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Comparison of distillation arrangement for the recovery process of dimethyl sulfoxide

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Abstract−In this study, computer modeling and comparative works have been performed to obtain highly pure dimethyl sulfoxide (DMSO) which is used for fiber spinning solvent for two different distillation sequences. These two distillation sequences remove methanol and water and recover DMSO solvent from the mixture of methanol and water using two distillation columns. Non random two liquid mixture (NRTL) liquid activity coefficient model was used for the modeling of each binary vapor-liquid equilibria for DMSO, methanol and water systems and we used PRO/II with PROVISION release 7.1 as a commercial chemical process simulator. As a result of computational simulation, we obtained a highly pure DMSO with its purity over 99.9 wt% and water contents which is main impurity was very low weight percent under 500 ppm.

Key words: Direct Sequence, Indirect Sequence, Dimethyl Sulfoxide, NRTL Liquid Activity Coefficient Model, Simulation, Modeling

INTRODUCTION

It can be possible to separate effectively a wanted product using distillation process from the mixture that exhibits thermodynamically highly non-ideal vapor-liquid equilibrium phase behaviors. However, it is inevitable to obtain vapor-liquid equilibrium data for each binary pairs and to select an appropriate thermodynamic model that can calculate these phase equilibrium data well among the various models in order to analyze these distillation processes accurately. DMSO has been used for fiber-spinning solvent and its fundamental physical properties are shown in Table 1.

If simple distillation column is used to separate a mixture consisted of ternary components into each pure components, it can be possible to choose one of the two distillation sequences as shown in Fig. 1(a) and Fig. 1(b) [1]. On the other hand, we can consider possibility of Fig. 2, which takes products from the middle part of

Table 1. The basic properties of dimenthyl sulfoxide

Properties	Values
Normal boiling point (K)	464.15
Molecular weight	78.129
Standard liquid density	1,103.8
Critical temperature (K)	720.00
Critical pressure (kPa)	5,700.00
Critical volume (m^3/k-mole)	0.20890
Critical compressibility factor	0.19891
Acentric factor	0.35
Heat of formation (kJ/k-mole)	−144,620
Free energy of formation (kJ/k-mole)	−82,797

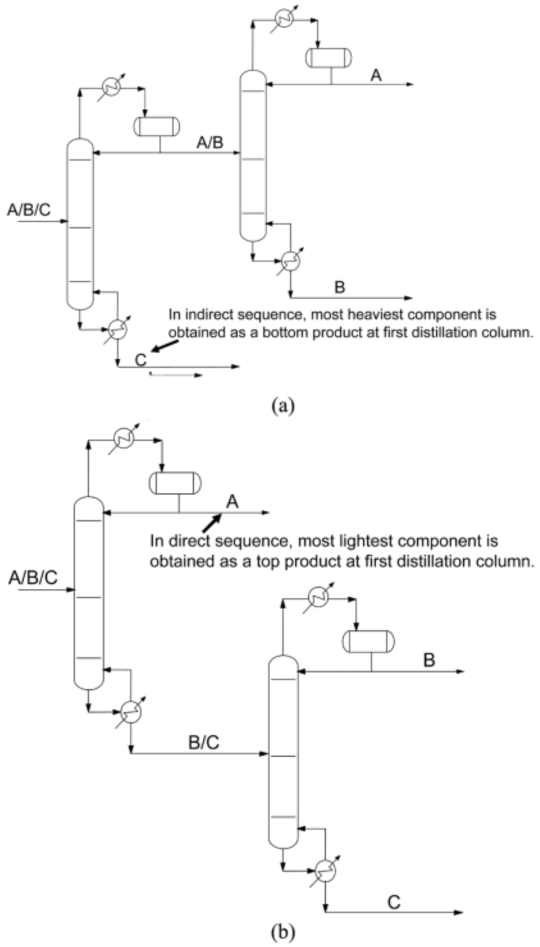

Fig. 1. (a) A schematic diagram of direct sequence. (b) A schematic diagram of indirect sequence.
A. Methanol, B. Water, C. DMSO

