

The Effects of Physical Property Estimation on Packed Column Distillation Simulation with a Rate-based Mode

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Abstract

Background/Objectives: we investigate the effects of estimation models for physical properties on the rate-based simulation and discuss what we should be aware of for obtaining better simulation results.

Methods/Statistical analysis: Three kinds of physical property models considered are an activity coefficient, a thermodynamic factor, and a liquid excess molar volume. We use experimental data obtained from a pilot-scale plant for comparison with numerical examples. We investigate the effects of estimation models for physical properties on the rate-based simulation and discuss what we should be aware of for obtaining better simulation results.

Findings: The thermodynamic factor models do not affect largely the simulation results in the distillation simulation where the mass transfer resistance of the vapor phase film is dominant.

The liquid excess molar volume of the ternary mixture of Methanol, Ethanol, and Water shows at most 3% deviations from the averaged molar volume. It affects the simulation results markedly where the composition of the liquid mixture passes through the region of the large excess molar volume.

Improvements/Applications: The simulation results indicate that even small difference in continuous operation becomes much pronounced in batch operation with multicomponent systems.

Keywords: Distillation, Rate-based model, Activity coefficient, Thermodynamic factor, Excess molar volume

1. Introduction

In order to meet increasing demands on rigorous simulation for distillation, a rate-based model has been developed by considering heat and mass transfer between vapor and liquid phases [1,2]. In order to conduct properly the rate-based simulation of distillation, we need a number of estimation models for physico-chemical properties.

In the following, we investigate the effects of estimation models for physical properties on the rate-based simulation and discuss what we should be aware of for obtaining better simulation results.

2. Estimation of Physical Properties of Mixtures

This work focuses on the effects of estimation models for physical properties on simulation results. The property models considered are an activity coefficient, a thermodynamic factor, and a liquid excess molar volume. The estimation models of mixture properties other than above are listed in Table 1.

Table 1: Estimation of mixture properties

| | |
|----------------------------|---|
| Vapor Diffusivity | Brokaw (Reid et al., 1987) |
| Liquid diffusivity | Raddy and Doraisway (Reid et al., 1987) |
| Vapor viscosity | Brokaw (Reid et al., 1987) |
| Vapor thermal conductivity | Lindsay-Bromley (Reid et al., 1987) |

| | |
|-----------------------------|-------------------------------------|
| Liquid thermal conductivity | Li (Reid et al., 1987) |
| Others | Molar average |
| Heat transfer coefficient | Chilton-Colburn (Bird et al., 1963) |

2.1. Activity Coefficient Models

We employ the NRTL model and the modified UNIFAC (m-UNIFAC) model for the estimation of liquid phase activity coefficients for vapor-liquid equilibrium calculations. The model parameters of NRTL are taken from Gmehling and Onken [3] and m-UNIFAC from Gmehling et al [4].

2.2. Activity Thermodynamic Factors Derived from Activity Coefficient Models

When a Maxwell-Stefan equation is solved for an analysis of multicomponent mass transfer in vapor and liquid films, thermodynamic factors are essential for considering nonideality of liquid mixtures. Expressions of the thermodynamic factors derived from NRTL are presented by Taylor and Kooijman [5]. In our simulation with the rate-based model, we employ NRTL as the activity coefficient model for evaluating the thermodynamic factors.

2.3. Liquid Excess Molar Volumes

The assumption of an averaged molar volume for real liquid mixtures is not applicable, because of the excess molar volume.

3. Numerical Examples and Discussion

The dimension of the column and the geometry of packing used for the experiments are listed in Table 2. The experimental and

calculation conditions are shown in Table 3 for continuous operation and in Table 4 for batch operation. In each operating condition, we investigate the simulation results obtained with the different combinations of the estimation models as follows.

