

A

THESIS ON

**“VAPOUR LIQUID EQUILLIBRIUM MODELING USING
UNIFAC GROUP CONTRIBUTION METHOD AND ITS
APPLICATION IN DISTILLATION COLUMN DESIGN AND
STEADY STATE SIMULATION”**

A Report Submitted In Partial Fulfilment of the Requirements for the Degree Of
Bachelor of Technology (Chemical Engineering)

SUBMITTED BY

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CERTIFICATE

This is to certify that the thesis entitled, **“vapour liquid equilibrium modeling using UNIFAC group contribution method and its application in distillation column design and steady state simulation”** submitted by Managobinda Behera in partial fulfilments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

For efficient design of distillation equipment or any other separation processes which are diffusional in nature requires quantitative understanding of vapour liquid equilibria. In VLE phases are expressed through vapour phase fugacity coefficients and the liquid phase activity coefficients. At low or modest pressures fugacity coefficient can be estimated easily for very simple mixtures or ideal solutions, but for non-ideal mixtures, estimation of liquid phase activity coefficient is quite difficult. Experimental mixture data are required to calculate activity coefficient. Since the variety of chemical species is separated out in chemical process industry and it is not necessary to every physicochemical and VLE experimental data are available in open database. In this regard researchers developed a new 'group contribution model which is able to predict the VLE data. The concept of group contribution method provide a correlation which correlate limited experimental data in such a way with confidence of activity coefficients of those mixtures where little or experimental data are not available. In this concept we have to know only about the each functional group of each molecule. Each molecule is considered as the sum of the functional groups which constituent that molecule; the thermodynamic properties of a solution are then correlated in terms of the functional groups which comprise the mixture. The particular promising method for calculating activity coefficient from group contributions method is provided by UNIFAC (universal quasi chemical functional group activity coefficient model). This method is a consequence of a model for activity coefficients called UNIQUAC (universal quasi chemical). The word UNIFAC stands for UNIQUAC functional group activity coefficients.

The activity coefficients of binary mixtures were successfully calculated by using UNIFAC model. And using these activity coefficients the design of distillation column was done for the separation of these binary mixtures.

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LIST OF SYMBOLS

SYMBOLS	MEANING
H	vapour phase enthalpy
h	liquid phase enthalpy
H_f	feed enthalpy
V	total vapour flow
V	component vapour flow
L	total liquid flow
L	component liquid flow
F	total feed
f	component feed
S^L	liquid side stream
S^V	vapour side stream.
a_{nm}	UNIFAC binary interaction parameter
$K_{n,i}$	equilibrium ratio of component i on stage n
Q_k	group area parameter of group k
R_k	group volume parameter of group k
x_i	mole fraction of component i in liquid phase
$y_i =$	mole fraction of component i in vapour phase

SYMBOLS	MEANING
γ_i	Activity coefficient of the component i in the mixture
Φ_i	Fugacity coefficient of the component i in the mixture
f_i^0	Fugacity of the pure component i
P	total pressure
p_i^s	saturation vapour pressure of component i
v_i	molar volume liquid
T	temperature
γ_i^C	combinatorial activity coefficient of component i
γ_i^R	residual activity coefficient of component i
θ_i	molecular surface area fraction
Φ_i	molecular volume fraction
$\mathbf{v}_k^{(i)}$	number of groups of kind k in molecular species i
r_i	molecular van der waals volume
q_i	molecular surface area
V_k	van der waals group volume
A_k	van der waals group surface area
Γ_k	group residual activity coefficient

SYMBOLS

MEANING

$\Gamma_k^{(i)}$	the residual activity coefficient of group k in a reference solution containing only Molecules of type i
X_m	fraction of group m in mixture;
Ψ_{mk}	UNIFAC parameter
$\eta_{n,i}$	murphee stage efficiency
Q_k	group area parameter for group k

CHAPTER-1

INTRODUCTION

INTRODUCTION

1.1 Vapour Liquid Equilibria

Vapour-liquid equilibrium (VLE), is a condition where a liquid and its vapour (gas phase) are in equilibrium with each other, a condition or state where the rate of evaporation (liquid converting to vapour) equals the rate of condensation (vapour converting to liquid) on a molecular level such that there is no net vapour-liquid inter-conversion. Although in theory equilibrium takes a very long time to reach, such equilibrium is practically reached in a relatively closed location if the liquid and its vapour are allowed to stand in contact with each other for a while with no interference or only gradual interference from the outside.

In process design, the required phase equilibrium information is commonly expressed by K values.

$$K_i = \frac{y_i}{x_i} \quad (1.1)$$

Where y_i , is the mole fraction of component i in the vapour phase and x_i , is the mole fraction of component i in the liquid phase. K_i is the equilibrium constant for the component i . Using thermodynamics

$$K_i = \frac{\gamma_i f_i^0}{P \Phi_i} \quad (1.2)$$

Where γ_i , is the liquid-phase activity coefficient Φ_i is the vapour-phase fugacity coefficient, and P is the total pressure of the mixture. For condensable components as considered here, f_i^0 is the fugacity of pure liquid i at system temperature T and pressure P . It is calculated from [Prausnitz, 1969]

$$f_i^0 = p_i^s \Phi_i^s \exp \int_{p_i^s}^P \frac{v_i dP}{RT} \quad (1.3)$$

Where, for pure liquid i , p_i^s is the saturation (vapour) pressure, Φ_i^s is the fugacity coefficient at saturation, and v_i , is the molar liquid volume, all at temperature T . Only pure- component

data are required to evaluate f_i^0 . The fugacity coefficients ϕ_i (in the mixture) and ϕ_i^s (pure i at saturation) are found from vapour-phase volumetric properties. Normally, at the low pressures considered here, these fugacity coefficients do not deviate much from unity. To determine K factors, the most difficult-to-estimate quantity is the activity coefficient γ_i .

