Research Journal of Applied Sciences, Engineering and Technology 5(19): 4769-4774, 2013
DOI:10.19026/rjaset.5.4317
ISSN: 2040-7459; e-ISSN: 2040-7467

Submitted: December 31, 2012 Accepted: January 23, 2013 Published: May 10, 2013

Research Article

Simulation of Extractive Distillation for Recycling Tetrahydrofuran from Pharmaceutical Wastewater with Chem CAD Software

Xiaoguang Wang and Yueyun Yang
Department of Chemistry, Zhoukou Normal University, Zhoukou Henan, 466001, China

Abstract: The functions and application of ChemCAD simulation software was introduced. Mathematical model of extraction distillation process was established. The extractive distillation process for preparation of tetrahydrofuran (THF) was simulated by SCDS rectification model in ChemCAD software, methanol-THF-solution and ethanedol-lithium chloride solution as extractant. Influence of extraction agent on vapor-liquid equilibrium curve of methanol-THF system and effects of theoretical plate number, feed and extractant input positions, extraction agent ratio (m(chlorinated lithium): v(ethanediol)), extractant ratio (m (extractant): m(feed)) and reflux ratio on tower top mass fraction of THF were investigated. The results of simulation were compared with experimental data. Under optimum extraction distillation conditions: theoretical plate 30, extractant plate 6, feed plate 18, extraction agent ratio 0.24g/mL, extractant ratio 2.7 and reflux ratio 5.0, mass fraction of THF on tower top can reach 97.2%. The distribution characteristic parameters of the column were simulated. The results of simulation and experimental data agree satisfactorily.

Keywords: ChemCAD, distillation, optimization, software application, tetrahydrofuran

INTRODUCTION

At present famous chemical process simulation software has AspenPlus, Pro/II and so on, but they are large chemical simulation software, higher cost of buying. ChemCAD chemical process simulation software was developed by Chemstations company, it with the graphical user interface way, basically have input Aspen Plus and Pro/II software all sorts of functions, but the price is cheap, suitable for normal small chemical enterprise. In ChemCAD software internal, there are four kinds of distillation modules, including TOWR Column, TOWR PLUS Column, SCDS Column and SHORTCUT Column. TOWR is strictly calculation model, TOWR PLUS applicable to with heat exchanger, circulating pump lateral-line system recovery. SCDS module can timely correct. SCDS module is mainly used for simulating nonideal K value. It can be used for Newton-Raphon mathematical convergence and calculation and strict derivation of equation, including the DK/DX (Derivation main mixture of K value main mixture of K value) aspects, that is, effective chemical simulation system.

THF is a good solvent and an important fine chemical raw materials. In industrial production, as solvent used often will bring impurities such as water (Liu, 2005), because of THF containing impurities and can not be reused, directly abandoned, waste and pollution of environment, do not accord with requirement of energy conservation and emissions reduction. In recent years, Along with expansion of market demand of high purity THF, at home and abroad, THF purification, dehydration is more and more attention (Ju *et al*., 2006). People have done much about extraction distillation recovery tetrahydrofuran work (Xu and Chen, 2002), especially in the vapor liquid equilibrium (Xu *et al*., 2001), the selection of extraction agent (Xu *et al*., 1999), simulation calculation (Wang and Yang, 2011), etc. Extraction agent and salt types, solvent ratio, extraction solvent feeding position, raw material feeding position and reflux ratio has obvious influence on the results. The simulation calculation of THF-methanol-water-composite extraction agent system and the study of adding salt extraction distillation recovery THF experimental less limited its application in industry. It is necessary to simulate the process on influence of the quality of factors, using advanced computer simulation technology, in order to attain process optimization.

