The Kinetic Modeling of Methane Hydrate Growth by Differential Scanning Calorimetry Measurements and Molecular Dynamic Simulations

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Abstract

In this work, a modified equilibrium approach based on calculation of multicomponent efficiencies is implemented for packed columns simulation. In this modified approach, distillation process non-idealities due to interphase mass transfer are considered while the algorithm remains simple and efficient. The whole method consists of a segment wise procedure which is performed iteratively in a computational MATLAB code to simulate an experimental packed distillation column with structured packings. In each iteration, the component efficiencies are determined to consider mass transfer effects through the packed segments. According to obtained profiles for temperature and component compositions, good agreement is observed between reported experimental data and simulation results, so that the average deviations are about 0.5% and 19% for temperature and compositions, respectively. This confirms that the presented modified equilibrium model can properly predict the performance of multicomponent distillation in the packed columns and therefore it can be employed as a valid and reliable tool for design and simulation of real distillation towers.

Keywords: Packed distillation column, Structured packing, Modified equilibrium model, Multicomponent packing efficiency

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1- Introduction

More than a century, researchers have focused on distillation as a significant unit operation for various applications [1]. This process is the most widely practiced method to separate mixtures of chemical species in the petroleum, natural gas, chemical and petrochemical industries [2]. Distillation process is an energy-consuming method that is used in many industries to separate compounds based on difference in volatility [3]. Distillation columns are mainly categorized to trayed type and packed type columns. Trayed towers are favored when the velocity of the liquid is low, whereas columns with random packings are efficient for high velocity of the liquid. Besides, the structured packings are preferred when the pressure drop is considered as a significant factor. In addition, they are a suitable alternative for trays when a higher separation degree or capacity is necessary [4]. According to these advantages, the attentions to the structured packed towers have highly increased in retrofitting or improving the existing stage columns [5].

Distillation towers may consume more than half of the plant energy required and thus account for a major portion of the project capital costs [6]. Due to high installation capacity and energy usage, distillation has a central effect on the overall performance of industrial plants. Due to the high capital and operating costs of distillation towers, it will be useful to use mathematical modeling tools for optimizing the column operating and design parameters simultaneously with the aim of minimizing costs.

However, engineers usually design the distillation columns based on experience and heuristics, with the help of rigorous stage-by-stage distillation models existing in commercial software for the process simulation [7]. An example can be seen in the Dai et al. work [8], where the economic assessment and optimization of different strategies for the ethanol-water azeotrope separation is down by Aspen Plus. Another recent work by Margarida et al. [9] has been used Aspen Plus to optimize a process consists of distillation towers for ethanol recovery and reactive distillation towers for conversion of the residual free fatty acids.

Hence, many researchers have tried to use modeling and simulation tools for optimizing the distillation process. A reliable model is important for evaluating the process performance. Since the control, management and operation of the distillation columns accompanied by various complexities, computer programs that properly describe this operation should be available throughout the industrial plant.

The two main modeling approaches used in distillation design are the equilibrium stage model and the rate-based model (known as the non-equilibrium model) [10]. Both methods use rigorous Mass, Equilibrium, Summation and Heat or enthalpy relations (MESH) at each stage. In the equilibrium stage model, it is assumed that the liquid and vapor streams from each stage reach the thermodynamic equilibrium. This means that the vapor and liquid phase have the same chemical potential and equal pressure and temperature. This modeling approach does not require the detailed design information. It needs only the data for calculating of equilibrium constants and enthalpies. The equilibrium modeling approach is a conventional method for simulation of packed distillation towers. Therefore, the packed distillation column is modeled like to a staged column, so that the height of packed bed is divided into several sections, each of them is considered as a separate stage. Here, the balance equations for any packing sections are identical to corresponded equations for a single stage in trayed columns [11].

Actually, the equilibrium modeling approach can be used together with Murphree efficiency method for trayed columns and HETP (height equivalent to a theoretical plate) method for packed towers [12]. These two concepts attach the equilibrium approach to actual equipment design, as the output streams from a stage may not reach thermodynamic equilibrium in practice. A distillation column is more accurately described by the rate-based approach than by the equilibrium method because it considers the interphase mass transfer between two phases under the assumption that the vapor-liquid equilibrium (VLE) is established only at the interfaces. Unfortunately, this increase in accuracy is dependent of the model size, so that an increasing the number of elements will significantly increase the computational load. The equilibrium stage method is still suitable and

widely used and represents the thermodynamic limit of the distillation process based on rigorous MESH calculations, even though it may not be as accurate as the rate-based method. Furthermore, it is also satisfactory for conceptual designs and optimization goals.

In fact, in an actual distillation operation, the output streams of a packed section or an actual tray are rarely in equilibrium. To overcome the discrepancy of the model with the actual situation and consequently consider the mass transfer effects, the first solution is to apply the efficiency concept into the equilibrium modeling approach. Accordingly, the deviation from the ideal state on any tray or packing section is accounted by introducing efficiency values into equilibrium relations. Indeed, efficiencies often are used to fit the results of equilibrium stage model with actual column operating data [13]. For designing a large-scale distillation column, the knowledge of distillation efficiencies and the ability to estimate accurate efficiencies are significant [14]. Efficiencies have a direct effect on the number of required stages and an indirect effect on the equipment running costs. Therefore, appropriate use of the efficiency concept leads to considerable savings in the capital and operation costs of the distillation process. In addition, it is important to predict the column efficiency in order to determine its performance and desired purity requirements [15]. Therefore, any factors that cause a decrease in the efficiencies will definitely change the whole column performance. So, it is important to correctly predict the efficiencies before construction or installation of distillation columns. It can be said that the increase of the separation efficiency, as well as its estimation, have been the main task in design and operation of distillation columns [16].

HETP concept for packed towers is used as a concept something similar to the stage efficiency in trayed towers. HETP is simply used into equilibrium modeling approach. According to this concept, the separation efficiency of a packed distillation tower is characterized for design purposes. In fact, the mass transfer efficiency of packed distillation columns is defined by HETP concept. Since the mass transfer efficiency of components in binary mixtures is similar, the HETP value of both components is equal. However, in multicomponent mixtures, HETP values of various components are different as the HETP depends on several factors such as components of the mixture, physical

properties of the system and operating conditions of the column. Therefore, this concept is not applicable to the multicomponent distillation, directly.

