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**Computer-Aided Preliminary Design and
Optimization of Distillation Column in
OPP's (O-phenylphenol) New Production
Process**

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Abstract

At present, the OPP production scale of China's chemical enterprises is small, and there is no obvious competitive advantage in cost, unit consumption and so on. The newly developed new OPP production process has made up for the shortcomings of other processes. The paper is on the preliminary design and optimization of the distillation column in this production process. The distillation column which meets the actual industrial production needs is designed by computer aided calculation.

The problem of missing physical data of Dibenzofuran was solved by using origin pro data fitting. The Newton iteration method was used to calculate the bubble and dew point temperatures involved in the design of distillation column with Matlab.

The whole design process is divided into three parts. Firstly, the FUG method is used to calculate the theoretical tray number, minimum reflux ratio, relative volatility and feed position of the distillation column. Then, using the above data, using Aspen simulation software to simulate the distillation column design. Finally, the sensitivity analysis of plate number, feed pressure, feed position and reflux ratio are used to optimize the design of distillation column, which can meet the separation requirements and save operation costs. The optimum design of distillation column is achieved.

The calculation method of bubble point and dew point in this study can be applied to the practical application of separation engineering. After obtaining reliable parameters of Antoni equation, the Newton iteration method can be used to calculate the bubble point and dew point temperature in multi-component system. It provides a reliable method for the calculation of vapor-liquid equilibrium.

Estratto

Attualmente, la scala di produzione OPP delle imprese chimiche cinesi è piccola e non vi è un evidente vantaggio competitivo in termini di costi, consumo unitario e così via. Il nuovo processo di produzione OPP recentemente sviluppato ha colmato le lacune di altri processi. Il foglio è sulla progettazione preliminare e l'ottimizzazione della colonna di distillazione in questo processo di produzione. La colonna di distillazione che risponde alle reali esigenze di produzione industriale è progettata mediante calcolo computerizzato.

Il problema dei dati fisici mancanti di Dibenzofuran è stato risolto utilizzando l'installazione di dati pro di origine. Il metodo di iterazione di Newton è stato utilizzato per calcolare le temperature di bolla e di punto di rugiada coinvolte nella progettazione della colonna di distillazione con Matlab.

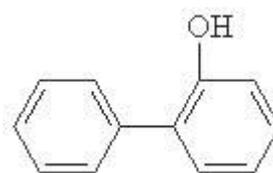
L'intero processo di progettazione è diviso in tre parti. In primo luogo, il metodo FUG viene utilizzato per calcolare il numero teorico del vassoio, il rapporto minimo di riflusso, la relativa volatilità e la posizione dei mangimi della colonna di distillazione. Poi, utilizzando i dati di cui sopra, utilizzando software di simulazione Aspen per simulare il disegno della colonna di distillazione. Infine, l'analisi di sensibilità del numero di piastra, della pressione dei mangimi, della posizione dei mangimi e del riflusso sono utilizzati per ottimizzare la progettazione della colonna di distillazione, che può soddisfare i requisiti di separazione e risparmiare i costi di funzionamento. La struttura ottimale della colonna di distillazione è ottenuta.

Il metodo di calcolo del punto di bolla e del punto di rugiada di questo studio può essere applicato all'applicazione pratica dell'ingegneria di separazione. Dopo aver ottenuto parametri affidabili dell'equazione Antoni, il metodo di iterazione Newton può essere utilizzato per calcolare il punto di bolla e la temperatura del punto di rugiada nel sistema multi-componente. Fornisce un metodo affidabile per il calcolo dell'equilibrio vapor -liquido.

1 Introduction

1.1 Overview of o-phenylphenol

O-phenylphenol (OPP), CAS No. 90-43-7, the formula is $C_{12}H_{10}O$, the molecular weight is 170.21. Chemical structure formula:



O-phenylphenol is a white flake crystal with a special odor. The purity of o-phenylphenol is 98%. Its relative density is 1.2130, melting point is 56-59 C, boiling point is 283-286 C, flash point is 127 C. It is slightly soluble in water, easily soluble in organic solvents such as ethanol, propanol, benzene, toluene, trichloroethylene and alkali solution.

1.2 Application of o-phenylphenol

O-phenylphenol is an important new type of fine chemical products and organic intermediates. It is widely used in sterilization, anti-corrosion, printing and dyeing auxiliaries and surfactants, in the synthesis of new plastics, resins and polymer materials stabilizers and flame retardants. In recent years, the actual demand for o-phenylphenol in the global market has increased year by year, and it has also promoted the further research

and development of o-phenylphenol, and its application field will be further broadened.

1.3 Existing mainstream production process and market conditions of o-phenylphenol

The companies that produce OPP in the world are mainly concentrated in Japan, the United States and Germany. The largest manufacturer of products is Bayer AG. OPP's global production is about 20,000 tons/year, with an average annual growth rate of 7%. OPP's market price is about 5,000 euros / ton, the market size is about 800 million, and the rapid development of environmentally friendly flame retardant materials is expected to drive the rapid increase of OPP demand.

The current main process method is cyclohexanone condensation dehydrogenation method: cyclohexanone liquid phase condensation synthesis dimer, dimer gas phase catalytic dehydrogenation into OPP, and then distillation, recrystallization to obtain pure OPP. Synthesis process:

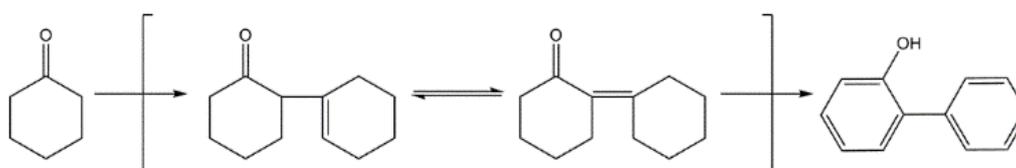


Figure 1.3.1 OPP synthesis process

1.4 Introduction of New Production Technology

At present, the OPP production scale of China's chemical enterprises is small, and there is no obvious competitive advantage in cost, unit consumption and so on. There are a lot of wastewater problems in the existing production process, and the pressure of environmental protection is high. But at the same time, the imbalance between supply and demand caused by this situation also brings market opportunities. Sinochem International Group has developed a new OPP production process, and the process has been optimized. While paying attention to environmental protection, the value of by-products in production process has been improved to cope with price changes flexibly and capture market share.

The new production process uses fluorene oxide (DBF) extracted from coal tar and washing oil as raw material to produce OPP.

Which follows:

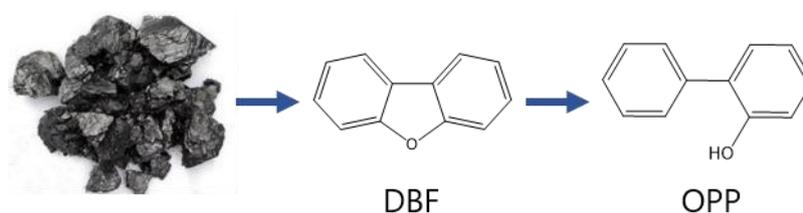


Figure 1.4.1 OPP synthesis

At present, the research and development of reaction catalyst has been

successfully completed. The process uses readily available toluene as a solvent. The reaction is carried out in a fixed-bed reactor. The conversion and yield of the reaction meet the needs of industrial production. The reaction products of the reaction are oxonium, biphenyl, OPP, toluene and phenol. Oxonium is the main reactant, toluene is the solvent, OPP is the target product, and biphenyl is obtained as an important by-product.

After the reaction is completed, the reaction product is sent to a distillation column to separate the desired product, after which the by-product is purified by a crystallization process and the solvent is recycled to the reactor. It should be noted that the boiling point of fluorene oxide and OPP is close and there is an azeotropic phenomenon, which will affect the separation efficiency of distillation column.

This paper focuses on the preliminary design and optimization of the distillation column in this production process. The distillation column which meets the actual industrial production needs is designed by computer aided calculation.

1.5 Problem Statement

When designing and optimizing the distillation column, simulation software such as Aspen Plus and Hysys is usually used to design and

simulate the operation of the tower equipment. However, simulation software usually relies heavily on its material database for simulation calculation, so once the database lacks the important reactant parameters, it will cause great design errors. This is not allowed.

As described in this paper, the Aspen Plus software is used for the distillation column design, but all the physical parameters of the oxygen oxime are not available in the database, then the subsequent calculation can only be performed by the physical property parameter simulated function of the Aspen Plus.

Therefore, in the process of designing the distillation column, it is necessary to fit the parameters of reactants (especially the parameters of Antoni equation, which are used to calculate the bubble and dew points of multi-components) and to compare and verify the accuracy of the simulation results of the Aspen Plus by matlab. Finally, the design optimization is carried out by Aspen Plus to achieve the goal. To the optimal distillation column. Then, Aspen Plus is used to optimize the design to achieve the optimal distillation column design.

2 Concepts

2.1 Vapor–liquid equilibrium (VLE)

For the calculation of the distillation column, the first concern is to solve the vapor-liquid equilibrium problem. The vapor–liquid equilibrium (VLE) describes the distribution of a chemical species between the vapor phase and a liquid phase. The equilibrium vapor pressure of a liquid is in general strongly dependent on temperature. Such vapor–liquid equilibrium information is useful in designing columns for distillation. Solving the vapor–liquid equilibrium problem is to calculate the bubble point and dew point temperature and the composition of the vapor–liquid phase.

