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Estimation of excess Gibbs free energy of multicomponent biofuel mixtures of Butan-1-ol using machine learning methods based on modified Raoult's law models

N. M. Buenaobra[1,2], G. A. Madlangbayan[1,3], K. T. A. Ong[1,4], L. A. Rovillos[1,5] and B. Doma Jr.[1,*]

[1]School of Chemical, Biological, and Materials Engineering and Sciences, Mapua University St., Intramuros, Manila, 1002, Philippines
[2]nmmbuenaobra@mymail.mapua.edu.ph, [3]gacmadlangbayan@mymail.mapua.edu.ph, [4]ktamong@mymail.mapua.edu.ph, [5]latrovillos@mymail.mapua.edu.ph

*btdoma@mapua.edu.ph

Abstract. In biofuels, the excess Gibbs free energy of mixing is a very important thermodynamic property as it is used in evaluating the efficiency and sustainability in terms of energy conversion. Multiple biofuel systems containing butan-1-ol were examined with oxygenate ether additives such as MTBE and DIPE using isothermal vapour-liquid equilibrium data at different temperatures (298.15K, 313.15K, 318.15K). Two activity coefficient models, Wilson and van Laar model were compared by determining the bubble pressure and vapor mole fractions of each system using Modified Raoult's Law and Machine Learning techniques. Besides, mole fractions and activity coefficients were used to identify the excess property. Results showed that Wilson model is appropriate for all the biofuel systems when using the Artificial Neural Network (ANN) resulting in an MSE of 3.2010e-09, 4.6792e-10, 1.6186e-10, and 5.3461e-07. In addition, van Laar model is more acceptable when Rational Quadratic GPR or Fine Tree algorithm were used with an average RMSE of 0.00582±0.01 and 0.02095±0.03 respectively. Lastly, the generated data for both activity coefficient models were also used to estimate the systems' excess Gibbs free energy of mixing across varying mole fraction of its components.

Keywords: Excess Gibbs free energy of mixing, Vapor–liquid equilibrium, Butan-1-ol, Modified Raoult's law, Machine learning.

1. Introduction

Analysis of the excess Gibbs free energy of mixing in biofuels is significant in the evaluation of efficiency and sustainability in energy conversion such that this thermodynamic property provides high stability to a system when low in value and is especially studied for the examination of bubble point pressure and fuel purification [1,2]. Synthesis of butan-1-ol for biofuel production has been studied through various biotechnological mechanisms due to the higher energy content leading to more efficiency compared to bioethanol [3]. The utilization of oxygenating additives on fuels is significant in terms of efficiency and environmental impacts. To lessen the dangerous emissions and increase octane levels, alkyl ether oxygenates additives such as methyl tert-butyl ether (MTBE) and diisopropyl ether

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(DIPE) are mixed with alcohols such as butan-1-ol and methanol [4]. The mixture composition of ether + alcohol + hydrocarbon of biofuel systems is significantly studied for potential efficient fuel energy sourcing [5]. In this study, biofuel systems containing butan-1-ol and oxygenate ether additives (MTBE or DIPE) are studied in terms of predicting thermodynamic property, excess Gibbs free energy, using isothermal vapor-liquid equilibrium (VLE) modelling. Additionally, a system with a hydrocarbon, benzene, and a system with additional alcohol, methanol, are considered with the criteria of having butan-1-ol as the main alcohol component. Furthermore, the potential of machine learning in modelling and predicting the system's behavior is relatively untapped. This paper aims to address such issues by incorporating machine learning in modelling four multiple biofuel systems of butan-1-ol.

VLE data for binary systems containing butan-1-ol and additive of DIPE was obtained and investigated at 318.15 K by Reddy et al [4]. The results from the experiment were correlated using activity coefficient models, including phi-gamma and phi-phi models. NRTL, Wilson, and UNIQUAC models with the truncated two-term virial equation of state were used to determine the activity coefficient, phi. For the phi-phi method of correlation, Peng-Robinson EOS was used based on Wong-Sander mixing rules. Methods used for the study yielded promising results, indicating that the approaches used are well fit to the measured values. In the prediction of P-x-y cuves, the approaches that yielded the best results are the UNIFAC (Dortmund) and the Predictive Soave–Redlich–Kwong (PSRK). Additionally, a study of binary mixture of butan-1-ol + MTBE was also studied by Park et al at 313. 15K using isothermal VLE data [6]. Properties such as activity coefficients and volume at infinite dilutions and partial molar and nonpartial excess enthalpies were obtained from experimental data. Measured data was then correlated with different models or empirical equations such as NRTL, van Laar, Margules, Wilson, UNIQUAC, and Redlich-Kister polynomial. The binary system of butane + MTBE was investigated to be an endothermic system. Another isothermal study was conducted in a ternary system of DIPE+butan-1-ol+benzene at 313.15K by Villamañan et al. evaluating total pressure in a cell [5]. Minimization of data by Barker's approach of reduction showed relations for excess Gibbs free energy based on Margules activity equation for systems with two components while systems with three components were based on the Wohl's expansion model. The approaches utilizing NRTL model, Wilson equation, and UNIQUAC model have been applied successfully in this mixture. Furthermore, a ternary system of biofuel butan-1-ol + MTBE + methanol was also published with isothermal VLE data at 2981.5K by Gonzales et al [7]. To analyze the data, DISQUAC model was utilized as it is commonly utilized for tertiary-alkyl ethers with organic solvent mixtures. In this study, the ternary interactions were neglected; hence, the VLE of this mixture was predicted correctly by this model using binary parameters. Also, it was found out that results from DISQUAC predictions are essentially independent of the ternary mixture considered.