In conventional approaches for the modeling of multicomponent distillations, the efficiencies or HETPs are often assumed equal for all components in each stage or packed section. However, it has been experimentally shown that in multicomponent distillations, the efficiencies could vary from stage to stage and even from component to component [17-19]. As the component efficiencies differ, the same separation would not be obtained using the assumption of constant efficiencies and consequently, introducing multicomponent efficiency calculations into the modeling algorithm is desirable. If the individual component efficiencies could be estimated during the simulation, the design of the column would be significantly improved by avoiding unnecessary over sizing and thus, capital and operation costs are diminished. According to our knowledge, none of the commercial simulation programs are capable of handling multicomponent efficiency calculations. The non-equilibrium simulators like the RateFrac of Aspen plus [20] and ChemSep [21] could only calculate efficiencies from the results of non-equilibrium simulations.

During past years, various researchers have attempted to use multicomponent efficiencies along with equilibrium modeling to include the distillation process non-ideality. Aittamaa [22] initially applied the multicomponent efficiency calculations in the distillation modeling. Later, Ilme [23] developed this approach further. Several researchers such as Klemola [24] and Jakobsson [25] comprehensively examined this method. Ilme et al. [18] and Jakobsson et al. [19] also applied efficiencies on the modeling of industrial columns. In our previous work [26], a simple non-equilibrium method based on rigorous efficiency calculations was also presented. Schubert et al.[27] present a comprehensive review of the existing theoretical efficiency prediction models along with the critical analysis of their strengths and weaknesses. The future of the tray efficiency modeling is expected to feature hybrid approaches, i.e. using theoretical models accompanied with fluid dynamics information from experimentally validated CFD models.

So far, most of studies conducted to multicomponent efficiency computations have been related to tray distillation columns, and the packed towers are rarely modeled based on this method. Among various researches, Keskinen et al. [28] focused on the equilibrium stage model with multicomponent efficiency factors and applied it for modeling of packed distillation columns at total reflux condition. However, they believed that the applied method still needs more works to be verified with extra laboratory data. The main challenge encountered in packed distillation modeling based on efficiency approach is to how component efficiencies are estimated for any packed section. Furthermore, their application on the simulation and design procedure are not clearly revealed.

The aim of the present paper is to discuss main characteristics of applying a rigorous efficiency-based distillation model on the simulation of packed distillation columns, focusing on temperature and composition profiles. This paper also provides a detailed comparison between the efficiency-based mass transfer model and reported data from an experimental packed distillation column. During the column simulation, individual component efficiencies are estimated for the packed column in question and then the obtained efficiencies are directly applied in the simulation procedure. The main characteristic of presented model is that the multi-component segment efficiencies are simultaneously calculated along with the complete distillation model. Subsequently, distillation process non-ideality due to mass transfer phenomena are accounted while the structure of equilibrium stage model is retained.

2- Model description

Basically, there are two main approaches proposed for modeling of packed columns: discrete approach and continuous approach. In the first approach, the packed bed as a continuous contact system is divided into some segments so that every segment is approximately considered as a separation stage in a tray tower. On the other approach, differential balance equations are written for a small packing element. Therefore, a numerical integration scheme is applied to solve these differential equations [29, 30]. In present work, the first approach is used so that the packed column

is divided into some separate segments. Then, each of them is considered as a discrete stage with considering their non-ideal behavior. In the model, the non-ideal behavior caused by deviation from the assumption of equilibrium state is regarded based on multicomponent efficiency calculations. In order to determine the efficiency of a packed column with mass transfer effects, one mass transfer stage should be initially defined. This requires the packed bed to be vertically discretized into a number of control volumes known as segments while any of them contains vapor and liquid phases with homogeneous composition and temperature. The model equations are then written for each segment. The configuration of a typical segment in the packed column is schematically shown in Figure 1.

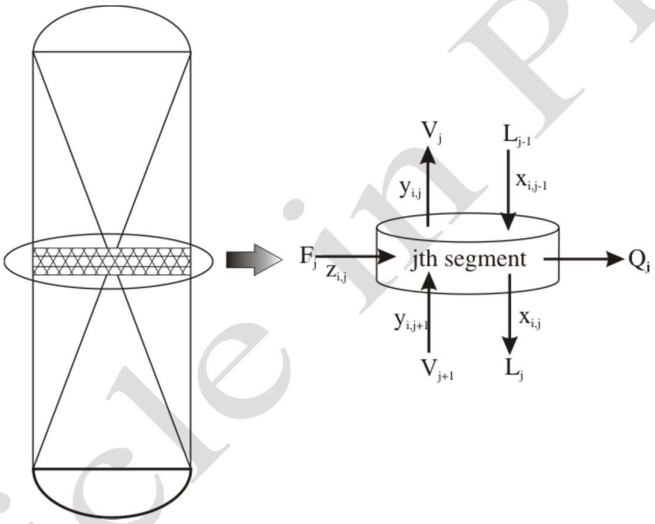

Figure 1. Schematic representation of a segment in the packed column

The equilibrium constants (K-values) are adjusted away from the thermodynamic equilibrium value when the efficiency-based equilibrium model is applied for the evaluation of the column non-ideal behavior. This modification is performed by incorporating the phenomena occurring in the packed bed (such as back-mixing) into a model for K-values while the structure of ideal stage model is preserved. This approach is inspired by the application of efficiency concept. Several types of efficiencies have been used in the modeling of distillation process, including Murphree [31], Hausen [32] and vaporization [33] efficiencies. However, among these types, the Murphree efficiency is the most widely used concept in the distillation column simulations. All of these

different types of efficiencies attempt to determine the deviation of real stages from the equilibrium state.

In the procedure of modeling, the whole packed bed is considered as a sequence of mass transfer stages, each of them corresponds to a special height of packing that represents a calculation segment. This segment height is then associated to a mass transfer stage by definition of multicomponent efficiencies. Each segment is numbered from the top to the bottom. The model governing equations according to Figure 1 are presented in Table 1.

