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APPLICATION OF THE UNIFAC AND MODIFIED UNIFAC (DORTMUND) MODELS TO PREDICT VAPOR–LIQUID EQUILIBRIUM IN BINARY SYSTEMS OF ACETONE + 1-BUTANOL, ACETONE + ETHANOL, AND ETHANOL + 1-BUTANOL

A. Mustain[1,*], B. T. Arta[1], A. A. Wibowo[1], P. H. Suharti[1], H. Hardjono[1], M. Effendy[2]

[1]*Department of Chemical Engineering, Politeknik Negeri Malang, Indonesia*
[2]*Department of Mechanical Engineering, Universitas Negeri Surabaya, Indonesia*

*asalil89@polinema.ac.id

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The production of biobutanol is typically conducted via a fermentation method known as the acetone–butanol–ethanol (ABE) process, which produces three primary products: acetone, butanol, and ethanol. In the purification of ABE fermentation products, vapor–liquid equilibrium (VLE) data for the binary mixtures of these components are crucial for accurate process design and optimization. Therefore, isobaric VLE data for the binary mixtures of acetone + 1-butanol, acetone + ethanol, and ethanol + 1-butanol were investigated in this study. The VLE data were predicted using group-contribution activity coefficient models, specifically the UNIQUAC Functional-group Activity Coefficients (UNIFAC) and the modified UNIFAC (Dortmund) models. Minor discrepancies were observed between the calculated values and the experimental measurements for both models. Nevertheless, the modified UNIFAC (Dortmund) model exhibited slightly better agreement with the experimental data, as evidenced by lower deviations in the predicted values. The results indicate that both models are suitable for predicting the VLE behavior of binary mixtures relevant to ABE fermentation products.

Keywords: *ABE fermentation, prediction model, UNIFAC, vapor-liquid equilibrium.*

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Introduction

Biobutanol is a biofuel that offers a viable alternative to fossil fuels. It is an alcohol-based compound produced through fermentation by *Clostridium acetobutylicum, Clostridium beijinrickii,* and other closely related species. This microorganism can utilize a broad spectrum of carbohydrate-rich substrates, including arabinose, xylose, mannose, cellobiose, galactose, fructose, and glucose, to synthesize butanol [1, 2]. Compared to bioethanol, biobutanol possesses several advantageous properties: it is less explosive, less toxic, less corrosive, and has a higher energy content [3]. Owing to these advantages, biobutanol is considered a potential environmentally friendly fuel for future energy applications.

The fermentation of biomass that yields biobutanol is commonly referred to as acetone-butanol-ethanol (ABE) fermentation [4, 5]. It produces not only butanol but also acetone and ethanol as primary products. This process employs specific bacterial strains to ferment carbohydrate sources such as starch and glucose into acetone, butanol, and ethanol. However, one of the major limitations of ABE fermentation is the low concentration of butanol produced, which necessitates further development in downstream separation and purification technologies [6, 7].

In recent years, researchers have conducted various experimental simulations to

enhance the efficiency of the ABE process. Upstream improvements have focused on biochemical pathways and microbial strain optimization, while downstream processes have explored techniques such as extraction, distillation, adsorption, and gas stripping. Among these, distillation remains the most widely used method due to its operational simplicity and ability to produce high-purity products [8–10].

