

Enhancement in Triethylene Glycol (TEG) Purity via Hydrocarbon Solvent Injection to a TEG + Water System in a Batch Distillation Column

Khadijeh Paymooni, Mohammad Reza Rahimpour,* Sona Raeissi, Mohsen Abbasi, and Mohammad Saviz Baktash

Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran

 Supporting Information

ABSTRACT: Triethylene glycol (TEG) is one of the most important liquid desiccants in the natural gas dehydration industry. In enhanced TEG regeneration processes, liquid hydrocarbons such as toluene and isooctane are added to the stripping column of natural gas dehydration unit in order to boost water volatility and regenerate TEG to higher purity. In this study, isooctane and toluene were selected as liquid hydrocarbon solvents and the effect of these two solvents on TEG purity and the outlet water concentration from the reboiler of tray column were experimentally investigated and mathematically modeled. The vapor–liquid equilibrium calculations were performed using the NRTL activity coefficient model and ideal gas equation of state to represent the liquid and vapor phases, respectively. Moreover, a comprehensive model was used to determine the liquid molar flow rate on each tray where it changed with time and tray by tray. The impact of various concentrations of solvents and different operating conditions (total and no reflux) on the performance of the tray column was investigated. The modeling results were validated with the experimental data, and good agreement was observed between them. Results showed that the least water concentration in the reboiler and the highest TEG purity were achieved by adding 0.15 wt % isooctane under total reflux conditions. The achieved results can provide an initial insight into designing equipments in enhanced TEG regeneration processes with hydrocarbon solvent injection.

INTRODUCTION

In this section, the main aspects of this study are outlined. As discussed later, the mathematical modeling was carried out in conjunction with experiments in order to achieve more reliable evaluation of triethylene glycol (TEG) dehydration unit performance.

Natural Gas Dehydration. Natural gas is an important source of primary energy and it is saturated with water vapor under normal production conditions.¹ The saturated water of natural gas can cause some operational problems such as hydrate formation, corrosion, etc.² Among different gas drying processes, absorption is the most common technique where the water vapor in the gas stream is absorbed in a liquid solvent stream. Glycols are the most widely used absorption liquids as they approximate the properties that meet commercial application criteria. Several glycols have been found suitable for commercial application.³ Actually, the main reason for glycols popularity is their superior absorption of water because the hydroxyl groups in glycols form similar associations with water molecules.⁴ Triethylene glycol (TEG) has gained universal acceptance as the most cost-effective glycol mainly due to more easy regeneration, less vaporization losses, lower capital and operating costs, higher initial theoretical decomposition temperature, etc.⁵ TEG is used in a counter-current mass transfer operation inside a contractor to establish the required water content in the outlet gas.⁶ Bahadori and Vuthaluru developed a simple-to-use method, by employing basic algebraic equations, to correlate water removal efficiency as a function of TEG circulation rate and TEG purity for appropriate sizing of the absorber at a wide range of operating conditions

of TEG dehydration systems.⁷ Furthermore, they developed the rapid estimation of the water dew point of a natural gas stream in equilibrium with a TEG solution at various temperatures and TEG concentrations.⁸ Darwish and Hilal simulated a typical process for natural gas dehydration using TEG as a desiccant using a steady state flowsheet simulator (Aspen Plus).⁹

Enhanced Regeneration Process. In spite of previously extensive investigations on typical natural gas dehydration units, several processes are available today while each applies different strategies to enhance glycol regeneration by reducing the effective partial pressure of water in the vapor phase.¹⁰ Enhanced regeneration could be the injection of stripping gas into the reboiler, azeotropic regeneration, or other processes.^{11,12} Pearce et al. investigated a gas dehydration process in which glycol used as dehydrating agent is subsequently regenerated with toluene (Drizo Process).¹³ The Drizo gas dehydration process uses high glycol concentrations to give low dew point temperatures and uses a solvent to recover extracted aromatics. The Drizo technology has evolved to overcome past reservations due to solvent losses, glycol losses, and glycol contamination of downstream low temperature ethane extraction units.¹⁴

Batch Distillation. Batch distillation is characterized as a system that is difficult to design because compositions are changing continuously with time. The design of a batch distillation column

Received: June 26, 2011

Revised: October 15, 2011

Published: October 17, 2011

Table 1. Specification of Materials Used in Experiments

chemical component	purity	water content	supplier
TEG	>99%	<0.3%	Arak Petrochemical Company
toluene, isoctane	>99%	<0.01%	Merck Company
distilled water			Shiraz University

is much more complex in comparison with that of a continuous distillation column as it requires consideration of unsteady-state behavior. The complexity of the problem increases with the number of components in multicomponent systems.¹⁵ Diwekar et al.¹⁶ presented optimization approaches using the shortcut method for the optimal design of single- and multiple-fraction batch columns operating under constant reflux and variable reflux conditions. Tapp et al.¹⁷ developed experimental method for obtaining distillation column concentration profiles at finite reflux using a batch apparatus. Stewart et al.¹⁸ investigated a theoretical and experimental study of the effect of certain design variables on the degree of separation obtainable in multicomponent batch distillation. Luyben¹⁹ investigated the effects of both design and operating parameters by using digital simulation, number of trays, reflux ratio (both fixed and variable), initial still charge, relative volatility, and product purity for multicomponent batch distillation.

Objectives. In this study, the effect of hydrocarbon solvent injection on TEG purity in water + TEG system was investigated both experimentally and theoretically. Experiments were conducted in a batch tray column under total and no reflux operating conditions and various concentrations of solvents. The effect of isoctane and toluene addition to a TEG + water system on TEG purity in the bottom product and TEG loss in the top product were compared. The concentration profiles of water and TEG in reboiler were determined. The modeling results were validated by the experimental data, and a good agreement was observed between them.

EXPERIMENTAL SECTION

Materials. The specification of materials used in experiments is reported in Table 1. Chemicals were used without further purification.

Apparatus and Procedure. In this study, experiments were conducted in a batch distillation column (see Figure 1). As seen, the column consists of twenty trays, a total condenser, and reboiler. Samples were taken from the reboiler in 5 min intervals. Different operating conditions and concentrations of water and solvents were considered to determine the effect of them on TEG purity. The specification of this column is reported in Table 2.

In order to gain a deep insight into conducting experiments, some samples were taken from the feed streamline to the stripping column of Farashband gas refinery (located in Iran) and analyzed by Karl Fischer Titrator (Mettler Toledo, DL31). The analyzing results showed that the water content of rich glycol was between 7 and 10 wt %; therefore three water concentrations of 7, 10, and 15 wt % were selected for the experiments. Furthermore, several experiments were conducted in order to recognize the best solvent concentration, and 0–0.05, 0.1, and 0.15 wt % solvent concentrations were chosen in the end. It was worth mentioning that a sudden blast was observed at a solvent concentration more than 0.3 wt %, and solvent did not show its effect at concentration less than 0.05%. Thus, the minimum solvent concentration of 0.05 wt % was considered during the experiments. Moreover, the effect of reflux ratio on TEG purity was investigated, and two reflux operating conditions including total reflux and no reflux were thoroughly investigated.