VLE in multiple systems containing butan-1-ol has been analyzed and compared through variations (e.g., additives, temperature, pressure); however, no published studies have analyzed and compared butan-1-ol systems with different numbers of components. Butan-1-ol systems are evaluated with other systems with the limitation of having the same number of components. In this study, binary systems are compared to a ternary system to analyze the behaviors of multiple component systems containing the same main biofuel component. This analysis approach in studying each multi-component system will help in establishing predictions on the behaviors between binary and ternary biofuel systems. The use of both Wilson and van Laar activity coefficient models in MRL and the subsequent integration of machine learning in modelling and predicting biofuel systems have not yet been studied. The use of machine learning is used in the analysis of the biofuel systems' behaviors in this paper.

Since there are limited published studies scoping the comparison of systems of VLE on biofuel systems with different numbers of components, mainly the butan-1-ol systems, this paper aimed to investigate and analyze multi-component modelling of butan-1-ol. The activity coefficient, gamma, in each system was solved using the Wilson and van Laar equation. The vapor mole fraction of every component was aimed to be solved using Modified Raoult's Law. From this, the thermodynamic property of the system, excess Gibbs free energy, is calculated. Additionally, different techniques in machine learning (e.g., Neural Net Fitting and Regression Learner) was used to predict the equilibrium

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data and led to the determination of the most appropriate technique for the given system. Hence, the study aimed to address the behavior of the VLE biofuel systems with the help of machine learning. Moreover, this study determined the best yielding model from the multiple component biofuel systems.

2. Methods

In the conduct of this study, MATLAB 2022a was used to execute simulations necessary for examining vapor-liquid equilibrium data for the binary and ternary systems. Given these isothermal VLE data, system pressure and vapor compositions were solved. The VLE data were modelled, and data were subsequently generated following Modified Raoult's Law using Wilson and van Laar correlation models for activity coefficient. Moreover, different machine learning techniques were also used to assess the accuracy and reliability of the generated data. The systems' thermodynamic properties, in this case, their excess Gibbs free energies were evaluated using the activity coefficients obtained from the models. Shown in figure 1 is a schematic diagram of the methods in this study.

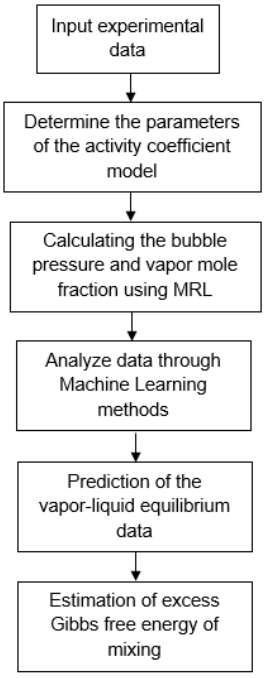

Figure 1. Schematic Diagram of the Methods.

2.1. Modified Raoult's law

Modified Raoult's law is a modified form of Raoult's law wherein activity coefficients are used and added to the equations in order to relate the non-ideality of the mixture. In this paper, the gas phase is expected to have an ideal gas behavior at low pressure value; thus, so $\overline{\phi}_{\mathrm{i}}^{\mathrm{v}} = 1$ and $f_i^L = P_i^{sat}$. The y_{i} and bubble pressure are calculated using the formula as expressed in equations (1) and (2).

$$y_{\mathrm{i}} = \frac{x_{\mathrm{i}}\gamma_{\mathrm{i}}P_{\mathrm{i}}^{sat}}{P} \tag{1}$$

$$P = \sum x_{\mathrm{i}}\gamma_{\mathrm{i}}P_{\mathrm{i}}^{sat} \tag{2}$$

To determine the saturation pressure of the individual components in the system, the Antoine equation was utilized, based on the given temperature as shown in equation (3). Antoine equation is an expression

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of the relationship between the temperature of a pure substance (°C) and the vapor pressure (mmHg). Antoine constants A, B, and C for butan-1-ol, DIPE, MTBE, benzene, and methanol were all lifted from the Iranian Chemical Engineers Website, as shown in table 1.

$$log_{10} P^* = A - \frac{B}{T + C} \tag{3}$$

Table 1. Antoine equation parameters for pure components (1).

Component	A	B	C
butan-1-ol	7.62121	1543.89	208.029
DIPE	7.20537	1354.97	245.019
MTBE	7.07597	1233.7	238.879
benzene	7.06437	1296.93	229.916
methanol	8.09126	1582.91	239.096

2.1.1. Activity coefficient models. In this study, two activity coefficient models—Wilson equation and van Laar equation—are used to evaluate gamma in the Modified Raoult's Law. MATLAB was utilized where the activity coefficients are determined based on the function fminsearch. The function includes establishing initial estimate values and acquiring the minimum variable's scalar function to estimate system parameters.