The success of a distillation process largely depends on the equilibrium established between the vapor and liquid phases of a mixture [11, 12]. In the context of acetone–butanol–ethanol mixtures, accurate binary VLE data must be known for all component pairs. Therefore, in this study, the binary vapor–liquid equilibrium (VLE) behavior of the acetone + 1-butanol, acetone + ethanol, and ethanol + 1-butanol systems was predicted. The UNIQUAC Functional-group Activity Coefficients (UNIFAC) model is one of the most widely used activity coefficient models for predicting VLE data in multicomponent systems. The UNIFAC model was introduced as a predictive modification of the universal quasi-chemical (UNIQUAC) model [13]. It follows the same fundamental approach as UNIQUAC by dividing the activity coefficient into combinatorial and residual contributions; however, instead of using interaction parameters for individual molecules, UNIFAC employs interaction parameters based on functional groups. Two types of UNIFAC models, namely the original UNIFAC model [14] and the modified UNIFAC (Dortmund) model [15], were employed in this study. The predictions were performed at a pressure of 101.3 kPa and compared with available experimental data. The accuracy of each model was evaluated based on the deviation between predicted values and experimental data. The predicted VLE data for the acetone + ethanol system were compared with the experimental measurements reported by Ku and Tu [16]. Similarly, the data for the ethanol + 1-butanol system were compared with experimental results obtained by Seo et al. [17]. In contrast, due to the limited availability of complete bubble point and dew point data for the acetone + 1-butanol system at 101.3 kPa in the open literature [18], the VLE data for this binary system were also measured in this study using an Othmer-type ebulliometer, serving as a comparison for the predicted values.

Experimental Section

For VLE measurements of the acetone + 1-butanol system in this study, analytical-grade acetone and 1-butanol obtained from commercial suppliers were utilized. The mass fraction purities of acetone and 1-butanol exceeded 0.998 and 0.995, respectively. Specifically, acetone and 1-butanol were sourced from Merck (Germany). All chemicals were used without further purification. Detailed information on the compounds used is provided in Table 1.

Table 1. Material specifications used in this study for VLE measurements of the acetone + 1-butanol system.

Component	Supplier	Mass Fraction Purity	MW (g/mol)	Purification Method
Acetone	Merck (Germany)	0.998	58.080	None
1-Butanol	Merck (Germany)	0.995	74.123	None

Isobaric vapor–liquid equilibrium (VLE) data for binary acetone + 1-butanol system were obtained using a modified Othmer-type recirculating still. The detailed operating procedure of the apparatus follows the methodology described by Hardjono et al. [19]. For each experimental run, a binary mixture of acetone and 1-butanol at predetermined compositions was prepared and introduced into an ebulliometer. Approximately 150 cm^3 of the solution was used per measurement. Heating and mixing were facilitated by a heater integrated with a magnetic stirrer to ensure uniform temperature distribution and solution homogeneity.

To maintain a constant pressure of (101.3 ± 0.2) kPa within the ebulliometer, a pressure regulation system was employed,

comprising a water reservoir for elevation control and a graduated burette connected to the still. This setup was necessary due to the local atmospheric pressure being lower than the standard atmospheric pressure. A barometer (Germany) with a precision of ±0.1 kPa was used to monitor the local atmospheric conditions. The pressure difference between the local and standard atmospheric pressures was compensated by adjusting the water level differential between the reservoir and the burette.

In the ebulliometer, the sample was circulated for at least one hour to ensure equilibrium conditions. Equilibrium was assumed to be achieved when stable readings of both temperature and pressure were observed. Upon reaching this condition, the equilibrium temperature was recorded. Temperature measurements were carried out using a calibrated Type-K digital thermometer with an accuracy of ±0.1 K. Subsequently, both condensed vapor and liquid phase samples were collected for analysis using gas chromatography.

Condensed vapor and liquid samples were injected into a gas chromatography using a syringe. The sample composition was subsequently analyzed using a gas chromatography (Hewlett Packard Model 5890, USA), which was equipped with a flame ionization detector (FID) and a capillary column with SGE Analytical Science BP-1. High-purity helium (mass fraction >0.999) was employed as the carrier gas, maintaining a constant flow rate of 30 $cm^3 \cdot min^{-1}$. The temperature settings for the gas chromatography were 343.15 K for the injector, 478.15 K for the oven, and 478.15 K for the detector. The chromatographic responses for each sample were recorded using 3390A Integrator Hewlett Packard). Calibration curves were constructed for the system under study to convert the area fraction data obtained from the gas chromatography into mole fraction values. Several standard solution compositions were prepared gravimetrically using an analytical balance (Mettler AE200, USA), with a precision of ±0.0001 g across the entire composition range. All gas chromatography measurements for the VLE samples, including both vapor-phase and liquid-phase compositions, were performed in triplicate under identical GC operating conditions to ensure the accuracy, repeatability, and reliability of the VLE composition data.