**Figure 1.** Batch distillation tray column used during the experiments.**Table 2. Specification of Tray Column**

outer diameter	8 cm
number of trays	20
pressure (condenser)	101.3 kPa
d	8 cm
WHS	1.3 cm
WLS	2.36 cm
Q_B	3587.2 kJ/h
initial weight fractions (TEG, isoctane/toluene, water)	0.85, 0.001, 0.15
	0.899, 0.001, 0.1
	0.929, 0.001, 0.07
	0.8485, 0.0015, 0.15
	0.8985, 0.0015, 0.1
	0.9285, 0.0015, 0.07
	0.8495, 0.0005, 0.15
	0.8995, 0.0005, 0.1
	0.9295, 0.0005, 0.07

A known amount of water, TEG, and solvents was mixed and introduced into the reboiler. According to the controlling section of the column, the column was started up and the mixture took 40–60 min to boil in the reboiler based on the composition distribution of components. When the top tray temperature reached steady state condition (the measurement uncertainty of the thermometer which was used in experiments was ± 0.1 °C), sampling was performed for 5, 10, 15, 20, 25, 30, 40, 50, and 60 min. Next, the water content of bottom samples was determined via Karl Fischer titrator with the measuring range of 50 ppm to 100% water (Figure 2) and the hydrocarbon content of the top samples was determined via total organic carbon (TOC) (Figure 3a)



Figure 2. Karl Fischer Titrator for determining the water content of the bottom product.



(a)



(b)

Figure 3. (a) TOC for determining the HC content of the top product. (b) GC for analyzing the HC content of the top product.

and analyzed by Varian Model 3800 GC (Figure 3b) for detecting special hydrocarbons. The column of the GC was 0.635 cm in diameter and 2 m in height packed by Porapak Q. Helium was used as a carrier gas, and a flame ionization detector (FID) was applied to obtain the composition of hydrocarbons.

MATHEMATICAL MODELING

A scheme of the batch distillation tray column is shown in Figure 4. Three basic assumptions are usually made in dynamic

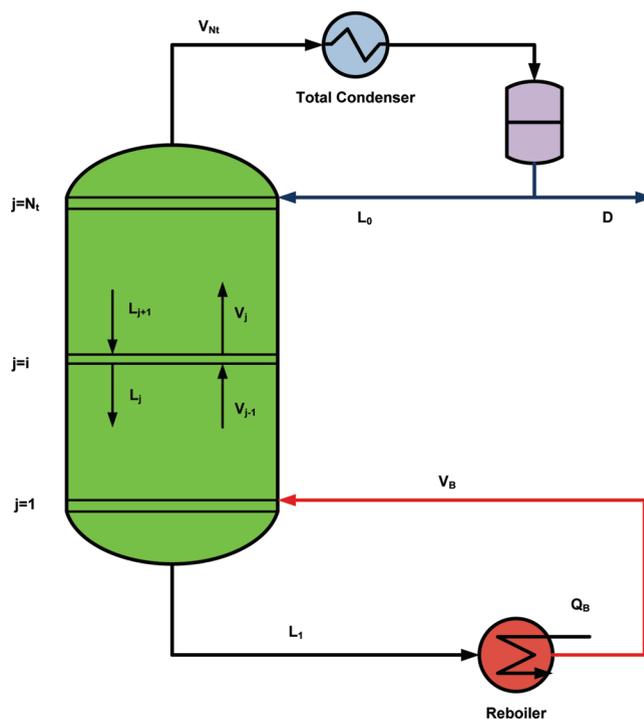


Figure 4. Scheme of the batch distillation tray column.

studies of nonreactive systems:²⁰

- The molar vapor holdup is negligible in comparison with the molar liquid holdup.
- Vapor and liquid on and leaving each tray are perfectly mixed, and the liquid on a tray has a concentration equal to that of the liquid leaving that tray.
- The theoretical equilibrium compositions are corrected for mixing effects, flow configuration, and mass transfer limitations by introducing tray efficiency (tray efficiency of the batch column considered in this study was 60%).

MASS AND ENERGY BALANCE EQUATIONS

The governing equations are composed of the total and partial material balances and the energy balance for the reboiler, the trays (first, intermediate, and top trays), and the total condenser. In the following equations, the usual assumption was made where vapor molar hold-up was negligible compared with liquid molar hold-up which may give erroneous results for very high column pressures.²¹

For the reboiler, total and component material balances and the energy balance are as follows (subscript B):

$$\frac{dM_B}{dt} = L_1 - V_B \quad (1)$$

$$\frac{d(M_B x_{B,j})}{dt} = L_1 x_{1,j} - V_B y_{B,j} \quad j = 1, \dots, N_c \quad (2)$$

and

$$\frac{d(M_B H_{L,B})}{dt} = L_1 H_{L,1} - V_B H_{V,B} + Q_B \quad (3)$$

The first tray (subscript 1):

$$\frac{dM_1}{dt} = V_B + L_2 - V_1 - L_1 \quad (4)$$

Table 3. Activity Coefficient Interaction Parameters for a Binary System of Water (1) and TEG (2)²³

pair	interaction parameters (NRTL)		
water–TEG	$A_{12} = 248.95$	$A_{21} = -172.96$	$\alpha_{12} = 2.3660$

$$\frac{d(M_1x_{1,j})}{dt} = V_B y_{B,j} + L_2 x_{2,j} - V_1 y_{1,j} - L_1 x_{1,j}$$

$$j = 1, \dots, N_c \quad (5)$$

and

$$\frac{d(M_1H_{L,1})}{dt} = V_B H_{V,B} - V_1 H_{V,B} + L_2 H_{L,2} - L_1 H_{L,1} \quad (6)$$

Intermediate trays (subscript i):

$$\frac{dM_i}{dt} = V_{i-1} + L_{i+1} - V_i - L_i \quad (7)$$

$$\frac{d(M_i x_{i,j})}{dt} = V_{i-1} y_{i-1,j} - V_i y_{i,j} + L_{i+1} x_{i+1,j} - L_i x_{i,j}$$

$$j = 1, \dots, N_c \quad (8)$$

and

$$\frac{d(M_i H_{L,i})}{dt} = V_{i-1} H_{V,i-1} - V_i H_{V,i} + L_{i+1} H_{L,i+1} - L_i H_{L,i} \quad (9)$$