Table 1. Equations of efficiency-based modified equilibrium model for the jth segment

Material balance equations $v_{i,j}\left(1+r_j^V\right)+l_{i,j}\left(1+r_j^L\right)-v_{i,j+1}-l_{i,j-1}-f_{i,j}=0$	c equations
Modified equilibrium equations $E_{ij}^{MV}K_{ij}\left(\frac{l_{i,j}}{\sum_{k=1}^{c}l_{k,j}}\right)\sum_{k=1}^{c}v_{k,j}-v_{i,j}+\left(1-E_{ij}^{MV}\right)\left(\frac{v_{i,j+1}}{\sum_{k=1}^{c}v_{k,j+1}}\right)\sum_{k=1}^{c}v_{k,j}=0$	c equations
Energy balance equation $H_j^V\left(1+r_j^V\right)\sum_{k=1}^{c}v_{k,j}+H_j^L\left(1+r_j^L\right)\sum_{k=1}^{c}l_{k,j}-H_{j+1}^V\sum_{k=1}^{c}v_{k,j+1}-$ $H_{j-1}^L\sum_{k=1}^{c}l_{k,j-1}-H_j^F\sum_{k=1}^{c}f_{k,j}+Q_j=0$	1 equation
Total number of equations	2c+1

In this table c is the number of species, $f_{i,j}$, $v_{i,j}$ and $l_{i,j}$ are the flow rate of components related to feed, vapor and liquid streams, respectively. r_j is the dimensionless side-stream flow rate and H_j is the enthalpy. E_{ij}^{MV} also stands for component Murphree efficiency.

In the simulation method, first stage (condenser) and last stage (reboiler) are considered as ideal equilibrium stages. So, equations written for these stages are different from equations of intermediate stages. The equations for top and bottom stages are represented in Table 2.

Table 2. Equations for the condenser and the reboiler as ideal stages

		condenser (j =1)	reboiler (j = N)
Material balance		$l_{i,1} + v_{i,1} - v_{i,2} - f_{i,1} = 0$	$l_{i,N} + v_{i,N} - l_{i,N-1} - f_{i,N} = 0$
Energy balance		$\sum_{k=1}^{c} l_{k,1} - RR \sum_{k=1}^{c} v_{k,1} = 0$	$\sum_{k=1}^{c} l_{k,N} - W = 0$
Equilibrium relation	Partial	$K_{i,1} \frac{l_{i,1}}{\sum_{k=1}^{c} l_{k,1}} - \frac{v_{i,1}}{\sum_{k=1}^{c} v_{k,1}} = 0$	$K_{i,N} \frac{l_{i,N}}{\sum_{k=1}^{c} l_{k,N}} - \frac{v_{i,N}}{\sum_{k=1}^{c} v_{k,N}} = 0$
	Total	$\sum_{p=1}^{c} \left(K_{p,1} \frac{l_{p,1}}{\sum_{k=1}^{c} l_{k,1}} \right) - 1 = 0$ *(bubble point equation)* $\frac{l_{i,1}}{\sum_{k=1}^{c} l_{k,1}} - \frac{v_{i,1}}{\sum_{k=1}^{c} v_{k,1}} = 0 \ \ (i = 2 : c)$	

In Table 2, RR is the reflux ratio and W is the bottom product flow rate.

Accordingly, for a packed distillation column consisting of N calculation segments, N (2c+1) non-linear equations are obtained. This value is equal to the number of equations for equilibrium stage model. So, using this modeling procedure it is possible to consider the effect of mass transfer on the column performance without changing the structure of equilibrium modeling approach. These sets of equations are solved simultaneously by the Newton–Raphson iterative method [34] in which successive sets of the output variables are computed. This calculation loop will continue until the sum of squares of discrepancy functions are inclined to the convergence criteria or zero.

2-1- Multicomponent packing efficiencies

For a dilute system in a packed column, the mass balance for the vapor phase could be written in matrix notation as follow [15]:

$$V \frac{d(y)}{dh} = -(J^V) a_e A_c \qquad (1)$$

where a_e is the effective interfacial area of the packing and A_c is the column surface area. By using the definition of the vector of diffusion fluxes,(J^V), based on the matrix of overall mass transfer coefficients for vapor phase, $[K^{OV}]$, Eq. (2) is achieved:

$$V\frac{d(y)}{dh} = c^v[K^{OV}](y^* - y)a_e A_c \tag{2}$$

where y^* is the vapor composition in equilibrium with the composition of the liquid leaving from the stage.

Based on the definition of the overall heights of transfer units (HTUs) for the vapor phase, equation (2) can be expressed as:

$$\frac{d(y)}{dh} = [H^{OV}]^{-1}(y^* - y) \tag{3}$$

In order to determine the vapor composition profile along the column, Eq. (3) should be integrated numerically. To avoid this, Keskinen [28] suggested that the term $(y^* - y)$ could be estimated with arithmetic average value for a certain segment height. This approximation leads to:

$$(y)_j - (y)_{j+1} = h_j\,[H^{OV}]_j^{-1}\left(\frac{[K]_j\,(x)_j + [K]_{j-1}\,(x)_{j-1}}{2} - \frac{(y)_j + (y)_{j+1}}{2}\right) \tag{4}$$

where $(y)_j$ and $(x)_j$ represent the composition vector of vapor and liquid streams leaving the segment j, and $(y)_{j+1}$ and $(x)_{j-1}$ indicate the composition vector of vapor and liquid streams entering the segment j. $[K]_j$ and $[K]_{j-1}$ are the diagonal matrix of K-values corresponding to liquid compositions x_j and x_{j-1}, respectively. $[H^{OV}]_j$ related to the overall HTUs matrix in segment j and h_j is the segment height.

