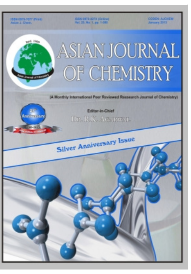
Asian Journal of Chemistry; Vol. 25, No. 5 (2013), 2774-2778

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13870



Separation of Tetrahydrofuran-Ethanol Azeotropic Mixture by Extractive Distillation

KE TANG*, PENG BAI, CHONGSHUN HUANG and WEIMING LIU

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P.R. China

*Corresponding author: E-mail: tangke1984@126.com

(*Received*: 9 April 2012; *Accepted*: 23 November 2012) AJC-12452

Tetrahydrofuran and ethanol formed a minimum azeotrope and extractive distillation should be a suitable method to separate their mixture. In this work, a systematic study of the separation of tetrahydrofuran-ethanol mixture with an entrainer by extractive distillation was performed. In order to break the original binary azeotrope, ethylene glycol was chosen as the entrainer. Vapour-liquid equilibrium of tetrahydrofuran-ethanol-ethylene glycol system was determined experimentally and NRTL model was the best one to predict this system. The feasibility analysis of this process was validated by simulation through chemical process simulation software-Aspen Plus and the optimal operating conditions of the extractive distillation process were valuable for industrial applications. Simulation results were then corroborated in a batch experimental packing column. In both the simulation and experiments, tetrahydrofuran, whose purity is more than 99.5 %, was obtained respectively.

Key Words: Tetrahydrofuran, Ethanol, Extractive distillation.

INTRODUCTION

Binary mixtures are commonly used in the pharmaceutical and fine chemical industries, form azeotropes or close-boiling mixtures and they are characterized as behaving like a pure component when submitted to a distillation process. It is impossible to achieve the separation of azeotropic mixtures through conventional methods. Therefore, extractive distillation is a common process used to separate these kinds of mixtures with a third component, a salt solution or a solvent as the entrainer[1]. The function of the entrainer is to increase the relative volatility of the mixture. In this way, the components will boil separately, which allows the collection of heavier components (solvent and heavy key) at the bottom of the distillation column and the light key component at the top[2,3].

Tetrahydrofuran-ethanol mixtures are commonly encountered in the fine chemical and pharmaceutical industries. The tetrahydrofuran-ethanol mixture forms a minimum boiling point azeotrope at a mole composition of 0.905 tetrahydrofuran and at a constant pressure of 101.3 kPa[4,5].

The aim of this work is to study the vapour-liquid equilibrium (VLE) of tetrahydrofuran-ethanol-ethylene glycol system and furthermore to establish industrial operating conditions for the extractive distillation process of tetrahydrofuran-ethanol by using ethylene glycol as the entrainer.

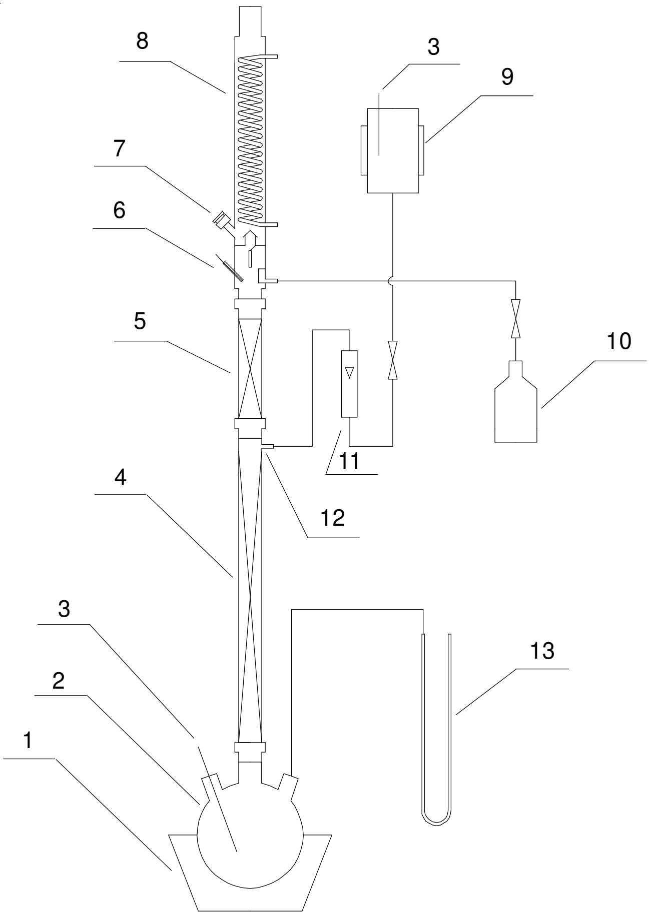
EXPERIMENTAL

The component mass fraction of raw material is 0.935 tetrahydrofuran and 0.065 ethanol. The purity of ethylene glycol is 0.998 (mass fraction).