Table 2: Dimensions of packed column and packing element

| Column | | |
|---------------------------------|--------------------------------------|--------------------------------------|
| Column height | 3.00 m | |
| Packed height | 2.16 m | |
| Diameter | 0.21 m | |
| Capacity of Still | 0.30 m ³ | |
| Heat transfer area of reboiler | 7.8 m ² | |
| Heat transfer area of condenser | 12.3 m ² | |
| Packing | MC-250S | MC-350S |
| Element diameter | 0.199 m | 0.202 m |
| Element height | 0.180 m | 0.180 m |
| Height of triangle | 9.9×10^{-3} m | 5.5×10^{-3} m |
| Base of triangle | 25.4×10^{-3} m | 19.3×10^{-3} m |
| Corrugation spacing | 15.6×10^{-3} m | 11.1×10^{-3} m |
| Specific surface area | 250 m ² / m ³ | 350 m ² / m ³ |
| Void fraction | 0.98 m ³ / m ³ | 0.98 m ³ / m ³ |
| Channel flow angle | 45 ⁰ | 45 ⁰ |

Table 3: Experimental conditions (Continuous distillation)

| | |
|--------------------|--|
| System | Methanol (1) / Ethanol (2) / Water (3) |
| Pressure | 102.5 kPa (top) 102.5kPa (bottom) |
| Feed | 0.605 mol/s (center feed) |
| Feed temperature | $t_F = 298.15$ K |
| Feed composition | 0.639 (1) / 0.332 (2) / 0.029 (3) |
| Distillate | 0.327 mol / s |
| Bottoms | 0.278 mol / s |
| Reflux ratio | $R_D = 1.28$ |
| Reflux temperature | $t_D = 294.55$ K |
| Packing | MC-350S |

Table 4: Experimental conditions (Batch distillation)

| | |
|---------------------------|--|
| System | Methanol (1) / Ethanol (2) / Water (3) |
| Pressure | 101.5 kPa (top) 101.5 kPa (bottom) |
| Heat duty of the reboiler | $38376 - 0.2207t - 5.4564 \times 10^{-5}t^2 + 3.7669 \times 10^{-9}t^3$ [W] (t [s]) |
| Condenser temperature | $T_1 = 299.05$ K (experiment) |
| Reflux temperature | $T_2 = 296.45$ K (experiment) |
| Charge | 12611 mol |
| Charge composition | 0.1013 (1) / 0.0471 (2) / 0.8516 (3) |
| Distillate | 6.767×10^{-6} m ³ / s (controlled) |
| Holdup | 8.00 × 10 ⁻³ m ³ / condenser 21.88 × 10 ⁻³ m ³ / reflux drum 50 mol / column |
| Packing | MC-250S |

3.1. Effect of Activity Coefficient Models

Figure 1 shows x, y-T diagrams of Methanol-Ethanol, Methanol-Water, and Ethanol-Water systems calculated at the total pressure of 101.3 kPa using NRTL and m-UNIFAC. A difference between the activity coefficient models can be seen in Figure1. In the following simulation, the thermodynamic factors are assumed to be unity, the liquid excess molar volumes are considered, and the other mixture properties are calculated as listed in Table 1.