2.2 Bubble point and dew point temperature

The liquid of a certain composition is heated under a constant pressure, and the temperature when the first bubble appears in the liquid phase is called the bubble point temperature. On the other hand, if a certain composition of the gas is cooled under a constant pressure, the temperature at which the first droplet appears is called the dew point temperature. Calculating the bubble point and dew point temperature is the most basic step in solving the separation process.

2.3 Newton's method

In numerical analysis, Newton's method, also known as the Newton-Raphson method, named after Isaac Newton and Joseph Raphson, is a root-seeking algorithm that continuously produces an approximation of the root (or zero) closer to the real-valued function. Newton's iteration method is one of the most important methods to find the root of the equation. Its greatest advantage is that it has a square convergence near the single root of the equation $f(x)=0$, and it can also be used to find the multiple and complex roots of the equation. In addition, this method is widely used in computer programming.

The idea is to start with an initial guess which is reasonably close to the true root, then to approximate the function by its tangent line using calculus, and finally to compute the x-intercept of this tangent line by elementary algebra. This x-intercept will typically be a better approximation to the original function's root than the first guess, and the method can be iterated.

The convergence criteria of the Newton iteration method applicable in this paper is set to 0.0001 to ensure the accuracy of calculation of bubble point and dew point temperature.

2.4 Key components in multicomponent distillation

The component separated are called the light key, which is the more volatile. The components more volatile than the light key are called light components and will be present in the bottoms in small amounts. The components less volatile than the heavy keys are called heavy components and are present in the distillate in small amounts. The two keys components are present in significant amount in both the distillate and bottoms.

2.5 FUG method

Fenske equation

The Fenske equation in continuous fractional distillation is an equation used for calculating the minimum number of theoretical trays required for the separation of a multicomponent feed stream by a distillation column that is being operated at total reflux (i.e., which means that no overhead product distillate is being withdrawn from the column). The equation was derived in 1932 by Merrell Fenske.

When designing large-scale, continuous industrial distillation columns, it is very useful to first calculate the minimum number of theoretical trays required to obtain the desired overhead product composition.

Underwood methods

The method is applied to all the i -components of a distillation, under the column's condition of minimum reflux. Minimum reflux is estimated using the Underwood method. The Underwood method assumes constant molar overflow and relatively constant relative volatilities. If these do not apply, caution is necessary when applying the results.

It also should be noted that this method uses Underwood constant, θ . The determination of the value of Underwood Constant will affect the calculation results of Minimum reflux.

Gilliland methods

Gilliland's (1940) method, which is developed into an equation by Molokanov (1972), is an empirical correction considered as an approximation method. It is utilized at the operating reflux ratio R (for flow rates at the column top) is correlated with the minimum reflux ratio obtained using the Underwood method, the minimum number of stages obtained by the Fenske method, and the number of stages N at the operating R

FUG stands for Fenske-Underwood-Gilliland method and it is the most

widely method used short cut method for determining number of equilibrium stages for multicomponent distillation.

3 Methodology

3.1 Newton's method

Newton's method, also known as Newton-Raphson method, is a method proposed by Newton in the 17th century to approximate the solution of equations in real and complex fields.

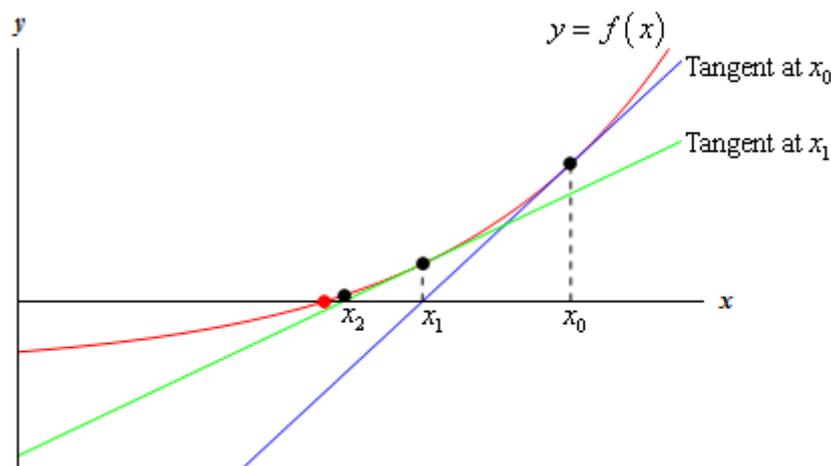


Figure 3.1.1 Newton-Raphson method curves

Let r be the root of $f(x)=0$, select x_0 as the initial approximation of r , and cross point $(x_0, f(x_0))$ as the tangent L of curve $y=f(x)$, $L: y = f(x_0) + f'(x_0)(x - x_0)$, then the abscissa $x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}$ at the intersection of L and axis x is called the first approximation of r . The crossing point $(x_1, f(x_1))$ makes the tangent of curve $y=f(x)$, and obtains the abscissa $x_2 = x_1 - \frac{f(x_1)}{f'(x_1)}$ of the intersection of the tangent and the x -axis, which is called the quadratic approximation of r . Repeat the above process to get the approximation sequence of r , where a is called a sub-approximation

of $x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$, and the upper formula is called Newton's iteration formula.

The Newton iteration method is an approximate method to solve the non-linear equation, which linearizes the non-linear equation $f(x)=0$.

Expand of $f(x)$ in a neighborhood of point x_0 into Taylor series

$$f(x) = f(x_0) + f'(x_0)(x - x_0) + \frac{f''(x_0)(x - x_0)^2}{2!} + \dots$$

$$+ \frac{f^{(n)}(x_0)(x - x_0)^n}{n!} + R_n(x)$$

Take its linear part (the first two terms of Taylor expansion), and make it equal to 0, then $f(x_0) + f'(x_0)(x - x_0) = 0$. Using it as an

approximate equation for the nonlinear equation $f(x)=0$. if $f'(x_0) \neq 0$,

Then the solution is $x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}$, thus an iteration formula of

Newton's iteration method is obtained: $x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$.

It has been shown that if it is continuous and the zero to be sought is isolated, there is an area around the zero point, and as long as the initial value is within this neighborhood, the Newton method must converge.

Also, if not 0, then Newton's method will have square convergence performance. Roughly speaking, this means that for each iteration, the effective number of Newton's method results will double.

It is worth noting that in the iterative calculation of bubble point and dew point, the selection of the appropriate iteration initial value x_0 will affect the accuracy of the calculation results of bubble point and dew point. Therefore, it is necessary to estimate an appropriate initial value of the iteration in advance.

3.2 Calculation of phase equilibrium constant K_i

According to the definition of ideal system, the saturated vapor phase composition y should conform to Dalton's law of partial pressure in equilibrium state: $P_{Vi}=PY_i$. The vapor phase composition conforms to Raoul's law: $P_{Li}=p_i^0 x_i$. In the case of two-phase equilibrium: $P_{Vi}= P_{Li}$. In the above formulae, the subscript i represents the component, the subscript V represents the vapor phase, and the subscript L represents the liquid phase.

In a multi-component equilibrium system, the ratio of the mole fraction of the i component in the vapor-liquid two phase is called the vapor-liquid equilibrium constant or the partition coefficient $K_i = \frac{Y_i}{X_i}$. The mathematical expression in the ideal system is $K_i = \frac{P_i^0}{P}$. Where P_i^0 is the saturated vapor pressure of pure component i at system temperature, and

P is the system pressure. The saturated vapor pressure of pure components can be calculated by the Antoine equation. The Antoine equation: $\ln P_i^0 = A_i - \frac{B_i}{C_i+T}$. A_i , B_i , and C_i are the three Antoine constants of component i , respectively. The Antoine formula applies only to low pressure systems (less than 0.2 MPa)

The known conditions of the process are the component number M , the composition of the material X_i (Y_i) and the system pressure P . It is necessary to calculate bubble point and dew point temperature and vapor phase (liquid phase) composition $Y_i(X_i)$ of phase equilibrium.

3.3 Bubble point calculation

A vapor-liquid equilibrium system with M components has $2M+2$ independent equations:

The phase equilibrium equation of component i is $K_i = \frac{Y_i}{X_i}$

Thermodynamic equation is $K_i = \frac{P_i^0}{P} = \frac{1}{P} \exp\left(A_i - \frac{B_i}{C_i+T}\right)$

Normalized equation is $\sum Y_i = 1$

It is assumed here that the Antoine equation applies. There are M equations for calculating the phase equilibrium constant. The variables of the system are $3M+2$, i.e. system temperature T , pressure P and X_i , Y_i and K_i of M components. When the liquid phase composition of the system

and the pressure of the system are determined, the temperature that satisfies the above three sets of equations is the bubble point temperature.

When calculating the bubble point temperature, the phase equilibrium equation and thermodynamic equation are substituted into the normalized equation, and the temperature T is derived by the Newton method until the objective function is satisfied: $F(T) = \sum Y_i - 1 = 0$.