1.2 Activity Coefficient

Activity coefficients may be measured experimentally or calculated theoretically, using the Debye-Hückel equation or extensions such as Davies equation or specific ion interaction theory (SIT) may also be used. Alternatively correlative methods such as UNIQUAC, NRTL or UNIFAC may be employed, provided fitted component-specific or model parameters are available.

1.2.1 Debye-Hückel equation

In order to calculate the activity of an ion in a solution, one must know the concentration and the activity coefficient, γ . The activity of some ion species C, a_c , is equal to dimensionless measure of the concentration of C, $[C]$ multiplied by the activity coefficient of C, γ [P. Debye and E. Hückel (1923)].

$$a_c = \gamma \frac{[C]}{[C^0]} \quad (1.4)$$

$[C^0]$ represents the concentration of the chosen standard state, e.g. 1 mol/kg if we work in molality.

1.2.2 Davies equation

The Davies equation is an empirical extension of the Debye–Hückel equation which can be used to calculate activity coefficients of electrolyte solutions at relatively high concentrations. The equation was refined by fitting to experimental data. The final form of the equation gives the mean molal activity coefficient, f_{\pm} , of an electrolyte which dissociates into ions having charges z_1 and z_2 as a function of ionic strength, I [Davies 1962].

$$-\log f_{\pm} = 0.5 z_1 z_2 \left(\frac{\sqrt{I}}{1+1.5\sqrt{I}} - 0.30 I \right) \quad (1.5)$$

The second term, $0.30 I$, goes to zero as the ionic strength goes to zero, so the equation reduces to the Debye–Hückel equation at low concentration. However, as concentration increases, the second term becomes increasingly important, so the Davies equation can be used for solutions too concentrated to allow the use of the Debye–Hückel equation. For 1:1 electrolytes the difference between measured values and those calculated with this equation is about 2% of the value for 0.1 m solutions. The calculations become less precise for electrolytes that dissociate into ions with higher charges. Further discrepancies will arise if there is association between the ions, with the formation of ion-pairs, such as $\text{Mg}^{2+}\text{SO}_4^{2-}$.

1.2.3 Non-Random Two Liquid model (NRTL)

The Non-Random Two Liquid model (NRTL model) is an activity coefficient model that correlates the activity coefficients γ_i of a compound i with its mole fractions x_i in the concerning liquid phase. It is frequently applied in the field of chemical engineering to calculate phase equilibria. The concept of NRTL is based on the hypothesis of Wilson that the local concentration around a molecule is different from the bulk concentration. This difference is due to a difference between the interaction energy of the central molecule with the molecules of its own kind and that with the molecules of the other kind. The energy difference introduces also non-randomness at the local molecular level. The NRTL model belongs to the so-called local composition models [Renon , Prausnitz 1968].

In the case of the description of a vapour liquid equilibria it is necessary to know which saturated vapour pressure of the pure components was used and whether the gas phases

was treated as an ideal or a real gas. Accurate saturated vapour pressure values are important in the determination or the description of an azeotrope. The gas fugacity coefficients are mostly set to unity (ideal gas assumption), but vapour-liquid equilibria at high pressures (i.e. > 10 bar) need an equation of state to calculate the gas fugacity coefficient for a real gas description.

1.2.4 UNIQUAC model

UNIQUAC (UNIversal QUAsiChemical) is an activity coefficient model used in description of phase equilibria [Abrams , Prausnitz 1975]. The model is a so-called lattice model and has been derived from a first order approximation of interacting molecule surfaces in statistical thermodynamics. The model is however not fully thermodynamically consistent due to its two liquid mixture approach. In this approach the local concentration around one central molecule is assumed to be independent from the local composition around another type of molecule.

It has been shown that while the local compositions are correlated, ignoring this correlation gives little effect on the correlation of activity coefficients [McDermott 1976]. Today the UNIQUAC model is frequently applied in the description of phase equilibria (i.e. liquid-solid, liquid-liquid or liquid-vapour equilibrium). The UNIQUAC model also serves as the basis of the development of the group contribution method UNIFAC, where molecules are subdivided in atomic groups.

1.2.5 The UNIFAC model

The UNIFAC method is a semi-empirical system for the prediction of non-electrolyte activity estimation in non-ideal mixtures. UNIFAC uses the functional groups present on the molecules that make up the liquid mixture to calculate activity coefficients. By utilizing interactions for each of the functional groups present on the molecules, as well as some binary interaction coefficients, the activity of each of the solutions can be calculated.

So, main objective of my project work is the calculation of activity coefficient of the binary mixture using UNIFAC model.

The calculated activity coefficient is compared with experimental activity coefficient and these calculated activity coefficient is used for steady state simulation of distillation column.

CHAPTER-2
THERMODYNAMICS AND
PREVIOUS WORK

THERMODYNAMICS OF THE MODEL

2.1 Origin And Range Of Applicability Of The UNIFAC Method

A large part of chemical engineering design is concerned with separation operations. Many of these are diffusional operations of the phase-contacting type, and distillation, absorption, and extraction are the most common. For rational design of such separation processes, we require quantitative information on phase equilibria in multi-component mixtures. Satisfactory experimental equilibrium data are only rarely available for the particular conditions of temperature, pressure, and composition required in a particular design problem. It is therefore necessary to interpolate or extrapolate existing mixture data or, when suitable data are lacking, to estimate the desired equilibria from some appropriate correlation. A very useful correlation for this purpose, UNIFAC, was recently proposed. The UNIFAC method was originally developed by Fredenslund [Fredenslund, Gmehling, Rasmussen (1977)]. Later the method was revised and its range of applicability considerably extended.