Top tray (subscript N_t):

$$\frac{dM_{N_t}}{dt} = V_{N_t-1} + L_0 - V_{N_t} - L_{N_t} \quad (10)$$

$$\frac{d(M_{N_t} x_{N_t,j})}{dt} = V_{N_t-1} y_{N_t-1,j} + L_0 x_{D,j} - L_{N_t} x_{N_t,j} - V_{N_t} y_{N_t,j}$$

$$j = 1, \dots, N_c \quad (11)$$

$$\frac{d(M_{N_t} H_{L,N_t})}{dt} = V_{N_t-1} H_{V,N_t-1} - V_{N_t} H_{V,N_t} + L_0 H_{L,D} - L_{N_t} H_{L,N_t} \quad (12)$$

Condenser (subscript D):

$$\frac{dM_D}{dt} = V_{N_t} - L_0 - D \quad (13)$$

$$\frac{d(M_D x_{D,j})}{dt} = V_{N_t} y_{N_t,j} - D x_{D,j} - L_0 x_{D,j}$$

$$j = 1, \dots, N_c \quad (14)$$

Modeling Assumptions

- Constant pressure throughout the column (101.3 kPa).
- Liquid is perfectly mixed on a tray.
- Adiabatic column.
- Constant liquid holdup in condenser (5 L).
- Vapor holdups are negligible.
- Tray liquid dynamics is calculated using the Francis Weir formula.

Table 4. Activity Coefficient Interaction Parameters for Ternary Systems of (a) Water (1), Toluene (2), and TEG (3) and (b) Water (1), Isooctane (2), and TEG (3)²³

pair	(a)		
	interaction parameters (NRTL)		
water–toluene	$A_{12} = 678.49$	$A_{21} = 378.24$	$\alpha_{12} = -0.1360$
water–TEG	$A_{13} = -1909.5$	$A_{31} = 14.769$	$\alpha_{13} = -0.8893$
toluene–TEG	$A_{23} = 172.05$	$A_{32} = 210.85$	$\alpha_{23} = -2.2000$

pair	(b)		
	interaction parameters (NRTL)		
water–isooctane	$A_{12} = -74.268$	$A_{21} = 407.46$	$\alpha_{12} = -1.3430$
water–TEG	$A_{13} = -145.63$	$A_{31} = -64.723$	$\alpha_{13} = -3.1110$
isooctane–TEG	$A_{23} = 1080.1$	$A_{32} = 1040.3$	$\alpha_{23} = 0.4810$

Table 5. (a) Vapor Pressure Constants for Pure Components^{24,25} and (b) Physical Properties for Pure Components

comp	(a)				
	C_1	C_2	C_3	C_4	C_5
water	73.649	-7258.2	-7.3037	4.1653×10^{-6}	2
toluene	80.877	-6902.4	-8.7761	5.8034×10^{-6}	2
isooctane	87.868	-6831.7	-9.9783	7.7729×10^{-6}	2
TEG	29.368	-8897.1	-1.4675	2.1263×10^{-6}	2

comp	(b)					
	Mw	T_c (K)	$P_c \times 10^{-6}$ Pa	V_c (m ³ /kmol)	Z_c	ω
TEG	150.20	769.50	3.3200	0.5347	0.2462	1.2540
H ₂ O	18.015	647.13	21.940	0.0560	0.2280	0.3430
toluene	92.141	591.80	4.1000	0.3140	0.2620	0.2620
isooctane	114.23	543.96	2.5600	0.4650	0.2640	0.3010

- Ideal gas behavior (atmospheric pressure system).
- Vapor–liquid equilibrium (VLE) is determined using the NRTL activity coefficient model and ideal gas equation of state.
- Negligible secondary heat effects (heat loss and heat of mixing).
- The condenser is a total condenser.
- Liquid in the reflux drum is well mixed, i.e., distillate and reflux have the same composition as the liquid in the reflux drum at any time.
- Liquid in the reboiler is well-mixed, i.e., the bottoms has the same composition as the liquid in the reboiler at any time.
- Known value of an input heat to the reboiler.
- Known value of the reflux ratio.

Francis Weir Formula.²¹ The liquid holdups of the trays are calculated based on the work of Luyben²¹ as follows:

$$LV = LMw_{Ave}/\text{density}_{Ave}$$

$$HFOW = \left(\frac{LV}{999WLS} \right)^{0.6667}$$

$$MV = \left(HFOW + \frac{WHS}{12} \right) \frac{\pi d^2}{4 \times 144}$$

$$M = MV \text{density}_{Ave}/Mw_{Ave} \quad (15)$$

Table 6. Constants of Equations 25, 26, and 27²⁶

comp	(a)				
	A	B	C	D	E
TEG	160.2	1.207	-3.064×10^{-3}	3.242×10^{-6}	0
isooctane	446.5	-4.343	2.431×10^{-2}	-5.287×10^{-5}	4.149×10^{-8}
toluene	256.5	-1.660	7.521×10^{-3}	-1.279×10^{-5}	8.356×10^{-9}
water	-22.42	0.877	-2.570×10^{-3}	2.484×10^{-6}	0

comp	(b)						
	A'	B' × 10	C' × 10 ³	D' × 10 ⁶	E' × 10 ⁹	F' × 10 ¹²	G' × 10 ¹⁶
TEG	75.98	1.169	0.177	-3.852	3.715	-1.756	3.284
isooctane	134.9	-5.957	4.531	-8.503	7.804	-3.557	6.417
toluene	47.37	-2.201	2.482	-4.918	4.604	-2.120	3.850
water	30.22	1.131	0	0	0	0	0

comp	(c)	
	A''	n
TEG	130.9	0.46
isooctane	48.09	0.38
toluene	50.14	0.38
water	54.00	0.34

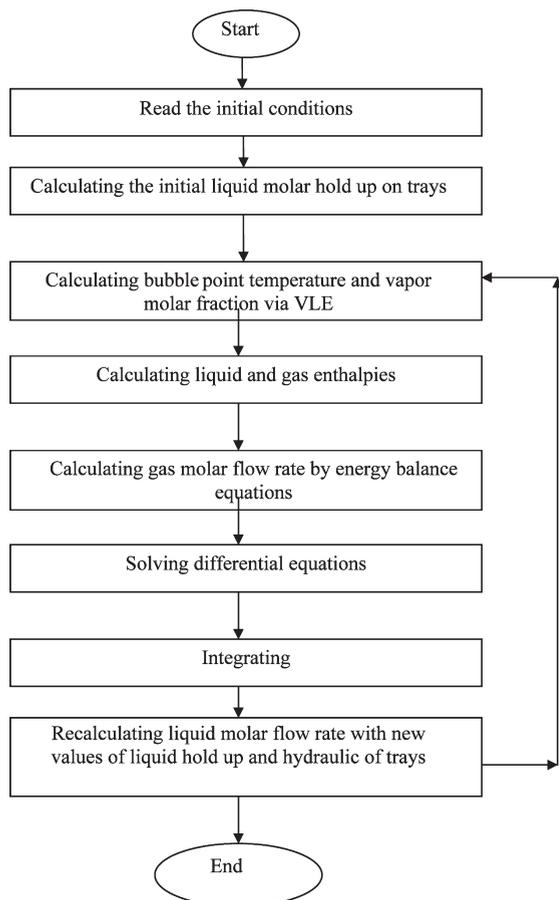


Figure 5. Calculation procedure.