The activity coefficients for components 1 and 2 in each system were calculated using equations (4) and (5). The activity coefficients for the three components in each system were obtained using equations (6), (7), and (8).

$$\ln \gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \tag{4}$$

$$\ln \gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) + x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \tag{5}$$

$$\ln \gamma_1 = 1 - \ln[x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}] - \frac{x_1}{x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}} - \frac{x_2\Lambda_{21}}{x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}} - \frac{x_3\Lambda_{31}}{x_1\Lambda_{31} + x_2\Lambda_{32} + x_3} \tag{6}$$

$$\ln \gamma_2 = 1 - \ln[x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}] - \frac{x_1}{x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}} - \frac{x_2\Lambda_{21}}{x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}} - \frac{x_3\Lambda_{31}}{x_1\Lambda_{31} + x_2\Lambda_{32} + x_3} \tag{7}$$

$$\ln \gamma_3 = 1 - \ln[x_1\Lambda_{31} + x_2\Lambda_{32} + x_3] - \frac{x_1\Lambda_{31}}{x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}} - \frac{x_2\Lambda_{23}}{x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}} - \frac{x_3}{x_1\Lambda_{31} + x_2\Lambda_{32} + x_3} \tag{8}$$

Equations (9) and (10) were used for binary systems and equations (11), (12), and (13) were used for the ternary systems to compute for the activity coefficient.

$$\ln \gamma_1 = \frac{A}{\left[1 + \frac{Ax_1}{Bx_2}\right]^2} \tag{9}$$

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$$\ln \gamma_2 = \frac{B}{\left[1 + \frac{Bx_2}{Ax_1}\right]^2} \tag{10}$$

$$\ln \gamma_1 = \frac{\left[x_2^2 A_{12}\left(\frac{A_{21}}{A_{12}}\right)^2 + x_3^2 A_{13}\left(\frac{A_{31}}{A_{13}}\right)^2 + x_2 x_3 \frac{A_{21}}{A_{12}}\frac{A_{31}}{A_{13}}\left(A_{12} + A_{13} - A_{32}\frac{A_{13}}{A_{31}}\right)\right]}{\left(x_1 + x_2\left(\frac{A_{21}}{A_{12}}\right) + x_3\left(\frac{A_{31}}{A_{13}}\right)\right)^2} \tag{11}$$

$$\ln \gamma_2 = \frac{\left[x_3^2 A_{23}\left(\frac{A_{32}}{A_{23}}\right)^2 + x_1^2 A_{21}\left(\frac{A_{12}}{A_{21}}\right)^2 + x_3 x_1 \frac{A_{32}}{A_{23}}\frac{A_{12}}{A_{21}}\left(A_{23} + A_{21} - A_{13}\frac{A_{21}}{A_{12}}\right)\right]}{\left(x_2 + x_3\left(\frac{A_{32}}{A_{23}}\right) + x_1\left(\frac{A_{12}}{A_{21}}\right)\right)^2} \tag{12}$$

$$\ln \gamma_3 = \frac{\left[x_1^2 A_{31}\left(\frac{A_{13}}{A_{31}}\right)^2 + x_2^2 A_{32}\left(\frac{A_{23}}{A_{32}}\right)^2 + x_1 x_2 \frac{A_{13}}{A_{31}}\frac{A_{23}}{A_{32}}\left(A_{31} + A_{32} - A_{21}\frac{A_{32}}{A_{23}}\right)\right]}{\left(x_3 + x_1\left(\frac{A_{13}}{A_{31}}\right) + x_2\left(\frac{A_{23}}{A_{32}}\right)\right)^2} \tag{13}$$

2.2. Machine learning methods

Through VLE data, bubble pressure and vapor mole fractions of every component in the system were obtained. With these input values, Artificial Neural Network (ANN), Fine Tree, Linear SVM, Rational Quadratic Gaussian Process Regression (GPR), SVM Kernel, and Boosted Trees Neural were utilized to predict equilibrium data. Using Machine Learning, the ANN, specifically Neural Net Fitting (NNF), were utilized to process the data generated. The ANN were utilized to solve a data fitting problem with a two-layer feed forward network trained with Levenberg-Marquardt and divided into a randomized data. For ANN, 65% of the data were used for training, 20% for validation, and 15% for testing. Besides, 7 input and 3 output variables were utilized with 15 hidden layers for binary system, while 10 input and 4 output variables for ternary system, as shown in figure 2. The root mean square error (RMSE) between calculated and predicted data and the model that suits the best in the given binary or ternary system was identified.

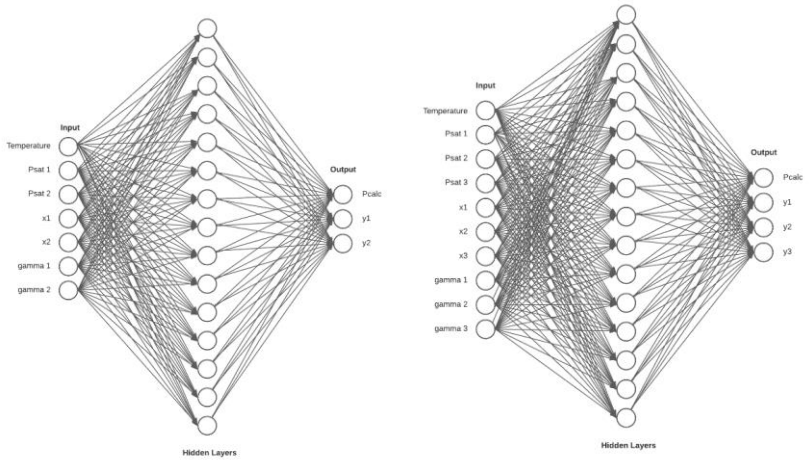

Figure 2. Artificial Neural Network for Binary and Ternary System

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2.3. Thermodynamic property

Evaluation of thermodynamic properties of mixtures are crucial especially when considering the mixture's performance for a certain function. The thermodynamic property determined for each system was the excess Gibbs free energy of mixing, G^{ex}. The excess Gibbs free energy of mixing were calculated based on the mole fractions of the components of each system and their corresponding activity coefficients. This excess property signifies the deviation of the mixture from an ideal assumption. It was obtained by utilizing the calculated mole fraction as well as the activity coefficient, as shown in equation (14).