The UNIFAC (UNIQUAC Functional Group Activity Coefficients) group-contribution method is a reliable and fast method for predicting liquid-phase activity coefficients in non-electrolyte, non-polymeric mixtures at low to moderate pressures and temperatures between 300 and 425 °K. It has become widely used in practical chemical engineering applications, most notably in phase equilibrium calculations in cases where little or no relevant experimental information is available.

2.2 Advantages And Disadvantages (of UNIFAC)

Advantages:

1. flexibility, because UNIFAC has a well founded basis for establishing group sizes and shapes.
2. simplicity, because UNIFAC parameters are nearly independent of temperature for the temperature range considered here.

3. large range of applicability, because UNIFAC parameters are now available for considerable number of different functional groups.

Disadvantages

1. All components must be condensable.
2. The temperature range considered is typically 30-125⁰C.
3. UNIFAC method does not presently apply to mixtures containing polymers.
4. It should rarely be applied to mixtures containing components with more than ten functional groups.

2.3 Application of UNIFAC Group Contribution Method

The UNIFAC method is most successful. It has been used in many areas, for example;

- (1) To calculate vapour-liquid equilibria (VLE).
- (2) For calculating liquid-liquid equilibria,
- (3) For calculating solid-liquid equilibria,
- (4) For determining activities in polymer solutions,
- (5) For determining vapour pressures of pure components,
- (6) For determining flash points of solvent mixtures,
- (7) For determining solubility's of gases,
- (8) For estimation of excess enthalpies.

2.4 UNIFAC Correlation (group contribution method)

A group contribution method uses the principle that some simple aspects of the structures of chemical components are always the same in many different molecules. The smallest common constituents are the atoms and the bonds. All organic components for example are built of carbon, hydrogen, oxygen, nitrogen, halogens, and maybe sulphur. Together with a single, a double, and a triple bond there are only ten atom types and three bond types to build thousands, of components. The next slightly more complex building blocks of components are functional groups which are themselves built of few atoms and bonds.

The large advantage of a group contribution method is that it enables systematic interpolation and extrapolation of vapor-liquid equilibrium data simultaneously for many chemically related mixtures. Most important, it provides a reasonable method for predicting properties of mixtures where no mixture data at all are available. For such mixtures it is not necessary to measure the intermolecular interactions because these can be calculated whenever appropriate group interaction parameters are known. These, however, are found from experimental data containing not the same molecules as those in the mixture of interest, but containing the same groups. The main advantage, then, is a form of "molecular scale-up." While there are many thousands of liquid non-electrolyte mixtures of interest in chemical technology, these mixtures can be constituted from a much smaller (around 50 or 100) number of functional groups. The UNIFAC correlation attempts to break down the problem of predicting interactions between molecules by describing molecular interactions based upon the functional groups attached to the molecule. This is done in order to reduce the sheer number of binary interactions that would be needed to be measured to predict the state of the system.

UNIFAC group contribution method is quite fast and accurate. This can be seen from the graph between the experimental and the value obtained by unifac model.

2.5 The Group Interaction Parameters

All group contribution method is necessarily approximation because any group within a molecule is not completely independent of the other groups within that molecule. But it is precisely this independence which is essential basis of group contribution method. Interdependence of groups within a molecule is allowed. Increasing distinction of groups however, also increases the number of group interactions that must be characterized. At last, if we carry group distinction to the limit we recover the individual molecules. In that event, the advantage of the group contribution method is lost. Only judgement and experience must tell how to define functional groups so as to achieve a compromise between accuracy of prediction and engineering utility.

2.6 The UNIFAC Model

UNIFAC provides a method for estimating activity coefficients in non electrolyte liquid mixtures. To use this method, no experimental data are required for the particular mixture of interest. In addition to the temperature and composition of the system, it is necessary only to know the molecular structure of every component in the mixture and the necessary group parameters. A large number of group-interaction parameters of different groups have been calculated.

UNIFAC is an abbreviation that indicates Universal quasi-chemical Functional Group Activity Coefficients. It is based on the quasi-chemical theory of liquid solutions.

Equations giving the activity coefficients as functions of composition and temperature are here stated. The UNIFAC model has a combinatorial contribution to the activity coefficients, essentially due to differences in size and shape of the molecules, and a residual contribution, essentially due to energetic interactions.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2.1)$$

Combinatorial residual

I. **Combinatorial Part:** The combinatorial contribution is

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\Phi_i}{\Phi_1} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (2.2)$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1); z=10$$

$$\theta_i = \frac{q_i x_i}{\sum_j x_j q_j}; \quad \Phi_i = \frac{r_i x_i}{\sum_j x_j r_j} \quad (2.3)$$

Pure-component parameters r_i and q_i are respectively measures of molecular van der Waals volumes and molecular surface areas. They are calculated as the sum of the group volume and group-area parameters, R_k and Q_k (Bondi, 1968)

$$r_i = \sum_k v_k^{(i)} R_k \quad ; \quad q_i = \sum_k v_k^{(i)} Q_k \quad (2.4)$$

Where $v_k^{(i)}$, always an integer, is the number of groups of type k in molecule i . Group parameters R_k and Q_k are obtained from van der Waals group volumes and surface area V_k and A_k , given by Bondi (1968)

$$R_k = V_k / 15.17; \quad Q_k = A_k / (2.5 * 10^9) \quad (2.5)$$

II. Residual part:

The contribution from group interactions, the residual part, is assumed to be the sum of the individual contributions of each solute group in the solution less the sum of the individual contributions in the pure component environment.