In the prediction of VLE data by using the UNIFAC and modified UNIFAC (Dortmund) models, the vapor phase was assumed to behave as an ideal gas, as the measured VLE data were determined at low pressure (101.3 kPa). Meanwhile, the liquid phase was treated as a non-ideal mixture. The following equation can be used to describe the VLE relationship under these conditions:

$$x_i P = y_i \gamma_i P_i^s \quad (1)$$

Where x_i represents the mole fraction of component i in the liquid phase, and y_i represents the mole fraction of component i in the vapor phase. γ_i denotes the activity coefficient of component i. P is the system pressure, and P_i^s is the vapor pressure of the pure component i, which is calculated using the extended Antoine equation:

$$\ln\left(P_i^s\right) = A + \frac{B}{T} + C\ln T + DT^E \quad (2)$$

The constants of the extended Antoine equation, namely A, B, C, D, and E, used in this study are listed in Table 2.

Table 2. The extended Antoine equation parameters for individual pure components [20, 21].

Component	A	B	C	D	E
Acetone	62.0982	-5599.6	-7.0985	6.224×10^{-6}	2
Ethanol	66.3962	-7122.3	-7.1424	2.885×10^{-6}	2
1-Butanol	99.3822	-9866.4	-11.655	1.083×10^{-17}	6

The predictive UNIFAC and modified UNIFAC (Dortmund) models were employed to estimate the activity coefficients (γ). For the UNIFAC model, the values of γ is calculated as

the sum of the combinatorial and residual contributions:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (3)$$

The combinatorial contribution is determined based on the molecular size and shape, as expressed in the following equation:

$$\ln \gamma_i^C = 1 - V_i + \ln V_i - \frac{z}{2} q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right) \quad (4)$$

where

$$V_i = \frac{r_i}{\sum_j^N r_j x_j}; \qquad F_i = \frac{q_i}{\sum_j^N q_j x_j} \quad (5)$$

x_i represents the liquid-phase mole fraction of component *i*, while *z* denotes the lattice coordination number, which is assumed to be constant and equal to 10. The surface area parameter (*q*) and volume parameter (*r*) of pure components are calculated from the relative van der Waals group parameters, R_k and Q_k, of subgroup *k* using the following equations:

$$r_i = \sum_k^N v_k^{(i)} R_k; \qquad q_i = \sum_k^N v_k^{(i)} Q_k \quad (6)$$

$v_k^{(i)}$ represents the number of functional groups of type *k* present in molecule *i*. Meanwhile, the residual contribution is determined from the intermolecular interactions according to the following expression:

$$\ln \gamma_i^R = \sum_k^N v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (7)$$

where Γ_k denotes the activity coefficient of group *k*, while $\Gamma_k^{(i)}$ represents the activity coefficient of group *k* in pure component *i*. The value of Γ_k can be calculated using the following expression:

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m^N \Theta_m \Psi_{mk} \right) - \sum_m^N \frac{\Theta_m \Psi_{km}}{\sum_n^N \Theta_n \Psi_{nm}} \right] \quad (8)$$

The same equation and approach are also applied to determine the values of $\Gamma_k^{(i)}$. In Eq. (8), Θ_m represents the group surface area fraction, while X_m denotes the group mole fraction, which are defined as follows:

$$\Theta_m = \frac{Q_m X_m}{\sum_n^N Q_n X_n}; \qquad X_m = \frac{\sum_j^N v_m^{(j)} x_j}{\sum_j^N \sum_n^M v_n^{(j)} x_j} \quad (9)$$

with

$$\Psi_{mn} = \exp\left(-\frac{a_{mn}}{T} \right) \quad (10)$$

For the Modified UNIFAC (Dortmund) model, the activity coefficient is also calculated using Eq. (3). However, the combinatorial contribution is modified as follows:

