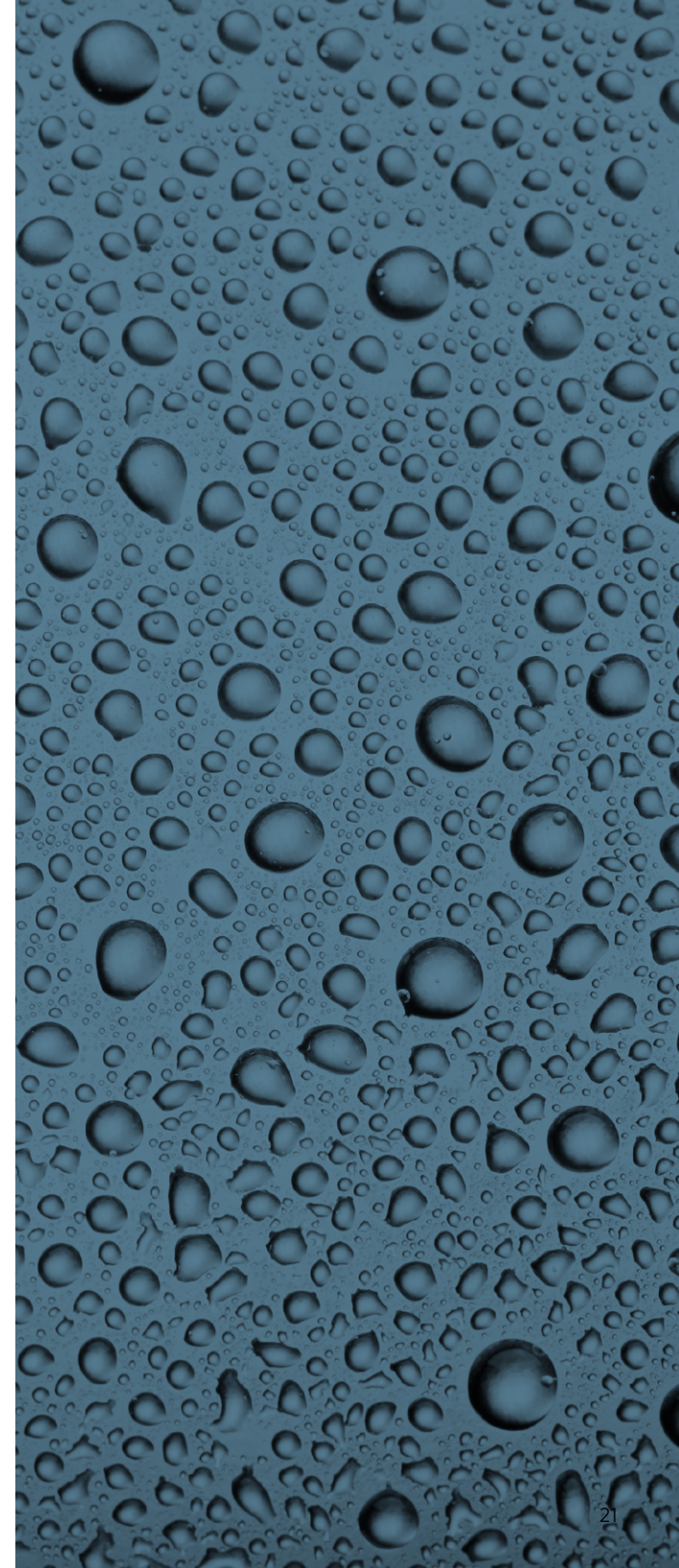
	Data¹⁴	Simulation
Wet Gas Flow Rate, MMscfd	29.2	29.2
Wet Gas Temperature, °F	69	69
Contactor Pressure, psia	305	305
Separator Pressure, psia	47	47
Stripper Temperature, °F	166	166
Stripper Pressure, psia	31	31
Reboiler Temperature, °F	355	355
Glycol Circulation Rate, gpm	2.34	2.34
Lean Glycol Temperature, °F	133	133