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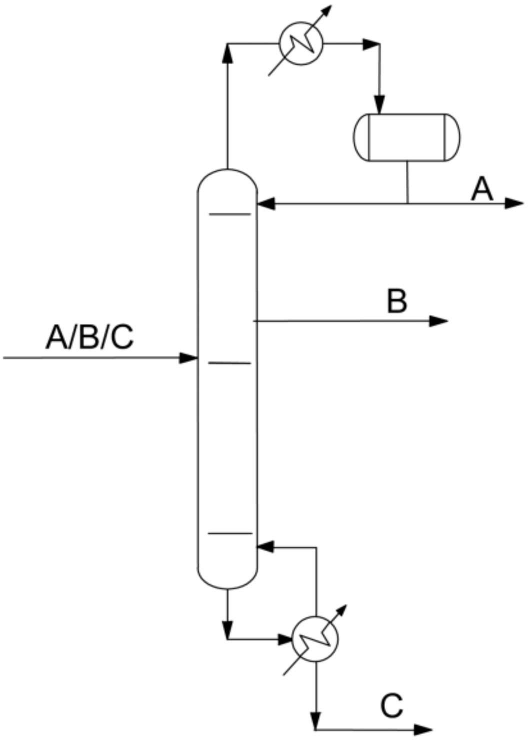

Fig. 2. One feed and three products scheme.
A. Methanol, B. Water, C. DMSO

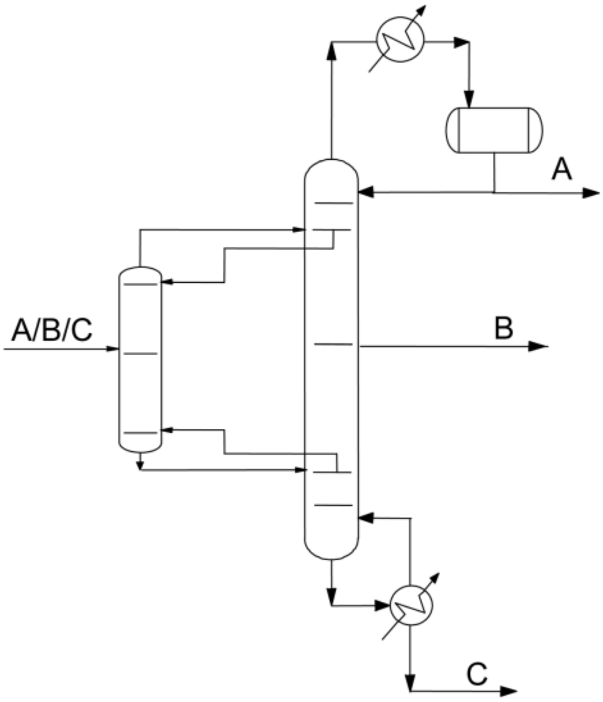

Fig. 3. One feed and three products scheme with a prefractionator.
A. Methanol, B. Water, C. DMSO

the distillation column as an alternative for the two simple distillation columns [2]. In this case, three products are produced from one distillation column. Additionally, arrangement having pre-separator as shown in Fig. 3 [3] and thermally coupled distillation column

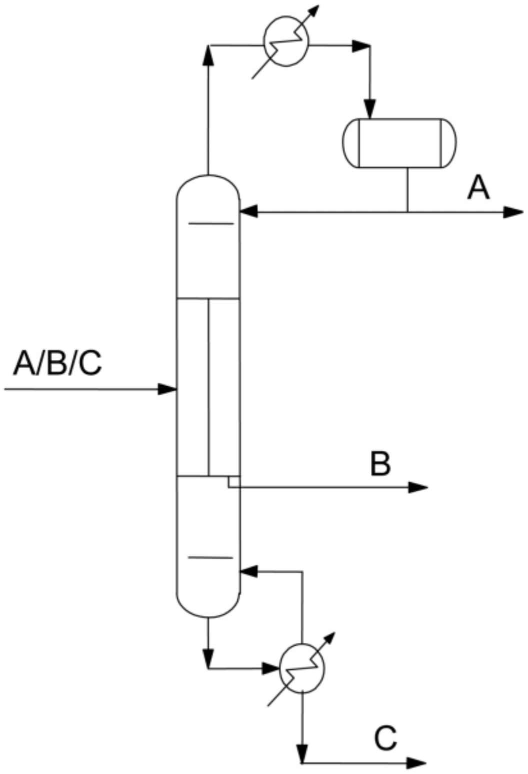

Fig. 4. One feed and three products scheme with an internal divided wall column.
A. Methanol, B. Water, C. DMSO