Now, it can be defined the packed bed efficiencies similar to the definition of Murphree plate efficiencies as follow:

$$E_j^{MV} = \frac{y_j - y_{j+1}}{y_j^* - y_{j+1}} \tag{5}$$

According to Eq. (5), a diagonal matrix $[A]_j$ is defined in which the reciprocals of term $\left(y_j^* - y_{j+1}\right)$ are its arrays:

$$[A]_j = \begin{bmatrix} \frac{1}{y^*_{1,j} - y_{1,j+1}} & 0 & \cdots & 0 \\ 0 & \frac{1}{y^*_{2,j} - y_{2,j+1}} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \frac{1}{y^*_{c-1,j} - y_{c-1,j+1}} \end{bmatrix} \quad (6)$$

Eventually, the following expression is obtained to calculate each component efficiency in any segment of the packed column:

$$(E^{MV})_j = [A]_j \frac{h_j}{2} [H^{OV}]_j^{-1} \left\{ [K]_j (x)_j + [K]_{j-1} (x)_{j-1} - (y)_j - (y)_{j+1} \right\} \quad (7)$$

Eq. (7) is our main equation during the modeling of the packed distillation column. This equation is applied to consider the deviation from the equilibrium state. The basic term in equation (7) is the matrix of overall HTUs, $[H^{OV}]$, that should be determined before calculating the segment efficiencies.

2-2- The overall HTUs matrix

The diffusion in a multicomponent system is very complex in comparison with the binary systems. In such systems, the diffusion rate of each component is affected by the diffusivity of all components in the mixture[23]. Therefore, the gradient of chemical potential is the driving force in calculations instead of the gradient of concentration [11, 35]. The component efficiencies are estimated based on the two-film theory in connection with multicomponent mass-transfer theory according to Maxwell-Stefan diffusion relationships [15]. In the mass transfer model of packed columns, the correlations of binary mass transfer coefficients are used to obtain the matrices of multicomponent height of transfer units (HTUs) for each phase. Then, the matrix of overall HTUs can be calculated. These calculations require some data about the geometry of the packed column and packing elements, the internal vapor and liquid flow rates and the physical properties of each phase. The matrices of HTUs for the liquid and vapor phases are determined as follows:

$$[H^L] = \frac{[R^L] u_{SL}}{a_e} \quad (8)$$

$$[H^V] = \frac{[R^V]u_{SV}}{a_e} \tag{9}$$

Where u_{SL} and u_{SV} are the superficial velocity for liquid and vapor phases, respectively. $[R^V]$ and $[R^L]$ are the inverse matrices of mass transfer coefficients with elements calculated by Eq. (10).

$$R_{i,i} = \frac{z_i}{k_{i,c}} + \sum_{\substack{m=1 \\ m \neq i}}^{c} \frac{z_m}{k_{i,m}}$$
$$R_{i,j} = -z_i \left(\frac{1}{k_{i,j}} - \frac{1}{k_{i,c}} \right) \tag{10}$$

In above equation, z is the considered phase mol fraction and $k_{i,j}$ is the binary mass transfer coefficient for the same phase.

Finally, the matrix of overall HTUs is determined using the multicomponent HTU matrices for vapor and liquid phases follows:

$$[H^{OV}] = [H^V] + \frac{V}{L}[K][H^L] \tag{11}$$

Here, $[K]$ represents a diagonal matrix consisting of vapor-liquid equilibrium (VLE) constants.

In order to calculate coefficients of binary mass transfer in Eq. (10), different correlations were presented for various commercial packings. In the present work, the relation of Bravo et al. (1985) [36] for structured packings is applied. By using this relation, the vapor and the liquid binary mass transfer coefficients are predicted by:

$$k^V = \frac{Sh_V \, D^V}{d_{eq}} \tag{12}$$

$$k^L = 2\sqrt{\frac{D^L u_{Le}}{\pi \, S}} \tag{13}$$

where Sh_V denotes the Sherwood number, d_{eq} represents the channel equivalent diameter, S is the spacing of corrugation (channel side), u_{Le} is the liquid effective velocity, and D is the diffusion coefficient.

There are also several correlations for calculation of the effective interfacial area per unit volume (a_e). This parameter is a complex function of various properties and operating conditions. Based on the method proposed by Bravo et al. (1985), the surface is considered completely wet. Hence, the interfacial area density (a_e) is considered equal to the apparent specific surface area (a_P). Consequently, the interfacial area is determined as a product of a_P and the volume of the jth segment.

3- Simulation procedure

In order to implement the multicomponent efficiency calculations for a packed distillation column, a sequence of steps is applied for all segments. The general outline of the segment-wise efficiency calculations is presented in Figure 2.

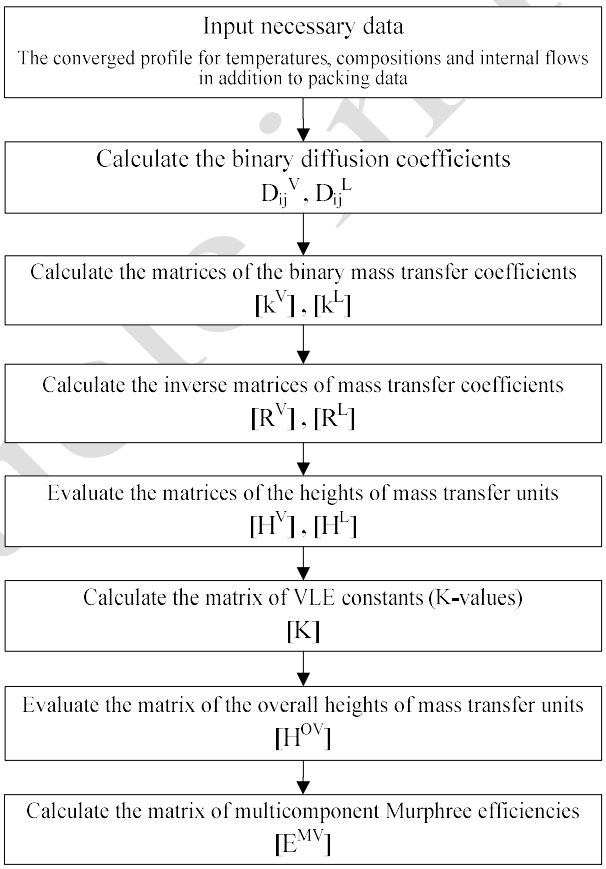

Figure 2. The sequence of multicomponent efficiency calculations for each segment

The whole calculation procedure for the packed column proceeds as follows. The height of packed bed is initially divided into a number of segments. Next, each segment is corresponded to a mass

transfer stage by introducing the efficiency values. In order to accomplish this, the segment-wise efficiency calculations according to Figure 2, is implemented in each iteration. Then, the obtained packing efficiencies are applied to correct the compositions at the equilibrium relations. The improved Newton-Raphson approach has been used to solve the set equations of model, simultaneously. This pattern is repeated until complete convergence of mathematical model for entire packed column. The detail of the modeling method is presented as a flowchart in Figure 3.