The liquid holdup in the reboiler at any time is calculated from an algebraic combination of the initial charge, the material in

the column, and the total material removed up to that instant in time:

$$M_B = M_{B0} + \sum_{i=1}^{Nt} M_{i0} - \sum_{i=1}^{Nt} M_i - \int D dt \quad (16)$$

Parameter Determination for VLE Calculation. As the column operated under atmospheric condition, the ideal gas equation of state could be used for the gas phase. Moreover, a nonrandom two-liquid (NRTL) model was used for the liquid phase as follows:²²

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ji}}{\sum_k x_k G_{kj}} \left(\tau_{ji} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right) \quad (17)$$

where

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$\tau_{ij} = \frac{A_{ij}}{T}$$

The parameters of the NRTL model have been used to predict the composition and temperature in this case. Khosravanipour Mostafazadeh et al.²³ measured experimentally the vapor–liquid equilibria data for systems water + TEG and water + TEG + toluene at 85 kPa and various temperatures. The column temperature was controlled by programming the temperature. After 1 min of holding at $t = 100$ °C, the column temperature was raised to the final temperature of 220 °C at the rate of 5 °C/min. The experimental data of the binary (water + TEG) and ternary systems (water + TEG + toluene) were tuned using Van Laar, quasichemical activity coefficient (UNIQUAC), and NRTL activity coefficients models. Good agreements were obtained for the water + TEG

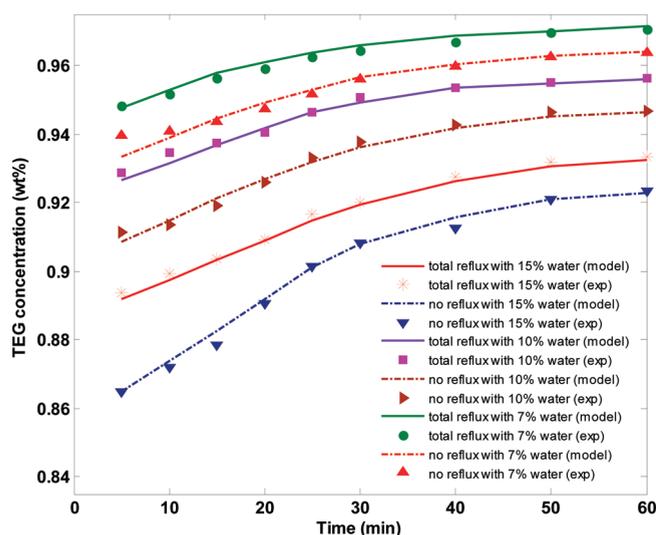


Figure 6. Effect of reflux ratio on TEG purity for different water concentrations.

system, but only NRTL and UNIQUAC models were suggested for the ternary system. The complete set of NRTL parameters for binary and ternary systems is reported in Tables 3 and 4.

According to the above-mentioned equations, a set of thermodynamic and thermophysical parameters such as vapor pressure, critical properties, etc. was required. The following equation was used for calculating vapor pressure:

$$\ln P_j = c_1 + \frac{c_2}{T} + c_3 \ln T + c_4 T^{c_5} \quad (18)$$

Vapor pressure constants and physical properties for pure components are reported in Table 5.

A trial and error method was used for determination of bubble point temperature of the mixture. The initial temperature was guessed via eq 19 and used in calculating the vapor pressure of components determined by eq 18. The activity coefficient parameters were calculated by eq 17. The modified vapor pressure could be recalculated by eq 18, and modified temperatures could be determined. The modified temperature was compared with the previously calculated temperature. If error between them was not acceptable, a calculation procedure should be performed until reaching the desired error value. Ultimately, the vapor mole fractions were determined by eq 21 and normalized.

$$T = \sum_{j=1}^{N_c} x_j T_j^{\text{sat}} \quad (19)$$

$$P = \sum_{j=1}^{N_c} x_j \gamma_j P_j^{\text{sat}} \quad (20)$$

$$y_j = \frac{x_j \gamma_j P_j^{\text{sat}}}{P} \quad (21)$$

NUMERICAL SOLUTION

A set of differential and algebraic equations (DEA) were solved simultaneously. The developed mathematical model had

Table 7. TOC Analysis of Top Product for Total Reflux and No Reflux Conditions

water concentration (wt %)	TOC (ppm)	TEG bottom (wt %)	reflux
7	352	97.05	total reflux
7	336	96.37	no reflux
10	324	95.62	total reflux
10	308	94.67	no reflux
15	291	93.32	total reflux
15	273	92.34	no reflux

88 state variables including the composition of 3 components on 20 trays, the composition of 3 components in the reboiler and condenser, liquid hold up on 20 trays and the reboiler, and the distillate amount. The input heat to the reboiler, the reflux ratio, and the condenser hold up were known variables.

In order to determine the concentration profiles of different components in the reboiler, the following calculation procedure was proposed:

Initial concentrations were assumed for components in reboiler and condenser and on 20 trays based on the reported values in Table 2. The initial concentrations were equal to the initial charge to the reboiler ($t = 0$), and it was assumed the same value for components in condenser and on 20 trays. The initial vapor and liquid molar flow rates were calculated based on eqs 22 and 23.

$$V = \frac{Q_B}{(H_{V,B} - H_{L,B})} \quad (22)$$

$$L = \frac{Rf}{Rf + 1} \quad (23)$$

The bubble point temperature and the vapor fraction of different components in the reboiler, condenser, and on 20 trays could be calculated based on VLE equation and physical property values. Now, the liquid and vapor enthalpies of different components could be determined by eqs 27 and 28 and by the help of bubble point temperature of mixture and vapor mole fractions. The constants of eqs 24, 25, and 26 are reported in Table 6. Liquid hold up could be calculated by determining the mixture density and molecular weight (eqs 29 and 30). The vapor molar flow rate was calculated by the energy balance and the liquid molar flow rate was calculated by the Francis formula²¹ (eq 31). The liquid and vapor molar flow rates changed with time and tray by tray. A comprehensive model was used to determine the liquid molar flow rate (eq 31). The concentration profiles of different components were determined at specific time by the help of new values of concentration, liquid hold up on all trays, liquid and vapor molar flow rates, etc. The calculation procedure is illustrated in Figure 5.