arrangement as shown in Fig. 4 [4-10] are also considerable; however, we restricted our focus on the Fig. 1(a) and Fig. 1(b) distillation column configurations. Even though distillation arrangements illustrated in Fig. 2 through Fig. 4. are superior to the two simple distillation column arrangements in the aspects of the initial capital and operating costs, it is common to add one more new distillation column to the existing operating column in the actual process. In this case, it will be designed to reuse the existing distillation column and auxiliary equipments to construct new small-scale distillation column to reduce extra expenses. Therefore, Fig. 1(a) or Fig. 1(b) arrangements are most commonly used at actual chemical processes because they are much better than the distillation arrangements shown in Fig. 2 through Fig. 4 in the viewpoint of initial equipment investment costs. The arrangement in Fig. 1(a) is called as the indirect sequence at which the heaviest component is produced as a bottom product in each distillation column. On the other hand, the arrangement shown in Fig. 1b is the direct sequence, at which the lightest component is produced as a top product in each distillation column. There can be big differences between the two distillation sequences in the viewpoint of initial investment costs and the annual operating expenses. In this study, we compared the initial investment costs of equipments, the utility consumptions, the purity of products and recovery ratio for the two distillation sequences.

Ternary system used in this study is the methanol, water and DMSO. Among these three components, DMSO is expensive component that is used as fiber spinning solvent. Hence, we simulated with the target purity over 99.9% by weight of DMSO and maximized the recovery ratio for DMSO as much as possible. In addition, methanol is side-product and its purity was set to simulate at the higher value than 99.9% by weight. To estimate the thermodynamically non-ideal vapor-liquid phase behavior for DMSO, methanol and water systems, we used NRTL liquid activity coefficient model [11]. We used PRO/II with PROVISION releases 7.1, which is a general-purpose commercial process simulator supplied by Simulation Science [12]. Throughout the simulation work performed in this study to obtain each pure component from the ternary mixture, direct sequence is superior to indirect sequence in the aspects of both the initial capital investment costs and annual operating utility consumptions. On the other hand, both distillation processes show similar purity and recovery ratio for the main product, DMSO. Separation process that recovers DMSO from mixture of water and methanol has been operating in the domestic petroleum company using one distillation column. The company could reduce the equipment invest cost and operating cost by direct sequence where added one distillation column to original one distillation column.

THEORY

NRTL (Non Random Two Liquid Mixture) liquid activity coefficient modeling equation, which was suggested by Renon and Prausnitz [11], has been used for the simulation of ternary-components distillation process of methanol, water and DMSO. Liquid activity coefficient formula of component ‘i’ in the mixture can be shown in Eq. (1)

$$\ln\gamma_i = \frac{\sum_j \tau_{ji}G_{ji}x_j}{\sum_k G_{ki}x_k} + \sum_j \frac{x_jG_{ij}}{\sum_k G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_k x_k\tau_{kj}G_{kj}}{\sum_k G_{kj}x_k}\right) \tag{1}$$

In Eq. (1), τ_{ij} and G_{ij} are optimum binary interaction parameters that minimize the deviations between the experimental data and the calculation values, respectively, and can be written as Eqs. (2) and (3):

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{2}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{3}$$

In Eq. (2), T is the absolute temperature, the NRTL model has five binary interaction parameters of a_{ij}, b_{ij}, a_{ji}, b_{ji} and α_{ij} including temperature dependent term for each binary pairs. Optimum NRTL binary interaction parameters were determined by regressing the experimental binary experimental vapor-liquid equilibria data [13,14] by using Pattern search method suggested by Nelder and Mead [15]. Optimum binary adjustable parameters are listed in Table 2. Objective function for the optimization was decided to minimize the summations of deviations in bubble temperatures and bubble compositions between the experimental and calculated ones as shown in Eq. (4)