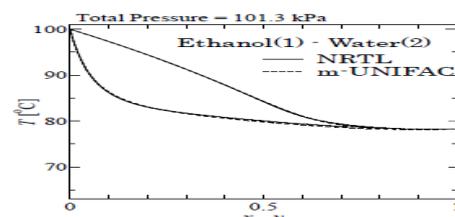
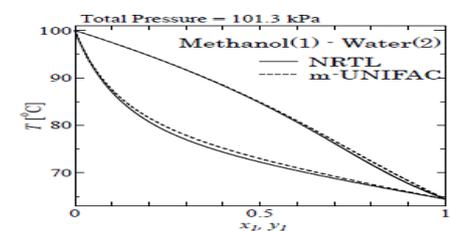
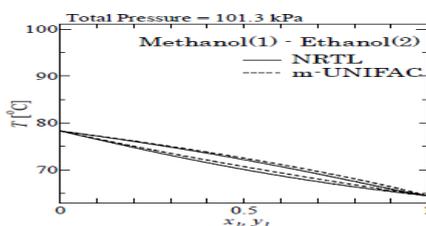
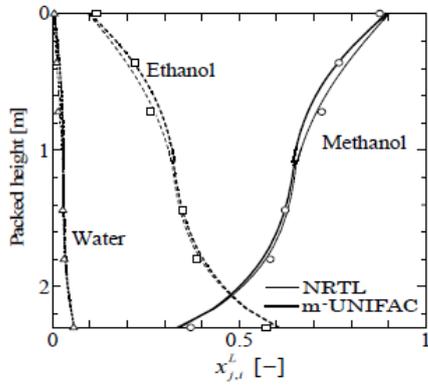
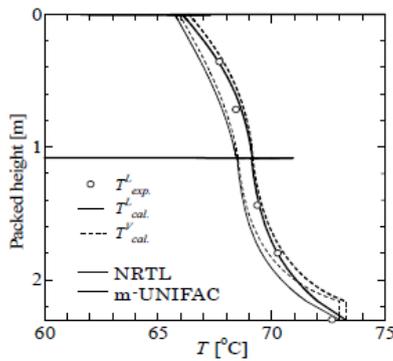


Figure 1: Vapor-liquid equilibrium with different activity coefficient models

The composition and temperature profiles in the continuous operation with NRTL and m-UNIFAC are shown in Figure 2 accompanied by the experimental results. The distillation curves and the time variation of the top vapor temperature in the batch operation are shown in the same order of magnitude in Figure 3. In Figure 2 and 3, a difference in the composition and temperature profiles is observed such as in the binary x , y - T diagrams.

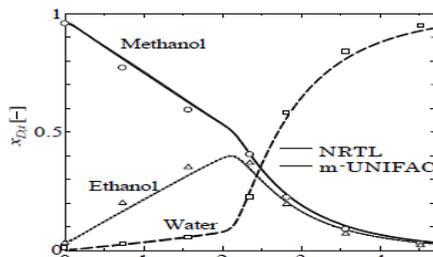


(a) Composition profiles

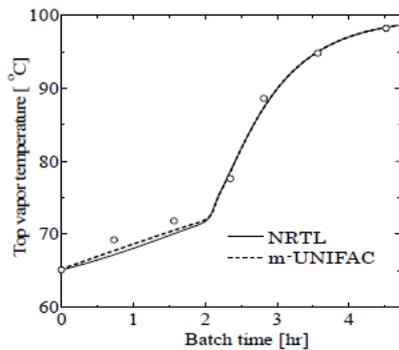


(b) Temperature profiles

Figure 2: Comparison of experimental and calculated results with different activity coefficient models(in continuous distillation)



(a) Distillate composition profiles



(b) Top vapor temperature profiles

Figure 3: Comparison of experimental and calculated results with different activity coefficient models (in batch distillation)

Contours for bubble point temperatures and composition profiles are shown in Figure 4 and Figure 5 for the continuous and batch operation, respectively. An appreciable difference in the contours for bubble point temperatures is observed in Figure 4 and Figure 5. The difference in the results of the batch operation in Figure 5 is significant compared with that in the results of the continuous operation in Figure 4.

Therefore, when we simulate a batch distillation, we should assess the effects of the activity coefficient model and parameters chosen on the vapor-liquid equilibria in the operating region.