$$C_{P_L} = A + BT + CT^2 + DT^3 + ET^4 \quad (24)$$

$$C_{P_V} = A' + B'T + C'T^2 + D'T^3 + E'T^4 + F'T^5 + G'T^6 \quad (25)$$

$$\text{HVAP} = A'' \left(1 - \frac{T}{T_c}\right)^n \quad (26)$$

$$H_L = H_L(T_{\text{Ref}}) + \sum_{j=1}^{N_c} x_j C_{P_{L_j}} (T - T_{\text{Ref}}) \quad (27)$$

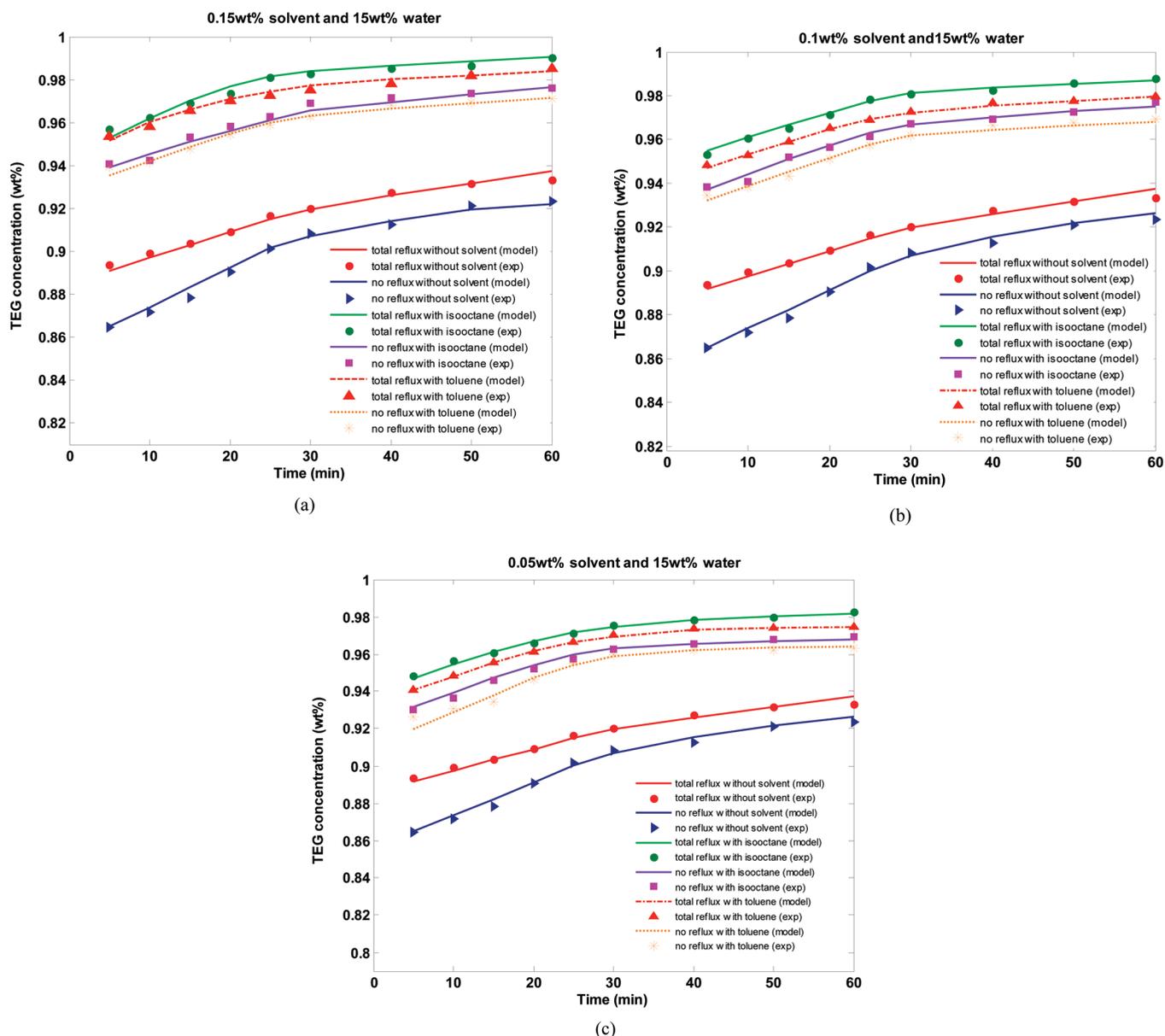


Figure 7. Variation of TEG concentration in reboiler with time for 15 wt % water and (a) 0.15, (b) 0.1, and (c) 0.05 wt % toluene and isooctane.

$$H_V = H_V(T_{\text{Ref}}) + \text{HVAP}(T_{\text{Ref}}) + \sum_{j=1}^{N_c} y_j(C_{P_{V_j}})(T - T_{\text{Ref}}) \quad (28)$$

$$M_{w_{\text{Ave}}} = \sum_{j=1}^{N_c} x_j M_{w_j} \quad (29)$$

$$\rho_{\text{Ave}} = \sum_{j=1}^{N_c} x_j \rho_j \quad (30)$$

$$L_i = \frac{999 \rho_{\text{Ave}} \text{WLS}[(183.2 M_j M_{w_{\text{Ave}}} / (\rho_{\text{Ave}} d^2)) - \text{WHS}/12]^{1.5}}{M_{w_{\text{Ave}}} \quad (31)$$

RESULTS AND DISCUSSION

Model Validation. The model validation has been investigated considering the obtained experimental data. Table A-1 (of the Supporting Information) reports the variation of glycol weight concentration with time in the presence of various solvent concentrations (0.15, 0.1, and 0.05 wt %) and various water concentrations (15, 10, and 7 wt %) under total reflux and no reflux conditions. In addition, Table A-2 (of the Supporting Information) presents the variation of various water concentrations (15, 10, and 7 wt %) with time in the presence of various solvent concentrations (0.15, 0.1, and 0.05 wt %) under total reflux and no reflux conditions. Furthermore, the effect of solvent addition to the TEG + water system was investigated in these tables. As seen, a good agreement was observed for both binary and ternary systems between the predicted values by the mathematical