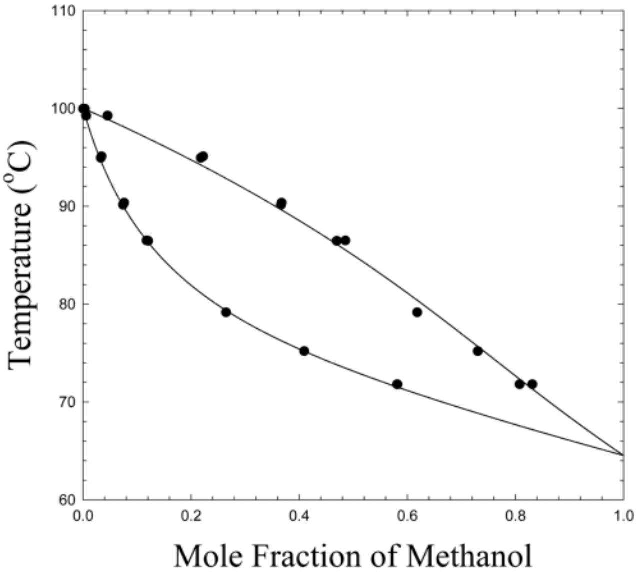

Fig. 5. Isobaric binary vapor-liquid equilibrium data for methanol-water system at 760 mmHg and its plot with NRTL model.

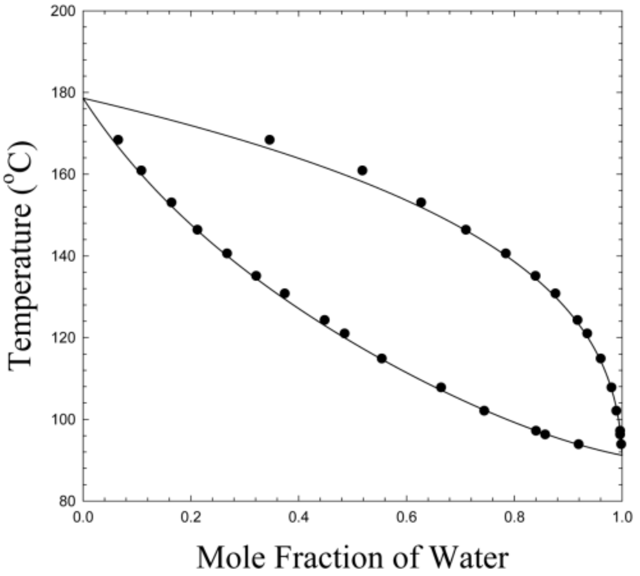

Fig. 6. Isobaric binary vapor-liquid equilibrium data for DMSO-water system at 550 mmHg and its plot with NRTL model.

$$\text{Objective} = \left[\sum_{j=1}^{N}\left(\frac{T_j^{exp} - T_j^{cal}}{T_j^{cal}}\right)^2 + \sum_{j=1}^{N}\left(\frac{y_j^{exp} - y_j^{cal}}{y_j^{cal}}\right)^2\right]\Big/N \tag{4}$$

Fig. 5 to Fig. 7 shows comparisons between the experimental isobaric vapor-liquid equilibrium data and its prediction with NRTL modeling equations for each binary pairs. It has been known that

Table 2. NRTL parameters for methanol-water, methanol-dimethyl sulfoxide and water-dimethyl sulfoxide binary pairs

Components	a_{ij}/K	a_{ji}/K	b_{ij}/K	b_{ji}/K	α_{ij}
Methanol-water	0.0000	0.0000	−371.1840	44.1837	0.2399
Methanol-DMSO	0.0000	0.0000	−524.8210	1,203.7700	0.6615
Water-DMSO	0.7361	0.5111	360.6920	199.8540	0.2442