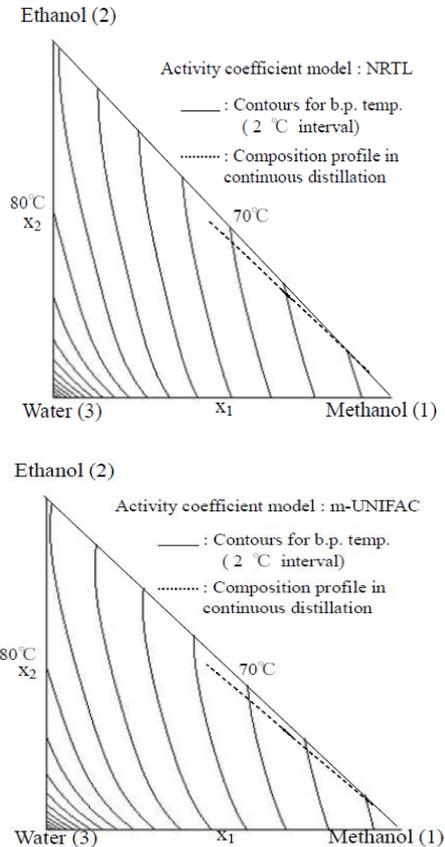


Figure 4: Contours for b.p. temperature and composition profiles in continuous distillation with different activity coefficient models

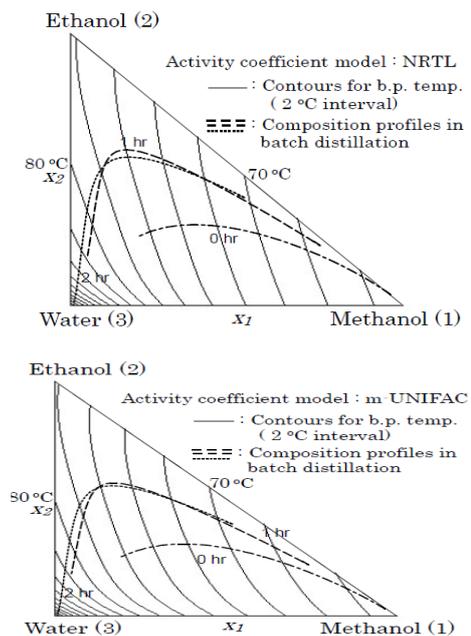
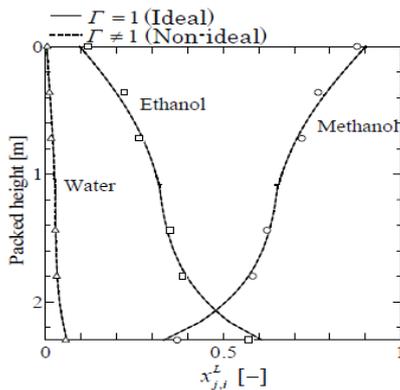


Figure 5: Contours for b.p. temperature and composition profiles in batch distillation with different activity coefficient models

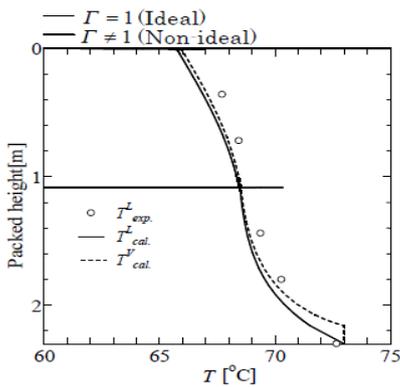
3.2. Effect of Thermodynamic Factors

In the simulation for studying the effects of the thermodynamic factor, the following assumptions are considered; the activity coefficient models employed is NRTL, the liquid excess molar volume is considered, and the other mixture properties are calculated as listed in Table 1.

The simulation results in the continuous operation are shown in Figure 6. Using the same physical properties as in the continuous operation, the simulation results in the batch operation are shown in Figure 7. For both continuous and batch operations, we hardly find the differences between the ideality and the non-ideality of thermodynamic factors in Figure 6 and Figure 7.