Simulation:

Mathematical model: Extraction rectification column includs stripping section, extraction section and rectifying section 3 parts. The equilibrium stage model of rectifying column to carry on the calculation, the whole tower has N equilibrium level, overhead condenser for the first, bottom reboiler for N level. Hypothesis:

Corresponding Author: Xiaoguang Wang, Department of Chemistry, Zhoukou Normal University, Zhoukou Henan, 466001, China

- Adding salt extraction distillation was a steady-state operation
- Each component had the same molar latent heat of vaporization
- Vapor and liquid were constant molar flow
- All levels of vapor and liquid no temperature gradient and the concentration gradient
- Leave plate, vapor and liquid mass transfer and heat transfer balance
- Lgnored heat loss. Mathematical model was established such as formula (1)-(4) shows (Wang *et al*., 2008)

Material balance equation:

$$q_{n,v_j} y_{ij} + q_{n,L_j} x_{ij} - q_{n,v_{j+1}} y_{ij+1} - q_{n,L_{j-1}} x_{ij-1} - q_{n,F} z_{ij} = 0 \quad (1)$$

Vapor-liquid equilibrium equation:

$$p_j y_{ij} = p_{ij}^s \gamma_{ij} x_{ij} \quad (2)$$

Normalization equation:

$$\sum_i x_{ij} - 1 = 0, \sum_i y_{ij} - 1 = 0 \quad (3)$$

Heat balance equation:

$$q_{n,V_j} H_j^V + q_{n,L_j} H_j^L - q_{n,V_{j+1}} H_{j+1}^V - q_{n,L_{j-1}} H_{j-1}^L - q_{n,F_j} H_j^F = 0 \quad (4)$$

For methanol-THF-water-composite extraction agent content system, NRTL equation than Wilson equation of higher calculation accuracy. Therefore, NRTL equation was used to calculate each composition activity coefficient.

Simulation of Vapor-liquid Equilibrium Phase Diagram: Through the group contribution methods that screening for ethylene glycol optimal extraction agent (Cui *et al*., 2004). In addition, salt effect (Huang, 1983; Pan *et al*., 2005; Sun and Sun, 2002) can change two components of the relative volatility, increase the two component separation ability (Fredenslung *et al*., 1975; Larsen *et al*., 1987; Ernesto *et al*., 1996; Polka and Gmehling, 1994). Through the menu "Plot", select the command "TPXY", respectively do vapor-liquid equilibrium phase diagrams of methanol-THF system, methanol-THF-chlorinated lithium system, methanol-THF-ethanediol system.

Simulation of distillation process: The extractive distillation process for preparation of THF was simulated by SCDS rectification model in ChemCAD software, ethanedol-lithium chloride solution as extractant. Effects of theoretical plate, feeding and extractant input positions, extraction agent ratio (m(chlorinated lithium): v(ethylene glycol)), extractant ratio (m(extractant): m(feed)) and reflux ratio on tower top mass fraction of THF were investigated. The process diagram as shown in Fig. 1.

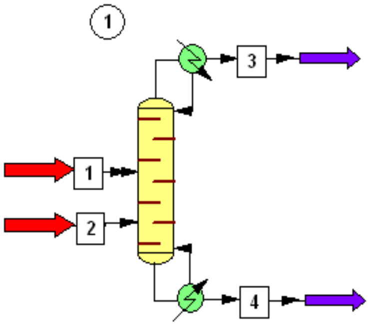

Fig. 1: Recovery process of THF

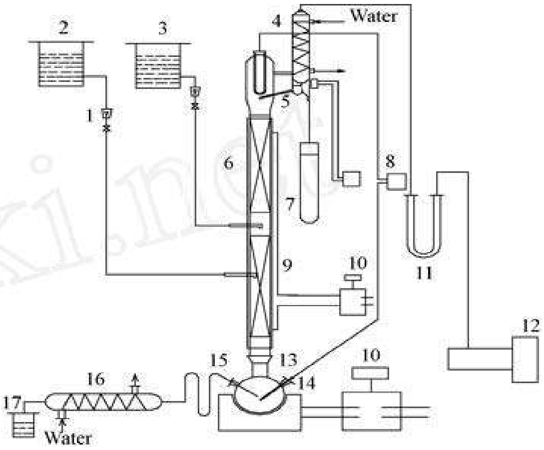

Fig. 2: Flow diagram of extractive distillation. 1 Rotameter; 2 Feed vessel; 3 Extractant vessel; 4 Condenser; 5 Refluxing; 6 Column; 7 Output tube; 8 Temperatue display; 9 Heater; 10 Voltage regulator; 11 Pressure gauge; 12 Vacum pump; 13 Reboiler; 14 Thermocouple; 15 U-tube; 16 Condenser; 17 Tank

Experimental: Extraction distillation was done to the mass fraction 38.31% THF, mass fraction 17.02% methanol aqueous solution. Extractive distillation tower diameter is 40 mm, the experiment device processes as shown in Fig. 2. Wang and Yang (2012) Demarcate rectifying column, determine the theoretical plate number 30. First full reflux operation, when stability, the partial backflow operation; when the tower top temperature and kettle temperature stability, distillate had been sampling analysised (Wang *et al*., 2008).