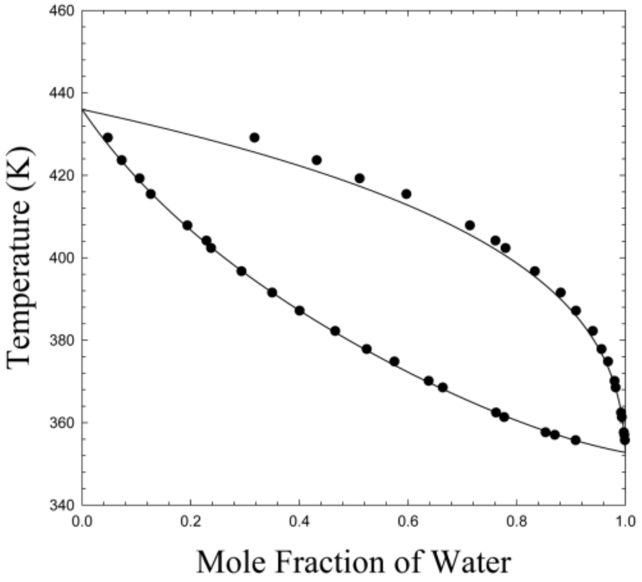

Fig. 7. Isobaric binary vapor-liquid equilibrium data for DMSO-methanol system at 350 mmHg and its plot with NRTL model.

newly decided NTRL liquid activity coefficient modeling equation by regression had calculated well the experimental data of each binary phase equilibrium from the Fig. 5 to Fig. 7.

SIMULATION OF DMSO RECOVERY DISTILLATION PROCESS

To simulate the process that separate DMSO from water and methanol using distillation process, feedstock information including stream composition, thermal conditions and flow rate are summarized in

Table 3. Feed stream information

Component	Flow rate (kg/hr)	Weight percent
Methanol	3,717.1	88.0
Water	169.0	4.0
DMSO	337.0	8.0
Temperature (°C)	25.0	
Pressure (bar)	1.013	
Flow rate (kg/hr)	4,224.0	

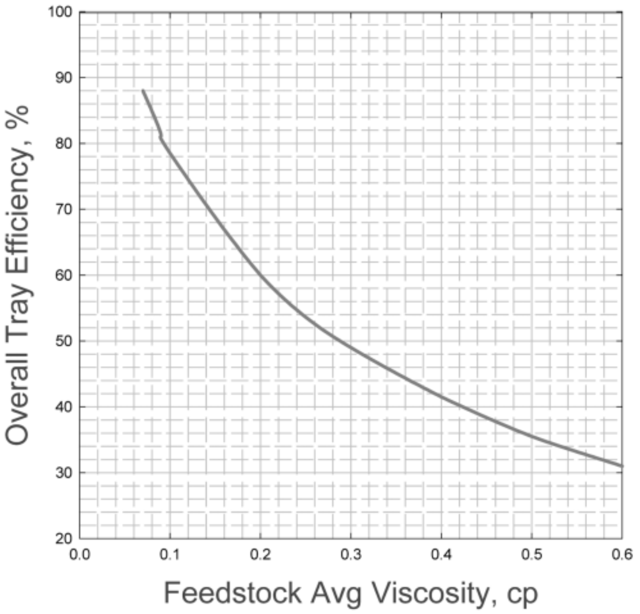

Fig. 8. Overall tray efficiencies as a function of average feedstock liquid viscosity (Viscosity is average of feed as top and bottom temperatures of the column).

Table 4. Input data, specified parameters and output data for direct sequence

Input/output data and specified parameters	Value
Input parameters for 1st distillation column	
Theoretical number of stages	13 including condenser and reboiler
Internal type	Sieve tray
Overhead reflux drum operating temperature	45.0 °C
Overhead reflux drum operating pressure	Atmospheric pressure
Column top pressure	0.26677 kg/cm^{2}G
Stage pressure drop	0.007 kg/cm^2
Reflux ratio	0.80 (by mole)
Input parameters for 2nd distillation column	
Theoretical number of stages	13 including condenser and reboiler
Internal type	Sieve tray
Overhead reflux drum operating temperature	45.0 °C
Overhead reflux drum operating pressure	−0.70 kg/cm^{2}G
Column top pressure	−0.50 kg/cm^{2}G
Reflux ratio	3.4878 (by mole)
Utility conditions	
Cooling water supply temperature	32.0 °C
Cooling water return temperature	40.0 °C
Steam condition	180.0 °C