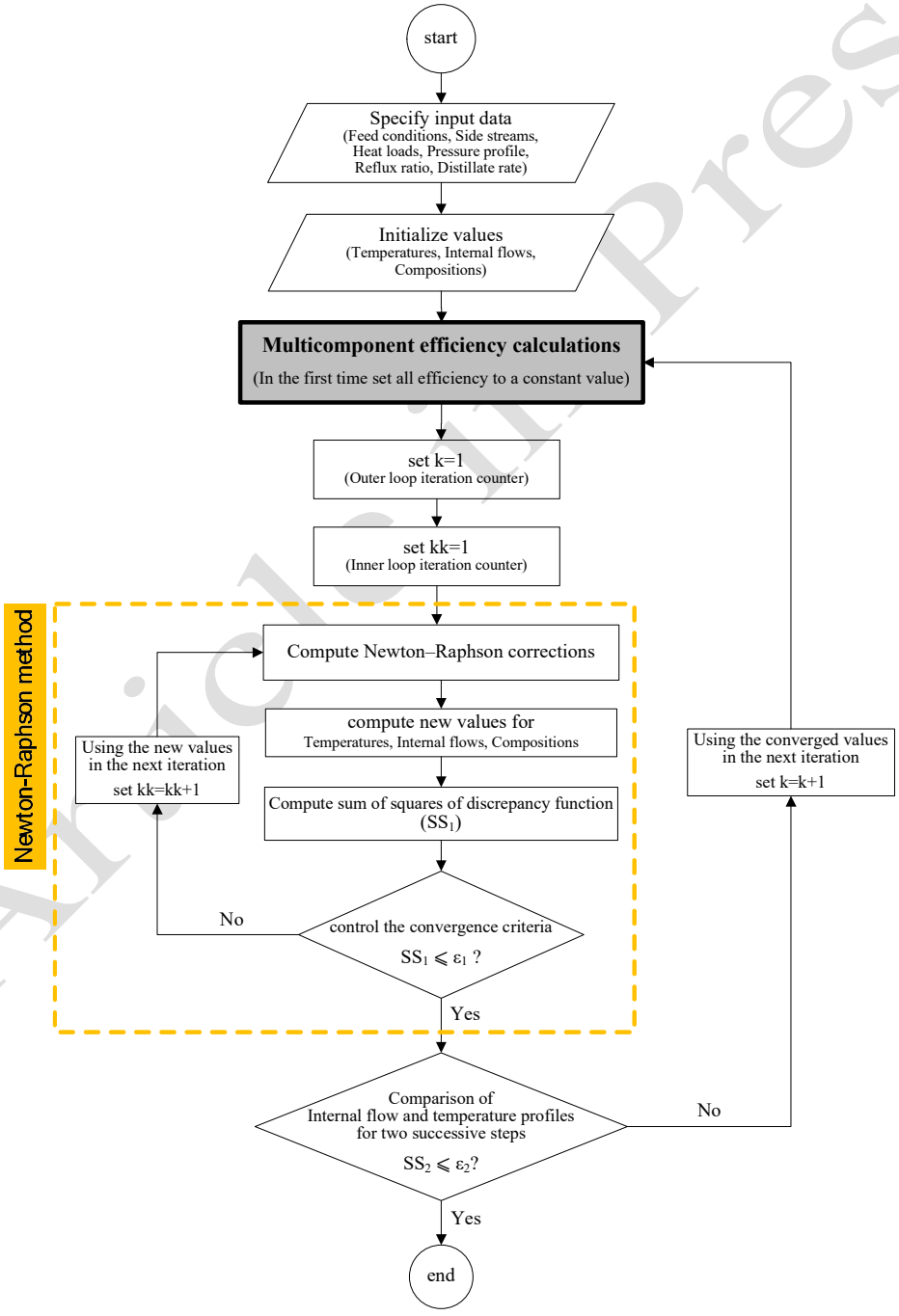

Figure 3. The sequence of whole simulation steps

The simulation model of the column was specified by defining main inputs such as the system thermodynamic, the flow rate, condition and composition of feed stream, the information about the column and structured packing elements. Vapor-liquid equilibrium (VLE) calculations is performed based on $\gamma - \phi$ approach [37]. In this approach, a liquid activity coefficient model is used to consider the liquid phase thermodynamic properties while an equation of state is used for the vapor phase. In the present work, the NRTL activity model [38] is applied for the liquid phase, and SRK equation of state [39] is applied for the vapor phase. In addition, the column is assumed to be adiabatic. The NRTL parameters used in this work presented in Table 3. The provided parameters are used together with $G_{ij} = exp(-\alpha_{ij}\tau_{ij})$ and $\tau_{ij} = B_{ij}/T$.

Table 3. NRTL parameters for binary mixtures at 101.3 kPa[40]

component i	component j	$B_{ij}\ [K]$	$B_{ji}\ [K]$	α_{ij}
Water	Ethanol	624.92	-29.17	0.294
Water	Methanol	594.63	-182.61	0.297
Ethanol	Methanol	73.41	-79.17	0.303

The modified equilibrium method with calculation of multicomponent packing efficiencies is executed in a computational home code in MATLAB. This computational code can simulate any packed column with any segment number including different type and size of packings in addition to various column diameters. One of the important advantages of our developed code is the possibility of easy modification to check the validity of different assumptions. Furthermore, the code has high flexibility to solve convergence issues.