RESULTS

Table 1 and 2 give the results of simulation and experimental of extraction distillation. The temperature of tower, flow rate, and mass fraction distribution as shown in Fig. 3 to 6.

Table 1: Simulation results of distillation

Flow	1	2	3	4
Temperature/°C	20.0	20.00	64.92	119.07
Pressure/kPa	101.3	101.3	101.3	101.3
Enthalpy/(MJ/h)	-52907.0	-26839.00	-3749.5	73995.00
Mole flow/(kmol/h)	120.000	100.000	17.0020	202.0080
Mass flow/(kg/h)	6810.87	2823.29	1134.12	8500.04
Liquid volume flow/(m^3/h)	5.82	3.08	1.28	7.62
Vapor volume flow/(m^3/h)	2689.64	2241.36	385.51	4545.48
Mass fraction/%				
Methanol	0.00	17.02	0.00	5.52
THF	0.00	38.31	99.20	0.02
Ethylene glycol	89.03	0.00	0.00	71.30
Water	2.58	44.6	0.80	16.44
Lithiumchloride	6.22	0.00	0.00	4.99

Table 2: Parameters of operating and results of experimental

Parameters	Value	Parameters	Value
Pressure/(kPa)	101.3	Extraction agent ratio /(g/mL)	0.24
Extractant input position	6	Extractant ratio	2.7
Feed input position	18	Mass fraction of THF/% (simulation)	97.2
Reflux ratio	5.0	Mass fraction of THF/% (experimental)	99.2

