Determination of Relative Volatility from Molecular Descriptor and its Application to Extractive Distillation Process

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Acetone and tetrahydrofuran are commonly used solvents and important raw materials in some organic synthetic process. Extractive distillation is proposed to separate the azeotropeofacetone-tetrahydrofuran. It is essential to determine the appropriate solvent to achieve efficient separation. Quantitative structure relative volatility relationship model established with discovery studio (Accelrys) software was developed using Genetic Function Approximation model to predict the relative volatility of abundant candidate solvents and determine the optimal solvent in the extractive process. The n-Octane was found as the suitable solvent compared the relative volatility withsolvent butyl ether. The total annual cost was used as the objective function to optimize the process. The parameters of the two processes using different solvents are obtained and compared.

1. Introduction

The separation of mixture is the key process in chemical industry and distillation is the most important separation method.The severe problem is that the separated mixture can generate azeotrope and simple distillation cannot achieve the separating task.To solve the problem, some widely used special distillation methods such as azeotropic distillation (Chienetet al.,2004), pressure-swing distillation (Wang et al.,2015)and extractive distillation (Zhu et al.,2016) are adapted to separate the azeotrope, Wang et al(2016) have also studied the control strategy of extractive distillation using relative gain array. Extractive distillation, whichinvolves a third component called solvent that help to get the effective separation, is commonly used method to separate binary azeotropes. Yuan et al (2015) studied the extractive distillation separating binary azeotropic mixture using relative volatility as the standard to select the solvent, and got the expected result,so in this paper the role of selecting solvent is that it can obviously enhance the relative volatility between the key components. The processsofextractivedistillationforseparatingbinary azeotropes mainlyinclude two distillation columns, one is called extractive column and the other is called the solvent recovery column.

In the extractive distillation, the difficulty is to select the efficient solvent among abundant solvents to make the separation easier, Andet et al. (2000) and Harper et al (1999) have applied some heuristic methods in the extractive process to select the optimal solvent. Solovev et al. (2011)have studied Quantitative Structure Property Relationship(QSPR) as the appearing of the subject of pharmaceutical chemistry, which is used to build the quantitative relationship between the chemical structure of compounds and biological activity, in which the method of mathematical statistics is introduced based on the biological activity as dependent variable and the physical and chemical parameters or structure parameters of compounds as independent variable. Now QSPR were gradually applied in the chemical engineering such as extractive distillation.Quantitative Structure-Relative Volatility Relationship (QSRVR) models was developedwith the help of Discovery Studio software based on multiple linear regressionwith genetic algorithm (GA-MLR) method and Artificial Neural Network (ANN) method (Kang et al., 2014). The industrial application of extractive distillation isusuallyconsider about one key factor: economics. In the estimate of the process economic, The total annual cost(TAC)has been proposed as an objective function to calculate the economics and confirm the optimal

steady state design (Douglaset al,1988). TAC consists of equipment cost and utilities cost. Luyben (2013) has paid attention to the minimal economic cost of different design to evaluate the different design with TAC. Acetone(ACT) and Tetrahydrofuran (THF) are both important raw material and can form minimum-boiling azeotropes in which ACT occupies 86.7 wt% and HTF occupies 13.3 wt% and the azeotropic temperature is 55°C. Yuan et al. (2013) has separated the system with butyl ether (BTE) as solvent through continuous extractive distillation(CED) by the simple simulation with Aspen Plus software and experiment，but the product purity of acetone is only 99 wt%,in this paper, through the preselection with the standard such asthermostability, boiling point and selectivity, n-Octane (OTE) was selected as new solvent. The purpose of this paper is to build QSRVR model for extractive distillation separating ACT and THF to estimate the relative volatility of new solvent OTE and former solvent BTE, TAC of the optimal flowsheets based on different solvents was calculated to verify the superiority of the new solvent.