$$\frac{G^{\mathrm{ex}}}{RT} = \sum_{\mathrm{i}} x_{\mathrm{i}} \ln \gamma_{\mathrm{i}} \tag{14}$$

3. Results and Discussion

3.1. Modified Raoult's law

Data from published articles were gathered and analyzed in MATLAB through determining the vapor pressure of each component and the parameters of each activity coefficient models. In determining the Wilson parameters for Wilson equation of binary systems, fmin values for the butan-1-ol + DIPE binary system is 1.6574×10^{-8} and 7.2572×10^{-10} for butan-1-ol + MTBE binary system. Meanwhile, the butan-1-ol + DIPE + benzene system and butan-1-ol + MTBE + methanol system has an fmin values of 1.2367×10^{-8} and 1.8448×10^{-9}, respectively. On the other hand, using the van Laar model on binary systems, the fmin values are found to be 0.1609 and 1.0510×10^{-9}, respectively. While for the ternary systems, they are 1.5520×10^{-8} and $2.6430\times10^{-8.}$

3.1.1. Equilibrium input data. Shown in table 2 are the experimental equilibrium data for biofuel systems obtained from published articles. The VLE data for butan-1-ol + DIPE system at 318.15 K was obtained from the study of Reddy et al. [4] and the data for butan-1-ol + MBTE at 313.15 K was obtained from the study of Park et al. [6]. Additionally, the VLE data for butan-1-ol + DIPE + benzene system at 313.15 K was obtained from the study of Villamañan et al. [5] while the data for butan-1-ol + MBTE + methanol at 298.15 K was obtained from the study of Antonio Gonza Âlez et al. [7].

Table 2. VLE data for biofuel systems.

System	Condition	Number of Data Points	References
butan1-ol+DIPE	318.15 K	9	Reddy et al.
butan-1-ol+MBTE	313.15 K	32	Park et al.
butan1-ol+DIPE+benzene	313.15 K	25	Villamañan et al.
butan1-ol+MBTE+methanol	298.15 K	26	Antonio Gonza Âlez et al.

Additionally, using randomized values of liquid compositions, table 3 shows the number of data points for each of the systems that were generated and correlated with the resulting parameters obtained from the previous data to compute for the desired output which are the bubble pressure and vapor mole composition. The data generated were used for the machine learning methods.

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Table 3. Number of generated data points for each biofuel system.

System	Model	Condition	Number of Data Points
butan1-ol+DIPE	Wilson	318.15 K	500
	Van Laar		500
butan-1-ol+MBTE	Wilson	313.15 K	500
	Van Laar		500
System	Model	Condition	Number of Data Points
butan1-ol+DIPE+benzene	Wilson	313.15 K	426
	Van Laar		426
butan1-ol+MBTE+methanol	Wilson	298.15 K	426
	Van Laar		426

3.2. Machine learning methods

Table 4. MSE and R^2 from ANN.

System	Model	MSE	R^2
butan1-ol+DIPE	Wilson	3.2010e-09	1.0000
	Van Laar	1.4761e-05	0.9999
butan-1-ol+MBTE	Wilson	4.6792e-10	1.0000
	Van Laar	4.9881e-09	1.0000
butan1-ol+DIPE+benzene	Wilson	1.6186e-10	1.000
	Van Laar	2.4605e-06	1.000
butan1-ol+MBTE+methanol	Wilson	5.3461e-07	1.000
	Van Laar	8.9330e-06	0.9998

Shown in table 4 are results for MSE and R^2 for all systems. As shown, all systems produce a value of r-squared equal to 1 or approximately equal to 1. This indicates that the predictions perfectly fit the data, making it have a great linear relationship, as observed in figures 3 and 4 for binary and ternary systems, respectively. In addition, despite both models performed a good fit to data, it was found out that Wilson activity model is more suitable in all four biofuel systems than the van Laar model as it produces a lower mean square error.