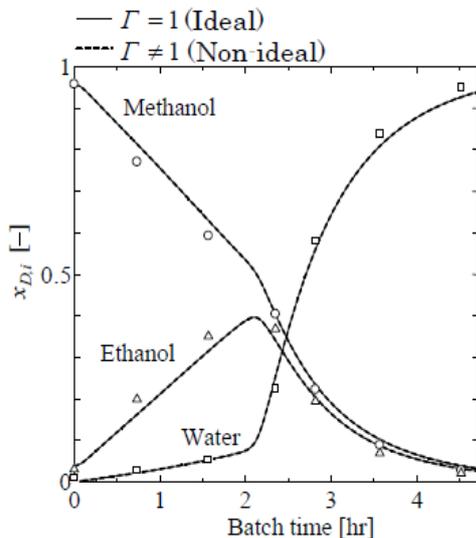


(a) Composition profiles

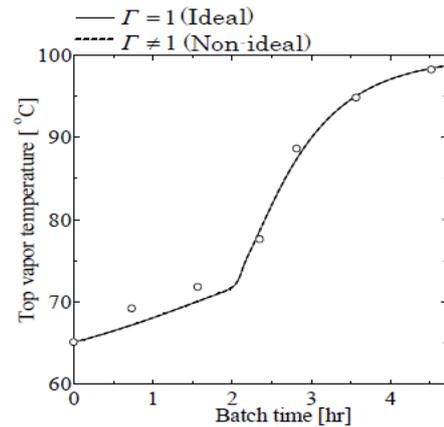


(b) Temperature profiles

Figure 6: Comparison of experimental and calculated results with different thermodynamic factor models (in continuous distillation)



(a) Distillate composition profiles



(b) Top vapor temperature profiles

Figure 7: Comparison of experimental and calculated results with different thermodynamic factor models (in batch distillation)

Figure 8 shows the profiles of liquid multicomponent mass transfer coefficients, and the ratio of the vapor / liquid mass transfer resistance, in the continuous operation. Although we can see the effect of the thermodynamic factors on, the overall mass transfer resistance is dominated by the vapor phase film, as the values of k_L are greater than 10. This results in the small effect in Figure 6 and Figure 7. When a operation with a wide boiling mixture which has a large temperature difference between vapor and liquid is performed, the effect of the thermodynamic factors on the simulation results will be significant, since the k_L will have smaller values.

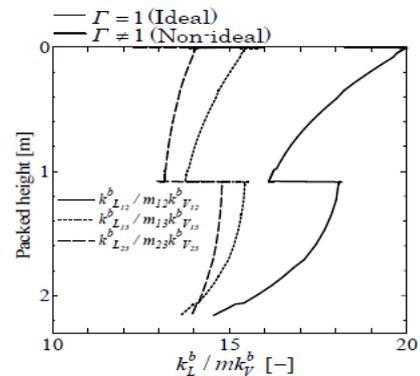
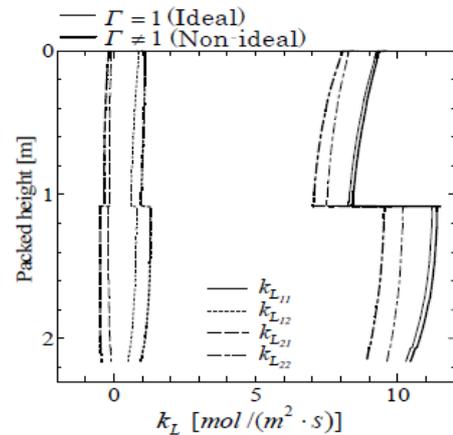


Figure 8: Multicomponent liquid mass transfer coefficients profiles and the ratio of the vapor / liquid mass transfer resistance (in continuous distillation)

3.3. Effect of Liquid Excess Molar Volume

In the batch simulation for comparing the results with or without the liquid excess molar volume, the activity coefficient models

employed is NRTL, the thermodynamic factors are assumed to ideal, and the other mixture properties are calculated as listed in Table 1.

The simulation results are shown in Figure 9. The difference in the composition and temperature between with or without the liquid excess molar volume becomes pronounced after the batch time of 2 hours. The molar holdup of the reflux drum and the distillate compositions are plotted in Figure 10. The distillation curves pass through the region of the large excess molar volume after 2 hours. This arises the change in the molar liquid holdup.