$$\ln \gamma_i^C = 1 - V_i' + \ln V_i' - \frac{z}{2} q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right) \quad (11)$$

where

$$V_i' = \frac{r_i^{3/4}}{\sum_j^N r_j^{3/4} x_j} \quad (12)$$

The residual contribution is described in the same manner as presented in Eq. (8). However, the parameter ψ_{mn} is defined using three group interaction parameters, namely a_{mn}, b_{mn}, and c_{mn}, as expressed below:

$$\Psi_{mn} = \exp\left(-\frac{a_{mn} + b_{mn} T + c_{mn} T^2}{T} \right) \quad (13)$$

The method used to calculate the VLE data in this study follows the procedure previously described in our earlier work [22]. In this approach, the pressure (*P*) and the liquid phase mole fraction (x_i) were predefined, and the corresponding temperature (*T*) was obtained through iterative bubble point calculations. Using the resulting *P*-*T*-x_i data, the value of y_i was subsequently computed.

Results and Discussions

As an initial step in this study, the VLE data for the binary system of acetone + 1-butanol was measured at a pressure of 101.3 kPa using a modified Othmer recirculating equilibrium still. This measurement was conducted due to the limited availability of existing data for this system, as most literature sources report VLE

data only at the bubble point region. The measured experimental data are shown in Table 3. Statistical analysis of the measured VLE data for the acetone + 1-butanol system was also performed in this study. The analysis was carried out by calculating the expanded uncertainties of the variables P, T, x_1, and y_1 using a coverage factor of $k = 2$, as presented in the footnote of Table 3.

Table 3. Vapor-liquid equilibrium data for the binary system of acetone (1) + 1-butanol (2) at 101.3 kPa measured in this study[a].

T (K)	x_1	y_1
390.9	0.0000	0.0000
384.1	0.0397	0.2375
382.4	0.0469	0.2724
380.9	0.0561	0.3203
369.5	0.1407	0.6113
355.3	0.2731	0.8122
350.0	0.3677	0.8726
348.0	0.3701	0.8785
342.3	0.5224	0.9265
333.8	0.7576	0.9725
332.3	0.8329	0.9824
330.7	0.9277	0.9933
329.3	1.0000	1.0000

[a]Expanded uncertainties calculated with a coverage factor of $k = 2$: $U(T) = 0.2$ K, $U(P) = 0.2$ kPa, $U(x_1) = 0.0075$, and $U(y_1) = 0.0096$.

The thermodynamic consistency of the measured binary acetone + 1-butanol systems in this study was evaluated using the L-W Wisniak test [23]. In this method, the consistency test is described by applying the Gibbs-Duhem equation, incorporating the general expression of the vapor-liquid equilibrium relationship along with the Clausius-Clapeyron equation [24]. The consistency criterion is evaluated using the parameters L_i and W_i, where the experimental data are considered thermodynamically point-to-point test consistent if the requirement for the L_i/W_i ratio to be between 0.92 and 1.08 is satisfied. The results of the thermodynamic consistency test are presented in Table 4, indicating that all experimental data are thermodynamically consistent.

Furthermore, VLE data were predicted at 101.3 kPa for three binary systems representing mixtures of the primary products of ABE fermentation: acetone + 1-butanol, acetone + ethanol, and ethanol + 1-butanol.

Table 4. Thermodynamic consistency test with the L−W Wisniak test for the binary system of acetone (1) + 1-butanol (2) at 101.3 kPa.

x_1	L_i	W_i	L_i/W_i	Consistency
0.0397	4.8556	5.2297	0.9285	Passed
0.0469	6.1985	6.0474	1.0250	Passed
0.0561	7.2410	7.2528	0.9984	Passed
0.1407	14.3876	15.4530	0.9311	Passed
0.2731	21.6746	21.6746	1.0000	Passed
0.3677	21.7644	22.3998	0.9716	Passed
0.3701	23.6492	22.8325	1.0358	Passed
0.5224	20.4326	20.4351	0.9999	Passed
0.7576	13.7025	13.3638	1.0253	Passed
0.8329	9.8720	9.8804	0.9991	Passed
0.9277	4.3993	4.7252	0.9310	Passed

The group volume (R_k) and surface area (Q_k) parameters for each component are provided in Table 5 for both predictive models. The group-interaction parameters applied in the UNIFAC and modified UNIFAC (Dortmund) models are listed in Tables 6 and 7, respectively. In both models, the group-interaction parameters between the same main groups are set to zero

Table 5. Group specifications for each component.