4- Validation method

In this paper, a laboratory scale packed distillation column (presented by Mori et al. [41]) for separation of a non-ideal ternary mixture containing methanol, ethanol, and water is considered to evaluate the modeling method. A schematic diagram of desired packed column is presented in

Figure 4. As shown in the Figure, feed enters from the middle of the packed bed. So, the height of stripping and enriching sections is the same and each section consists of six structured packing elements. The geometry of used packings is similar to other commercial corrugated sheet-type packings. However, its sheets are sandwiched by gauze. Therefore, the wetting properties are similar to gauze-type packings. Packed column characteristics and the geometry of the structured elements are specified in Table 4. The operational conditions used in the experiment are also given in Table 5.

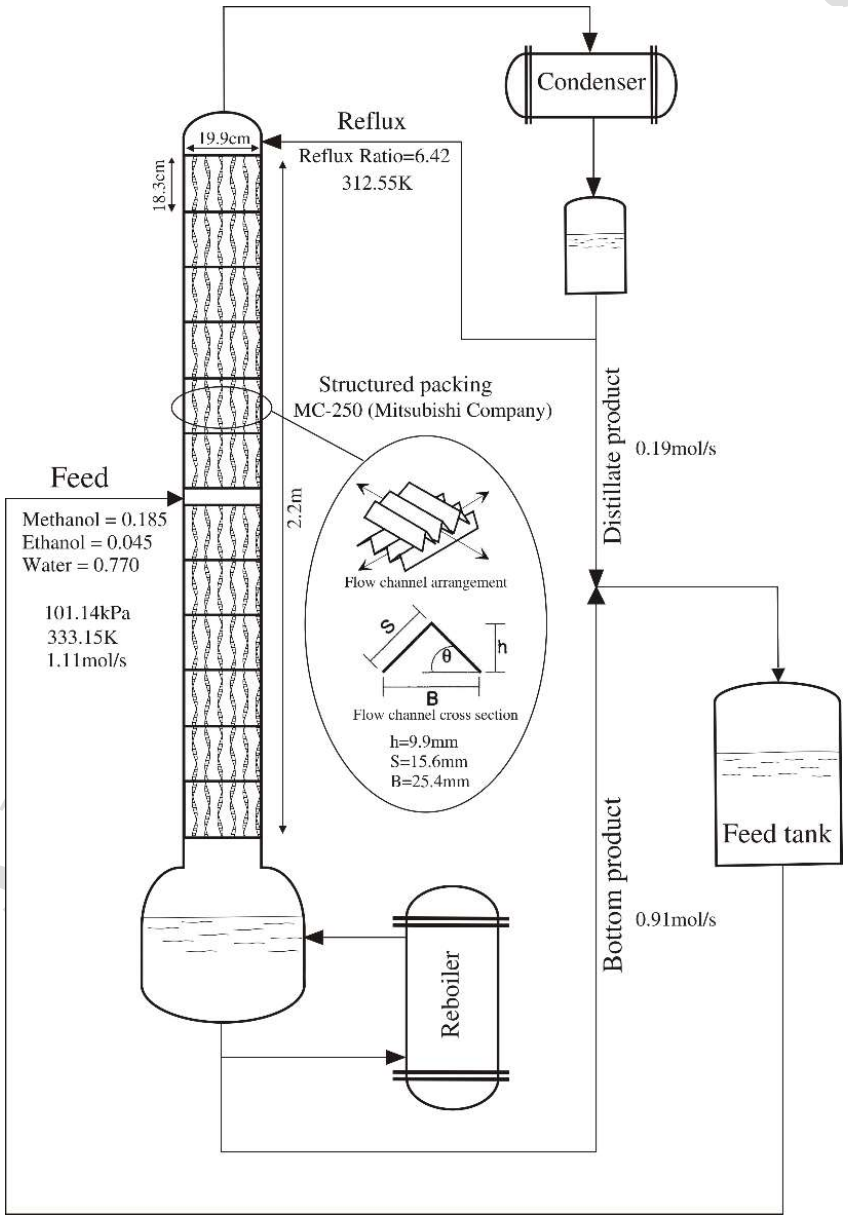

Figure 4. Schematic representation of the packed distillation column in addition to packing specifications

Table 4. Specifications of the packed column and information of packing elements

Column specifications	
Column height	3 m
Packed height	2.2 m
Diameter	0.21 m
Packing elements information	
type	MC-250 (Mitsubishi Company)
Element diameter	0.199 m
Element height	0.183 m
Height of triangle	9.9×10^{-3} m
Base of triangle	25.4×10^{-3} m
Corrugation spacing	15.6×10^{-3} m
Specific surface area	250 m^2/m^3
Void fraction	0.98
Channel flow angle	45°

Table 5. Operating condition of the packed distillation column

specification	**value**	
Reflux ratio	6.42	
Reflux temperature	312.55 K	
Column pressure	101.4 kPa	
Feed flow rate	1.11 mol/s	
Feed composition (mole fraction)	Methanol	0.185
	Ethanol	0.045
	Water	0.770
Feed temperature	333.15 K	
Distillate flow rate	0.19 mol/s	

The physical properties for mixture and pure components are estimated with several methods presented in Table 6. Moreover, Table 6 presents relationships used for calculation of binary mass transfer coefficients and effective interfacial area for the used commercial structured packing.

Table 6. Methods for estimating physical and mass transfer properties

Physical properties [42]	
Vapor molar density	Equation of State (SRK)
Liquid molar density	Modified Rackett method
Pure gas viscosity	Chung method
Mixture gas viscosity	Wilke method
Pure liquid viscosity	Correlation based on experimental data [Reid et al., 1987]
Mixture gas viscosity	Grunberg and Nissan method
Pure surface tension	Sastri-Rao method
Mixture surface tension	Tamura method
Mass transfer properties	
Binary gas diffusion coefficient	Brokaw method
Binary liquid diffusion coefficient	Reddy and Doraisway method
Binary mass transfer coefficient	Bravo et. al. (1985)
Effective interfacial area	equal to the specific packing surface ($a_e = a_p$)

5- Results and discussion

According to the presented efficiency-based modified equilibrium model, a packed distillation column is chosen to implement the simulation procedure. This column separates a ternary non-ideal mixture consist of methanol, ethanol, and water. The goal of simulations is to study the behavior of the desired packed column under operational conditions with the modified modeling method.