Batch distillation experiments were carried out in a small laboratory column to evaluate the performance of the solvent. The column has a total height of 1.2 m and an internal diameter of 25 mm. It is packed with stainless steel θ-rings of Φ 3 mm × 3 mm. The total packing height is about 30 theoretical plates and the total liquid hold up is 30 mL. The bottom is a flask of 4000 mL with three openings. The solvent is fed to the column near the top section. The flow rate is controlled by a flow meter. The reflux ratio is provided at the top of the column by a solenoid valve. The sketch map is showed in Fig. 1.

The tetrahydrofuran, ethanol, ethylene glycol and other high boiling organic impurity composition are determined by a GC-SP-6890 gas chromatograph with a FID detector and with a GDX-102 column. The injector and detector temperature are held 210 ºC while the column temperature is set equal to 125 ºC.

Experiment procedure: 540 mL original tetrahydrofuran-ethanol mixture was charged into the bottom. Then it was heated and kept under total reflux for 0.5 h. The condenser was subcooled to and the power for boiler heating is 400 W. When the temperature of the bottom and the condenser was steady, ethylene glycol was charged into the column near the top section of the column at a speed of 20 mL/min and then kept total reflux 0.5 h again. The purpose of this step was to bring down the concentration of ethanol at the top product. After the total reflux, the distillate was withdrawn at a reflux ratio of 3. The analysis of the distillate composition was repeated about every 5 min. The temperatures of the top and the bottom of the column were recorded every 5 min. When the top temperature exceeded 66 ºC, it showed that the tetrahydrofuran in the raw material had been withdrawn completely. At this moment, the solvent should be stopped to charge. The top product will be transition distillate in turn. When ethylene glycol began to appear in the top product, this solvent at the bottom was collected for recycle.



1) Heating jacket; 2) Flask; 3) 6-Thermometer; 4) Extractive rectifying section with insulation; 5) Rectifying section with insulation; 7) Sample connection; 8) Condenser; 9) Storage tank of solvent; 10) Distillate receiver; 11) Flowmeter; 12) Solvent inlet; 13) U-type pressure meter

Fig. 1. Experiment equipment

Experiment results: The experimental results are shown in Figs. 2 and 3. Time 0 started from the qualified distillate withdrawn step. It can be seen that, at the beginning, the concentration of tetrahydrofuran in distillate maintained a high value that is over 99.9 % wt averaged and the yield is about 80 %. When processed for 80 min, the tetrahydrofuran mass fraction at the top decreased while the concentration of ethanol increased gradually. But the solvent in the distillate was close to zero all the time. This distillation cut was transition distillate. As there was lots of tetrahydrofuran in this part of distillate, it could not be thrown away but recycled with the mixture in the next process. After 80 min, the concentration of methanol in the distillate decreased sharply while the toluene mass fraction increased. The tetrahydrofuran concentration in transition distillate cut is high which lead to decreased yield. In the experiment, the temperature of the top is stable at the qualified tetrahydrofuran withdrawn step. The top temperature is nearly the temperature of pure tetrahydrofuran. While the solvent is charged into the column, ethanol is carried to the bottom by ethylene glycol. There is more and more solvent at the bottom, so the bottom temperature rises all the time.