Table 5. Input data, specified parameters and output data for indirect sequence

Input/output data and specified parameters	Value
Input parameters for 1st distillation column	
Theoretical number of stages	13 including condenser and reboiler
Internal type	Sieve tray
Overhead reflux drum operating temperature	39.4 °C (bubble temperature)
Overhead reflux drum operating pressure	-0.70 kg/cm^{2}G
Column top pressure	-0.50 kg/cm^{2}G
Stage pressure drop	0.007 kg/cm^2
Reflux ratio	0.30 (by mole)
Input parameters for 2nd distillation column	
Theoretical number of stages	13 including condenser and reboiler
Internal type	Sieve tray
Overhead reflux drum operating temperature	45.0 °C
Overhead reflux drum operating pressure	Atmospheric pressure
Column top pressure	0.30 kg/cm^{2}G
Reflux ratio	4.5077 (by mole)
Utility conditions	
Cooling water supply temperature	32.0 °C
Cooling water return temperature	40.0 °C (36 °C for 1st column)
Steam condition	180.0 °C

the Table 3. Cooling water was used for cold utility, where supply temperature was assumed as 32 °C and return temperature was set as 40 °C. Saturated steam at the condition of 180 °C was used for hot utility and reboiler was assumed to be operated to supply only latent heat. Actual stages for distillation column were set to 22 stages because this was based on the actual situation to reuse the existing distillation column. Efficiency of each distillation column was assumed to 50%, which is based on the correlation that the stage efficiency is a function of the liquid feedstock viscosity at the average temperature between top and bottom section of the distillation column shown in Fig. 8. According to Fig 8, due to the feedstock average viscosities are 0.29694 cP and 0.30295 cP of first and second distillation column in direct sequence, the efficiency of distillation column at 0.3 cP shows 50% and this value was decided to the typical efficiency of the two distillation columns. The necessary input data for the simulation of direct sequence and indirect sequence are summarized in Table 4 and Table 5.

1. Direct Sequence

In case of first distillation column in direct sequence, the methanol is separated first from the top of the column, since it is the lowest boiling component, we can treat it as a separation process between water and methanol. Separation of water and methanol was simulated at the atmospheric conditions because the top product methanol can be subcooled at atmospheric pressure. However, in the second distillation column, it will be a separation between water and DMSO. According to Table 1, since the normal boiling temperature of DMSO is very high value, 191.0 °C, the available 180 °C saturated steam cannot be used at atmospheric condition of distillation column. Hence, in this case, the second distillation column has to be operated below atmospheric pressure with vacuum pump. The vapor pressure curve versus temperature of DMSO is shown in Fig. 9. To maintain temperature difference between saturated steam and the reboiler return stream, the operation pressure of the column bottom section was set to -0.50 Kg/cm^{2}G. According to Fig. 9, when the operating pressure at the bottom of distillation column is -0.50 Kg/cm^{2}G, operation temperature is maintained at 167 °C. Hence, the logarithmic mean temperature difference of reboiler is approximately 24 °C, which considered the operating pressure of distillation column with margin. In this case of simulation, pressure drop along the distillation column was ignored but the condenser pressure drop was assumed to 0.20 Kg/cm^2.

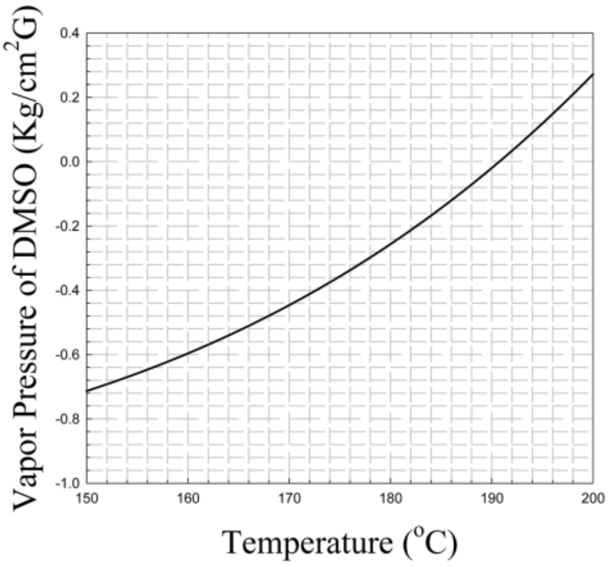

Fig. 9. A plot of DMSO liquid vapor pressure versus temperature.