In order to obtain the basic equation (7) for the estimation of packing efficiencies, it is mainly assumed that the integral solution of equation (3) is approximated with arithmetic mean value of the term $(y^* - y)$. It is obvious that the equation (7) becomes close to the integral solution as the height of segments is reduced. Therefore, the number of calculation segments have significant impact on the precision of the results. Furthermore, the segments size directly affects the total computation time. Besides, if the height of segments is too small, the segment efficiencies will be very low. This results in some numerical instabilities due to large fluctuations in the model variables. Meanwhile, more computation time is needed. Contrarily, if the height of calculation segments is too high, numerical problems may easily arise during the calculations and the accuracy of obtained results declines. A good insight about suitable segment height leads to reasonable results. Accordingly, the

impact of the number of calculation segments is comprehensively investigated on the results by changing the number of divisions along the packed column.

Figure 5 depicts the predicted temperature profiles along the column for different size of segments. Also, the measured temperatures along the packed bed are shown. As expected, the temperature decreases from the bottom to the top of the column. As is clear, a considerable change is seen at the feed inlet. This change becomes more visible as the number of segments is increased. Figure 5 also shows an excellent agreement between predicted results and measurement temperatures. The quantitative comparisons between simulation results and experimental data (for the number of segments 25) confirms this as shown in Table 7. The mean relative error for temperature data is approximately 0.5%.

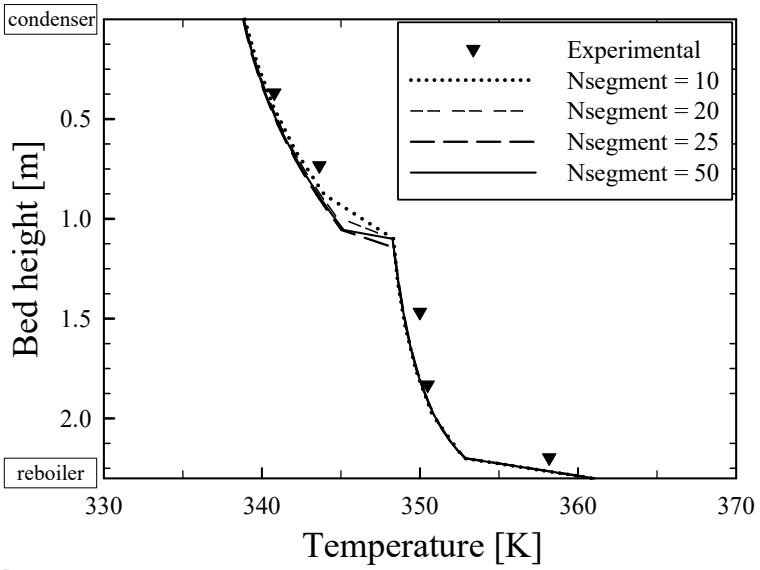

Figure 5. The predicted temperature profiles along the packed height based on several segment size.

Table 7. The quantitative comparison between simulation and experimental temperature data (Nsegments=25)

h [m]	T_exp.	T_sim.	(%e)
0.37	340.8	340.2	-0.18
0.73	343.6	342.3	-0.38
1.47	350.0	349.0	-0.29
1.83	350.5	350.1	-0.11
2.20	358.2	352.8	-1.51
	% mean error		**0.5**

On the other side, the effect of segment size on the prediction of column performance is more inspected by comparing the composition profile of each component with measurement compositions along the column. Thus, a comparison between predicted liquid compositions for various segment sizes with experimental data is presented in Figure 6. The experimental data consist of four liquid compositions taken along the length of the packed bed. As seen in the Figure, it is found that the efficiency-based modeling approach fairly expects the composition of all species. The quantitative comparisons between simulation and measurement compositions along the column (for the number of segments 25), presented in Table 8, confirm this matter. The major discrepancy between the plant data and the simulation results is related to the concentration of ethanol. Moreover, it can be seen from Figure 6 that increasing the number of segments can reduce the errors in the predicted compositions, particularly at the middle of column. Figure 6 also shows that the difference in the profiles between various segment sizes at top and bottom sections is less than that of the middle section.

According to obtained results, the deviation of compositions and temperatures from the experimental data through the packed bed is so small. Thus, the modified approach is confidently recommended for design purposes of packed distillation columns.

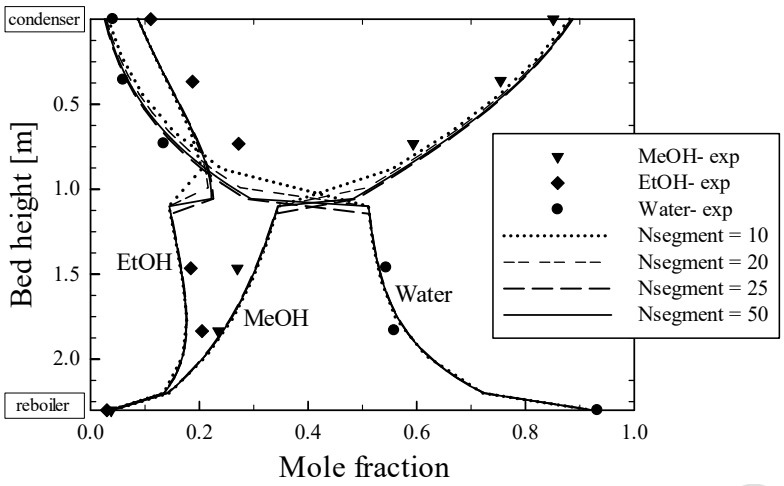

Figure 6. Liquid mole fraction profiles of all components along the packed height for different segment size

According to our findings, when the number of segments is increased, both temperature and composition profiles significantly change at the middle section of the column. However, the difference between profiles is not very noticeable when the number of segments is highly increased. Therefore, according to resulting profiles for different segment sizes, it can be concluded that the simulation according to 25 segments (8.8 cm for each segment) is efficient for the acceptable prediction of experimental profiles.