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (2.6)$$

All groups

Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i .

The individual group contributions in any environment containing groups of kinds 1,2 ...N are assumed to be only a function of group concentrations and temperature.

$$\ln \Gamma_k = Q_k [1 - \ln (\sum_m \theta_m \Psi_{mk}) - \sum_m (\theta_m \Psi_{km} / \sum_n \theta_n \Psi_{nm})] \quad (2.7)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} ; \quad X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i} \quad (2.8)$$

x_m is the fraction of group m in the mixture.

$$\Psi_{mk} = \exp[-(a_{nm}/T)] \quad (2.9)$$

Parameter a_{nm} characterizes the interaction between group's n and m . For each group-group interaction, there are two parameters: $a_{nm} \neq a_{mn}$. No ternary (or higher) parameters are needed to describe multi-component equilibria.

PREVIOUS WORK

Jurgen Gmehling et al. (1982) Used the UNIFAC model for predicting the activity coefficient for many non-electrolyte liquid mixtures. In his work some of the gaps in the group-interaction parameter table have been filled, and parameters were reported for seven new groups.

Henrik K. Hansen et al. (1991) presented the revised UNIFAC interaction parameters for 74 pairs of groups, finally they added six main groups so that UNIFAC cover the mixtures of chlorofluorohydrocarbons, amides, glycol ethers, sulphides, morpholine and thiophenes.

Jurgen Gmehling et al. (1993) proposed a modified UNIFAC model, for increase the range of its applicability, the temperature-dependent group interaction parameters of the modified UNIFAC have been fitted for 45 main groups using phase equilibrium information (VLE, H^E , γ^{cc} LLE) stored in the Dortmund data bank. It was found that the results of other group contribution methods confirm the high reliability of the modified UNIFAC method.

CHAPTER-3
VLE CALCULATION
USING UNIFAC

VLE CALCULATION USING UNIFAC

3.1 Case 1(A) System is Di-ethyl Ketone (1) And n-Hexane (2)

Table-3.1: VLE data for diethyl ketone (1) and n-hexane (2) at 338.15k [Smith, Van Ness, Abbott 2005]

P/kpa	X ₁	Y ₁	ln γ_1 (Experimental)
90.15	0.0	0.0	-----
91.78	0.063	0.049	0.901
88.01	0.248	0.131	0.472
78.89	0.443	0.215	0.278
76.82	0.508	0.248	0.257
73.39	0.561	0.268	0.190
66.45	0.64	0.316	0.123
57.70	0.763	0.412	0.072
50.16	0.834	0.490	0.016
45.7	0.874	0.570	0.027
29.00	1.00	1.00	0.000

Here we have n-hexane is made up of two CH₃ and four CH₂ group where as di ethyl ketone is made up of one CH₂CO ,one CH₃ and one CH₂ groups.

Table 3.2 group size (R_k) and group surface area (Q_k) [Fredenslund, Gmehling, Rasmussen 1977]

GROUPS	NUMBERS	R_k	Q_k
CH ₃	1	0.9011	0.848
CH ₂	2	0.6744	0.540
CH ₂ CO	3	1.4457	1.180

RESULTS:

Solving the equations of UNIFAC model in MATLAB we will get the calculated activity coefficient.

Table 3.3 Activity Coefficient of The System Using UNIFAC

P/kpa	X1	Y1	$\ln \gamma_1$ (Theoretical)
90.15	0.0	0.0	-----
91.78	0.063	0.049	0.8589
88.01	0.248	0.131	0.5394
78.89	0.443	0.215	0.3034
76.82	0.508	0.248	0.2428
73.39	0.561	0.268	0.1992
66.45	0.64	0.316	0.1430
57.70	0.763	0.412	0.0746
50.16	0.834	0.490	0.0446
45.7	0.874	0.570	0.0310
29.00	1.00	1.00	0.000

3.2 Case 1(B) System is n-Hexane (1) And Di-ethyl Ketone (2)

Table 3.4 VLE data for n-hexane (1) and diethyl ketone (2) at 338.15k [Smith, Van Ness, Abbott 2005]

P/kpa	X1	Y1	$\ln \gamma_1$ (Experimental)
90.15	0.0	0.0	0.000
91.78	0.063	0.049	0.033
88.01	0.248	0.131	0.121
78.89	0.443	0.215	0.210
76.82	0.508	0.248	0.264
73.39	0.561	0.268	0.306
66.45	0.64	0.316	0.337
57.70	0.763	0.412	0.462
50.16	0.834	0.490	0.536
45.7	0.874	0.570	0.548
29.00	1.00	1.00	-----

Here we have n-hexane is made up of two CH_3 and four CH_2 group where as diethyl ketone is made up of one CH_2CO , one CH_3 and one CH_2 groups. With the same values of R_k and Q_k mentioned above we can calculate the theoretical values of the activity coefficient using UNIFAC group contribution method.

RESULTS:

Solving the equations of UNIFAC model in MATLAB we will get the calculated activity coefficient.