2. Indirect Sequence

In the indirect sequence, first distillation column can be regarded as a separation process between water and DMSO because the highest boiling material, DMSO, is produced from bottom of the distillation column. Since the second distillation column can be considered as a separation process between methanol and water, therefore, they can be subcooled and condensed at the atmospheric pressure condition, simulation was performed at the atmospheric condition for the second distillation column. However, in the first distillation column, it is a separation between water and DMSO. Similar way in the direct sequence, if the first distillation column operates at atmospheric pressure, it is impossible to use 180 °C saturated steam. Therefore, in this case, first distillation column should be operated at reduced pressure with vacuum pump. According to Fig. 9, same way with direct sequence, operation pressure of bottom of the first distillation column was set to -0.50 Kg/cm^{2}G. Considering condenser pressure drop to 0.20 Kg/cm^2, overhead reflux drum operation pressure was set to -0.70 Kg/cm^{2}G. In that case, return temperature of cooling water cannot be 45 °C because bubble point temperature of the top product stream is as low as 39.4 °C under this condition. Hence, cooling water return temperature should be lowered to 36 °C. When we operate it at this condition, bottom section of the distillation column will be 170 °C and the temperature difference between steam and the reboiler return stream will maintain at 10 °C, we cannot increase the operating pressure of the distillation column. As a result, the indirect sequence uses much more cooling water in the first distillation column than direct sequence.

RESULTS AND DISCUSSIONS

Changing the feed stage location both for direct and indirect sequence minimized the heat duty of reboiler in each distillations column. Fig. 10 shows a plot of reboiler heat duty versus feed stage location for direct sequence. Solid line with solid circle shows the heat duty change for reboiler as a function of feed stage location in the first distillation column. On the other hand, dotted line with solid triangle shows heat duty change for the reboiler in the second distillation column. In case of first distillation column, as lowering the position of the feed stage, heat duty of reboiler decreases until the stage number 7, where the reboiler heat duty is minimum and then show the trends to increase. When feedstock input to the stage number 7 (actually 12 stage from the column top), heat duty of reboiler show the minimum value of 1.9387×10^6 Kcal/hr. In case of the second distillation column, as lowering the position of feedstock input stage, the value increases up to the maximum value at the stage number 7. After then, start to decrease until the minimum value at stage number 11 and show abruptly increasing trends at the final 12 stage. In the second distillation column (actually first stage from top column), when fed into the second stage, the heat duty of reboiler shows minimum value of 0.3794×10^6 Kcal/hr. In Fig. 11, heat duty change of each distillation column was drawn as changing the position of feed stage for the indirect sequence. In case of the first distillation column, even though the feed stage changes, heat duty of the reboiler almost not changed. However, in case of the second distillation column, if the position of feed stage lowered from top to bottom, the heat duty of reboiler decreasing monotonically, show the minimum value of 1.8247×10^6 Kcal/hr at 7 stage (actually 12 stage from column top) and show the trends to increasing again. Therefore, in this arrangement, we decided to feed at stage 7 for both fist and second distillation column.