Component	Main Group	Sub Group	No.	$v_k^{(i)}$	R_k	Q_k
UNIFAC [25]						
Acetone	1	CH3	1	1	0.9011	0.848
	9	CH3CO	19	1	1.6724	1.488
Ethanol	1	CH3	1	1	0.9011	0.848
	1	CH2	2	1	0.6744	0.540
	5	OH	15	1	1.0000	1.200
1-Butanol	1	CH3	1	1	0.9011	0.848
	1	CH2	2	3	0.6744	0.540
	5	OH	15	1	1.0000	1.200
Modified UNIFAC (Dortmund) [26]						
Acetone	1	CH3	1	1	0.6325	1.0608
	9	CH3CO	18	1	1.7048	1.6700
Ethanol	1	CH3	1	1	0.6325	1.0608
	1	CH2	2	1	0.6325	0.7081
	5	OH (p)	14	1	1.2302	0.8927
1-Butanol	1	CH3	1	1	0.6325	1.0608
	1	CH2	2	3	0.6325	0.7081
	5	OH (p)	14	1	1.2302	0.8927

Table 6. UNIFAC group-interaction parameters, a_{mn}, in K [25].

Main Group	n = 1	5	6
m = 1	0	986.5	697.2
5	156.4	0	-137.1
6	16.51	249.1	0

Table 7. Modified UNIFAC (Dortmund) group-interaction parameters [26].

m	n	a_{mn} (K)	b_{mn}	c_{mn} (K^{-1})	a_{nm} (K)	b_{nm}	c_{nm} (K^{-1})
1	1	0	0	0	0	0	0
1	5	2777.0	-4.6740	0.1551×10^{-2}	1606.0	-4.7460	0.9181×10^{-3}
1	6	2409.4	-3.0099	0	82.593	-0.4857	0
5	5	0	0	0	0	0	0
5	6	346.31	-2.4583	0.2929×10^{-2}	-1218.2	9.7928	-0.1616×10^{-1}
6	6	0	0	0	0	0	0

In order to assess the predictive activity coefficient model's accuracy, the agreement between experimental VLE data and the values predicted by the UNIFAC and modified UNIFAC (Dortmund) models were examined by calculating the root mean square deviation (RMSD). The comparison results are provided in Table 8 and illustrated in Figures 1-3. Overall, the predicted VLE values are in reasonable alignment with the experimental data, suggesting that the UNIFAC and modified UNIFAC (Dortmund) models remain a valuable tool for estimating VLE phase behavior in the binary mixtures of ABE fermentation products, particularly under operating conditions where experimental measurements are unavailable. Based on the RMSD values, as well as the graphical analysis, the modified UNIFAC (Dortmund) model provides better predictions than the UNIFAC model. The modified UNIFAC (Dortmund) model generally offers improved accuracy over the original UNIFAC model due to several key enhancements. One of the primary reasons is the revised group interaction parameters, which are based on a significantly larger and more diverse set of experimental data. These updated parameters allow the model to better capture specific

intermolecular interactions, especially in systems involving polar or associating compounds, such as alcohols and acids commonly found in ABE fermentation products. The modified UNIFAC (Dortmund) model also incorporates temperature-dependent interaction parameters, which enhance its ability to predict phase behavior across a wider range of temperatures. This feature is particularly important in practical applications where temperature variations can significantly influence equilibrium behavior [15]. Furthermore, in the case of components containing OH groups, such as alcohols, the modified UNIFAC (Dortmund) model provides improved accuracy due to the classification of the main OH group into primary, secondary, and tertiary subgroups [22].