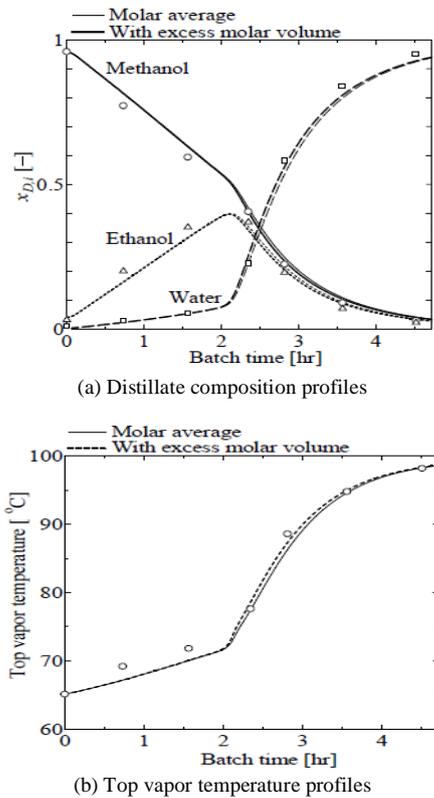


Figure 9: Comparison of experimental and calculated results with or without the liquid excess molar volume (in batch distillation)

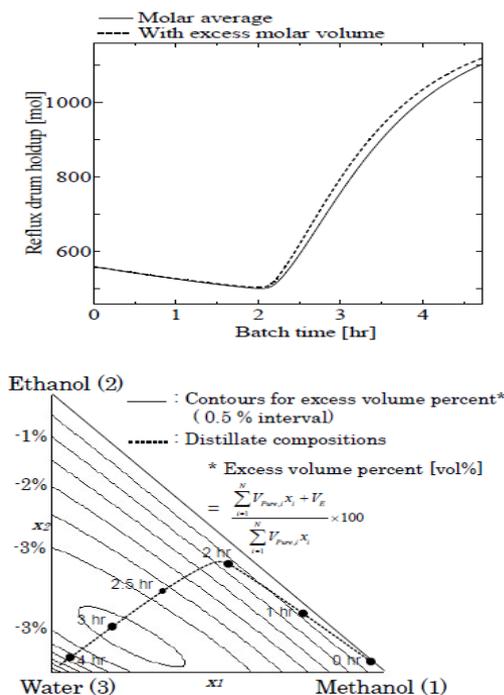


Figure 10: Time variation of the reflux drum molar holdup and contours for excess volume percent and distillate compositions in batch distillation

4. Conclusion

We discussed how the different estimation models of the three physical properties affect the simulation results in distillation simulations with the rate-based model. When we use the activity coefficient models with the parameters to estimate the vapor-liquid equilibrium relationship in batch operation, we should confirm how the models affect the results and employ the parameters with great care.

The thermodynamic factor models do not affect largely the simulation results in the distillation simulation where the mass transfer resistance of the vapor phase film is dominant.

The liquid excess molar volume of the ternary mixture of Methanol, Ethanol, and Water shows at most 3% deviations from the averaged molar volume. It affects the simulation results markedly where the composition of the liquid mixture passes through the region of the large excess molar volume. A proper estimation of the liquid mixture molar volume is required in the distillation simulation when the liquid composition varies with the time such as a batch operation.

5. Nomenclature

| | |
|-------|--|
| k | = multicomponent mass transfer coefficient [mol/(m ² ·s)] |
| k^b | = binary mass transfer coefficient [mol/(m ² ·s)] |
| m | = vapor-liquid equilibrium ratio [-] |
| N | = number of components [-] |
| T | = temperature [K] |
| V | = molar volume [cm ³ /mol] |
| x | = mole fraction in liquid phase [-] |
| y | = mole fraction in vapor phase [-] |

<Subscripts>

| | |
|--------|-----------------------------|
| E | = excess property |
| i | = component number |
| j | = segment number |
| L | = referring to liquid phase |
| $Pure$ | = pure substance property |
| V | = referring to vapor phase |

<Super scripts>

| | |
|-----|-----------------------------|
| I | = referring to interface |
| L | = referring to liquid phase |
| V | = referring to vapor phase |

References

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