2. Quantitative Structure Relative Volatility Relationship model

2.1 Data set for QSRVR and molecular descriptor

To build a QSRVR model, the first step is to get the date of relative volatility based on candidate solvents, then divide the candidate solvents into two subsets called training set and test set with a simple random sampling. The training set was used to develop the QSRVR model and the test set was used to verify the predictability of the model. In this study, the data of the previous literature published by Young-Mook Kang was used to set up the subsets.Molecular descriptor is a concept to describe the physical and chemical property of compounds and is the crucial element to establish the QSRVR model, in this study, the Discovery Studio software was used to calculate the molecular descriptors and hundreds of molecular descriptors were calculated. The three-dimensional (3D) structures were also optimized with the Merck Molecular Force Field.

2.2 The selection of molecular descriptor using Genetic Function Approximation Algorithm

The selection of genetic algorithm method has a significant influence for the QSPR model development, contrast with many techniques such as Friedman's multivariate adaptive regression splines algorithm, principle components analysis, the Genetic Function Approximation Algorithm use a large number of models and test the final, fully-constructed model, the modified model is set up by executing the genetic crossover operation to reunited the items of the models which perform better than before, the Friedman lack-of-fit (LOF) function to reduce the hidden trouble of overfitting to scale the mean-squared error, the Discovery Studio software uses a modified version of the Friedman LOF measurement, as shown followed：

$$LOF = \frac{\sum_{i=1}^{N}\left(\alpha_i^{exp} - \alpha_i^{pred}\right)}{\left[N - 0.99\left\{\frac{P + dC(N - p_{max})}{p_{max}}\right\}\right]^2} \tag{1}$$

Where α_i^{exp} and α_i^{pred} are the experimental and predicted relative volatility values of i; N is the number of samples in the training set; P represent the number of descriptors in each equation; d is the LOF smoothness parameter; C is a measure of equation complexity that is equal to the total number of features in the equation; and P_{max} is the maximum equation length.

2.3 Results and discussion after the calculation with the Discovery Studio software

A series of QSRVR models have been set up sorted by coefficient of determination squared correlation coefficient (R^2) values, the molecular descriptor in the top one function is shown in the Table 1

Table 1: the molecular descriptors and means of the function built by GFA

Molecular descriptor	coefficient	code	R^2 of the function
constant	1.0858	A	
AlogP	0.013049	B	
CHI_3_C	0.066769	C	
CHI_V_3_C	-0.11539	D	
Dipole_X	0.0070809	E	
JX	0.22049	F	0.9611
JY	-0.1901	G	
Jurs_PNSA_2	-0.00013735	H	
Jurs_RNCG	0.061155	I	
Shadow_zlength	-0.018643	J	
Strain_energy	-0.0047651	K	

The R^2 in the table is the degree of regression and the higher it is, the better the model is. In which the AlogP is on behalf of hydrophobicity of the molecule, CHI_3_C and CHI_V_3_C are the type of the molecular that is defined with aspects of atom connectivity within a molecule, JX and JY are highly discriminating descriptor whose evaluation begins with the D-matrix. The model consists of ten molecular descriptors and the detail mean is shown in the Table 2.

Table 2: the description of molecular descriptors using in the model

Molecular descritor	Description
AlogP	Log of the octanol-water partition coefficient using Ghose and Crippen's method.
CHI_3_C	Connectivity Indices
CHI_V_3_C	Connectivity Indices
Dipole_X	3D electronic descriptors that indicates the strength and orientation behaviour of a molecule in an electrostatic field
JX	Balaban Indices
JY	Balaban Indices
Jurs_PNSA_2	Partial negative solvent-accessible surface area multiplied by the total negative charge
Jurs_RNCG	Charge of most negative atom divided by the total negative charge
Shadow_zlength	Length of molecule in the z dimension
Strain_energy	Gives the point strain energy. Strain_Energy is the difference between Energy and Minimized_Energy.

The descriptor of B, D, E, F, I, have the positive effect on the RV, while the descriptor of C, G, H, J, K, have the negative effect on the RV, this results give the direction of the solvent selection.