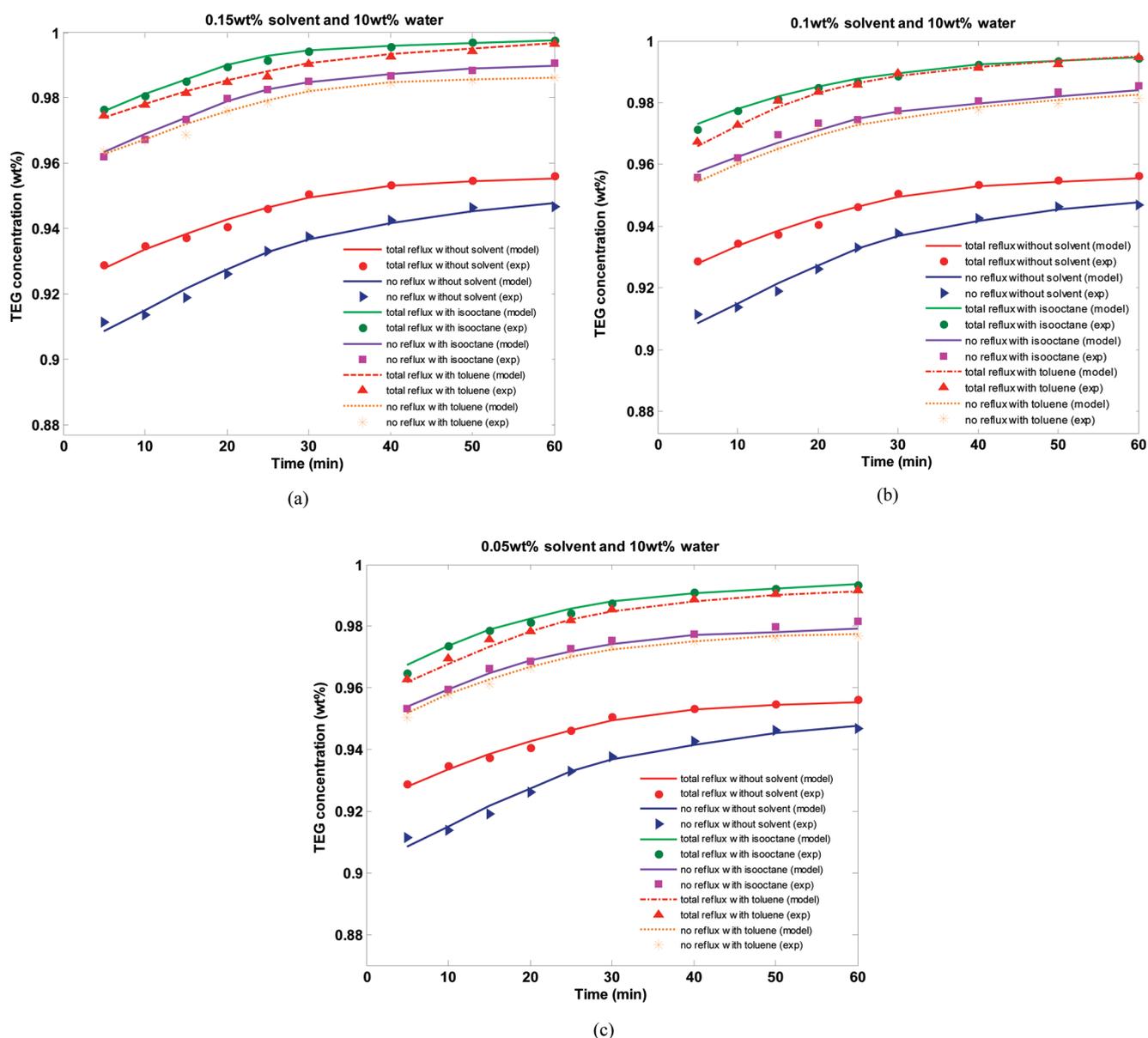


Figure 8. Variation of TEG concentration in the reboiler with time for 10 wt % water and (a) 0.15, (b) 0.1, and (c) 0.05 wt % toluene and isoctane.

model and the experimental data. More details could be found in the Supporting Information section.

Reflux Ratio Effect on TEG Purity without Solvent Injection. For the binary system of TEG + water, the effect of reflux ratio on TEG purity at various water concentrations is shown in Figure 6. As seen, higher purity of TEG is achieved under total reflux condition in the course of time in comparison with no reflux conditions. A remarkable difference in boiling point temperatures of water (373.15 K) and TEG (561.5 K) is the main reason for the rising TEG purity with time which causes water to vaporize swiftly while TEG remains in the liquid phase simultaneously. Thus, this considerable difference in boiling point temperatures causes water to vaporize in the course of time with receiving thermal energy from reboiler and leaving from the top of column which enhances TEG concentration. Table 7 reports the TEG concentration of the top product under

total and no reflux operating conditions. As seen, TEG loss decreases considerably under total reflux condition.

Effect of Solvent Concentration on TEG Purity and Its Loss. The variation of TEG concentration in the reboiler with time for 15 wt % water and various concentrations of solvents (i. e., toluene and isoctane) is depicted in Figure 7a–c. As seen, solvent addition can effectively enhance TEG purity in comparison with no solvent injection. In addition, glycol purity is boosted directly with increasing solvent concentration where higher TEG concentration is achieved at 0.15 wt % isoctane and toluene. As obviously recognized from the figures, isoctane can enhance TEG purity in the bottom product and reduce its loss from the top product more remarkably than toluene. Moreover, operating under total reflux conditions in the presence of solvent is obviously more effective than no reflux conditions on enhancing TEG purity. In fact, the liquid hydrocarbon solvent increases