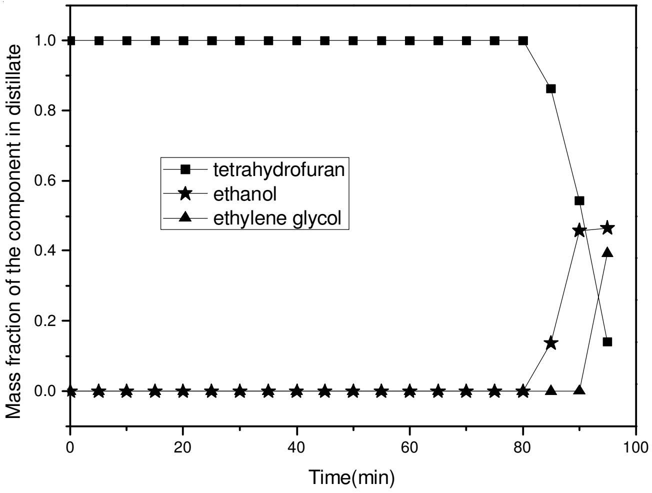


Fig. 2. Variation of the distillate composition in the experiment

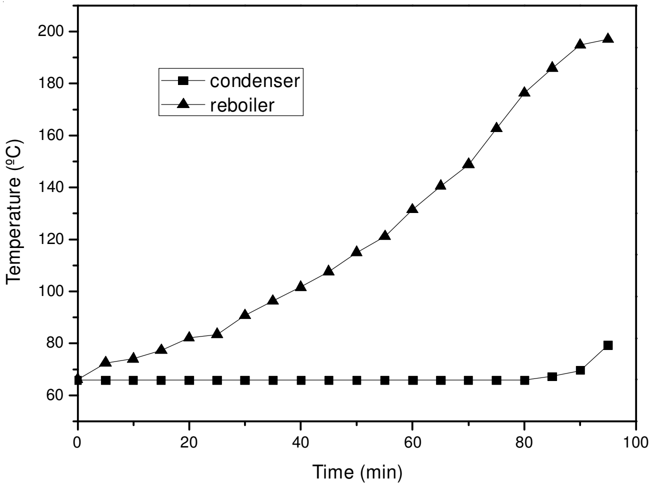


Fig. 3. Temperature of reboiler and condenser in the experiment

RESULTS AND DISCUSSION

Vapour-liquid equilibrium of tetrahydrofuran-ethanol-ethylene glycol system: The ternary vapour-liquid equilibrium of tetrahydrofuran-ethanol-ethylene glycol system was determined experimentally. Briefly, mixtures of tetrahydrofuran-ethanol with ethylene glycol at 101.3 kPa were prepared in a vapour-liquid equilibrium still. After the vapour-liquid equilibrium was achieved (constant temperature throughout the system), samples of condensed vapour and liquid were taken for GC analysis. Each assay was made in duplicate. Fig. 4 shows the pseudo-binary diagram obtained for a solvent to feed molar ratio (E/F) of 5.Three thermodynamic models (Wilson, NRTL and UNIQUAC) were analyzed to determine which was the best model to predict the system performance. The obtained results show that the NRTL model presented the highest accuracy.

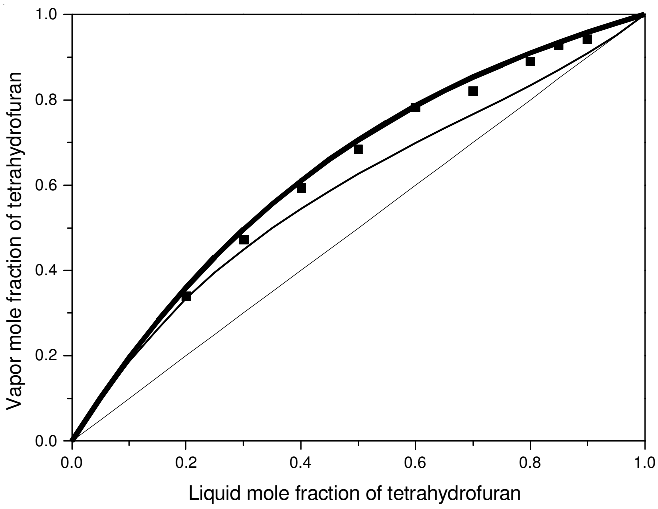


Fig. 4. Pseudo-binary equilibrium curve for tetrahydrofuran-ethanol with ethylene glycol at 101.3 kPa. Thick and thin lines predicted by NRTL model for the pseudo-binary and binary systems, respectively. ■ experimental data

Simulation of the process: The separation of tetrahydrofuran-ethanol mixture was carried out with the help of an entrainer, ethylene glycol. The simulation of the process was performed with the chemical process simulation software-Aspen Plus V7.0. The NRTL model was used to predict the activity coefficients and ideal gas model to predict the fugacity coefficient. The binary interaction parameters of tetrahydrofuran-ethanol, tetrahydrofuran-ethylene glycol and ethanol-ethylene glycol were from "APV70VLE-IG" databank in Aspen.