Table 8. The root mean square deviations (RMSD) in boiling temperature (ΔT) and vapor-phase mole fraction (Δy_1) between the predicted results obtained from the UNIFAC and Modified UNIFAC (Dortmund) models and the experimental data at 101.3 kPa.

System	Source	RMSD T (K)		RMSD y_1	
		UNIFAC	Modified UNIFAC (Dortmund)	UNIFAC	Modified UNIFAC (Dortmund)
Acetone + 1-Butanol	This work	1.1	1.1	0.0274	0.0082
Acetone + Ethanol	Ku and Tu [16]	0.9	0.1	0.0203	0.0082
Ethanol + 1-Butanol	Seo et al. [17]	0.6	0.6	0.0128	0.0121

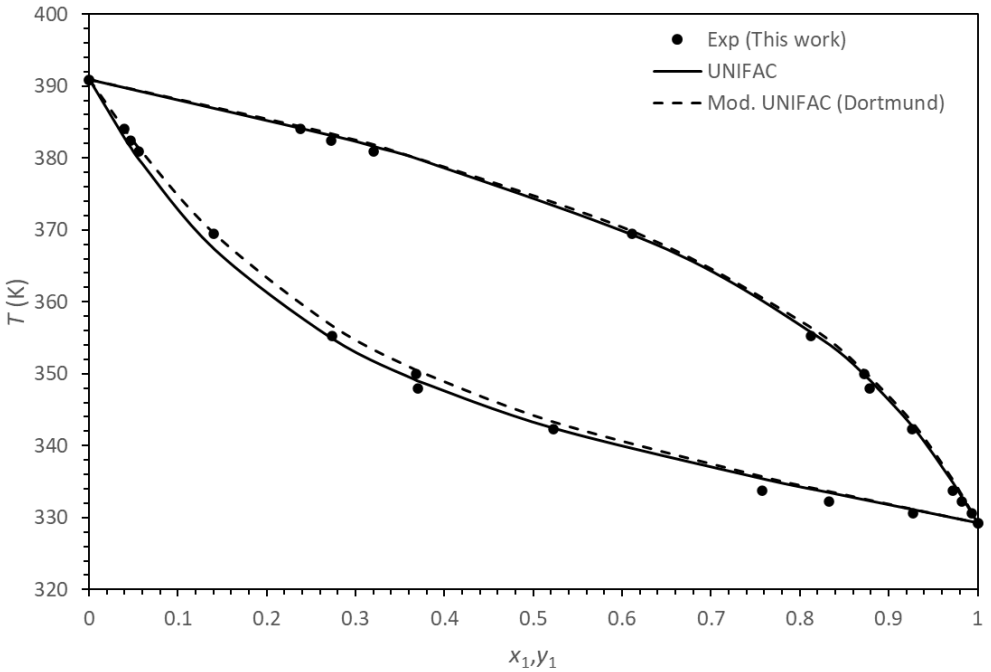

Fig.1. Predicted VLE diagram for binary system of acetone (1) + 1-butanol at 101.3 kPa compared with experimental data from this work.

As observed in Figures 1-3, the binary mixtures of acetone + 1-butanol, acetone + ethanol, and ethanol + 1-butanol do not exhibit azeotropic behavior, which is beneficial for the separation of ABE fermentation products. The absence of azeotropes enables complete separation of these components through conventional distillation methods, thereby simplifying process design and reducing both energy requirements and operational complexity. Moreover, it eliminates the need for more advanced separation techniques, such as azeotropic or extractive distillation.