Table 8. The quantitative comparison of liquid compositions between simulation and experimental data (Nsegments=25)

h [m]	MeOH			EtOH			Water		
	Exp.	Sim.	(%e)	Exp.	Sim.	(%e)	Exp.	Sim.	(%e)
condenser	0.85	0.89	4.3	0.11	0.09	-20.4	0.04	0.02	-41.6
0.36	0.75	0.79	5.3	0.19	0.14	-23.1	0.06	0.06	3.7
0.73	0.59	0.65	9.9	0.27	0.20	-25.3	0.13	0.14	6.8
1.47	0.27	0.31	13.3	0.18	0.17	-9.7	0.54	0.53	-2.9
1.83	0.23	0.25	4.8	0.20	0.18	-13.4	0.56	0.58	3.0
reboiler	0.04	0.04	5.0	0.03	0.04	20.5	0.93	0.92	-0.9
% mean error			**7.1**			**18.7**			**9.8**

In Figure 7, the calculated component efficiencies for considered packed column are depicted as a function of the packed bed length for 25 segments. Based on these efficiency values, the mass transfer in each segment is corrected and then, the temperature and concentration profiles are

obtained. As it is clear in the Figure 7, the component efficiencies are different from each other. This results that each component can have different mass transfer properties along the column. Furthermore, an oscillation can be seen in component efficiencies at the column middle section. This is caused by the fluctuations of compositions at feed inlet.

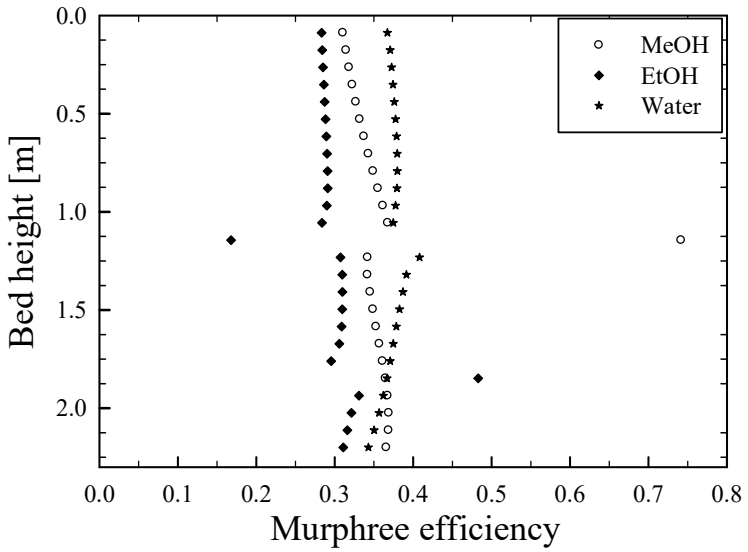

Figure 7. Calculated efficiencies for different components as a function of the packing height

It is worthy to note that the packing efficiencies are a function of the segment size so that efficiencies are reduced with the decrease in the size of segments. This means that it would not expect a special trend for the efficiency profile along the packed bed, just contrary with trayed columns. Indeed, efficiency profile across the height of a trayed column is unique due to the constant number of stages.

Conclusion

A simulation algorithm using equilibrium model modified by multicomponent packing efficiencies is implemented as a rigorous method for performance evaluation of packed distillation columns. The main feature of the modified method is to preserve the simple structure of equilibrium model. In the present model, the non-ideality of a real distillation column as a result of mass transfer phenomena was considered by using multicomponent efficiency calculations. For modeling purpose, the packed column was divided into some separate segments and then, the multicomponent efficiencies were determined for each segment. A basic equation was introduced to evaluate the

packing efficiencies. To implement the simulation process, an experimental packed column with structured packings to separate a ternary non-ideal mixture is chosen. For validation of the modified approach, obtained results are compared with reported measurement data. The effect of segment size on the precision of results was investigated, and it would be concluded that the simulation with 25 segments could properly predict the reported experimental data. The qualitative and quantitative comparisons displayed good agreement between simulation results and experimental data, so that the average deviations between results are about 0.5% for temperature and 18% for component compositions. These results obtained according to estimated component efficiencies. The resulted efficiency profiles confirmed that each component can have distinct mass transfer characteristics due to difference between component efficiencies along the column.

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Nomenclature

V_j	vapor flow rate, mol/s
$v_{i,j}$	component vapor flow rate, mol/s
L_j	liquid flow rate, mol/s
$l_{i,j}$	component liquid flow rate, mol/s
F_j	feed flow rate, mol/s
$f_{i,j}$	component feed flow rate, mol/s
r_j	the dimensionless side-stream flow rate
y	the vapor mole fraction
y^*	the vapor composition in equilibrium with the outlet liquid composition
x	the liquid mole fraction
z	the mole fraction of appropriate phase
H_j	the enthalpy, J/mol
Q_j	heat load, J/mol
RR	Reflux Ratio
W	bottom product flow rate
h_j	the segment height, m
a_e	the effective interfacial area, m^2/m^3
a_p	the apparent specific surface area, m^2/m^3
A_c	the column surface area, m^2
$[K]$	the matrix of vapor-liquid equilibrium constants (K-values)
$[K^{OV}]$	the matrix of overall mass transfer coefficients, m/s
(J^V)	the vector of diffusion fluxes, $mol/(m^2.s)$
$[H^{OV}]$	the matrix of overall HTUs
$[H]$	the matrix of HTUs for each phase
$[R]$	the inverse matrix of mass transfer coefficients
E^{MV}	Murphree vapor phase segment efficiency
$k_{i,j}$	the binary mass transfer coefficient, m/s
Sh	Sherwood number, dimensionless
D	the diffusion coefficient, m^2/s
d_{eq}	the equivalent diameter of a channel, m
S	the corrugation spacing, m
u_{Le}	the effective liquid velocity, m/s
u_{SV}	the superficial vapor velocity, m/s
u_{LV}	the superficial liquid velocity, m/s

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