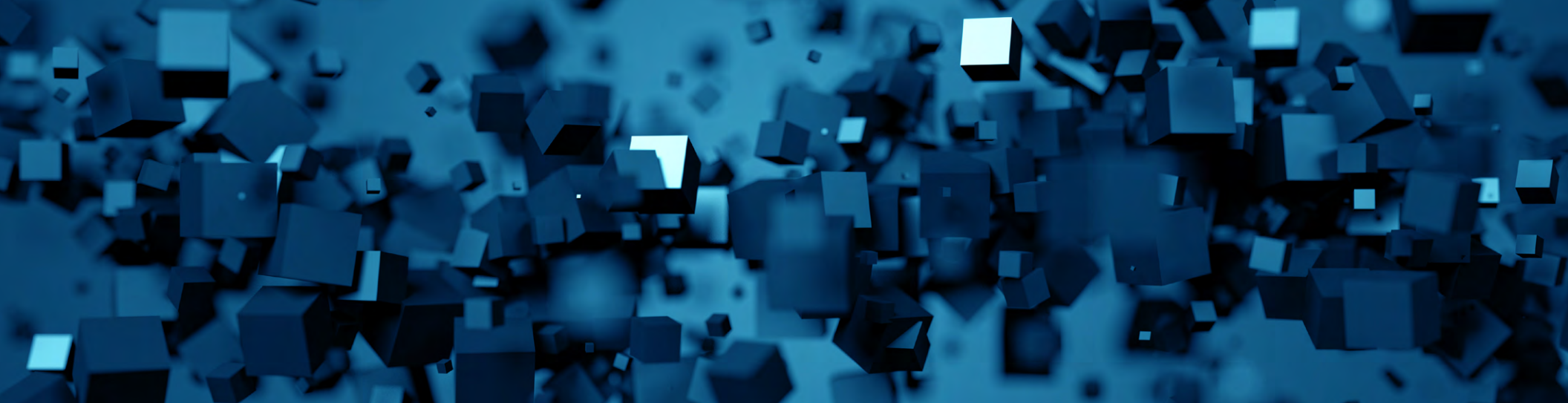
Table 7:
Operation conditions
used in the validation

	Data¹⁴	CPA
Water Content of Dry Gas (lb/MMSCF)	3.00	3.00
Benzene Emissions (tons/year)	0.47	0.34
Toluene Emissions (tons/year)	1.17	0.95
Ethylbenzene Emissions (tons/year)	0.06	0.25
Total Xylene Emissions (tons/year)	0.76	0.37
Total BTEX Emissions (tons/year)	2.46	1.92

Table 8:
Comparison of water
content of dry gas and
BTEX emission between
data and CPA calculation

Since the feed compositions of plant data for ethylbenzene and xylene are not accurately provided, the prediction of ethylbenzene and xylene could not match the data. However, the prediction of water contents and benzene and toluene emission rate are predicted close to plant data. If we could match the real stripping gas composition, which has a possibility to have a trace of BTEX composition or reflect individual component efficiency in the contactor, benzene and toluene prediction would be improved, matching the data more accurately.





Conclusion

In Aspen HYSYS V10 and above, the CPA property package, which is based on the Cubic-Plus-Association (CPA) equation of state, is available and is recommended for modeling dehydration processes with EG, DEG and TEG.

The CPA property package and the glycol dehydration flowsheet model in Aspen HYSYS were tested with various experimental and plant data. The results from validation with binary and multi-component systems and patterns of physical properties as well as simulation model show a good prediction with wide range of conditions.

Gas treating is crucial for meeting regulations. Better process understanding can help guide decisions to reduce costs and prevent costly damage to equipment. As engineers continue to drive improvement in plant operations, it is imperative they have the right simulation tools in place to help make informed decisions and remain competitive.

Plant issues arise all too frequently, and in order for organizations to ensure the best action is taken, operators need access to an integrated software platform. With the right technology, the engineers can make the right decisions for their plants to ensure profits outweigh costs. Additionally, with these solutions, organizations can minimize risk against unplanned events, as they will have the tools to adjust day-to-day activities to find the most effective and efficient way to run the facility.

References

- ¹ Folas, G.K., Technical University of Denmark, Thesis, 2006, Modeling of Complex Mixtures Containing Hydrogen Bonding Molecules
- ² Braek, A.M.; Almehaideb, R.A.; Darwish, N.; Hughes, R., Process Safety and Environmental Protection, Volume 79, Issue 4, July 2001, 218-232, Optimization of Process Parameters for Glycol Unit to Mitigate the Emission of BTEX/VOCs
- ³ Arnold, K.; Stewart, M., Surface Production Operations – Design of Gas-Handling Systems and Facilities, Volume 2, Second Edition, 1999, Chapter 8 - Gas Dehydration
- ⁴ USEPA Natural Gas Star, Lesson learned, “Optimize Glycol Circulation and Install Flash Tank Separators in Glycol Dehydrators,” 2006
- ⁵ Soave, G. Chem. Eng. Sci., Vol. 27, (1972), pp. 1196-1203, Equilibrium Constants for Modified Redlich-Kwong Equation of State
- ⁶ Kontogeorgis, G.M., Voutsas, E., Yakoumis, I.; Tassios, D.P., Ind. Eng. Chem. Res., 1996, 35, 4310, An Equation of State for Associating Fluids
- ⁷ Kontogeorgis, G.M.; Folas, G.K., John Wiley & Sons, 2010, Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories
- ⁸ Arya, A.; Maribo-Mogensen, B.; Tsvintzelis, I.; Kontogeorgis, G.M., Ind. Eng. Chem. Res. 2014, 53, 11766–11778, Process Design of Industrial Triethylene Glycol Processes Using the Cubic-Plus-Association (CPA) Equation of State
- ⁹ Aspen Plus® V10, Aspen Technology, Inc. Bedford, MA
- ¹⁰ International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering Vol:7, No. 6, 2013
- ¹¹ Hlavinka, M.W.; Collie, J. and Ashworth A., 1998, An Analysis of BTEX Emissions from Amine Sweetening and Glycol Dehydration Facilities, Proceedings of the 1998 Laurance Reid Gas Conditioning Conference, University of Oklahoma
- ¹² Bahadori, A. Technology and Engineering Design, 2014, 441-481, Chapter 9 - Natural Gas Dehydration
- ¹³ Ballard, D. American Institute of Chemical Engineers Spring National Meeting, New Orleans, LA, USA, 6 Apr 1986, The Fundamentals of Glycol Dehydration
- ¹⁴ Ebeling, H.O.; Lyddon, L.G.; Covington, K.K., Bryan Research and Engineering, Inc., 1998, Reduce Emission and Operating Costs with Appropriate Glycol Selection
- ¹⁵ Hernandez-Valencia, V.N.; Hlavinka, M.W.; Bullin J.A., Bryan Research & Engineering, Inc., 1992, Design Glycol Units for Maximum Efficiency
- ¹⁶ R.K. Abdulrahman and I.M. Sebastine, Natural Gas Dehydration Process Simulation and Optimization: A Case Study of Khurmala Field in Iraqi Kurdistan Region
- ¹⁷ Hlavinka, M.W; Hernandez-Valencia, V.N.; Bullin, J.A., Bryan Research & Engineering, Inc., 1992, Influence of Process Operations on VOC and BTEX Emissions from Glycol Dehydration Units
- ¹⁸ C.I.C. Anyadiegwu, A. Kerunwa, P. Oviawe, Petroleum & Coal 56(4) 407-417, 2014, Natural Gas Dehydration Using Triethylene Glycol (TEG)