The R^2 of the best QSRVR model is 0.9611 closing to 1 which express a better regression, the Figure 1 show the predicted relative volatilities of EB to PX by GFA method versus experimental relative volatilities of EB to PX.Based on the model, the RV of OTE and BTE were calculated using the model and the results are 1.15 and 1.14.
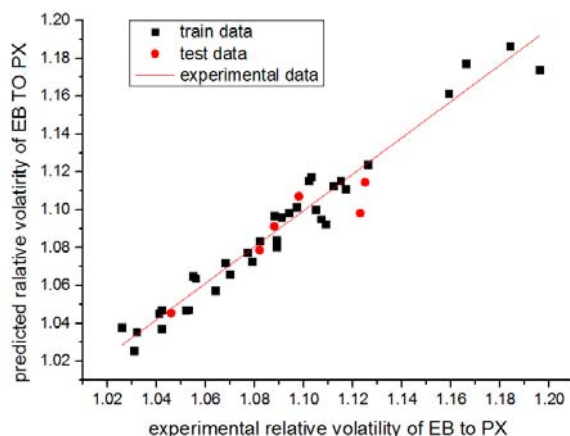

Figure 1: Predicted relative volatilities of EB to PX by GFA method versus experimental relative volatilities of EB to PX

3. Steady state process considering TAC

The optimal solvent in extractive distillation can lead to a minimal TAC in traditional thought, to verify the veracity of the calculation of the relative volatility with OTE and BTE, the feasibility of new solvent in extractive distillation is studied and the calculation of TAC with different solvents is carried out.

3.1 Solvent selection

A suitable solvent has the far-reaching influence on the extractive distillation, and is worthy to pay more attention on the selection of the solvent. The relative volatility is an important indicator to confirm the feasibility

of solvent on the system. Relative volatility is the ratio of volatilities of the light and heavy components when the solvent was added into the mixture. The higher relative volatility can lead to easier separation.

Triangular diagram containing RCM is used to describe the equilibrium relationships of the separated system and some feasibility analyses of separation process were all carried out with RCM. The RCM of the OTE/ACT/THF ternary system drawn by Aspen Plus with the built-in UNIQUAC model is displayed in Figure 2.
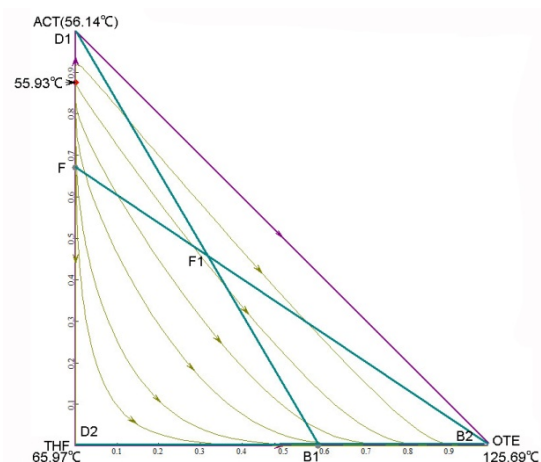

Figure 2: Residue curve map (mass basis) of the OTE/ACT/THF ternary system

From Figure 3, both ACT and THF are saddles, while OTE is the stable node, the azeotrope of ACE and THF was unstable node. The yellow residue curves were all point to OTE in the end, which indicated that there was no distillation boundary in the separating process, and the extractive distillation has the feasibility.The blue line shows the material balance lineand separating process can be clearly shown from the trace of the material balance line, the F1 was fed into the first column and was separated into stream D1 and stream B1, then the stream B1 was fed into the second column and was separated into stream D2 and stream B2.