Introduce the Antoine equation and derive the temperature T :

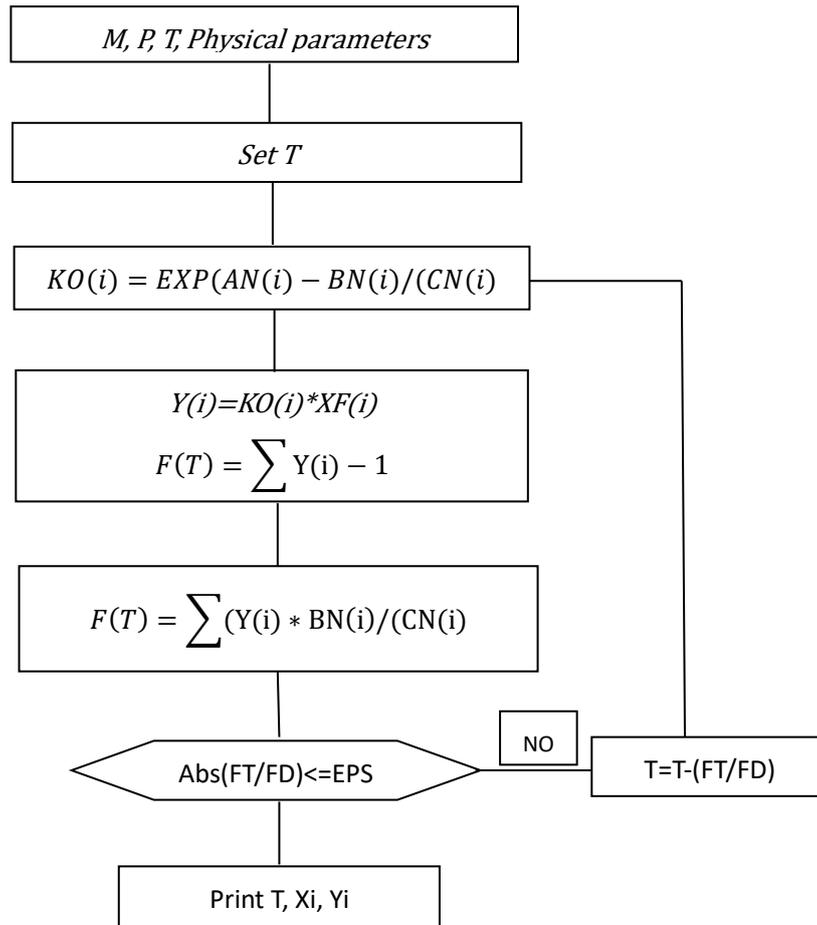
$$\frac{dF(T)}{dT} = \frac{1}{P} \sum_i X_i \exp \left[A_i - \frac{B_i}{C_i + T} \right] \cdot \frac{B_i}{(C_i + T)^2}$$

$$\frac{dF(T)}{dT} = \sum_i Y_i \frac{B_i}{(C_i + T)^2}$$

Firstly, the initial temperature T is set and the equilibrium constant K is obtained, then the vapor phase composition Y_i of the phase equilibrium can be obtained, which can be distinguished by the normalized equation.

If the accuracy requirement is not met, the Newton iteration method can be used to iterate until the accuracy requirement is met.

The calculation process of bubble point temperature using matlab program is as follows.



3.4 Dew point calculation

The procedure for calculating the dew point temperature is similar to calculating the bubble point temperature. When the vapor phase composition of the system and the pressure of the system are determined, the temperature that satisfies the above three sets of equations is the dew point temperature.

The phase equilibrium equation of component I is $K_i = \frac{Y_i}{X_i}$

Thermodynamic equation is $K_i = \frac{P_i^0}{P} = \frac{1}{P} \exp\left(A_i - \frac{B_i}{C_i + T}\right)$

Normalized equation is $\sum X_i = 1$

Then $F(T) = \sum X_i - 1 = \sum_i P Y_i \exp \left[A_i - \frac{B_i}{C_i + T} \right]^{-1} - 1 = 0$.

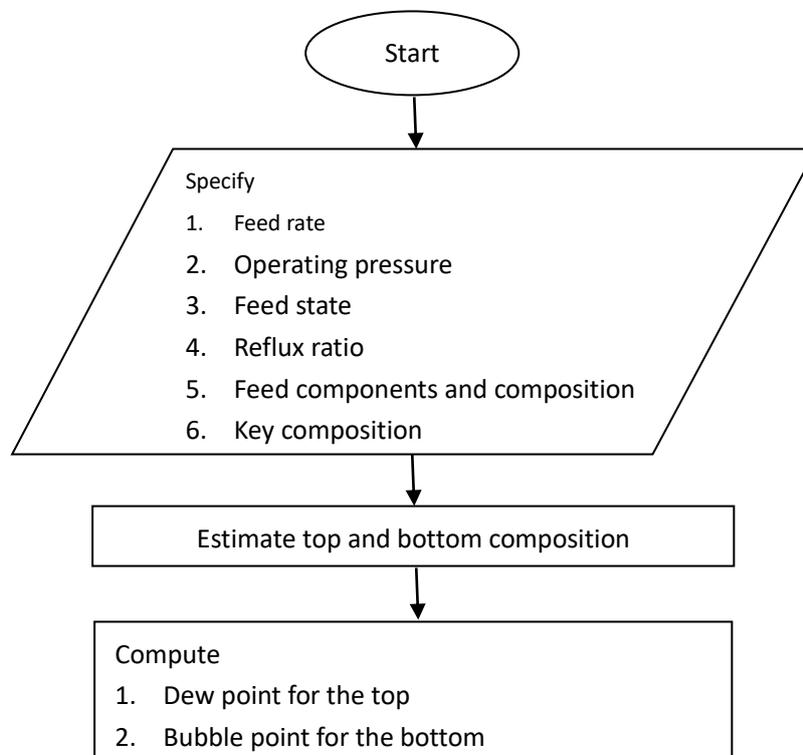
Introduce the Antoine equation and derive the temperature T:

$$\frac{dF(T)}{dT} = P \sum_i \left(-Y_i \exp \left[A_i - \frac{B_i}{C_i + T} \right]^{-2} \exp \left[A_i - \frac{B_i}{C_i + T} \right] \frac{B_i}{(C_i + T)^2} \right)$$

Similarly, Newton iteration method is used to iterate until the accuracy requirement is satisfied, and the dew point temperature is obtained.

3.5 FUG method

The flow chart is as follows:





1. Minimum number of stages at total reflux ratio using Fenske
2. Minimum reflux ratio using Underwood
3. Theoretical numbers of stages at operating reflux ratio using Gilliland
4. Location of feed tray

Equilibrium in the multicomponent distillation

Raoult's law can be used to determine the composition of vapor in equilibrium with the composition of liquid for a multicomponent system that can be considered ideal.

$$p_i = P_i x_i$$

Where p_i is the partial pressure of component i in the vapour in Pa (atm). P_i is the vapour pressure of pure i in Pa (atm) and x_i is the mole fraction of i in the liquid. In hydrocarbon systems, because of non-idealities, the equilibrium data are often represented by:

$$y_i = K_i x_i$$

Where K_i is the vapor-liquid equilibrium constant

It should be noted that for ideal system:

$$K_i = \frac{P_i^0}{P}$$

The relative volatility α_i for each individual component in a multicomponent mixture can be defined in a manner similar to that for a binary mixture. If component C in a mixture of A, B, C, D and E is selected as the base component

$$\alpha_i = \frac{k_i}{k_c}, \alpha_A = \frac{k_A}{k_c}, \alpha_B = \frac{k_B}{k_c}, \alpha_C = \frac{k_C}{k_c} = 1.0, \alpha_D = \frac{k_D}{k_c}, \alpha_E = \frac{k_E}{k_c}$$

Boiling point and dew point calculation

For the calculation of bubble point and dew point temperature, Newton iteration can be performed on the composition and temperature of the components by matlab to calculate the exact bubble point and dew point temperature.

Data fitting

However, it is worth noting that since the feed components in the distillation column case contains substances that are not commonly used in the industry: fluorene and o-phenylphenol. It requires to find the exact Antoine equation parameters for the feed components to calculate the bubble point and dew point temperature. In this case, the data fitting method was performed by Origin data processing software to determine the Antoine parameters of each component.

Due to the lack of physical data of fluorene in Aspen's database, the Antoine equation parameters of fluorene are selected, which are provided by DDB (Dortmund Data Bank), in the form of three parameters. The parameters of the other four components can be obtained by searching Aspen's database of PLXANT-1 physical parameters. The extended Antoine vapor pressure model is applicable in Aspen.

$$\ln p_i^{*,l} = C_{1i} + \frac{C_x}{T + C_{3i}} + C_{4i}T + C_{5i} \ln T + C_{6i}T^{C_\pi} \text{ for } C_{8i} \leq T \leq C_{9i}$$

Therefore, it is necessary to fit the data into three-parameter Antony equation model.

Minimum number of stages at total reflux ratio using Fenske equation

The Fenske equation is applicable to any two components in a multi-component system. When applied to HK and LK

$$N_m = \frac{\log|(x_{LD}D/x_{HD}D)(x_{HW}W/x_{LW}W)|}{\log(\alpha_{L,av})}$$

Where $x_{LD}D$ = mole fraction of light key in distillate.

x_{LW} = Mole fraction of the light component in bottoms.

x_{HD} = Mole fraction of heavy component in bottoms.

The average value $\alpha_{L,av}$ (is the relative volatility) of the light key is calculated from the α_{LD} at the top temperature (dew point) of the tower and α_{LW} at the bottoms temperature (bubble point):

$$\alpha_{L,av} = \sqrt{\alpha_{LD}\alpha_{LW}}$$

We can see that the minimum number of theoretical trays is independent of the feed composition and is only determined by the separation requirements. As the separation requirements increase (ie, the distribution ratio of light key components increases, the distribution ratio of heavy key components decreases), and the relative volatility between key

components approaches 1, the minimum number of theoretical trays required will increase.