The flow sheet of the extractive distillation process is presented in Fig. 5. The process has two columns, one for extractive distillation and the other for solvent recuperation. The azeotropic mixture and the solvent are fed to the first column, in which the components boil separately which allows the less volatile components to be collected at the bottom and the light key component at the top. The bottom product is fed to the second column, in which the solvent is recovered and recycled to the extractive distillation column.

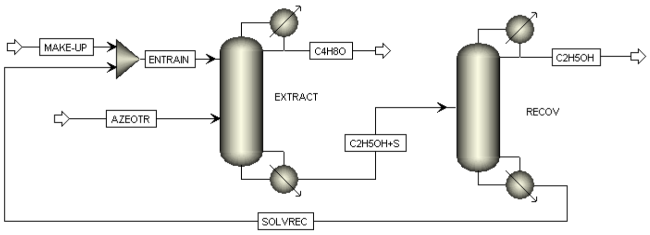


Fig. 5. Extractive distillation flow sheet

Sensitivity analysis: To establish the operating conditions for the extractive distillation process, a sensitivity analysis was conducted.

Effect of azeotropic mixture feed stage: In Fig. 6, the effect of azeotrope feed stage on the molar composition of distillate in the extractive column and reboiler energy consumption is presented. It can be observed that, as the azeotropic feed stage was closer to the reboiler, the mole fraction of tetrahydrofuran in distillate increased; so did the reboiler energy consumption. The purity and energy consumption reached a maximum when feed stage is 19. This meant that the biggest separation took place in the rectifying section. In order to obtain the tetrahydrofuran composition required in the distillate and decrease the reboiler energy consumption, the stage near the reboiler should be chosen as the suitable azeotrope feed stage.

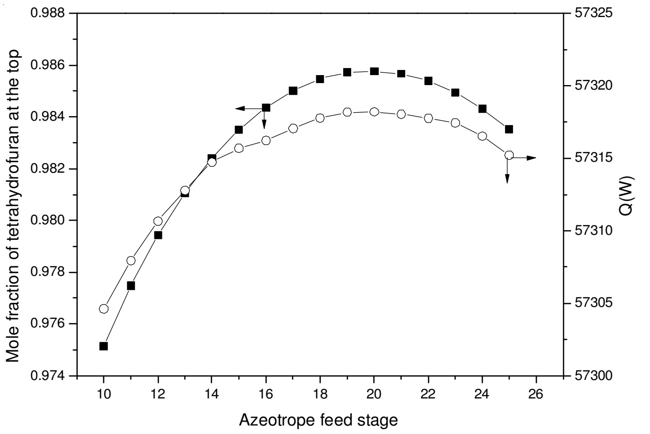


Fig. 6. Effect of azeotrope feed stage in the extractive distillation column with ethylene glycol on distillate composition and reboiler energy consumption

Effect of reflux ratio: Fig. 7 shows that the change of molar reflux ratio exerted a great infuence on the distillate composition and reboiler energy consumption. The results showed that the purity reached a maximum with the increasing molar reflux, because as the reflux rate increased, the solvent was diluted in the column. The results also showed that the reboiler energy consumption increased sharply as the molar reflux ratio increased. The liquid brought by reflux should be vapourized; therefore, the molar reflux ratio could be as low as possible to bring down the reboiler energy consumption.