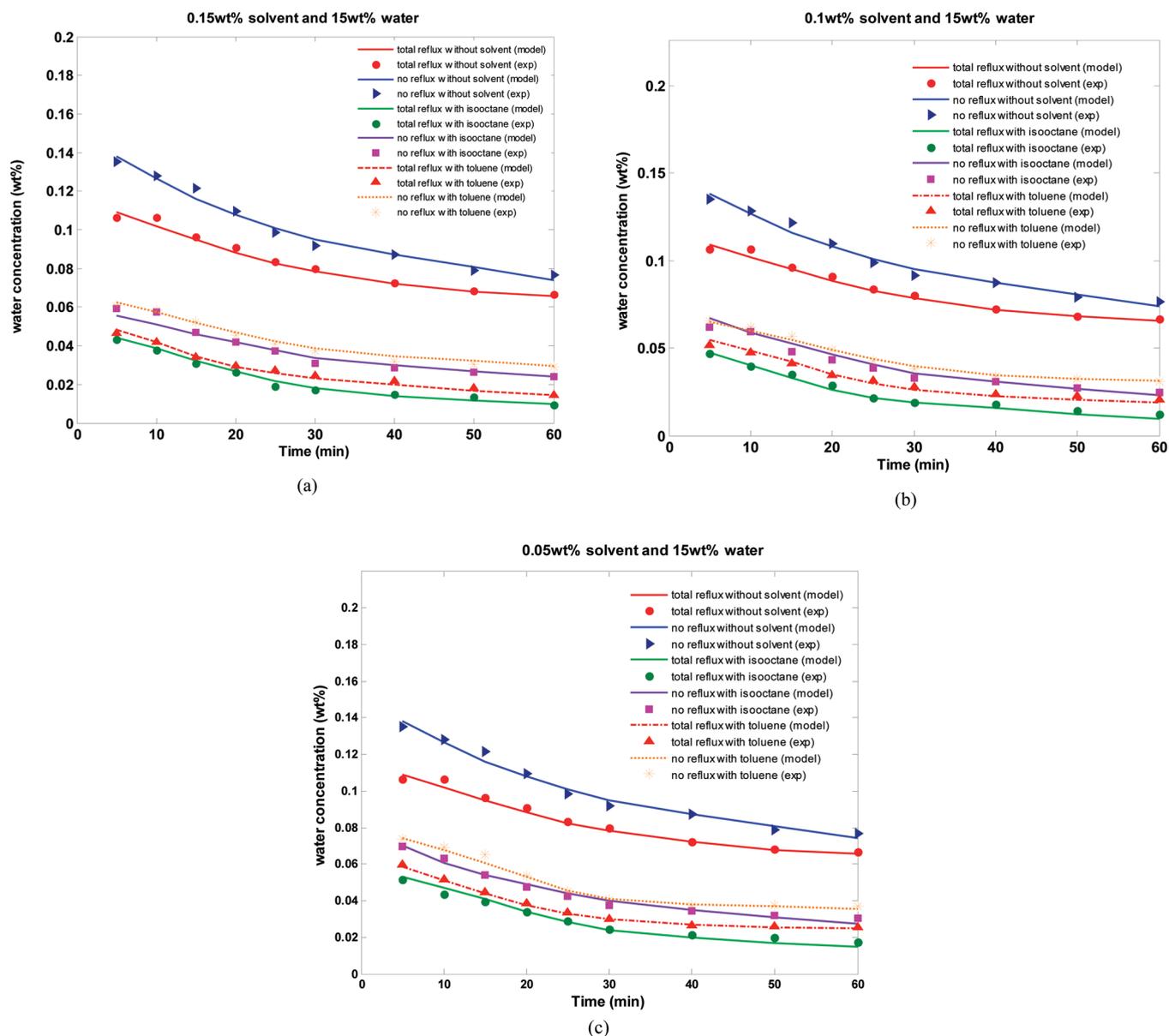


Figure 9. Effect of injecting (a) 0.15, (b) 0.1, and (c) 0.05 wt % isooctane and toluene on 15 wt % water in the reboiler.

the water volatility in the water + TEG solution because isooctane and toluene can form an azeotropic mixture with water and act as a stripping gas after vaporization in the reboiler and consequently enhance TEG purity in the reboiler. In addition, the field test experiments proved that the water content of glycol + water solution could be decreased to less than 1000 ppm by an azeotropic regeneration of glycol via toluene.¹³ The same results are demonstrated for 10 wt % water in Figure 8. Conducting experiments in conjunction with the mathematical modeling of the column at different operating conditions including total and no reflux as well as solvent and no solvent addition for 10 and 7 wt % water highlight the significant effects of solvent addition and total reflux conditions on achieving remarkably higher TEG purity.

Effect of Solvent Concentration on Water Concentration in the Reboiler. In order to investigate the impact of solvent addition on the outlet water concentration from the reboiler, the

following figures were depicted under total and no reflux conditions and various concentrations of solvents.

Figure 9a–c shows the effect of adding various solvent concentrations on 15 wt % outlet water concentration from the reboiler. As seen, the least water concentration is achieved under total reflux conditions by adding isooctane. Furthermore, the least water concentration is achieved at the highest solvent concentration (0.15 wt %). A remarkable decrease in water concentration in the reboiler in the presence of hydrocarbon solvents in comparison with no solvent injection implies the impact of solvent addition which enhances the water volatility in the TEG + water system and consequently boosts TEG purity. Furthermore, isooctane can enhance water volatility more effectively than toluene which can be obviously realized in the figures.

Similarly, Figure 10 illustrates the effect of various solvent concentrations on 10 wt % water. Investigating different operating conditions and solvent concentrations for 10 wt % water revealed