Estimate top and bottom composition

To determine the distribution or concentration of other components in the top and the bottoms at total reflux, the equation is used for any other component i as follows.

$$\frac{x_{iD}D}{x_{iW}W} = (\alpha_{L,av})^{N_m} \frac{x_{HD}D}{x_{HW}W}$$

The accuracy of Fenske equation obviously depends on the reliability of relative volatility data. The calculation methods of bubble and dew point introduced earlier in this paper can provide accurate relative volatility.

Minimum reflux ratio using Underwood

The Underwood shortcut method to calculate R_m uses constant average α values and also assumes constant flows in both sections of the tower.

This method provides a reasonably accurate value. The two equations to be solved to determine the minimum reflux ratio are:

$$1 - q = \sum \frac{\alpha_i x_{iF}}{\alpha_i - \theta}$$

$$R_m + 1 = \sum \frac{\alpha_i x_{iD}}{\alpha_i - \theta}$$

Where α_i Relative volatility of component i

- q Liquid fraction of feed
 R_m Minimum reflux ratio
 x_{iF} Molar fraction of component i in feed mixture
 x_{iD} Molar fraction of component i in distillate at minimum reflux ratio
 θ The roots of equations

To solve R_m , the value of θ should be calculated first. θ value should be between a value of light and heavy key components. If the light and heavy key components are not adjacent components, two or more θ values can be obtained, and R_m can be calculated separately, taking the larger one.

The composition of distillate at the minimum reflux ratio is needed for calculating R_m , but it is difficult to know the composition. In practice, the composition under the condition of total reflux is often used to replace the composition under the condition of total reflux.

Real reflux ratio and theoretical tray number

The minimum number of theoretical trays and the minimum reflux ratio are two limiting conditions under full reflux condition. They determine the allowable range of theoretical trays and operating reflux ratio, which is helpful to select specific operating conditions.

The choice of actual reflux ratio is based on economic considerations.

The optimal value of R/R_m is about 1.05, but it is close to the optimal condition within a certain range slightly larger than this value. In practice, if $R/R_m=1.10$ is often required, many theoretical trays are required; if the value is 1.50, fewer theoretical trays are required. According to experience, the median value is generally 1.30.

Gilliland's shortcut method, which is developed into an equation by Molokanov, is an empirical correction considered as an approximation method.

Gilliland correlation: Number of ideal plates at the operating reflux

$$\frac{N - N_{\min}}{N + 1} = f\left(\frac{R_D - R_{Dm}}{R_D + 1}\right)$$

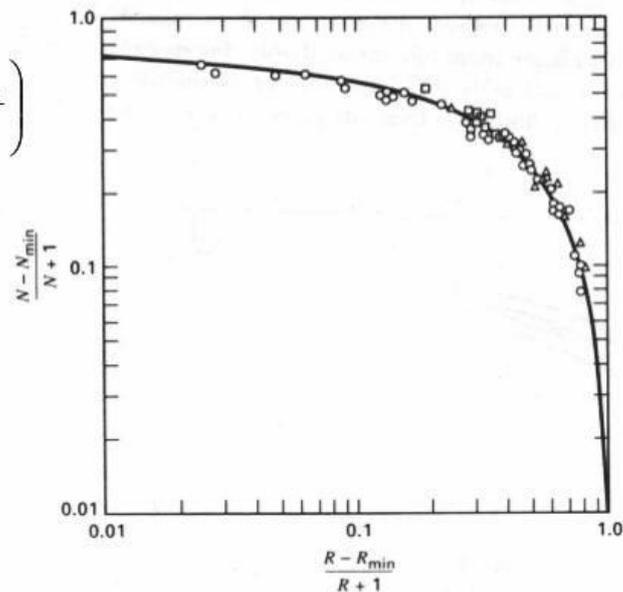


Figure 3.5.1 Gilliland correlation

It is utilized at the operating reflux ratio R is correlated with the minimum R_m obtained using the Underwood method, the minimum number of stages N_m obtained by the Fenske method, and the number of

stages N at the operating R , given

$$\frac{N - Nm}{N + 1} = 1 - \exp \left\{ \left(\frac{1 + 54.4\psi}{11 + 117.2\psi} \right) \left(\frac{\psi - 1}{\psi^{0.5}} \right) \right\}$$

Where $\psi = \left(\frac{R - R_m}{R + 1} \right)$

Estimation of Feed tray Location

The calculation of the theoretical tray number by the short cut method also includes determining the appropriate feed position. The principle of determining the suitable feed position is that the ratio of theoretical tray number of distillation section to stripping section is equal to the ratio of theoretical tray number of distillation section to stripping section calculated by Fenske equation under the condition of full reflux. This empirical relation is as follows:

$$\log \frac{N_R}{N_S} = 0.206 \log \left[\left(\frac{x_{HF}}{x_{LF}} \right) \frac{W}{D} \left(\frac{x_{LW}}{x_{HD}} \right)^2 \right]$$

Where N_R is the number of theoretical stages above the feed tray

N_S is the number of theoretical stages below the feed tray.

The combination of the above parts constitutes a FUG

(Fenske-Underwood-Gilliland) short cut method for a multicomponent distillation calculation.

3.6 Hypothesis and limitations of FUG method

It presumes the most basic assumptions that are generally made while designing that is constant molar flow of components, i.e., for each stage, molar latent heat of vaporization of liquid phase is equal to molar latent heat of condensation of vapour phase. Hence moles of liquid vaporized over each theoretical stage are equal to moles of vapour condensed on that stage. This implies that, molar flow rate of liquid and vapours in distillation section (L and V) and also in stripping section (\dot{L} and \dot{V}) remains constant.

It also assumes that the physical properties of components remain constant throughout the column.

It assumes system to be non-foaming, non-corrosive, non-azeotropic and well thermally insulated, i.e., no heat loss.

4 Case Studies and Results

4.1 Fitting of Antoni Equation Parameters

For the design of the distillation column, the Antoine equation parameters are the basis for calculating the phase equilibrium relationship in a multi-component system. Since the feed components involved in this case are partially missing in the Aspen software property database, the parameter source is divided into two parts: 1. Provided by DDB (Dortmund Data Bank). 2. Aspen physical property database.

The parameters of the Antoni equation for Dibenzofuran are as follows:

DDB format: $\log (P/\text{Torr}) = A - B / (C + T/^{\circ}\text{C})$			
	A	B	C
Fluorene	6.94368	1885.05	178.793

Table 4.1.1 Dibenzofuran Antoni equation parameters

Converted to the standard Antonio equation form as follows:

Standard format: $\log (P/\text{KPa}) = A - B / (C + T/\text{K})$			
	A	B	C
Fluorene	6.94368	1885.05	178.793

Table 4.1.2 Dibenzofuran standard Antoni equation parameters

The other five components of the Antoine equation are obtained from Aspen's physical property database. Since it is a five-parameter form, it

needs to be processed by OriginPro and fitted to a standard three-parameter form.

For Aspen formal: Extended Antoine Equation

Parameters for many components are available for the extended Antoine equation from the Aspen Physical Property System pure component databank.

$$\ln p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i} \ln T + C_{6i}T^{C_{7i}} \text{ for } C_{8i} \leq T \leq C_{9i}$$

Biphenyl:

Components			Temperature Units			Property Units		
Biphenyl			K			KPa		
1	2	3	4	5	6	7	8	9
62.6334	-9415.99	0	0	-6.41553	1.58601e-18	6	528.15	773

Table 4.1.3 Biphenyl Aspen Antoni equation parameters

By OriginPro fitting, it is as follows:

A		B		C		Statistics	
Value	Standard Error	Value	Standard Error	Value	Standard Error	Value	Standard Error
14.64311	0.00689	4532.69004	5.55163	-75.84895	0.22288	2.57785E-5	1

Table 4.1.4 Biphenyl standard Antoni equation parameters

Fitted curves plot:

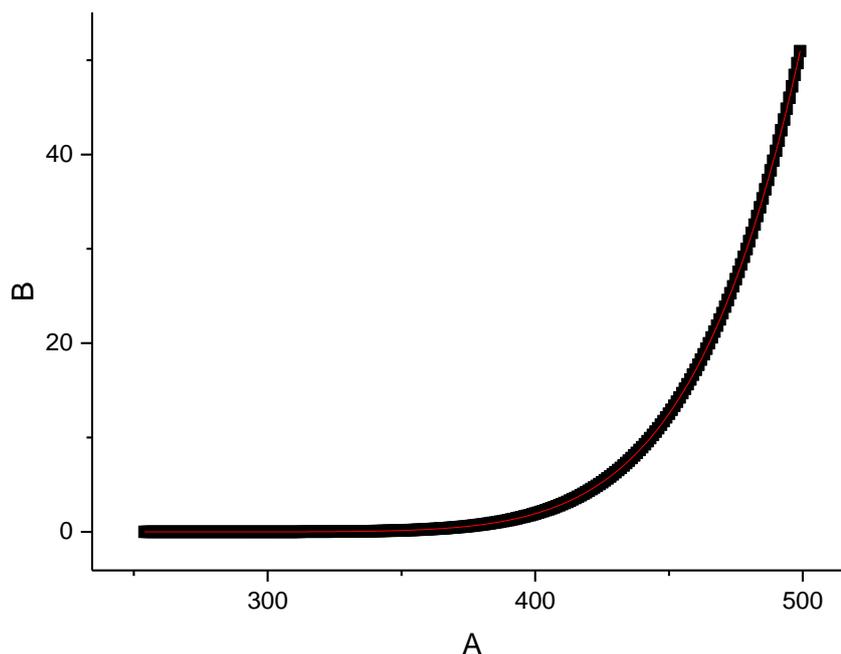


Figure 4.1.1 Biphenyl Antoni equation parameters fitted curves

O-phenylphenol:

Components			Temperature Units			Property Units		
Biphenyl			K			KPa		
1	2	3	4	5	6	7	8	9
86.1307	-12445.3	0	0	-9.365964170	1.76859e-18	6	556.793	792

Table 4.1.5 O-phenylphenol Antoni equation parameters

By OriginPro fitting, it is as follows:

A		B		C		Statistics	
Value	Standard Error	Value	Standard Error	Value	Standard Error	Value	Standard Error
15.74237	0.00862	5124.21229	7.01682	-95.90413	0.24863	1.32878E-5	1

Table 4.1.6 O-phenylphenol standard Antoni equation parameters

Fitted curves plot:

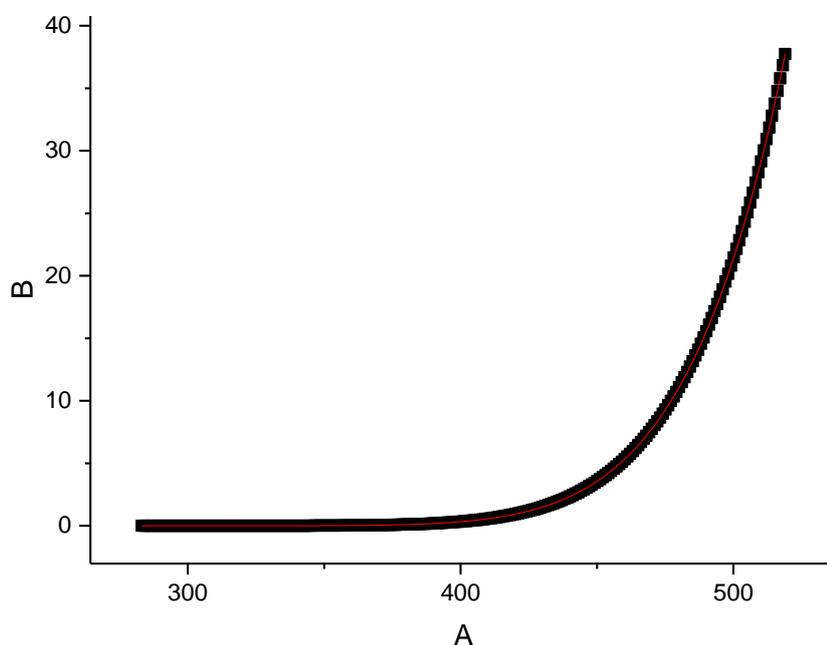


Figure 4.1.2 O-phenylphenol Antoni equation parameters fitted curves

Phenol:

Components			Temperature Units			Property Units		
Biphenyl			K			KPa		
1	2	3	4	5	6	7	8	9
61.0673	-8794.66	0	0	-6.822057360	3.14272e-18	6	454.99	694.25

Table 4.1.7 Phenol Antoni equation parameters

By OriginPro fitting, it is as follows:

A		B		C		Statistics	
Value	Standard Error	Value	Standard Error	Value	Standard Error	Value	Standard Error
15.62165	0.00753	4299.95098	5.18058	-63.99415	0.1852	7.87848E-6	1

Table 4.1.8 Phenol standard Antoni equation parameters

Fitted curves plot:

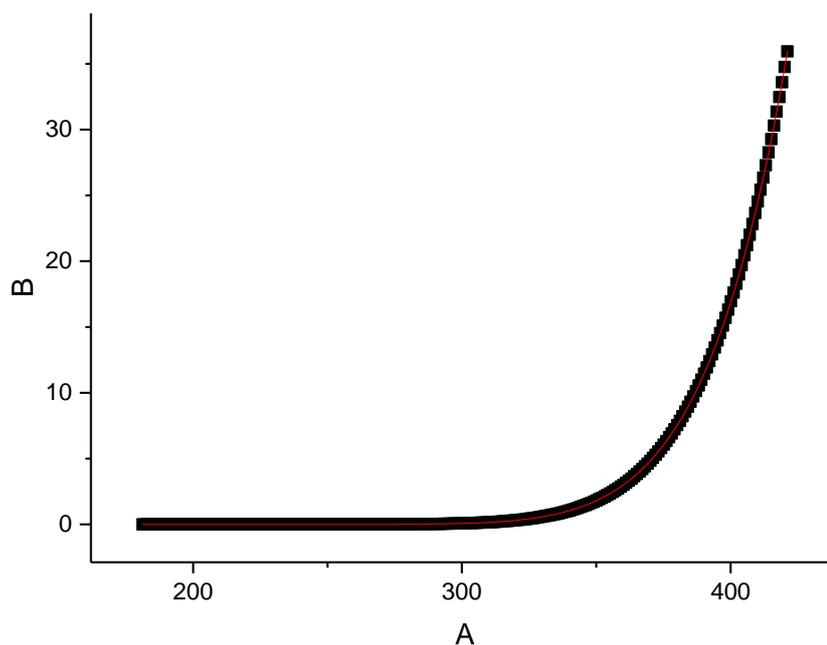


Figure 4.1.3 Phenol Anton equation parameters fitted curves

Toluene:

Components			Temperature Units			Property Units		
Biphenyl			K			KPa		
1	2	3	4	5	6	7	8	9
47.8456	-5962.51	0	0	-4.657420650	6.51866e-18	6	383.78	591.75

Table 4.1.9 Toluene Anton equation parameters

By OriginPro fitting, it is as follows:

A		B		C		Statistics	
Value	Standard Error	Value	Standard Error	Value	Standard Error	Value	Standard Error
14.80654	0.0064	3533.12749	3.49026	-36.25931	0.12055	2.91969E-7	1

Table 4.1.10 Toluene standard Anton equation parameters

Fitted curves plot:

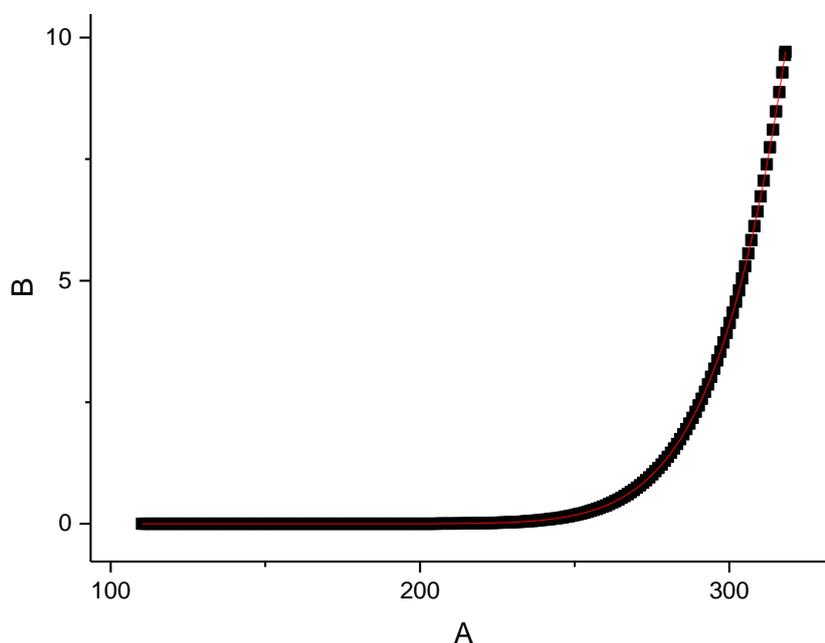


Figure 4.1.4 Toluene Antoni equation parameters fitted curves

4.2 Distillation column feed condition calculation

In the new OPP production process, the raw material is dibenzofuran produced by downstream refineries with an annual yield of 1000t. In the reaction for producing OPP, the selectivity was 72.7%.

The distillation column feed composition is:

component	Formula	Mole fraction
Dibenzofuran	C ₁₂ H ₈ O	0.0196
Biphenyl	C ₁₂ H ₁₀	0.0021
O-phenylphenol	C ₁₂ H ₁₀ O	0.006
Phenol	C ₆ H ₅ OH	0.0003
Toluene	C ₇ H ₈	0.9719

Table 4.2.1 The distillation column feed composition

Calculate the amount of feed by moles:

$$\frac{1000 \times 1000 \times 70\%}{365 \times 168 \times 24} / 0.0196 = 24.2677 \text{ mole/h}$$

The operating pressure of the distillation column is 110KPa, Feeding condition is bubble point feeding i.e. liquid fraction of feed $q = 1$

Calculate the feed bubble point temperature using the bubble point calculation program written in Matlab $T_{\text{feed}} = 386.8488 \text{ K}$.

The program uses Newton iteration method to calculate the bubble point of multi-component system, and uses the software of MATLAB to call the Antonio equation parameters in Excel file and the status of feed components.