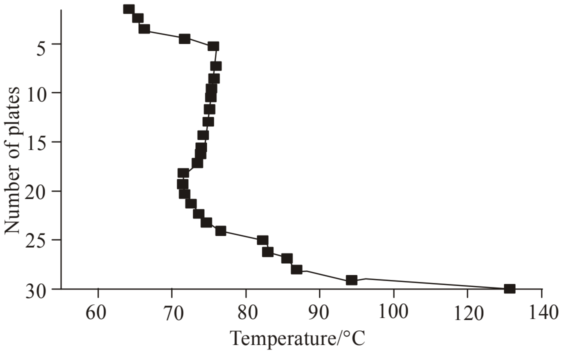

Fig. 3: Temperature distribution

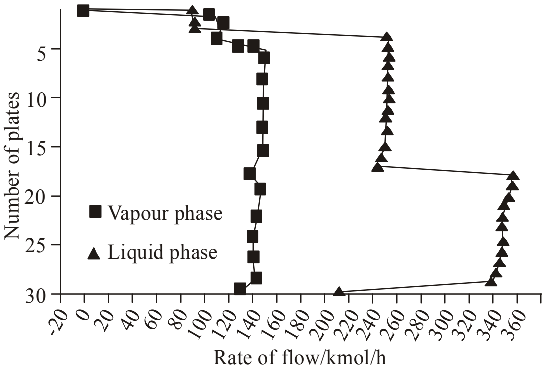

Fig. 4: Vapor-liquid flow distribution

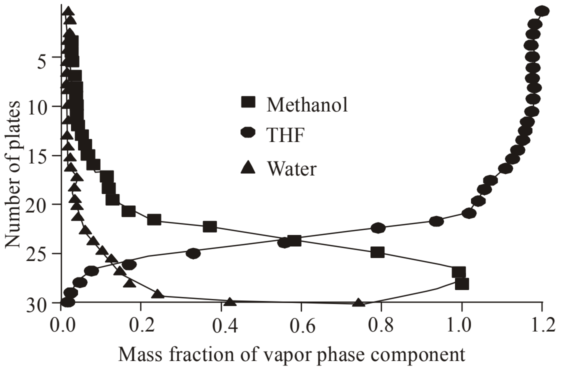

Fig. 5: Mass distribution of vapor phase

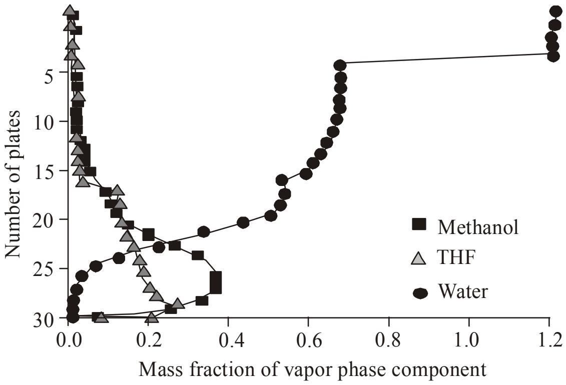

Fig. 6: Mass distribution of liquid phase

DISCUSSION

Influence of extraction agent on the vapor liquid equilibrium phase diagrams: Figure 7 to 9 along with molar fraction increases of lithium chloride and ethanediol in methanol-THF solution, equilibrium curve away from the diagonal line that the volatility of methanol relative THF also gradually increases. Ethanediol and lithium chloride eventually can all make methanol-THF solution from the bondage of azeotropic.

Influence of theoretical plate number on tower top content of THF: Figure 10 when the theoretical plate number increases to 27, the effect on separation is small. Therefore, the whole tower theory plate selected 30 is appropriate.

Influence of extraction agent feed position on tower top content of THF: Figure 11 extraction agent feed position at the 4th to the 6th theoretical plate, along with the extraction agent feed position down, tower top content of THF increases slightly; From the 6th theoretical plate, as extraction agent feeding position downs, tower top content of THF reduces and aggravate along with extraction agent feed position downs. This is because when extracting agent feeding position distances tower top too close, there will be part of the

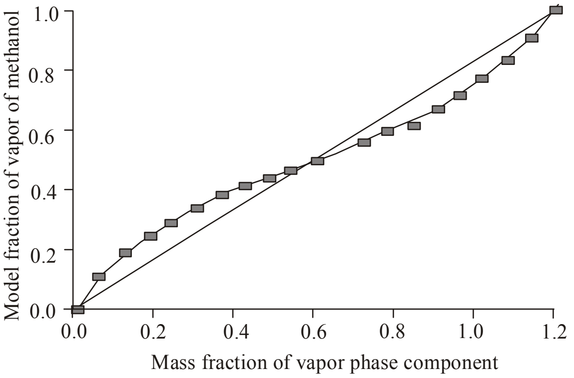

Fig. 7: Vapor-liquid equilibrium curve of methanol-THF

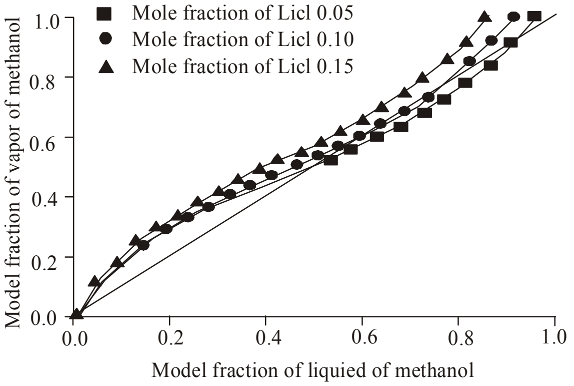

Fig. 8: Vapor-liquid equilibrium curve of methanol-THF

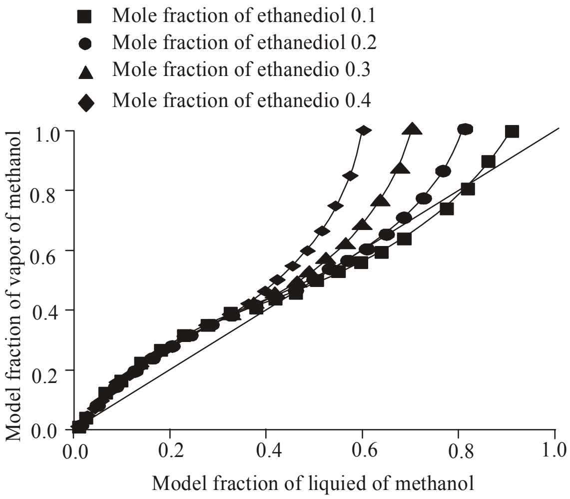

Fig. 9: Vapor-liquid equilibrium curve of methanol-THF

extraction agent is taken out from the tower top by the raise vapor, thus affecting the separation effect. When extraction agent feeding position more than the 6th theoretical plate, extraction period of theoretical plate number decreases, methanol and THF separation effect was reduced. Therefore, the content of THF on tower top dropped. So optimum extraction agent feed position was 6th.