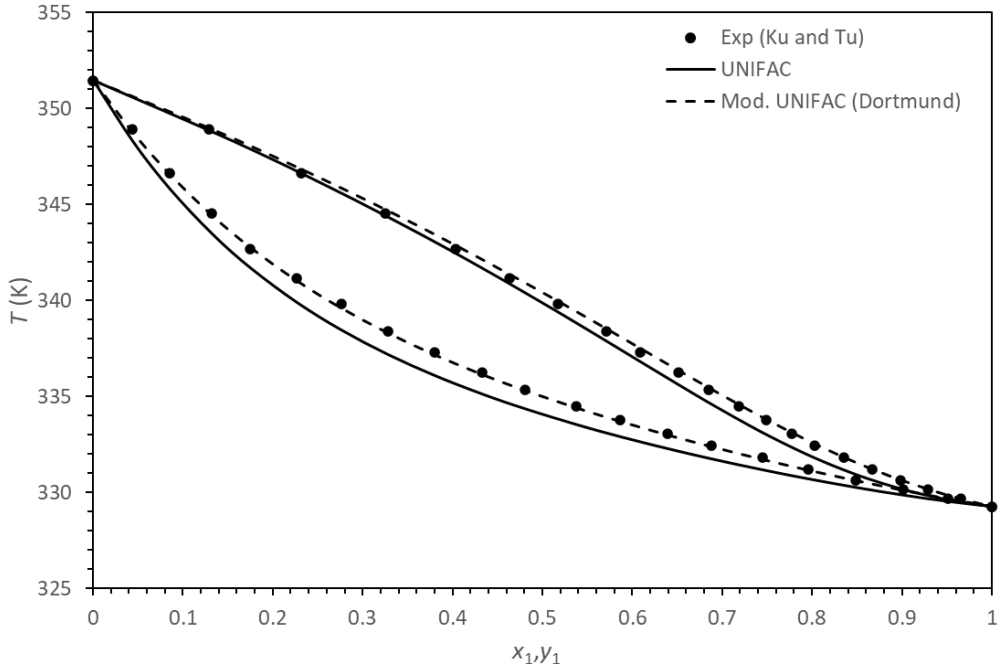

Fig. 2. Predicted VLE diagram for binary system of acetone (1) + ethanol at 101.3 kPa compared with experimental data from Ku and Tu [16].

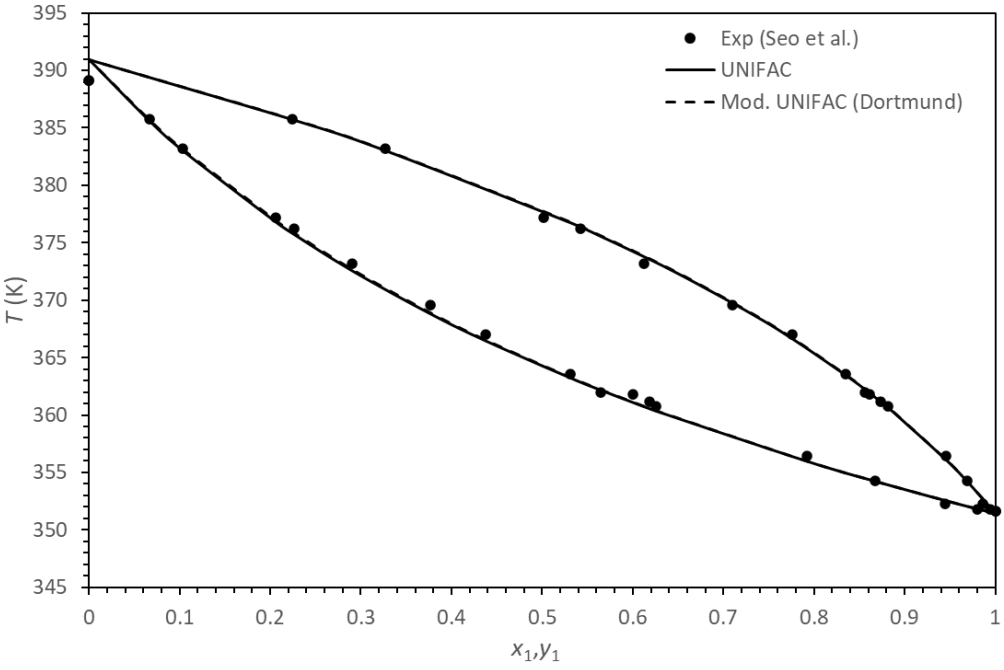

Fig. 3. Predicted VLE diagram for binary system of ethanol (1) + 1-butanol (2) at 101.3 kPa compared with experimental data from Seo et al. [17].