Component number	Component	A	B	C
1	Dibenzofuran	14.56505	4716.6129	-84.6091
2	Biphenyl	14.64311	4532.69	-75.849
3	O-phenylphenol	15.74237	5124.2123	-95.9041
4	Toluene	14.80654	3533.1275	-36.2593
5	Phenol	15.62165	4299.951	-63.9942

Table 4.2.2 components Antoni equation parameters

Dibenzofuran	Biphenyl	O-phenylphenol	Toluene	Phenol	P
0.0196	0.0021	0.006	0.9719	0.0003	110 KPa

Table 4.2.3 The distillation column feed condition

4.3 FUG method by Matlab

Dibenzofuran was selected as the light key component (LK) and O-phenylphenol as the heavy key component (HK) according to the

bubble point temperature and separation requirements.

Using the Fenske equation to solve the minimum number of theoretical trays requires knowing the concentration of light and heavy key components in the top and bottom of the column. That is, you must first calculate $x_{1,D}$ (top) and $x_{3,B}$ (bottom) by material balance.

The feed amount was 24.2677 moles. Assume that the division is clear and the following table is based on the material balance relationship:

According to separation requirements, assume $b_1=0.85B$, $d_3=0.003D$

	component	Feed, f_i	b_i	d_i
1	Dibenzofuran	$0.0196*24.2677$	0.85B	$0.0196*24.2677-0.85B$
2	Biphenyl	$0.0021*24.2677$	0	$0.0021*24.2677$
3	O-phenylphenol	$0.006*24.2677$	$0.006*24.2677-0.003D$	0.003D
4	Phenol	$0.0003*24.2677$	0	$0.0003*24.2677$
5	Toluene	$0.9719*24.2677$	0	$0.9719*24.2677$
	Σ	24.2677	B	D

Table 4.2.4 The distillation column compositions

Solve D, B and complete the material balance as follows.

By mass:

	component	Feed, f_i	b_i	d_i
1	Dibenzofuran	$0.0196*24.2677$	0.420970306	0.054676614
2	Biphenyl	$0.0021*24.2677$	0	0.05096217
3	O-phenylphenol	$0.006*24.2677$	0.074288878	0.071317322
4	Phenol	$0.0003*24.2677$	0	0.00728031
5	Toluene	$0.9719*24.2677$	0	23.58577763
	Σ	24.2677	0.495259184	23.77244082

Table 4.2.5 The distillation column feed condition by mass

By molar fraction:

	component	Feed, f_i	b_i	d_i
1	Dibenzofuran	0.0196	0.85	0.0023
2	Biphenyl	0.0021	0	0.00214375
3	O-phenylphenol	0.006	0.15	0.003
4	Phenol	0.0003	0	0.00030625
5	Toluene	0.9719	0	0.992147917

Table 4.2.6 The distillation column feed condition by molar fraction

Calculating relative volatility

Firstly, the relative volatility of the key components, α_D and α_B , was calculated at the top temperature (dew point) and bottom temperature (bubble point).

$$\alpha_D = 1.780715592; \alpha_B = 0.937846241$$

Average Relative Volatility of Light and Heavy Key Components:

$$\alpha_{LH,av} = \sqrt{\alpha_D * \alpha_B} = 0.835$$

Calculate the minimum number of trays:

$$N_m = \frac{\lg\left[\left(\frac{0.0023}{0.003}\right) / \left(\frac{0.15}{0.85}\right)\right]}{\lg 0.835} = 12.89699009 \approx 13$$

Calculating the Minimum Reflux Ratio:

In order to solve the minimum reflux ratio, the root θ of Underwood equation is first required: $\theta = 1.103709042$

Then
$$R_m = \sum \frac{\alpha_i x_{iD}}{\alpha_i - \theta} - 1 = 0.009868$$

Calculate the position of the feed tray:

$$\log \frac{N_R}{N_S} = 0.206 \log \left[\left(\frac{0.006}{0.0196} \right) \frac{0.4677}{23.8} \left(\frac{0.85}{0.003} \right)^2 \right]$$

$$\frac{N_R}{N_S} = 3.57$$

$$N_R + N_S = 13$$

Then $N_S = 2.84463895 \approx 3$. That is, the number of feeding trays should be the tenth tray.

4.4 Design of Aspen RadFrac Simulated Distillation Column

The results of FUG calculation are used as the initial design parameters of Aspen RadFrac simulation to simulate the distillation column design as follows:

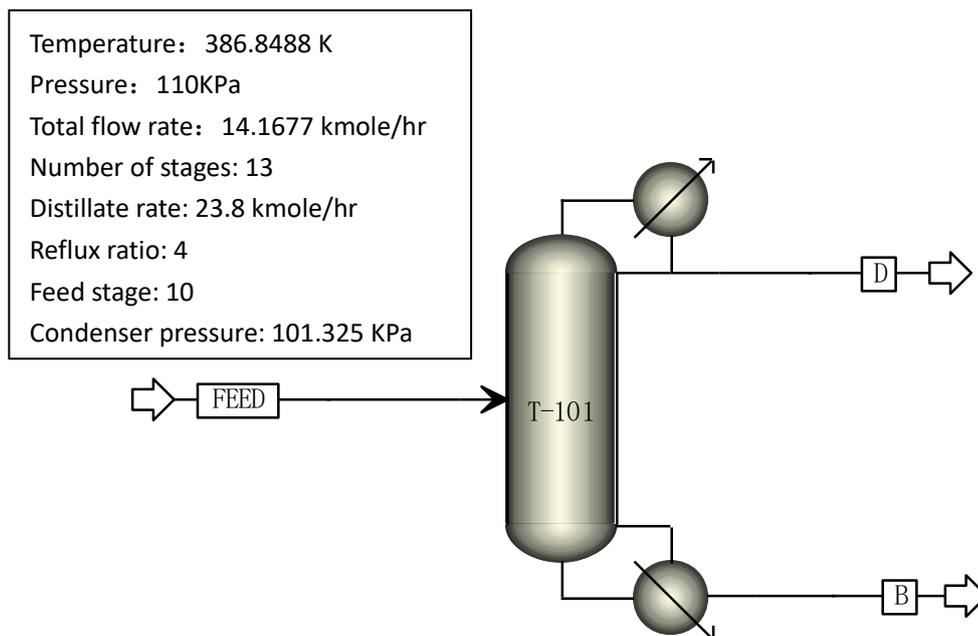


Figure 4.4.1 Initial parameters of distillation column

The components composition of each tray was obtained by simulation of the distillation column by Aspen:

Stage	Dibenzofuran	Biphenyl	O-phenylphenol	Toluene	Phenol
1	0.003345	0.002136	0.003115	0.991098	0.000306
2	0.249188	0.058601	0.26973	0.421566	0.000916
3	0.457276	0.050977	0.448741	0.042826	0.000181
4	0.515136	0.028792	0.43759	0.018444	3.82E-05
5	0.559515	0.01601	0.408442	0.016013	1.95E-05
6	0.600083	0.009039	0.375105	0.015756	1.69E-05
7	0.638335	0.005287	0.340612	0.015749	1.65E-05
8	0.674563	0.003278	0.306364	0.015779	1.63E-05
9	0.708731	0.002205	0.273232	0.015815	1.62E-05
10	0.740691	0.001632	0.241807	0.015854	1.61E-05
11	0.786695	0.000916	0.211664	0.000723	2.04E-06
12	0.818762	0.000505	0.1807	3.29E-05	2.55E-07
13	0.846901	0.000277	0.152821	1.50E-06	3.17E-08

Table 4.2.7 The components composition of each tray of the distillation column

In the simulation results of distillation column, the temperature, pressure, heat condition and gas-liquid flow rate of each tray are as follows:

Stage	Temperature	Pressure	Heat duty	Liquid from (Mole)	Vapor from (Mole)
	K	kPa	kJ/hr	kmol/hr	kmol/hr
1	384.44	101.325	-4.5584E+06	119	0
2	413.948	102.025	0	45.0558	119
3	513.924	102.725	0	50.8413	68.8558
4	536.197	103.425	0	56.1777	74.6413
5	539.49	104.125	0	56.992	79.9777
6	540.565	104.825	0	57.2373	80.792
7	541.308	105.525	0	57.4234	81.0373
8	541.964	106.225	0	57.6008	81.2234
9	542.577	106.925	0	57.7715	81.4008
10	543.163	107.625	0	78.5491	81.5715
11	559.023	108.325	0	85.8658	78.0814
12	560.379	109.025	0	86.5409	85.3981
13	561.018	109.725	4.57E+06	0.4677	86.0732
Liquid feed (Mole)	Liquid product (Mole)	Liquid enthalpy	Vapor enthalpy	Liquid flow (Mole)	Vapor flow (Mole)
kmol/hr	kmol/hr	kJ/kmol	kJ/kmol	kmol/hr	kmol/hr
0	23.8	26341.8	60299.3	95.2	0
0	0	13810.4	64648	45.0558	119
0	0	28280.8	84344.4	50.8413	68.8558
0	0	33773.3	88732.6	56.1777	74.6413
0	0	34876	88557.7	56.992	79.9777
0	0	36169.3	88782.9	57.2373	80.792
0	0	37823.2	89533.4	57.4234	81.0373
0	0	39655.8	90580.6	57.6008	81.2234
0	0	41531.1	91762.6	57.7715	81.4008
24.2677	0	43365.8	92981.7	78.5491	81.5715
0	0	50517.9	101877	85.8658	78.0814
0	0	52600.9	104056	86.5409	85.3981
0	0.4677	54282.7	105730	0.4677	86.0732

Table 4.2.8 the simulation results of distillation column

4.5 Summary and Check

Checking the preliminary simulation results of Aspen, the separation requirements were basically met. O-phenylphenol and Dibenzofuran were concentrated in the bottom liquid of the bottom of the column to achieve purification of the target product and recovery of unreacted dibenzofuran.