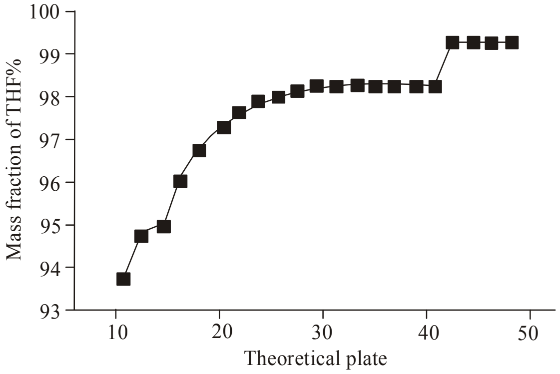

Fig. 10: Influence of theoretical plate number on tower top mass fraction of THF

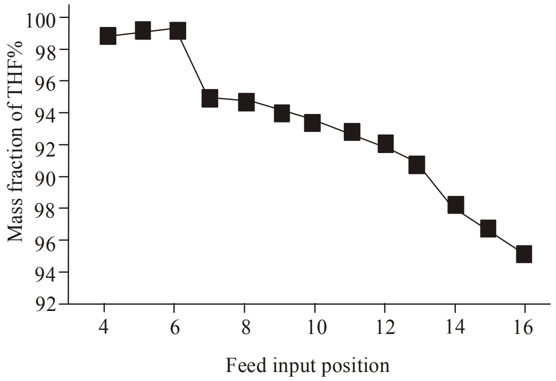

Fig. 11: Influence of extractant input position on tower top mass fraction of THF

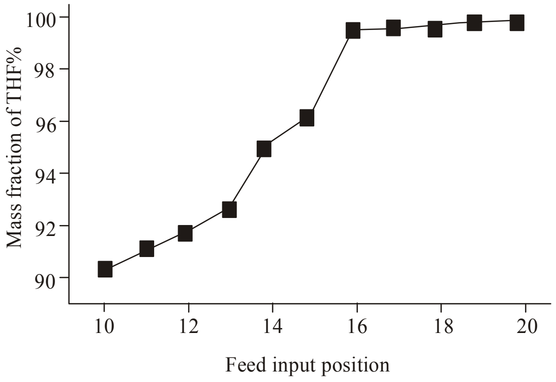

Fig. 12: Influence of feed input position on tower top mass fraction of THF

Influence of raw material feed position on tower top content of THF: Figure 12 when raw material feed position moves down, overhead THF content increases. Feed at the 16th to 20th theoretical plate has little effect on the content of overhead THF. This is because as raw material feed position down, extraction period of theoretical plate number increases, methanol and THF separation effect enhancement, the content of overhead THF increases; At the 18th theoretical plate feeds,

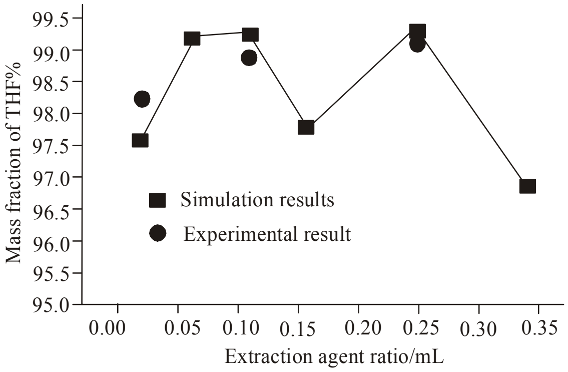

Fig. 13: Influence of extraction agent ratio on tower top mass fraction of THF. (Operation conditions: number of theoretical plate is 30, feed input position at 18th theoretical plate, extractant feed input position at 6th theoretical plate, extractant ratio 2.7, reflux ratio 5.0)