Conclusions

This study demonstrates that the UNIFAC and modified UNIFAC (Dortmund) models can be effectively applied to predict the VLE for the binary systems of acetone + 1-butanol, acetone + ethanol, and ethanol + 1-butanol. Furthermore, isobaric VLE data for the binary system of acetone + 1-butanol at 101.3 kPa were also determined using a modified recirculating Othmer equilibrium still in this study. The experimental data passed the thermodynamic consistency test, evaluated

using the L-W Wisniak test. The predicted results from both models showed good agreement with experimental data, as indicated by low RMSD values in both temperature and vapor phase composition. Overall, the modified UNIFAC (Dortmund) model provided more accurate predictions compared to the conventional UNIFAC model. Therefore, both models, particularly the modified UNIFAC (Dortmund), can be considered reliable predictive tools for the design and analysis of separation processes in the ABE fermentation systems.

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ASETON + 1-BUTANOL, ASETON + ETANOL VƏ ETANOL + 1-BUTANOL BİNAR SİSTEMLƏRİNDƏ BUXAR-MAYE TARAZLIĞININ PROQNOZLAŞDIRILMASI ÜÇÜN UNIFAC VƏ MODİFİKASİYA EDİLMİŞ UNIFAC (DORTMUND) MODELLƏRİNİN TƏTBİQİ

A. Mustain, B. T. Arta, A. A. Wibowo, P. H. Suharti, H. Hardjono, M.Effendy

Biobutanolun istehsalı adətən aseton-butanol-etanol (ABE) prosesi kimi tanınan fermentasiya üsulu ilə həyata keçirilir və bu üsul üç əsas məhsul - aseton, butanol və etanol istehsal edir. ABE fermentasiya məhsullarının təmizlənməsi mərhələsində bu komponentlərin binar qarışıqları üçün buxar–maye tarazlığı (VLE) məlumatları prosesin dəqiq layihələndirilməsi və optimallaşdırılması baxımından mühüm əhəmiyyət kəsb edir. Buna görə də, bu tədqiqatda aseton + 1-butanol, aseton + etanol və etanol + 1-butanol binar qarışıqları üçün izobarik buxar–maye tarazlığı məlumatları araşdırılmışdır. VLE göstəricilərinin proqnozlaşdırılması qrup töhfələri prinsipinə əsaslanan aktivlik əmsalı modelləri, xüsusilə də UNIQUAC Funksional Qrup Aktivlik Əmsalları (UNIFAC) modeli və modifikasiya edilmiş UNIFAC (Dortmund) modeli vasitəsilə həyata keçirilmişdir. Hər iki model üzrə hesablanmış nəticələrlə eksperimental ölçmələr arasında yalnız kiçik fərqlər müşahidə edilmişdir. Bununla belə, proqnozlaşdırılmış qiymətlərdə daha aşağı sapmaların əldə olunması modifikasiya edilmiş UNIFAC (Dortmund) modelinin eksperimental məlumatlarla bir qədər daha yaxşı uyğunluq göstərdiyini ortaya qoymuşdur.
Əldə edilən nəticələr göstərir ki, həm UNIFAC, həm də modifikasiya edilmiş UNIFAC (Dortmund) modelləri ABE fermentasiya məhsulları ilə əlaqəli ikili qarışıqların buxar–maye tarazlığı davranışının proqnozlaşdırılması üçün yararlıdır və etibarlı nəticələr verir.

Açar sözlər: *ABE fermentasiyası, proqnozlaşdırma modeli, UNIFAC, buxar-maye tarazlığı.*