Table 3.5 Activity Coefficient of the System Using UNIFAC

P/kpa	X1	Y1	$\ln \gamma_1$ (calculated)
90.15	0.0	0.0	0.000
91.78	0.063	0.049	0.0044
88.01	0.248	0.131	0.2139
78.89	0.443	0.215	0.2239
76.82	0.508	0.248	0.2636
73.39	0.561	0.268	0.2959
66.45	0.64	0.316	0.3714
57.70	0.763	0.412	0.4728
50.16	0.834	0.490	0.5434
45.7	0.874	0.570	0.5808
29.00	1.00	1.00	-----

3.3 Comparison Between Experimental Value And Theoretical Values:

Case 1(A): System Is Di-ethyl Ketone (1) And n-Hexane (2) At 65⁰c

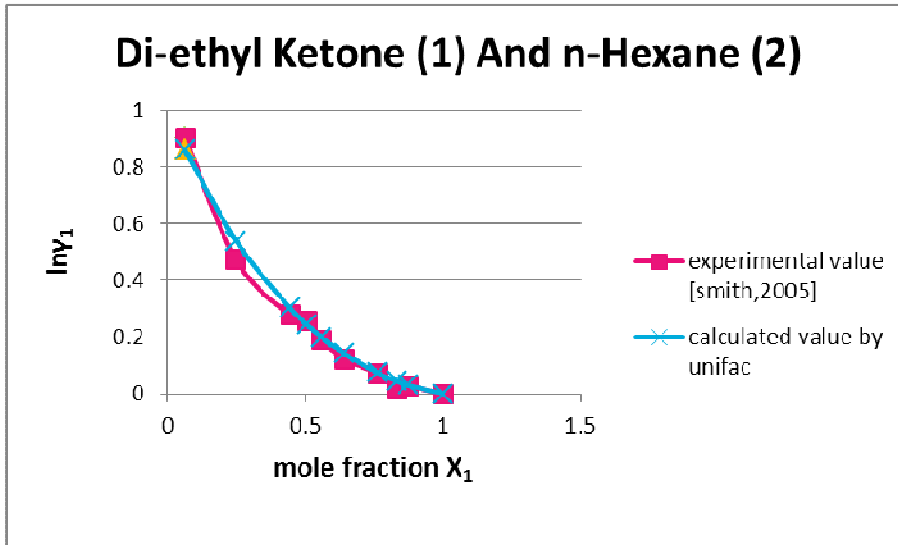


FIGURE 3.1 comparisons between the theoretical and experimental activity coefficient for case1 (a)

Case 1(B): System Is n-Hexane(1) And Di-ethyl Ketone (2) At 65⁰c

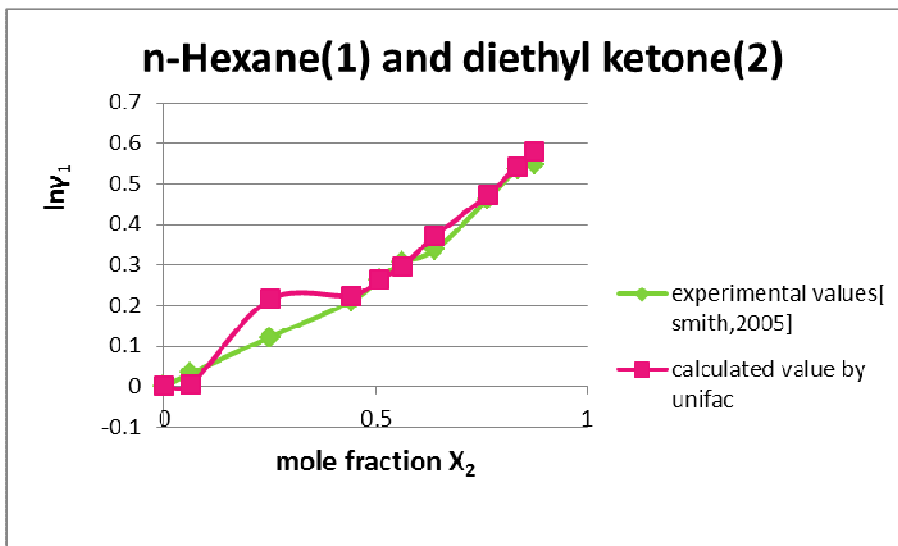


FIGURE 3.2 comparisons between the theoretical and experimental activity coefficient for Case 1(b)