3.2 Process design and economic analysis

In this paper, the separated mixture was 1,000 kg/h with 62 wt% ACT and 38 wt% THF, in the columns of the process, the pressure of the two columns are all set at 1 atm with a tray pressure drop of 0.0068 atm, the purity of two products was set no less than 99.9 wt% and the annual working time was set 8,000 h, the design of steady state was executed by commercial software Aspen Plus and UNIQUAC activity model was chosen as the property package based on the build-in binary interaction parameters in the two processes with the solvents of OTE and BTE. Figure 3 shows that there is a maximum ACT purity at a optimum reflux ratio (RR1) on a certain solvent rate with OTE and BTE as solvent. We can see that to get the specified purity, the solvent rate of OTE should be no less than 755 kg/h and the BTE is no less than 2,180 kg/h.
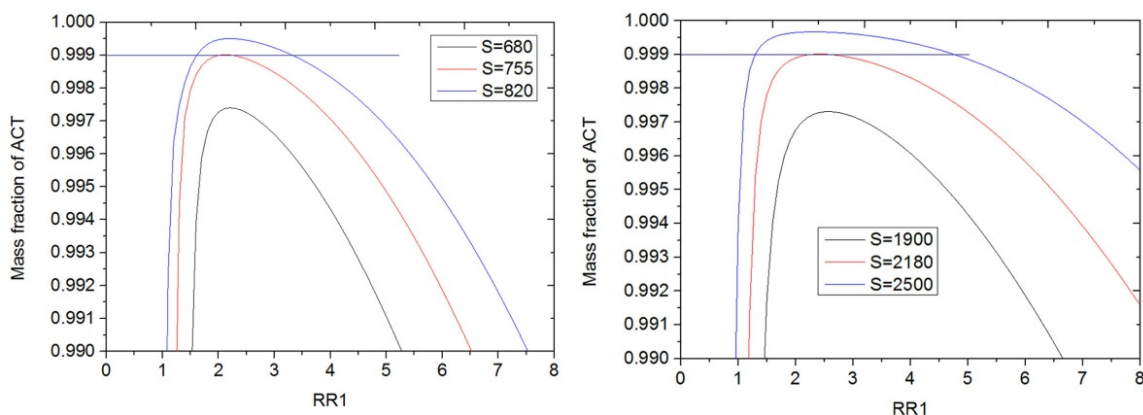

Figure 3: Effect of RR1 and solvent flow rates of OTE and BTE on ACT content in distillate product of extractive column

In this paper, the distillation composition specification of ACT in extractive column is 99.9 wt% and the goal value is achieved by manipulating the RR1 and bottom composition specification is 10^{-5} wt% ACT by manipulating the distillation rate. In the solvent recovery column, the distillation composition specification of THF is set at 99.9 wt% by manipulating the RR2 to get the goal value and the bottom composition specification was set at 10^{-5} wt% by manipulating the distillation rate to achieve that. The TAC was defined as follow:

$$TAC = C_V + 0.3FCI \tag{2}$$

Where the C_V was on behalf of the utilities consumption and the FCI is the fixed capital investment, the time of pay back with capital investment is set at three years.

The capital investment in the separation process is mainly made up by the two columns, two reboilers, and two condensers. The tray spacing was set at default value (0.61m) in the simulator and the sieve plate was used. The area of the condensers and reboilers are calculated by the heat duty, the overall heat coefficient, and the differential temperature driving. The overall heat transfer coefficient used in this paper are 0.852 kW/(K•m^2) for condensers and 0.568 kW/(K•m^2) for reboilers. There are five design variables including total stages (NT1), feed location (NF1), and recycle solvent feed location (NFE) of the extractive distillation column, total stages (NT2), and fresh tray location (NF2) of the solvent recovery column that can be used to optimize the TAC for the two extractive distillation processes. A calculation sequence was set up for optimizing so many variables. Figure 4 shows the TAC trend as the change of the S/F ratio with NT1 and NFE fixed based on different solvents. There is a minimum value in the path of the TAC and it is observed that the optimum S/F ratio is 0.84 with OTE as solvent, when the NT1 and NFE fixed at 70 and 56, respectively, and 2.52 with BTE as solvent, when the NT1 and NFE fixed at 60 and 42. According to the sequential iterative optimization procedure, the optimal values of five design variables and the extra information of the two flowsheets were shown in the Figure 5
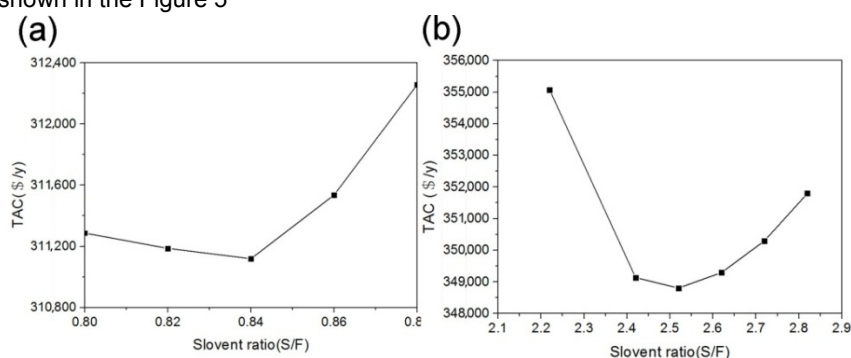