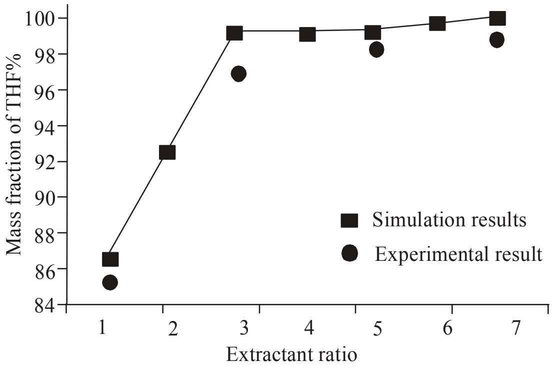

Fig. 14: Influence of extractant ratio on tower top mass fraction of THF. (Operation conditions: number of theoretical plate 30, feed input position at 18th theoretical plate, extractant feed input position at 6th theoretical plate, extractant agent ratio 0.24 g/mL, reflux ratio5.0.)

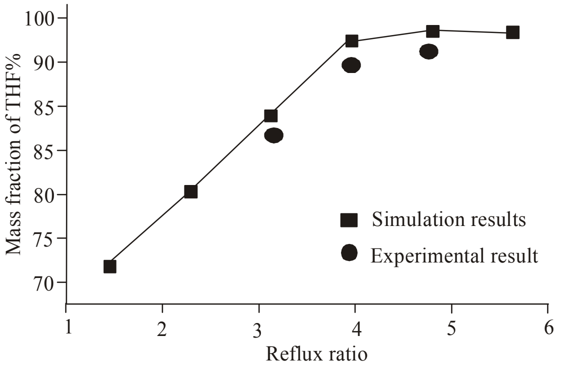

Fig. 15: Influence of reflux ratio on tower top mass fraction of THF. (Operation conditions: Number of theoretical plate 30, feed input position at 18th theoretical plate, extractant feed input position at 6th theoretical plate, extractant agent ratio 0.24 g/mL, extractant ratio 2.7)

extraction period of theoretical plate number already can make the extraction agent give full play to the effect, the content of overhead THF changes little. So optimum raw material feed input position was 18th.

Influence of extraction agent ratio on tower top content of THF: Figure 13 along with lithium chloride concentration increases in the composite extraction agent, salt effect enhancement. Due to its solubility reasons, concentration can not be too big, concentration is too high may appear crystallization in the tower, reducing plate efficiency. So optimum extraction agent ratio was 0.24 g/mL. Add 0.04 g/mL, 0.12 g/mL, 0.24g/mL composite extraction agent respectively, the results of experiment and simulation have some difference, may be due to rectifying column itself caused by the error.

Influence of extractant ratio on tower top content of THF: Figure 14 along with extractant ratio increases overhead THF content increased; When the extractant ratio more than 2.7, the overhead THF content increases tend to be gentle. When solvent ratio more than 2.7, composite extraction agent for THF-methanol-water system of dilution effect reaches balance, thus separation effect is not obvious. So optimum extractant ratio was 2.7. Extractant ratio respectively was 1.4, 2.7, 4.1, 5.4, the results of experiment and simulation have some difference, may be due to rectifying column itself caused by the error.

Influence of reflux ratio on tower top content of THF: Figure 15 along with reflux ratio increase overhead THF content increases; When the reflux ratio is small, overhead THF content increases quickly; When the reflux ratio more than 4.0, overhead THF content increases little. Reflux ratio more than 4.0, already satisfies the separation requirements. So optimum reflux ratio was 5.0. Reflux ratio respectively was 3.0, 4.0, 5.0, the results of the experiment and simulation results of experiment and simulation have some difference, may be due to rectifying column itself caused by the error.

CONCLUSION

- NNRTL requation was used to calculate vapor-liquid equilibrium data of methanol -THF-water system, salt extraction distillation mathematical model was established.
- Vapor-liquid equilibrium data of methanol-THF system was determined; Compared vapor-liquid equilibrium of methanol-THF changes before and after adding salt or extraction agent. The results shows that the ethylene glycol, lithium chloride was suitable extracting agent for separation methanol-THF system.