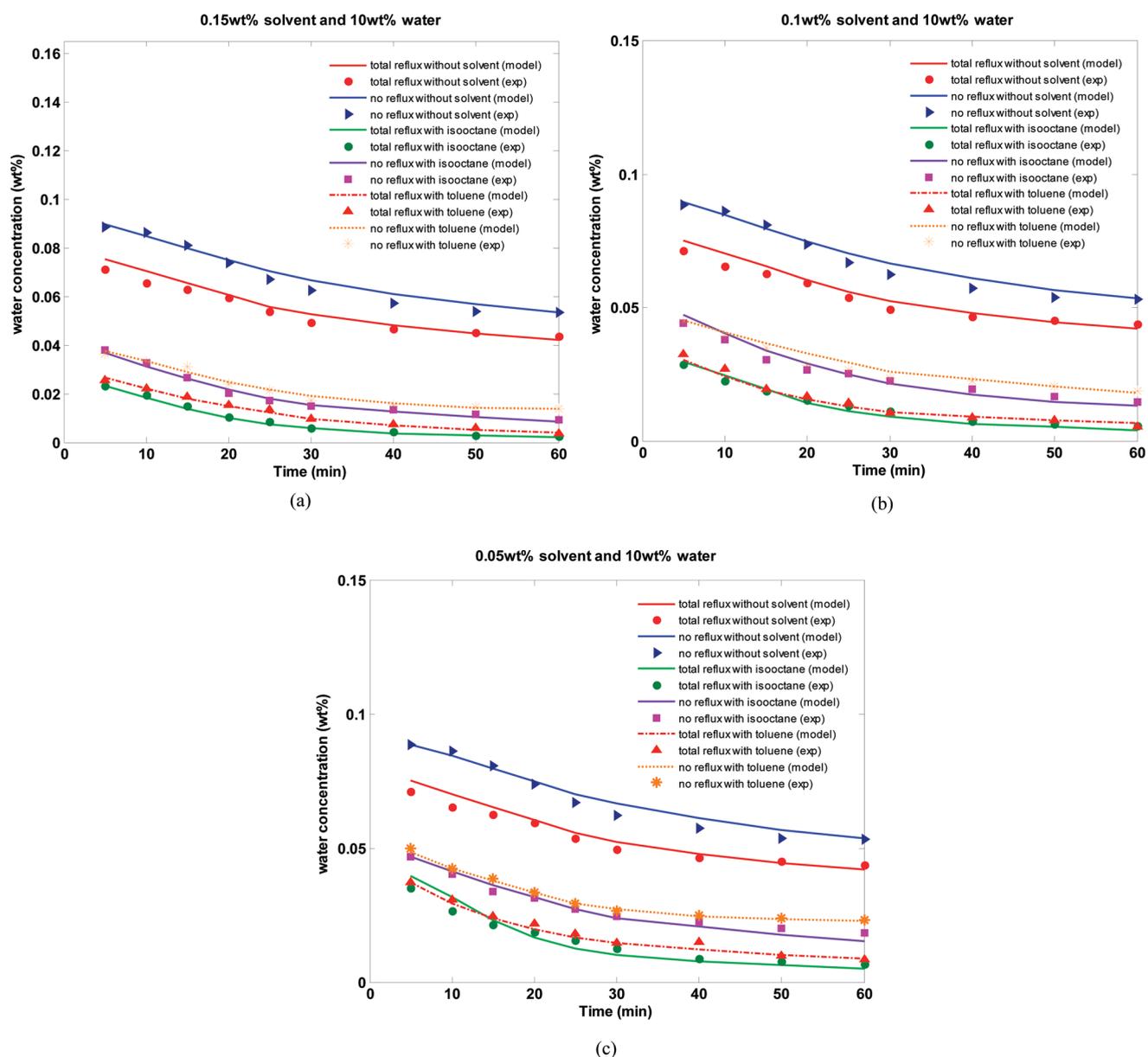


Figure 10. Effect of injecting (a) 0.15, (b) 0.1, and (c) 0.05 wt % isooctane and toluene on 10 wt % water in the reboiler.

Table 8. Reboiler Duty in the Presence of Toluene Injection

water (wt %)	toluene (wt %)	time (min)	energy consumption (kJ)	energy saving (kJ)	energy saving (%)
7	0	39.71	7147	0	0
7	0.05	36.77	6619	528	7.39
7	0.10	35.91	6464	683	9.56
7	0.15	35.40	6372	775	10.84
10	0	43.69	7865	0	0
10	0.05	41.01	7382	483	6.14
10	0.10	40.22	7240	625	7.94
10	0.15	39.92	7186	679	8.63
15	0	48.84	8791	0	0
15	0.05	46.56	8380	411	5.84
15	0.10	46.11	8300	491	5.59
15	0.15	45.75	8235	556	6.32

Table 9. Reboiler Duty in the Presence of Isooctane Injection

water (wt %)	isooctane (wt %)	time (min)	energy consumption (kJ)	energy saving (kJ)	energy saving (%)
7	0	39.71	7147	0	0
7	0.05	36.22	6520	627	8.77
7	0.10	35.27	6349	798	11.17
7	0.15	34.61	6229	918	12.81
10	0	43.69	7865	0	0
10	0.05	40.39	7271	594	7.56
10	0.10	39.64	7135	730	9.28
10	0.15	39.01	7021	844	10.73
15	0	48.84	8791	0	0
15	0.05	45.99	8278	513	5.84
15	0.10	45.46	8183	608	6.92
15	0.15	45.05	8109	682	7.75

that the solvent addition and total reflux condition could effectively decrease the water concentration in the TEG + water system. Particularly, isooctane was superior to toluene in terms of enhancing water volatility in the TEG + water system and boosting TEG purity.

Effect of Solvent Concentration on Reboiler Duty. In order to determine the required reboiler duty under solvent injection and no solvent injection conditions, the time which the first tray temperature reached steady state conditions was measured via a chronometer. These times were multiplied to the reboiler duty so that the consumed reboiler duty was achieved. Thus, the saving in reboiler duty was determined by a comparison between the reboiler duty with and without solvent injection. The experimental results are reported in Tables 8 and 9. As seen, 12.8% and 10.8% savings in reboiler duty could be achieved by isooctane and toluene injection, respectively. According to the previous investigations, the azeotropic regeneration process needed a considerably lower energy consumption rate in comparison with other regeneration processes.²⁷ As seen, the obtained experimental data justified previously achieved results.

CONCLUSIONS

In this study, the effect of solvent injection on TEG purity and its loss in the tray column were investigated. Experiments were conducted in a batch tray column under different operating conditions and solvent concentrations at atmospheric pressure. The modeling and experimental results showed that the liquid hydrocarbon solvent addition can remarkably enhance TEG purity and water volatility in the bottom product and considerably reduce TEG loss in the top product. Furthermore, isooctane performed better than toluene, and a higher TEG concentration, lower water concentration, and duty of reboiler were achieved with isooctane injection. In addition, 0.15 wt % solvent concentration was the ideal solvent concentration in these experiments because the best results were achieved at this value. In fact, liquid hydrocarbon solvent vaporized rapidly in the reboiler and increased the water volatility which enhanced TEG concentration in the reboiler. This modeling and experimental results can provide a good initial insight into future pilot plant design of natural gas dehydration columns with solvent injection.

ASSOCIATED CONTENT

Supporting Information. Variations of glycol and various water concentrations (15, 10, and 7 wt %) with time in the presence

of various solvent concentrations (0.15, 0.1, and 0.05 wt %) under total reflux and no reflux conditions: Tables A-1 and A-2, respectively. Variation in TEG concentration and the outlet water concentration (the initial 7 wt % water concentration) and various concentrations of solvents: Figures B-1 and B-2, respectively. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +98 711 2303071. Fax: +98 711 6287294. E-mail address: rahimpour@shirazu.ac.ir.

ACKNOWLEDGMENT

The authors would like to appreciate financial support of the South Zagros Oil and Gas Production Company.

NOTATION

C_{P_L} = liquid specific heat capacity (J/mol·K)
 C_{P_V} = gas specific heat capacity (J/mol·K)
 d = column diameter (cm)
 $\text{density}_{\text{Ave}}$ = average density (kg/m³)
 D = distillate flow rates (kmol/h)
 j = component number
 H_L = gas enthalpy (J/mol)
 H_V = liquid enthalpy (J/mol)
 HVAP = heat of vaporization (kJ/mol)
 L = liquid molar flow rate (kmol/h)
 M = molar liquid hold up on tray (kmol)
 MV = volumetric liquid holdup on tray (cm³)
 Mw_{Ave} = average molecular weight (kg/kmol)
 P = total pressure (kPa)
 P_j^{sat} = vapor pressure of j component (kPa)
 Q_R = reboiler heat input (kJ/h)
 R_f = reflux ratio
 V = vapor flow rates (kmol/h)
 WHS = Weir height (cm)
 WLS = Weir length (cm)
 x = liquid weight fraction
 y = gas weight fraction

Definitions

comp = component

exp = experiment

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