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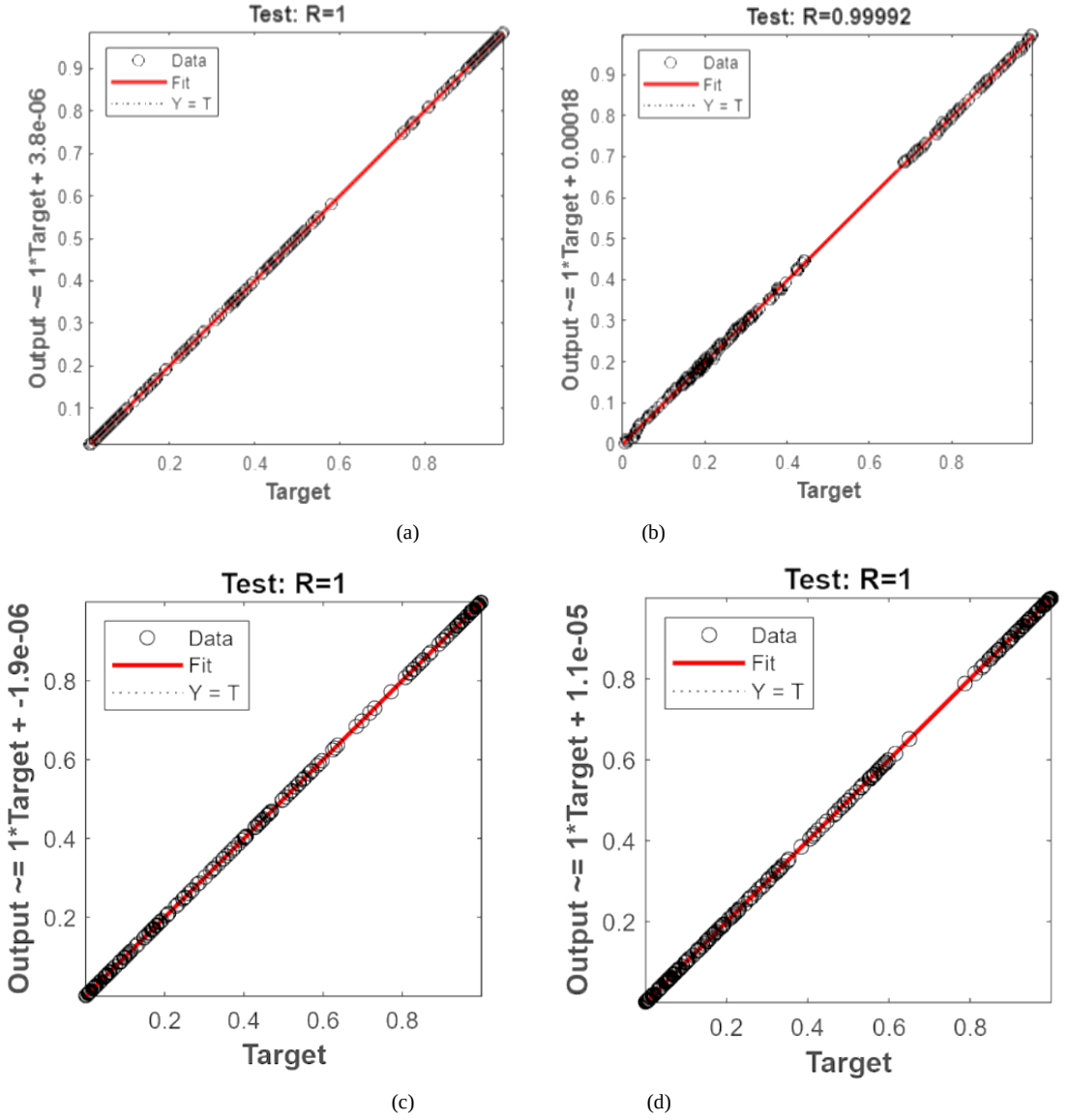

Figure 3. Regression Plot for testing binary system (a) butan-1-ol+DIPE – Wilson, (b) butan-1-ol+DIPE – van Laar, (c) butan-1-ol+MBTE – Wilson, and (d) butan-1-ol+MBTE – van Laar.

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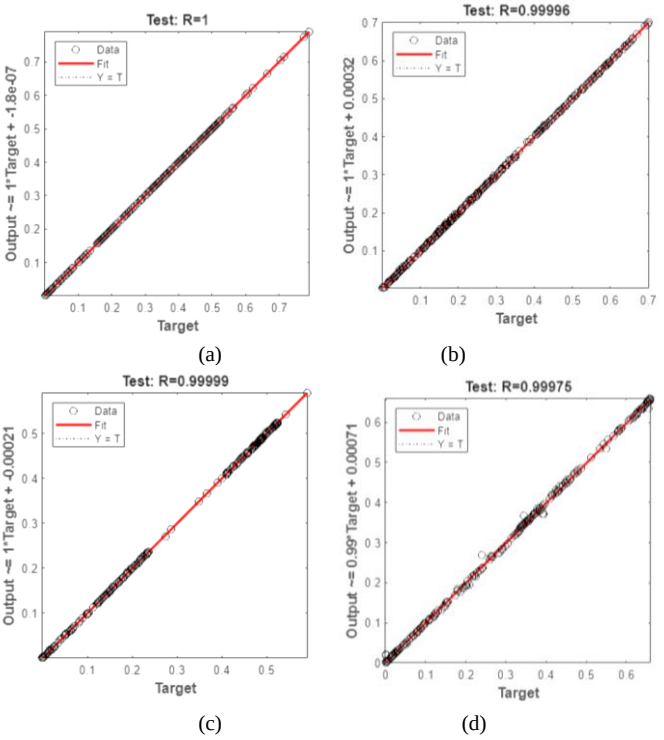

Figure 4. Regression Plot for testing ternary system (a) butan-1-ol+DIPE+benzene – Wilson, (b) butan-1-ol+DIPE+benzene – van Laar, (c) butan-1-ol+MBTE+methanol – Wilson, and (d) butan-1-ol+MBTE+methanol – van Laar.