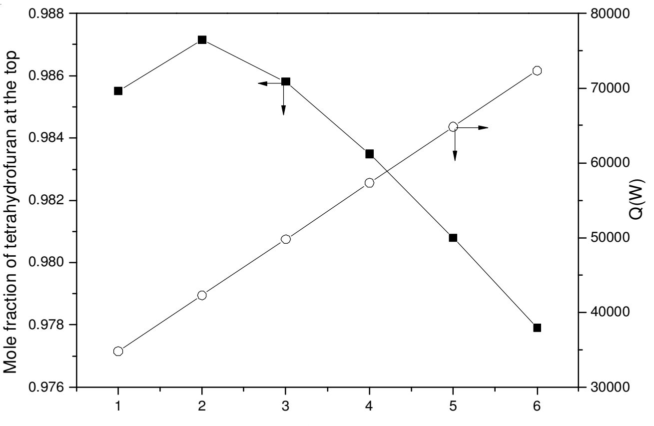


Fig. 7. Effect of molar reflux ratio in the extractive distillation column with ethylene glycol on distillate composition and reboiler energy consumption

Effect of solvent to feed ratio (S/F): Solvent to feed ratio (S/F) exerts a direct effect on the distillate purity. In Fig. 8, before S/F molar ratio reached to 5, tetrahydrofuran content kept increasing, but after that point, it remained stable. This occurred because more solvent may enlarge the relative volatility of the tetrahydrofuran-ethanol mixture; however, the purity of tetrahydrofuran was so high that it is not necessary to increase S/F sequentially. Rising S/F increased the liquid flow in the reboiler. Although the liquid brought by the solvent remained in liquid phase in column, it may absorb heat there. Taking into consideration the situation that high S/F ratios increased the energy consumption in reboiler, S/F should not be too large.

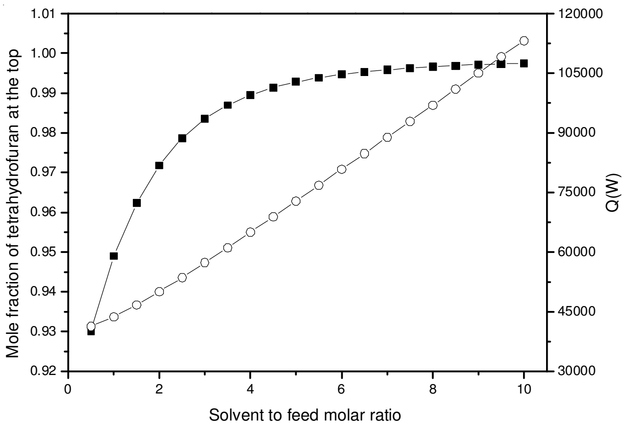


Fig. 8. Effect of S/F molar ratio in the extractive distillation column with ethylene glycol on distillate composition and reboiler energy consumption

Effect of entrainer feed stage: The results shown in Fig. 9 allow establishing a maximum in the distillate molar fraction for all the tested conditions when the solvent is fed on stage 3. As the solvent feed stage approached to the condenser tetrahydrofuran content went up to a maximum, after which point it decreased. The reason why this decrease occurred was that the vapourization of the ethylene glycol entered the column, which became part of the vapour that flowed up to the condenser and that was withdrawn as distillate.

Based on the sensitivity analysis above, the best configuration and operating conditions of the columns was established and presented in Table-1.

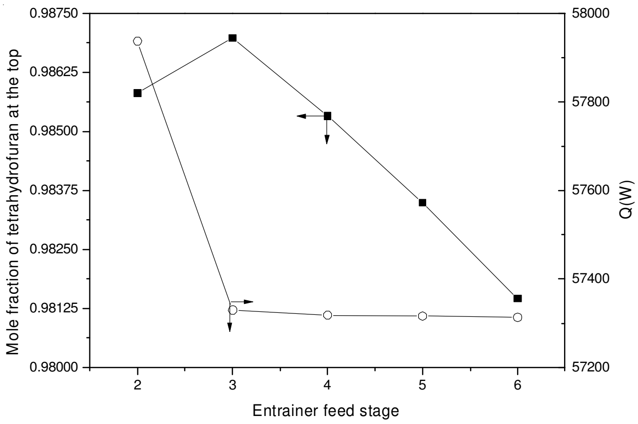


Fig. 9. Effect of solvent feed stage of the distillation column with ethylene glycol on distillate composition and reboiler energy consumption

TABLE-1
OPTIMAL DATA FOR THE DISTILLATION COLUMNS

Parameter	Extractive column	Recovery column
Azeotropic feed flowrate (kmol/h)	1	-
Number of stages	30	10
Solvent feed stage	3	-
Azeotrope feed stage	19	5
Solvent feed temperature (ºC)	25	-
Azeotrope feed temperature (ºC)	25	-
Mole fraction of tetrahydrofuran in azeotropic feed	0.905	-
Solvent feed flow rate (kmol/h)	5	-
Mole fraction of ethylene glycol in solvent feed	1	-
Reflux ratio	2	3

Simulation results: The simulation results were presented in Table-2. It was shown that the obtained tetrahydrofuran mole composition at the top of the extractive column was 0.9963 and the ethanol mole composition at the recovery column top was 0.9644. Meanwhile, the ethylene glycol which was 1 in mole composition was obtained at the bottom of the recovery column.