Figure 4: The influence of S/F on TAC with OTE (a) and BTE (b) as solvent

By the work of simulation with BTE as solvent, the former solvent can also improve the purity of ACT by raising the solvent rate, compared the final results, the minimum TAC is 311,120 $/y with OTE as solvent and the optimal minimum TAC is 348,802 $/y with BTE as solvent, the new solvent can result a 10.8 %, it is more obvious that in the extractive distillation separating ACT and THF system, OTE is superior to BTE.
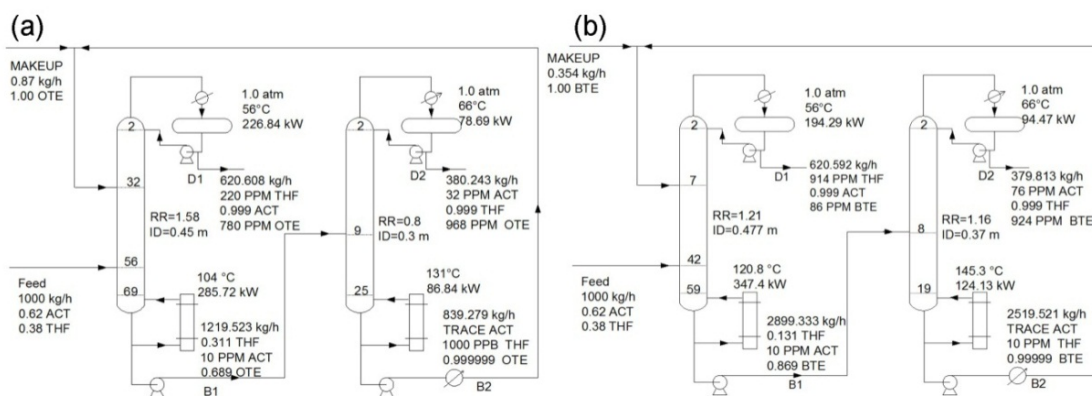

Figure 5: The optimal flowsheets of extractive distillation with OTE (a) and BTE (b) as solvent

4. Conclusion

Extractive distillation was used to separate the azeotropic mixture of ACT-THF in this paper. QSRVR model was set up to calculate the relative volatility of solvents avoiding the experiment, the model of relative volatility (RV) wasestablished with the help of GFA method. The squared correlation coefficient (R2) was introduced to explain the degree of the regression and the final value is 0.9611,TAC was used to examine the validity of the model,in the optimization of the processes, the feed flow is 1000 kg/h with 62 wt% ACT and 38 wt% THF and the purity of products were set at 99.9 wt%, the relative volatilities of ACT-THF with OTE and BTE as solvent, respectively, were predicted using the established QSRVR model, TAC is 311,120 $/ywith OTE as solvent, which is lower than 348,802 $/y of TAC with BTE as solvent, the new solvent has the advantage in extractive distillation separating the mixture of ACT-THF.QSPR is an efficient method in predicting some chemical characters and if introducing it into the extractive distillation field, the design of extractive distillationcan get intensification.

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