Table 5. *RMSE* results of bubble pressure output from other machine learning methods.

System	Model	Fine Tree	Linear SVM	Rational Quadratic GPR	SVM Kernel	Boosted Trees
butan-1-ol+DIPE	Wilson	9.1942	35.7080	9.3024	9.2185	9.1973
	Van Laar	0.0453	0.0157	0.0055	0.1964	0.0640
butan-1-ol+MBTE	Wilson	0.0679	0.0306	0.0029	0.3437	0.0892
	Van Laar	0.0524	0.2955	0.0886	0.3035	0.0750
butan-1-ol +DIPE+benzene	Wilson	0.0841	0.0313	0.0132	0.2088	0.0981
	Van Laar	0.0466	0.0173	0.0057	0.1223	0.0571
butan-1-ol +MBTE+methanol	Wilson	0.0210	0.0044	0.0037	0.0910	0.0330
	Van Laar	0.0751	0.0164	0.0039	0.1904	0.0860

Additionally, five different methods were used to compare their root mean square error (RMSE). In examining the bubble pressure as an output, as shown in table 5, most all biofuel systems obtained the lowest RMSE through rational quadratic GPR method with a value of 0.00582 ± 0.01. The binary

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systems of butan-1-ol+DIPE (Wilson) and butan-1-ol+MBTE (van Laar) gained the lowest error using the Fine Tree method with RMSE values of 9.1942 and 0.052368, respectively. On the other hand, the ternary systems of butan-1-ol+DIPE+benzene (Wilson) and butan-1-ol+MBTE+methanol (van Laar) yielded an acceptable error with RMSE values of 0.084072 and 0.075105 correspondingly through the same method. Although, it is noticed that the lowest RMSE values from Fine Tree were quite identical to the RMSE obtained in the rational quadratic GPR in these binary systems. Therefore, it can be concluded that rational quadratic GPR is the most acceptable method in these biofuel systems in both activity coefficient models.

Table 6. *RMSE* results of vapor composition output from other machine learning methods.

System	Model	Compo-nent	Fine Tree	Linear SVM	Rational Quadratic GPR	SVM Kernel	Boosted Trees
	Wilson	1	0.0150	478.06	0.3200	0.1211	0.0153
butan1-ol		2	0.0150	447.44	0.3200	0.1371	0.0543
+DIPE	Van Laar	1	0.0181	0.0385	0.0029	0.1995	0.0204
		2	0.0181	0.0408	0.0029	0.1962	0.0610
	Wilson	1	0.0118	0.0227	0.0037	0.2174	0.0128
butan-1-ol		2	0.0118	0.0273	0.0037	0.2253	0.0542
+MBTE	Van Laar	1	0.0054	19.452	0.9120	0.1324	0.0070
		2	0.0054	19.557	0.9120	0.1618	0.0479
	Wilson	1	0.0195	0.1702	0.0098	0.4859	0.0213
butan1-ol		2	0.0280	0.1093	0.0123	0.3280	0.4847
+DIPE+		3	0.0201	0.0979	0.0331	0.1533	0.0247
benzene	Van Laar	1	0.0263	0.0070	0.0007	0.1098	0.0258
		2	0.0594	0.0119	0.0038	0.2613	0.0818
		3	0.0332	0.0137	0.0039	0.1478	0.0184
	Wilson	1	0.0070	0.0424	0.0083	0.1329	0.0078
butan1-ol		2	0.0457	0.0288	0.0122	0.0814	0.0572
+MBTE+		3	0.0301	0.0692	0.0386	0.0654	0.0340
methanol	Van Laar	1	0.0067	0.0815	0.2832	0.0564	0.0073
		2	0.0046	0.1606	0.6212	0.1870	0.0340
		3	0.0038	0.2069	0.3265	0.0590	0.0156

Aside from bubble pressure, vapor mole composition is another output determined in this study. Results are quite similar to the bubble pressure, as Fine Tree and Rational Quadratic GPR are the most likely appropriate method in determining the compositions of every component in the biofuel systems, as observed in table 6. In the binary system butan-1-ol+DIPE, Fine Tree method is appropriate for the Wilson model with a *RMSE* value of 0.01502 while Rational Quadratic GPR for the van Laar model with a *RMSE* value of 0.0029231. With this, the van Laar model is more suitable than the Wilson as it generates a lower value with 0.0121 difference, indicating that the training and testing data were much closer. For the second binary system, butan-1-ol+MBTE, it is the opposite of the first binary system since Wilson model produces a lower *RMSE* value of 0.0037113 in Rational Quadratic GPR method while Fine Tree method suits the van Laar model with 0.005412 *RMSE*. Since the error is much lower in Wilson with 0.0017 difference, it is the more acceptable model for this binary system.

For the first ternary system, butan-1-ol+DIPE+benzene using Wilson, the compositions of components 1 and 2 have a lowest *RMSE* in Rational Quadratic GPR with 0.0098495 and 0.012262 *RMSE*, while component 3 have a lowest *RMSE* in Fine Tree method with 0.020074. While the ternary system using van Laar obtained the lowest *RMSE* in all components in the Rational Quadratic GPR with a value of 0.00069374, 0.003891, and 0.0038508. Comparing their *RMSE*, van Laar model gives the lowest value than the Wilson, therefore van Laar is more suitable in this ternary system. On the other

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hand, the second ternary system, butan-1-ol+MBTE+benzene produces a lower *RMSE* using the Fine Tree method both in Wilson and van Laar models except for the composition of component 2 in Wilson model which gives a lowest *RMSE* of 0.012184 using Rational Quadratic GPR. Through analyzing their errors, the van Laar model is more acceptable in this ternary system due to its *RMSE* values being lower than 0.01.