CHAPTER-4
SIMULATION OF
DISTILLATION
COLUMN

SIMULATION OF DISTILLATION COLUMN

4.1 Equations for Distillation Column Design

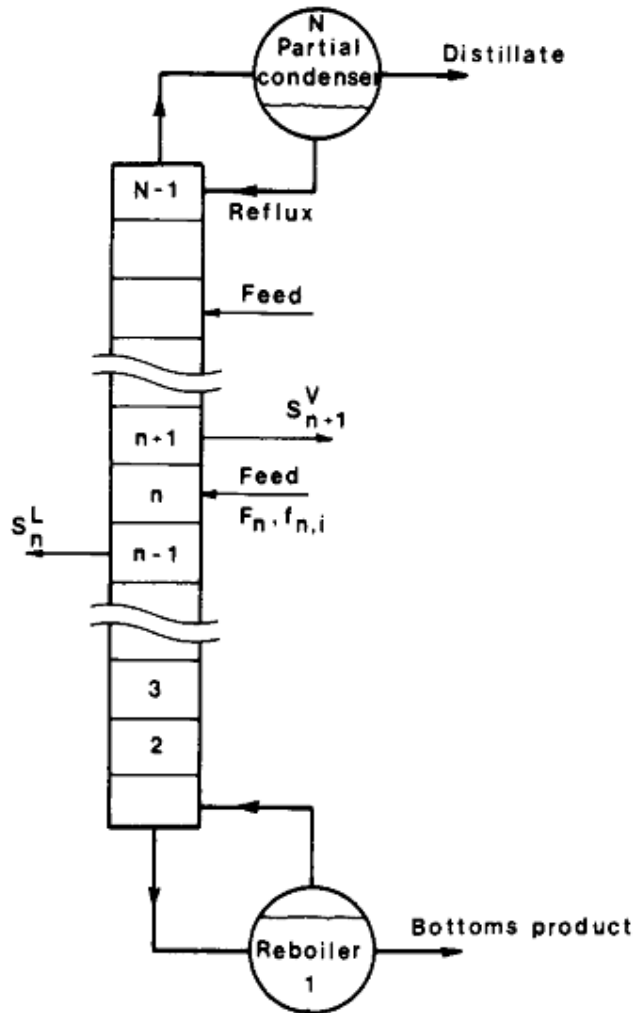


FIGURE 4.1 Distillation Column Configurations

Distillation columns with up to 50 (actual) stages, up to ten components, a partial condenser, and any number of feed- and side streams may be considered. In our “operating column analysis”, the user must specify: (a) the number of actual stages, (b) stage efficiencies, (c) feed- and side stream locations, (d) feed compositions, flow rates, and thermal states, (e) distillate flow rate, (f) side stream phase conditions and flow rates, (g) reflux ratio, and (h) column pressure. The nomenclature for an arbitrary stage n , which includes the possibility of feed- and side streams, is given below [Naphtali and Sandholm (1971)].

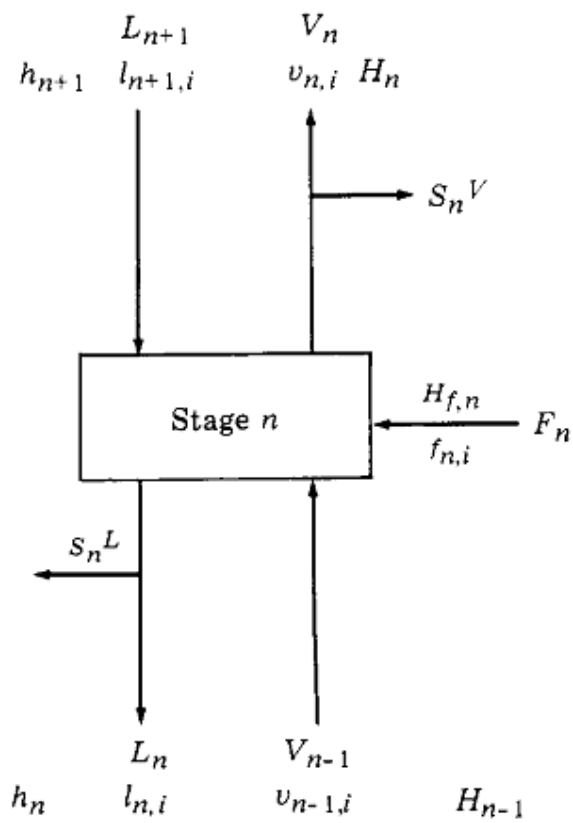


FIGURE 4.2 n^{TH} Stage of The Distillation Column

Subscript n : flow from stage n , $n = 1, 2, \dots, N$;

Subscript i : component i , $i = 1, 2, \dots, M$;

4.2 General Relations with Enthalpy Balances

For stage n one obtains the following set of dependent relationships (test functions $F_{1(n,i)}$) which must be satisfied. $L_{n,i}$

Component Balances. (Total: $N \times M$ relations)

$$F_{1(n,i)} = \left(1 + \frac{S_n^L}{L_n}\right) l_{n,i} + \left(1 + \frac{S_n^V}{V_n}\right) v_{n,i} - v_{n-1,i} - l_{n+1,i} - f_{n,i} = 0 \quad (4.1)$$

Enthalpy Balances. (Total: N relations)

$$F_{2(n)} = \left(1 + \frac{S_n^L}{L_n}\right) h_n + \left(1 + \frac{S_n^V}{V_n}\right) H_n - H_{n-1} - h_{n+1} - H_{f,n} = 0 \quad (4.2)$$

Equilibrium Conditions with Murphree Stage Efficiencies: (Total: $N \times M$ relations).

$$F_{3(n,i)} = \eta_{n,i} K_{n,i} V_n l_{n,i} / L_n - v_{n,i} + (1 - \eta_{n,i}) v_{n-1,i} V_n / V_{n-1} = 0 \quad (4.3)$$

$$K_{n,i} = \left(\frac{y_i}{x_i}\right)_n = \left(\frac{Y_i f_i^0}{p \Phi_i}\right)_n$$

The above relationships comprise a vector of test functions

$$\mathbf{F}(\mathbf{x}) = \begin{Bmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \\ \mathbf{F}_3 \end{Bmatrix} = \mathbf{0} \quad (4.4)$$

This contains $N \times (2M + 1)$ elements, and which may be solved for equally many unknowns.

$$\mathbf{x} = \begin{Bmatrix} \mathbf{1} \\ \mathbf{v} \\ \mathbf{T} \end{Bmatrix} \quad (4.5)$$

Where the vector $\mathbf{1}$ contains all the elements $l_{n,i}$, \mathbf{v} all elements $v_{n,i}$ and \mathbf{T} all elements T_i . Once all $l_{n,i}$, $v_{n,i}$ & T_i are known, the product compositions and product flow rates and the concentration- and temperature profiles in the column follow readily.