However, it is still necessary to optimize the operation conditions of distillation column, find the appropriate number of trays, reflux ratio, feed position, operation pressure, etc. to meet the separation requirements while controlling the energy consumption of distillation column, and determine the optimal design scheme of distillation column.

In addition, it is necessary to verify the accuracy of the matlab programming method for the bubble point temperature calculation of each tray according to the composition, pressure and temperature results of each tray simulated by Aspen.

Number of plates	Aspen simulates the bubble point temperature of each tray	Matlab calculates the bubble point temperature of each tray according to the composition	deviation
1	384.4400	383.3479	1.0921
2	413.9480	415.1417	-1.1937
3	513.9240	512.5010	1.4230
4	536.1970	535.8647	0.3323

5	539.4900	539.1873	0.3027
6	540.5650	540.0045	0.5605
7	541.3080	540.4507	0.8573
8	541.9640	540.8054	1.1586
9	542.5770	541.1240	1.4530
10	543.1630	541.4259	1.7371
11	559.0230	560.3528	-1.3298
12	560.3790	561.6877	-1.3087
13	561.0180	562.1261	-1.1081

Table 4.2.9 the deviation of the temperature of the tray obtained by the two methods

By verifying the deviation of the temperature of the tray obtained by the two methods, it is found that the deviation is basically maintained at about one degree (maximum of 1.73 degrees, minimum of 0.3 degrees), which proves that the previous bubble point calculation is correct, and the result is trustworthy.

5 Optimization Design of Distillation Case Studies and Results

The optimization of the distillation process is based on the objective function to solve the optimal design parameters, such as the number of plates, the feed position, the reflux ratio, the operating pressure, etc., to solve the process and equipment design problems. Under the premise of ensuring product quality and stable operation, the yield is improved by changing the reflux ratio, feed position, feed state, etc., saving energy and reducing consumption.

5.1 Sensitivity Analysis of Tray Number

It presumes the most basic assumptions that are generally made while designing that is constant molar flow of components, i.e., for each stage, molar latent heat of vap

The most important design parameter of distillation column is the number of trays. The more theoretical trays, the better separation effect and the higher manufacturing cost. This needs to find a balance between separation effect and manufacturing cost, to meet the separation requirements of actual production, while reducing the number of trays is to reduce manufacturing costs.

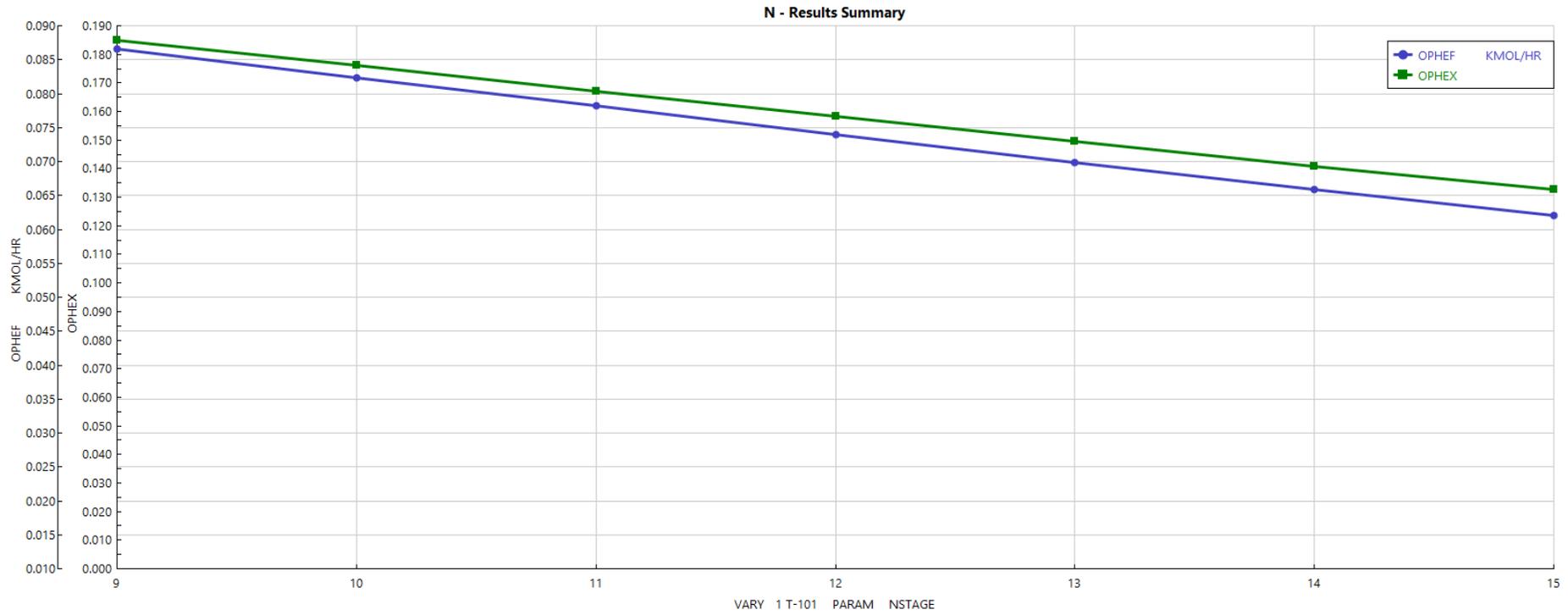


Figure 5.1.1 Sensitivity Analysis of Tray Number

OPHEF represents the flow rate of the target product O-phenylphenol, and OPHEX is its molar fraction.

Analysis of these two data shows that when the number of trays varies from 9 to 15, with the increase of the number of trays, the molar fraction of the target product we hope to obtain decreases, but because the molar fraction of O-phenylphenol in the components is quite small, the effect of the change of the number of trays on the separation effect is negligible. Therefore, the number of trays is not the main factor to consider, only to meet the production requirements.

In addition, considering the need to recycle unreacted dibenzofuran and the separation requirements of solvent toluene, the number of trays in the distillation column should be kept at 13.

5.2 Sensitivity Analysis of Feed Tray Position

It is necessary to find the most suitable feed position at the same number of plates and reflux ratio so that the separation purity of the top and bottom products is highest.

At the same tray number and reflux ratio, the effect of feed position on O-phenylphenol content is shown in the figure below.

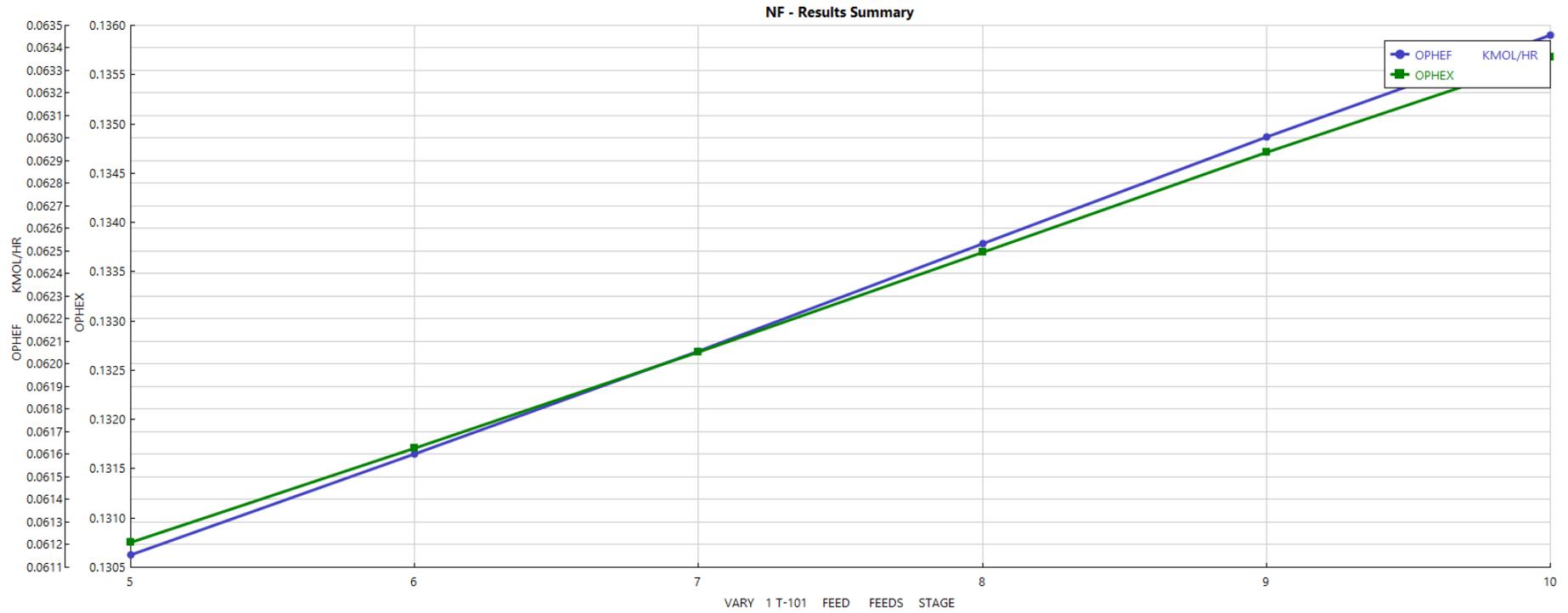


Figure 5.2.1 Sensitivity Analysis of Feed Tray Position

It can be seen that the content of O-phenylphenol increases with the decrease of feed position. It is proved that in this distillation system, too high a stripping section will affect the efficiency of the column.