3.3. Estimation of excess Gibbs free energy

The generated data using each of the van Laar and Wilson models for activity coefficients were used to solve for the excess Gibbs free energy of the systems. The resulting values for the excess property were plotted as functions of the mole fractions. These graphs are shown below.

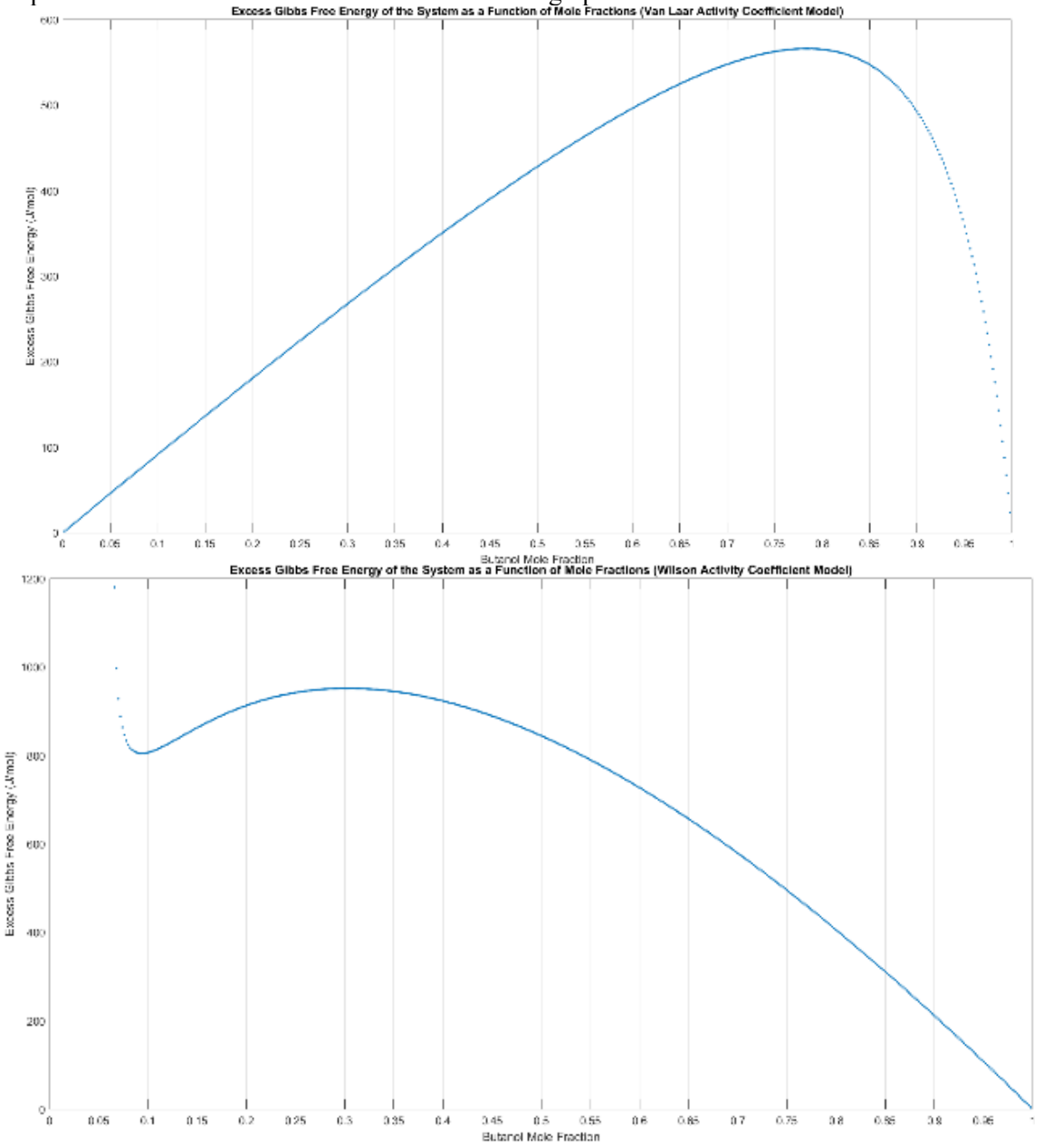

Figure 5. Excess Gibbs free energy as a function of butanol mole fraction in the system butan-1-ol+DIPE ($T = 318.15\ K$) using van Laar (left) and Wilson (right) activity coefficient models.

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Figure 5 shows the excess property as a function of the mole fraction of our component of interest, butan-1-ol, in the butan-1-ol + DIPE system. In both models, the excess Gibbs free energy experienced an initial rise followed by a gradual decrease for the Wilson model and a more abrupt one in the van Laar model. For the van Laar model, the peak of the plot occurred at $x_1 = 0.776$ where $G^{ex} = 565.99\, J/mol$. At lower mole fractions of butan-1-ol, the excess property experienced a gradual decrease. At higher mole fractions, the decrease was more abrupt. For the Wilson model, excluding the trailing part on the left side of the graph, the peak of the plot occurred at $x_1 = 0.302$ where $G^{ex} = 952.25\, J/mol$. At lower mole fractions of butan-1-ol, the decrease was abrupt followed by a trail towards infinity. At higher mole fractions, the decrease was more gradual.