- Optimum extraction distillation conditions: theoretical plate 30, extractant plate 6, raw material feed plate 18, extraction agent ratio 0.24 g/mL, extractant ratio 2.7 and reflux ratio 5.0. Under this condition, on tower top mass fraction of THF can reach 97.2%. Simulation results and experimental data agree satisfactorily.

FOOTNOTES

$q_{n,F}$ = Feed flow, kmol/h
H = Enthalpy, kJ/kmol
$q_{n,L}$ = Liquid flow, kmol/h
p = Pressure, Pa
$q_{n,V}$ = Vapor flow, kmol/h
x = Liquid molar fraction
y = Vapor mole fraction
z = Feed molar fraction
γ = Activity coefficient
Superscript: F = Feed
V = Vapor
L = Liquid
s = Saturation state
Subscript: i = Component
j = Theoretical plate number

ACKNOWLEDGMENT

The authors wish to thank the helpful comments and suggestions from my leaders and colleagues in department of chemistry, Zhoukou Normal University. And also thank the support of my family. This study is supported by the study fund (No. 2012QNB12 and K201211).

REFERENCES

Cui, X., Y. Zhai and Z. Yang, 2004. Solvent selection for extractive distillation by the universal quasichemical functional group activity coefficient (UNIFAC) group contribution method. Chinese J. Chem. Eng., 12(6): 862-868.

Ernesto, V., P.M. Pilar and M.A. Antoni, 1996. Isobaric vapor-liquid equilibrium data for ethanol + water + potassium nitrate. J. Chem. Eng. Data, 41(1): 66-69.

Fredenslung, A., R. Jones and J.M. Prausnitz, 1975. Group contribution estimation of activity coefficients in nonideal liquid mixtures. AIChE J., 21: 1086-1099.

Huang, Z., 1983. Introduction of Electrolyte Solution Theory. Science Press, China, Beijing.

Ju, S., J. Liu and H. Zhang, 2006. Study on purification of mmll amount of water from tetrahydrofuran on 4A molecular sieves by adsorption. Chem. Eng., 129(6): 1-3.

Larsen, B., P. Rasmussen and A. Fredenslund, 1987. A modified UNIFAC group contribution model for prediction of phase equilibria and heats of mixing. Ind. Eng. Chem. Res., 26(11): 2274-2286.

Liu, B., 2005. Simulation of double-effect distillation for purification of tetrahydrofuran. J. Zhejiang Univ., Technol., 33(5): 560-562.

Pan, X., G. Xiao and Z. Yang, 2005. The separation process of distillation coupled with salt extraction. J. Chem. Eng. Chinese Univ., 19(5): 598-602.

Polka, H.M. and J. Gmehling, 1994. Effect of calcium n itrate on the vapor-liquid equilibria of ethanol + water and 2-propanol + water. J. Chem. Eng. Data, 39(3): 621-624.

Sun, R. and Q. Sun, 2002. Verification of vapor-liguid equilibrium data for salt-containing sysrms. J. Chem. Ind. Eng. (China), 53(8): 875-878.

Wang, H., C. Li, J. Fang and Z. Wang, 2008. Simulation of salt extractive distillation for preparation of anhydrous ethanol. Petrochem. Technol., 37(3): 258-261.

Wang, X. and Y. Yang, 2011. Simulation of salt extractive distillation for preparation of anhydrous ethanol with ChemCAD software. Chem. Eng., 39(9): 98-102.

Wang, X. and Y. Yang, 2012. Simulation of salt extractive distillation for recycling tetrahydrofuran from pharmaceutical wastewater. Mod. Chem. Ind., 32(12): 108-112.

Xu, J., W. Duan, C. Wang, Z. Duan and S. Ji, 1999. Application of special distillation in the recovery of tetrahydrofuran from waste pharmaceutical liquor. Env. Protect. Chem. Ind., 19(1): 12-16.

Xu, W. and X. Chen, 2002. New separation methods in pharmaceutical waste recycling tetrahydrofuran. Chem. Eng., 30(1): 17-19.

Xu, W., X. Zou and S. Zheng, 2001. A new separate method for methanol-tetrahydrofuran-water system. J. Yantai Univ., Nat. Sci. Eng., 14(3): 198-200.