- 19 Jou, F.Y.; Deshmukh, R.D.; Otto, F.D.; Mather, A.E. *Fluid Phase Equilib.*, 1987, 36, 121 Vapor-Liquid Equilibria for Acid Gases and Lower Alkanes in Triethylene Glycol
- 20 Wilson, L.C.; Wilding, W.V.; Wilson, G.M. *AIChE Symp. Ser.*, 1989, 85, 25-43 Vapor-Liquid Equilibrium Measurements on Four Binary Mixtures
- 21 Herskowitz, M.; Gottlieb, M.J. *Chem. Eng. Data*, 1984, 29, 450, Vapor-Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 1. Triethylene Glycol
- 22 Tsuji, T.; Hiaki, T.; Hongo, Masaru. *Ind. Eng. Chem. Res.*, 37 (5), 1998, Vapor-Liquid Equilibria of the Three Binary Systems: Water +Tetraethylene Glycol (TEG), Ethanol + TEG, and 2-Propanol + TEG
- 23 Parrish, W.R.; Wonk, W.; Baltatu, M.E. *Proc. Ann. Conv. Techn. Papers GPA*, 1986, Phase Behavior of the Triethylene Glycol - Water System and Dehydration/Regeneration Design for Extremely Low Dew Point Requirements
- 24 Rafflenbeul, L.; Hartmann, H. *Forschungsber. Landes Nordrhein-Westfalen*, 2888, 1979, A Method for Selecting Solutes for the Extractive Distillation
- 25 Bestani, B.; Shing, K.S. *Fluid Phase Equilib.*, 50, 1989, 209-221, Infinite-Dilution Activity Coefficients of Water in TEG, PEG, Glycerol and Their Mixtures in the Temperature Range 50-140 Degrees Centigrade
- 26 Ikari, A.; Ayabe, N. *Kagaku Kogaku*, 31(11), 1967, 1067-1070, Activity Coefficients at Infinite Dilution of Water in Glycerol and Triethylene Glycol
- 27 Folas, G.K.; Kontogeorgis, G.M.; Michelsen, M.L.; Stenby, E.H.; Solbraa, E.J. *Chem. Eng. Data*, 2006, 51, 977-983
- 28 Gupta, S.K.; Rawat, B.S.; Goswami, A.N.; Nanoti, S.M.; Krishna, R. *Fluid Phase Equilib.*, 1989, 46, 95-102 Isobaric Vapor-Liquid Equilibria of the Systems: Benzene-Triethylene Glycol, Toluene-Triethylene Glycol and Benzene-N-Methylpyrrolidone
- 29 Hughes, M.A.; Haoran, Y.J. *Chem. Eng. Data*, 1990, 35, 467-471 Liquid-Liquid Equilibria for Separation of Toluene from Heptane by Benzyl Alcohol Tri(ethylene glycol) Mixtures
- 30 Ng, H.J.; Chen, C.J.; Robinson, D.B., *GPA Research Report RR-131, The Solubility of Selected Aromatic Hydrocarbons in Triethylene Glycol*, DB Robinson Research Ltd., 1991
- 31 Holoboff, J.L.; Khoshkbarchi, M., *Process Ecology Inc.*, 2009, Prediction of BTEX Emission and Water Content in TEG Dehydration Units

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