Therefore, in the actual production, under the premise of ensuring the production quality and within the range of possible feed trays, the feeding position can be lowered as much as possible to obtain a better separation effect.

5.3 Sensitivity Analysis of Reflux Ratio

For distillation column, optimizing reflux ratio and theoretical tray number can obtain reasonable temperature distribution in the column, so as to achieve the best separation effect. If the reflux ratio is too low, not only the dry plate of the distillation tray will appear, but also the separation effect will be poor. Too high will result in waste of energy.

The effect of reflux ratio on O-phenylphenol content is shown in the figure below.

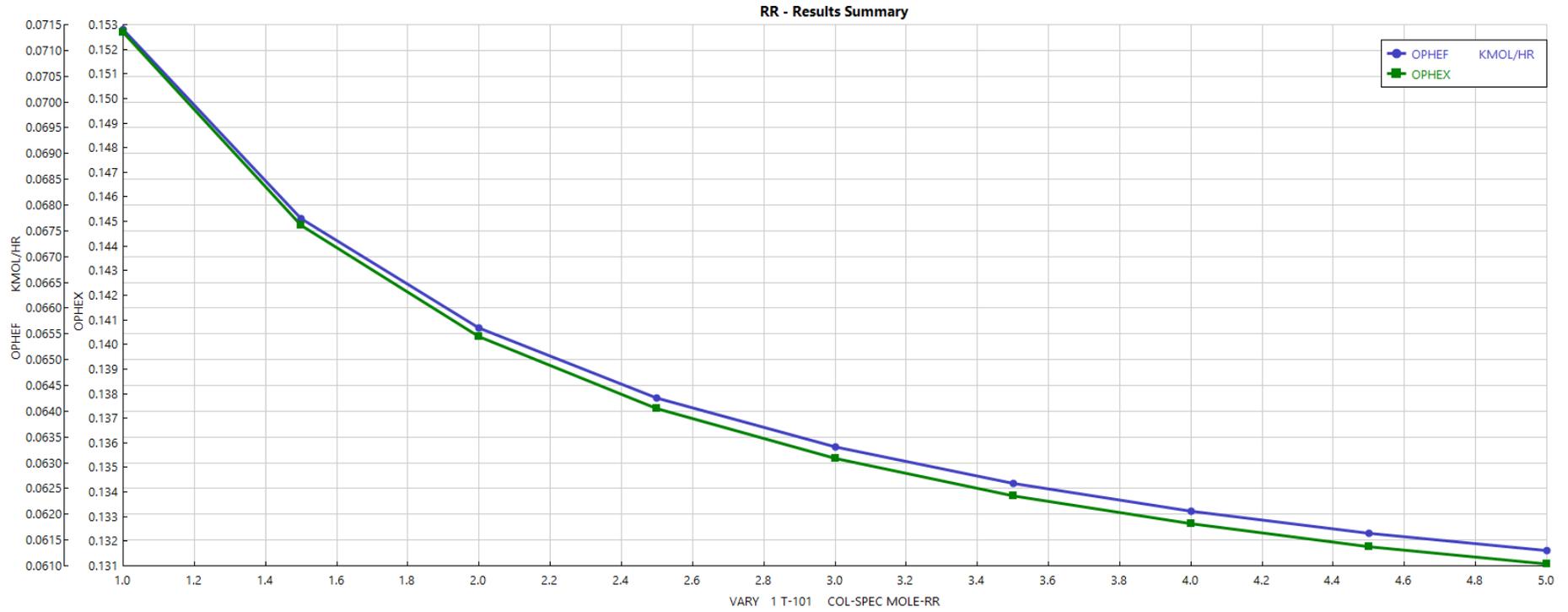


Figure 5.3.1 Sensitivity Analysis of Reflux Ratio

It can be seen that as the reflux ratio increases, the content of the top O-phenylphenol decreases, and there is a tendency to decrease sharply between 1 and 1.6, so decreasing the reflux ratio increases the content of the target product. Simultaneously reducing the reflux ratio reduces the load on the overhead condenser and the bottom reboiler. However, it should also be noted that too small a reflux ratio will affect the normal operation of the distillation column. Therefore, under the premise of ensuring the normal operation of the rectification column, it is necessary to prevent the occurrence of dry plate conditions, moderately reduce the reflux ratio, separate the appropriate O-phenylphenol content and reduce the operation cost.

5.4 Sensitivity Analysis of Feed Pressure

The standard atmospheric pressure is 101 KPa, so for sensitivity analysis of the feed pressure, standard atmospheric pressure is selected as the initial value to find the feed pressure that is most suitable for the separation of the distillation column. Smaller feed pressures reduce operating costs and energy consumption but also require acceptable separation.

The effect of feed pressure on O-phenylphenol content is shown in the figure below.

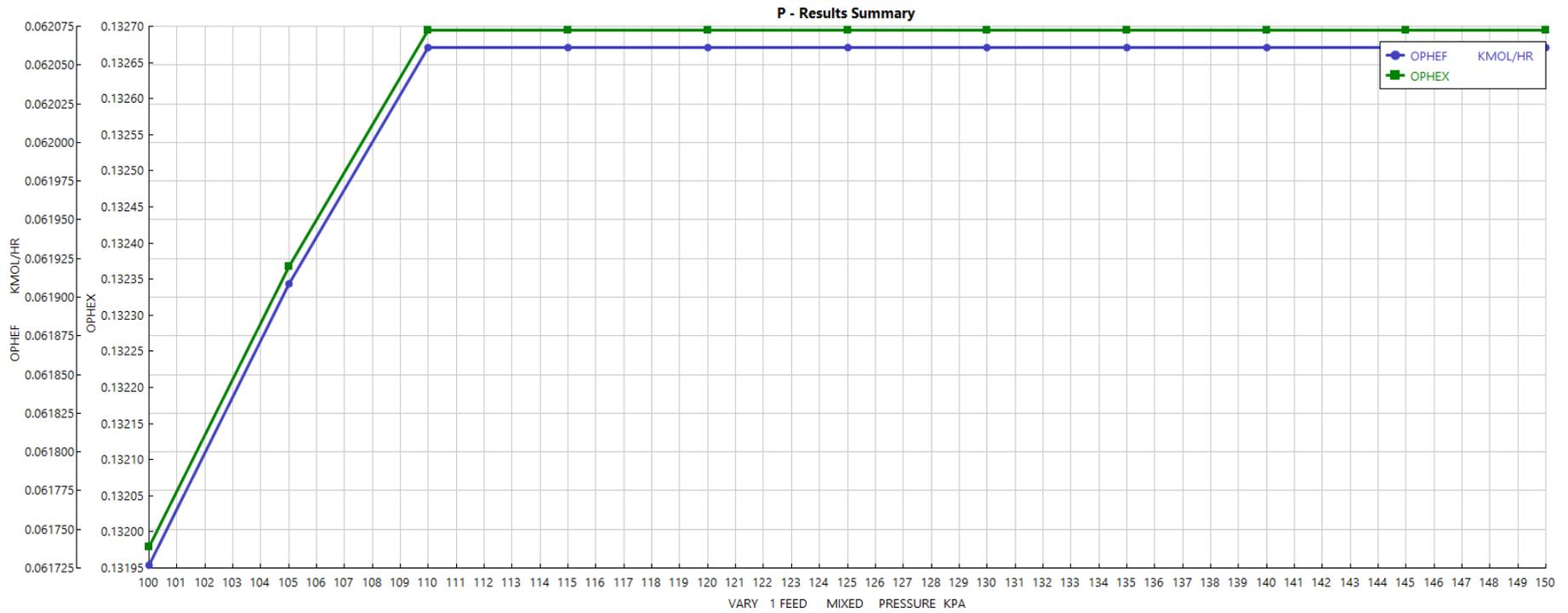


Figure 5.4.1 Sensitivity Analysis of Feed Pressure

It can be seen that with the increase of feed pressure, the content of O-phenylphenol will increase until the pressure increases to 110 KPa. Therefore, the optimum feed pressure is to increase the pressure to 110 KPa instead of choosing the normal feed pressure in order to obtain the optimum separation effect.

6 Concluding Remarks

In the industrial design of the distillation column, it is often encountered that a certain physical property data of the component involved is missing. Therefore, besides the method of querying physical property database, it also needs to rely on reasonable mathematical model and separation theory of chemical engineering to simulate, obtain reasonable design scheme, and then use Aspen and other process simulation software to simulate and optimize the design parameters of distillation column.

For the design optimization of the rectification column, it is necessary to consider the separation effect and obtain the best separation effect, and also need to consider the operating cost of the equilibrium rectification column. Increasing the feed pressure, the number of trays, and increasing the reflux ratio tend to optimize the separation, but at the same time increase the energy consumption and cost of the distillation column.

However, when reducing the reflux ratio, it is also necessary to prevent the occurrence of dry plates in the rectification column, affect the normal operation of the rectification column, and increase the risk factor.

In addition, this paper involves the use of Newton iteration to calculate the bubble point and dew point temperature of a multi-component system.

The calculation of bubble point and dew point temperature is the most basic problem that needs to be solved in vapor-liquid separation operation. However, this method requires accurate Antonii equation parameters as a prerequisite to ensure the accuracy of the calculated bubble point and dew point temperature.

Reference