4.3 Newton-Raphson Iteration

Solving equation 4(B) or 9(B) means finding the set of values of the independent variables, x , which makes the set of test functions become equal to zero

$$F(x) = 0$$

In Newton-Raphson iterations, a new set of values of the test functions $F^{(new)}$, regenerate from a previous estimate in the following fashion

$$F^{(new)}(x^{(new)}) = F^{(old)}(x^{(old)}) + \left(\frac{\partial F}{\partial x}\right)_{x=x^{(old)}} (x^{(new)} - x^{(old)}) = 0 \quad (4.6)$$

This equation is used to estimate $x^{(new)}$. When $(x^{(new)} - x^{(old)})$ is sufficiently small, the correct set of values of x has been found, and the iteration stops.

The variation between subsequent iterations is arbitrarily limited as follows:

- (1) Negative component molar flow rates are equated to zero,
- (2) Component flow rates exceeding L_n are equated to L_n ,
- (3) The maximum change in the temperature at each stage, T_n is 10K.

The initial guess values for the independent variables, x_0 must be supplied by the user. Wild initial guesses can make the Newton-Raphson linearization approximation invalid to such an extent that the method fails to convergence characteristics far from the correct solution.

4.4 Disadvantages of Newton-Raphson Method

Newton's method is an extremely powerful technique—in general the convergence is quadratic: the error is essentially squared (the number of accurate digits roughly doubles) at each step. However, there are some difficulties with the method.

1. Newton's method requires that the derivative be calculated directly. In most practical problems, the function in question may be given by a long and complicated formula, and hence an analytical expression for the derivative may not be easily obtainable. In these situations, it may be appropriate to approximate the derivative by using the slope of a line through two points on the function. In this case, the Secant method results. This has slightly slower convergence than Newton's method but does not require the existence of derivatives.
2. If the initial value is too far from the true zero, Newton's method may fail to converge. For this reason, Newton's method is often referred to as a local technique. Most practical implementations of Newton's method put an upper limit on the number of iterations and perhaps on the size of the iterates.
3. If the derivative of the function is not continuous the method may fail to converge.
4. It is clear from the formula for Newton's method that it will fail in cases where the derivative is zero. Similarly, when the derivative is close to zero, the tangent line is nearly horizontal and hence may overshoot the desired root.
5. If the root being sought has multiplicity greater than one, the convergence rate is merely linear (errors reduced by a constant factor at each step) unless special steps are taken. When there are two or more roots that are close together then it may take many iterations before the iterates get close enough to one of them for the quadratic convergence to be apparent.
6. Newton's method works best for functions with low curvature. For linear function with zero curvature, Newton's method will find the root after a single iteration.

4.5 Steady State Simulation of Distillation Column Procedure

The calculation procedure may be outlined as follows:

- (1) Input value was taken (pure-component data, thermodynamic data for the mixture, and detailed column specifications such as feed plates, reflux ratio, etc)
- (2) Initial temperature and component flow profiles was guessed.
- (3) Then all K-factors, stream enthalpies, and their derivatives with respect to temperature and composition were determined.
- (4) The discrepancy functions $F(x)$ was set.
- (5) The elements of the jacobian matrix were determined and the block tri-diagonal system of equations was solved.
- (6) The correlations to the temperature and component vapour and liquid flow profiles were determined. New profiles were determined.
- (7) Check, whether the correlated value is smaller than a specified value.

If no, go to step (3) with the newly determined profiles.

If yes, go to step (8)

- (8) Print final output and stop.

4.6 Problem Statement

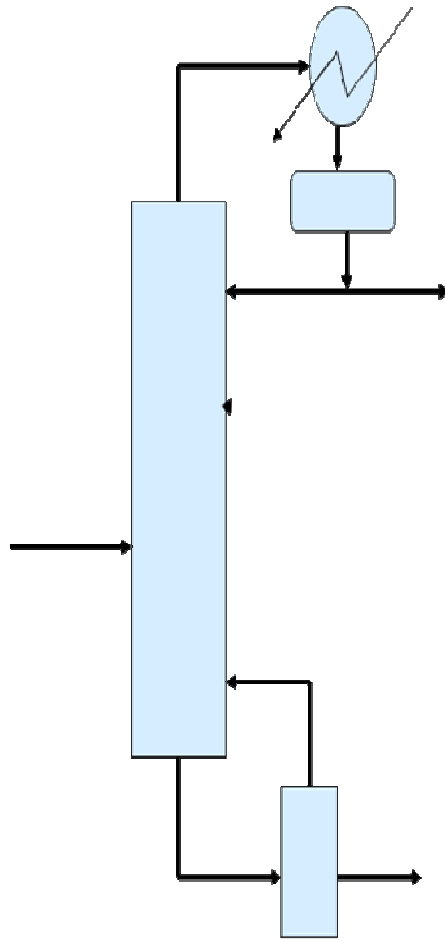


FIG 4.3. DISTILLATION COLUMN

MIXTURE: Binary mixture of n-pentane (1) and Acetone (2)

Table 4.1 Antoine Constants for acetone and n-Pentane

COMPONENTS	A	B	C
Acetone	6.8	1064.63	232
n-Pentane	7.23	1277.03	237.23

4.6.1 Design of Distillation Column Assuming No Temperature Variance:

Number of plates: 10 (including the reboiler and condenser)

Feed plate: 5

Feed flow rate: 100 moles/hr

Mole fraction of n-pentane x_f : 0.5

Column pressure: 101kpa

The top temperature: 323.4 K

The bottom temperature: 303.3 K

The reflux ratio =2.5

There is no side stream taken.

SOLUTION:

The boiling point of n-pentane is less than that of the acetone so n-pentane is more volatile than acetone. The top product will be n-pentane and the bottom product will be acetone.