TABLE-2
SIMULATION RESULTS FOR THE PROCESS FLOWSHEET

	C_4H_8O	C_2H_5OH	SOLVREC
T (ºC)	65.86	77.1	197.8
Mole flow kmol/h	0.905	0.095	5
Mole fraction			
Tetrahydrofuran	0.9963	0.0356	0
Ethanol	0.0036	0.9644	0
Ethylene glycol	0.0001	0	1.000

In Fig. 10, the temperature profile in the extractive distillation column showed a temperature change at stage 3 due to the entrainer inlet, whereas at stage 19 the temperature had a minimal decrease due to the azeotropic mixture feeding. A significant temperature increase was observed at stages 29 and 30 due to the reboiler proximity.

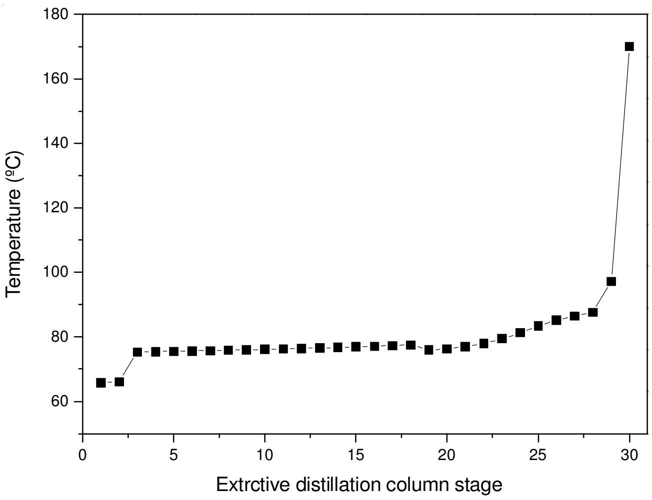


Fig. 10. Extractive distillation column temperature profile

Fig. 11. presents the liquid and vapour molar flow rate profiles in the extractive column. The liquid molar flow exposed two significant changes due to the solvent and the

azeotropic mixture feed at stages 3 and 19, respectively. Meanwhile, the vapour molar flow rate remained constant along the column, except at stage 3 where the solvent was fed. This change was caused by the liquid-phase vapourization due to the ethylene glycol inlet temperature.

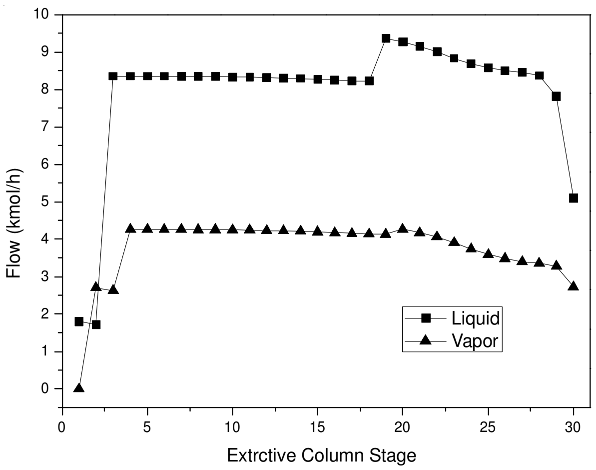


Fig. 11. Liquid and vapour molar flow rate profiles in the extractive distillation column

Fig. 12 showed that tetrahydrofuran concentration kept decreasing, from the top of the column to the bottom. Ethanol composition kept increasing, from the top of the column to the bottom. The ethylene glycol composition was approaching to zero, from the top of the column to the bottom. The main product at the top of the column was tetrahydrofuran and at the bottom the main components were ethanol and ethylene glycol. Meanwhile, in Fig. 13, for the liquid molar composition profiles, tetrahydrofuran and ethylene glycol had an important change at stage 3, in which the tetrahydrofuran composition decreased rapidly and ethylene glycol increased due to the entrainer inlet. The feed of azeotropic mixture at stage 19 caused an increase in tetrahydrofuran composition, whereas a decrease in ethylene glycol composition was observed. The tetrahydrofuran composition decreased along the column and at the bottom only ethylene glycol and ethanol were present. Ethanol exposed only one significant change at stage 19 where the binary mixture was fed.