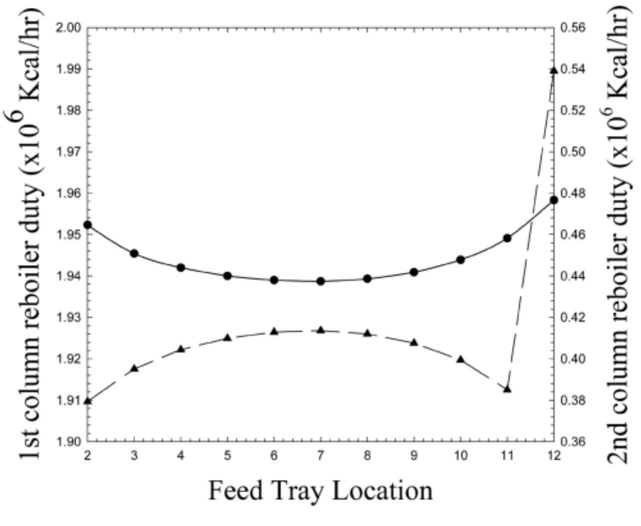

Fig. 10. Plots of each distillation column reboiler heat duties versus feed stage location for direct sequence.

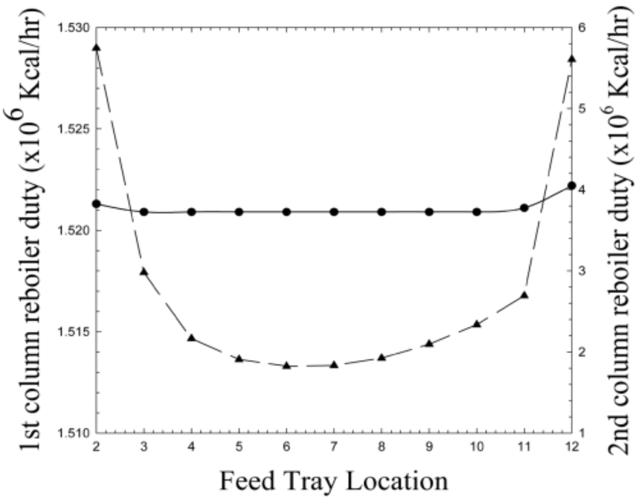

Fig. 11. Plots of each distillation column reboiler heat duties versus feed stage location for indirect sequence.

Table 6 shows a summary of the simulation result for direct sequence and indirect sequence. According to Table 6, direct sequence shows superior results for the purity of the main product, DMSO and byproduct, methanol, diameter of distillation column and utility consumptions. Recovery ratio of DMSO and methanol shows nearly similar results.

CONCLUSIONS

In this study, we concluded as followings after the comparative study for the direct sequence and indirect sequence to separate DMSO over 99.9 wt% purity from water and methanol using distillation process.

1. Direct sequence shows superior purity of the DMSO and methanol to indirect sequence.
2. Indirect sequence shows a little better recovery ratio of DMSO and methanol, but their differences are small and could be neglected.

Table 6. Simulation results summary for direct sequence and indirect sequence

Input/output data and specified parameters	Direct sequence	Indirect sequence
DMSO purity in weight percent	99.9543	99.5000
DMSO recovery ratio	99.9994	100.0000
Methanol purity in weight percent	Stream 5	Stream 3
Methanol recovery ratio	99.6118	99.5993
Methanol draw	99.7967	99.9000
Total reboiler heat duties in 10^6 Kcal/hr	2.3519	3.9894
Total condenser heat duties in 10^6 Kcal/hr	3.8009	3.9066
Cooling water consumptions in Tons/hr	1,380	2,314
Steam consumptions in Tons/hr	7.60	7.82
1^{st} column diameter in mm	1,219	1,372
2^{nd} column diameter in mm	800	1,067
Water impurity in weight percent at DMSO product	0.0457	0.5000

3. Direct sequence shows superior efficiency of utility consumptions and initial equipment investment costs to indirect sequence.

NOMENCLATURE

N	: number of experimental data points
P	: pressure [KPa]
R	: gas constant [J/gmole-K]
T	: absolute temperature [K]
G	: binary interaction parameter in Eq. (1)
a	: binary interaction parameter in Eq. (2)
b	: binary interaction parameter in Eq. (2)
x	: liquid phase mole fraction
y	: vapor phase mole fraction

Greek Letters

α	: interaction parameter in Eq. (1)
γ	: activity coefficient in Eq. (1)
τ	: interaction parameter in Eq. (1)

Superscripts

exp	: experimental value in Eq. (4)
cal	: calculated value in Eq. (4)

Subscript

i, j, k	: component i, j and k

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