Taking the average temperature in the column $T = (303.3+323.4)/2 = 313.5^0\text{K}$

Calculating the saturation pressure of both of the components using Antoine equation

P^{sat} acetone = 105.9 kpa

P^{sat} n-pentane=82.5 kpa

Calculating the activity coefficient at the average temperature for both of the components using UNIFAC group contribution method in MATLAB

Activity coefficient $\gamma_{\text{n-pentane}} = 1.2192$

Activity coefficient $\gamma_{\text{acetone}} = 1.7259$

RESULTS:

Solving the mass, energy and equilibrium equations in MATLAB, we get the results as follows:

Table 4.2 Results for temperature independent distillation column design

No. of Plates	Liq. Flow Rate Of n-pentane (moles/hr)	Liq. Flow Rate of Acetone(moles/hr)	Mole Fraction of n-pentane
1	16.5071	0.1949	0.988
2	35.2652	0.7856	0.978
3	56.5813	2.5754	0.956
4	80.8040	7.999	0.91
5	108.3299	24.4346	0.815
6	139.60	74.2392	0.65
7	118.33	73.647	0.61
8	94.1615	71.8524	0.56
9	66.69	66.4146	0.501
10	35.47	49.9357	0.41

4.6.2 Design of Distillation Column Assuming Ideal Case with Temperature Variance

Number of plates: 5 (including the reboiler and condenser)

Feed plate: 3

Feed flow rate: 100 moles/hr

Mole fraction of n-pentane x_f : 0.5

Column pressure: 101kpa

The top temperature: 323.4 K

The bottom temperature: 303.3 K

The reflux ratio =2.5

There is no side stream taken.

For the ideal case the activity coefficient $\gamma = 1$ for both the components.

SOLUTION:

For solving the mass, energy, and equilibrium relation equations by Newton-Raphson method we have to assume the initial values of the independent variables.

Here the variables are component liquid flow rates, component vapour flow rates and temperature.

The top and the bottom temperature are known so we can assume the intermediate temperatures. Similarly from the top and bottom liquid and vapour flow rates we can assume the intermediate flow rates.

The condenser is counted as the number one plate and the boiler is the 5th plate. The condenser is partial one.

Table 4.3 The assumed initial values of the independent values

NO. OF PLATES	TEMPERATURE (^o C)	TOTAL LIQ. FLOW RATES (moles/hr)	TOTAL VAPOUR FLOW RATES (moles/hr)
1	303.3	44	110
2	308.32	74.25	99
3	313.35	104.5	88
4	318.37	134.75	77
5	323.4	165	66

Now using these initial guess values of the variables and forming the jacobian matrix and solving the mass, energy and equilibrium relation by Newton-Raphson method, the results will come like this

Table 4.4 Results for ideal distillation column design

No. of Plates	Temperature (^o C)	Component Liq. Flow Rates (l ₁) (moles/hr)	Component Liq. Flow Rates (l ₂) (moles/hr)	Component Vapour Flow Rates (v ₁) (moles/hr)	Component Vapour Flow Rates (v ₂) (moles/hr)
1	278.7	163.02	1.98	65.99	0.000142
2	288.8	128.8	5.95	76.99	0.0025
3	298.71	85.16	19.33	87.94	0.0554
4	308.6	41.58	32.67	98.62	0.38
5	318.1724	18	25.96	109.25	0.7464

4.6.3 Design of Distillation Column Assuming Non-Ideal Case with Temperature Variance

Number of plates: 5 (including the reboiler and condenser)

Feed plate: 3

Feed flow rate: 100 moles/hr

Mole fraction of n-pentane x_f : 0.5

Column pressure: 101kpa

The top temperature: 323.4 K

The bottom temperature: 303.3 K

The reflux ratio =2.5

There is no side stream taken.

RESULTS:

Solving the mass, energy and equilibrium equations using Newton-Raphson method in MATLAB, we get the results as follows:

Table 4.5 Results for the non ideal distillation column design

Plate No.	Temperature(k)	Liquid Acetone Flow Rate (moles/hr)	Vapour Acetone Flow Rate (moles/hr)	Liquid N-Pentane Flow Rate (moles/hr)	Vapour N - Pentane Flow Rate (moles/hr)
1	267.67	30.53	9.6377	7.522	2.37
2	253.8115	114.93	36.282	38.05	12.01
3	242.06	135.79	77.08	122.45	38.65
4	270.24	93.31	63.59	93.31	29.45
5	321.28	42.478	47.62	50.58	15.96

CHAPTER-5
CONCLUSION AND
FUTURE
RECOMMENDATION

CONCLUSION

The average percentage of error in determining the activity coefficient by UNIFAC group contribution method varies from 9- 15% with respect to the experimental values. So with this much percentage of error the VLE data generated by UNIFAC can be successfully implemented in designing separation processes. UNIFAC model is a thermodynamic framework to describe the non-linearity in vapour-liquid equilibrium prediction. Presently UNIFAC model cannot apply to all type of mixtures containing polymers. Future study and research are required so that this method can be applied to all types of mixtures. The steady state simulation of binary distillation (n-pentane + acetone) column (10 plates, including reboiler and condenser) has been done assuming temperature independence. The temperature dependent simulation could not reach convergence.

FUTURE RECOMMENDATION

- The temperature dependent steady state simulation of the distillation column is to be done.
- The VLE data can be generated for ternary or quaternary mixtures using UNIFAC model,
- And steady state simulation for the multi component mixtures is to be done and the results should be compared with the other models.

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