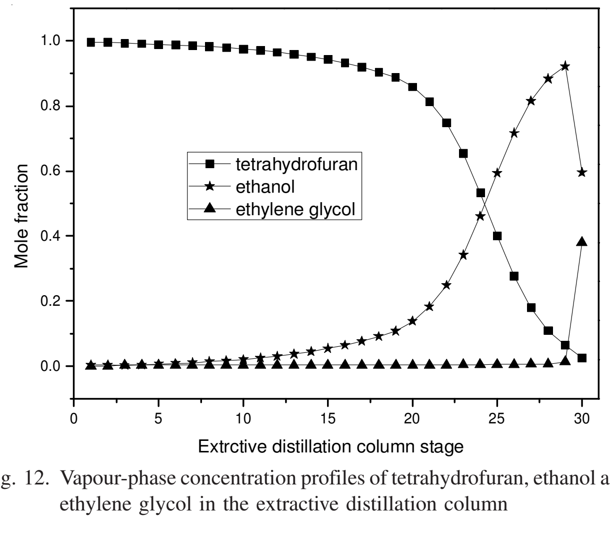


Fig. 12. Vapour-phase concentration profiles of tetrahydrofuran, ethanol and ethylene glycol in the extractive distillation column

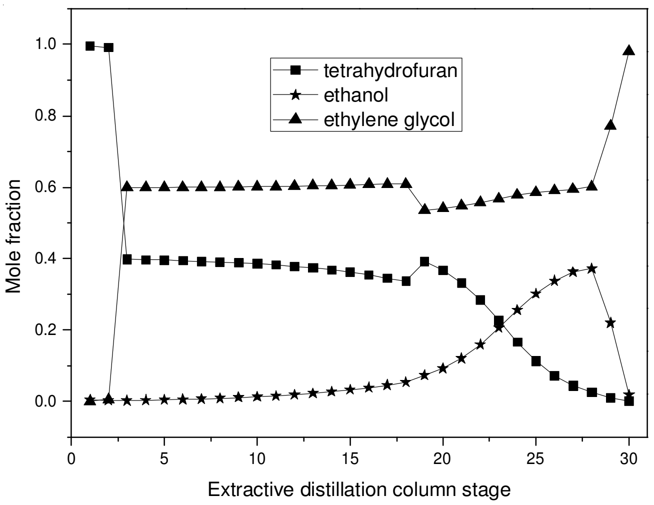


Fig. 13. Liquid-phase concentration profiles of tetrahydrofuran, ethanol and ethylene glycol in the extractive distillation column.

Conclusion

Ethylene glycol was chosen as the entrainer to achieve the separation of the azeotropic mixture tetrahydrofuran-ethanol by extractive distillation. NRTL model was the best model to predict vapour-liquid equilibrium of tetrahydrofuran-ethanol-ethylene glycol system. The feasibility of the process was confirmed via simulation and experiments. Sensitivity analysis was done to obtain the best conditions and configuration for extractive and recovery columns. The temperature, composition and molar flow profiles obtained for the extractive distillation column were consistent. In both the simulation and experiments, high purified tetrahydrofuran and ethanol were obtained.

REFERENCES

1. B. Kotai, P. Lang and G. Modla, *Chem. Eng. Sci.*, **62**, 6816 (2007).
2. E. Batista and A. Meirelles, *J. Chem. Eng. Jpn.*, **3**, 45 (1997).
3. P. Langston, N. Hilal, S. Shingfield and S. Webb, *Chem. Eng. Process.*, **44**, 345 (2005).
4. Y. Yoshikawa, A. Takagi and M. Kato, *J. Chem. Eng. Data*, **25**, 344 (1980).
5. B. Erwln and G.R.S. Andreas, *J. Chem. Eng. Data*, **29**, 28 (1984).