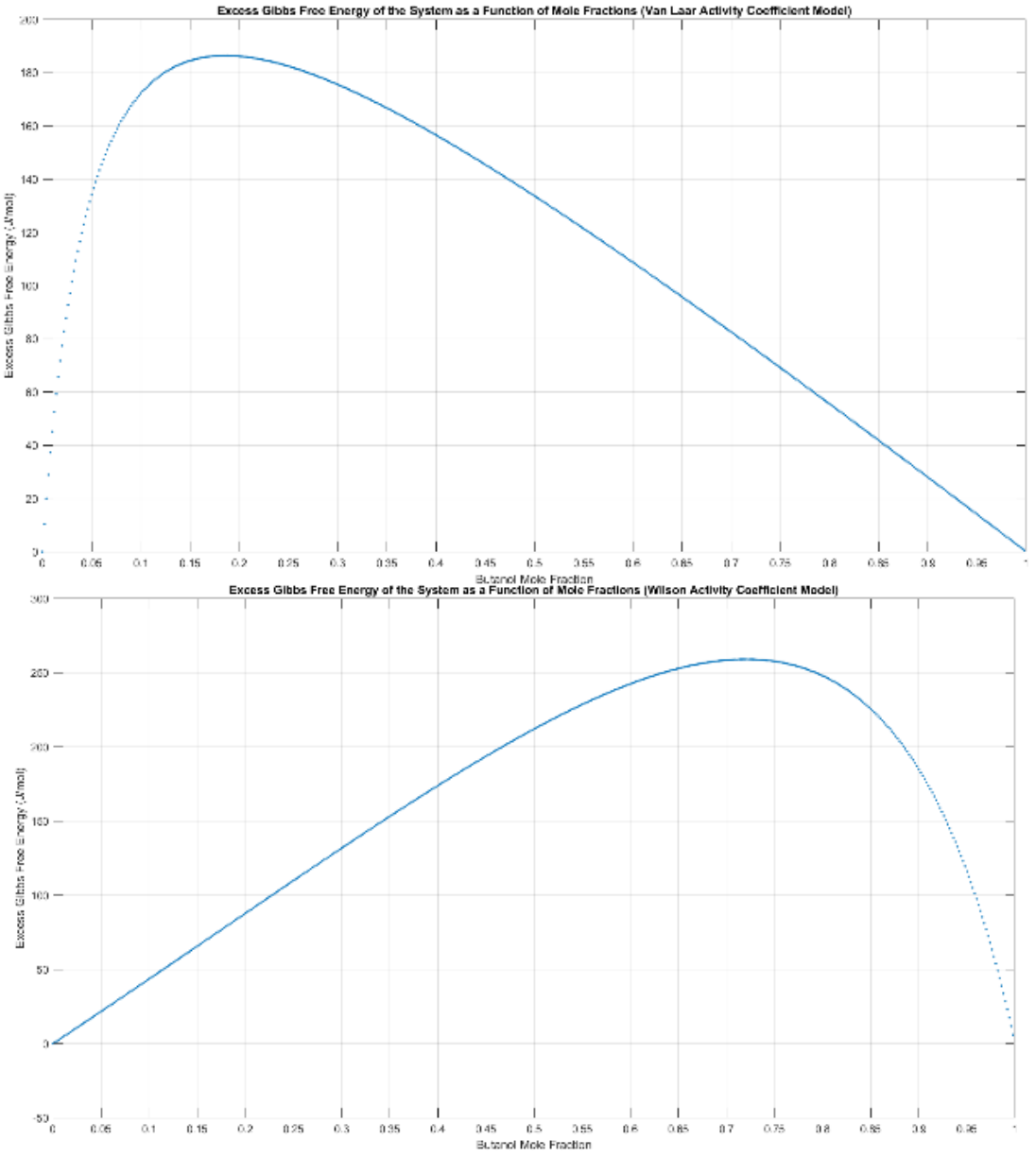

Figure 6. Excess Gibbs free energy as a function of butanol mole fraction in the system butan-1-ol+MBTE ($T = 313.15\, K$) using van Laar (left) and Wilson (right) activity coefficient models.

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Figure 6 shows the excess property as a function of the mole fraction of butan-1-ol, in the butan-1-ol + MBTE system. In the van Laar model, the excess Gibbs free energy experienced a more abrupt rise and a gradual fall as the butan-1-ol mole fraction increased. In the Wilson model, the rise was gradual, but the fall is more abrupt. For the van Laar model, the peak of the plot occurred at $x_1 = 0.186$ where $G^{ex} = 186.43\, J/mol$. At lower mole fractions of butan-1-ol, the excess property experienced an abrupt decrease. At higher mole fractions, the decrease was more gradual. For the Wilson model, the peak of the plot occurred at $x_1 = 0.720$ where $G^{ex} = 259.11\, J/mol$. At lower mole fractions of butan-1-ol, the excess property experienced a gradual decrease. At higher mole fractions, the decrease was more abrupt.

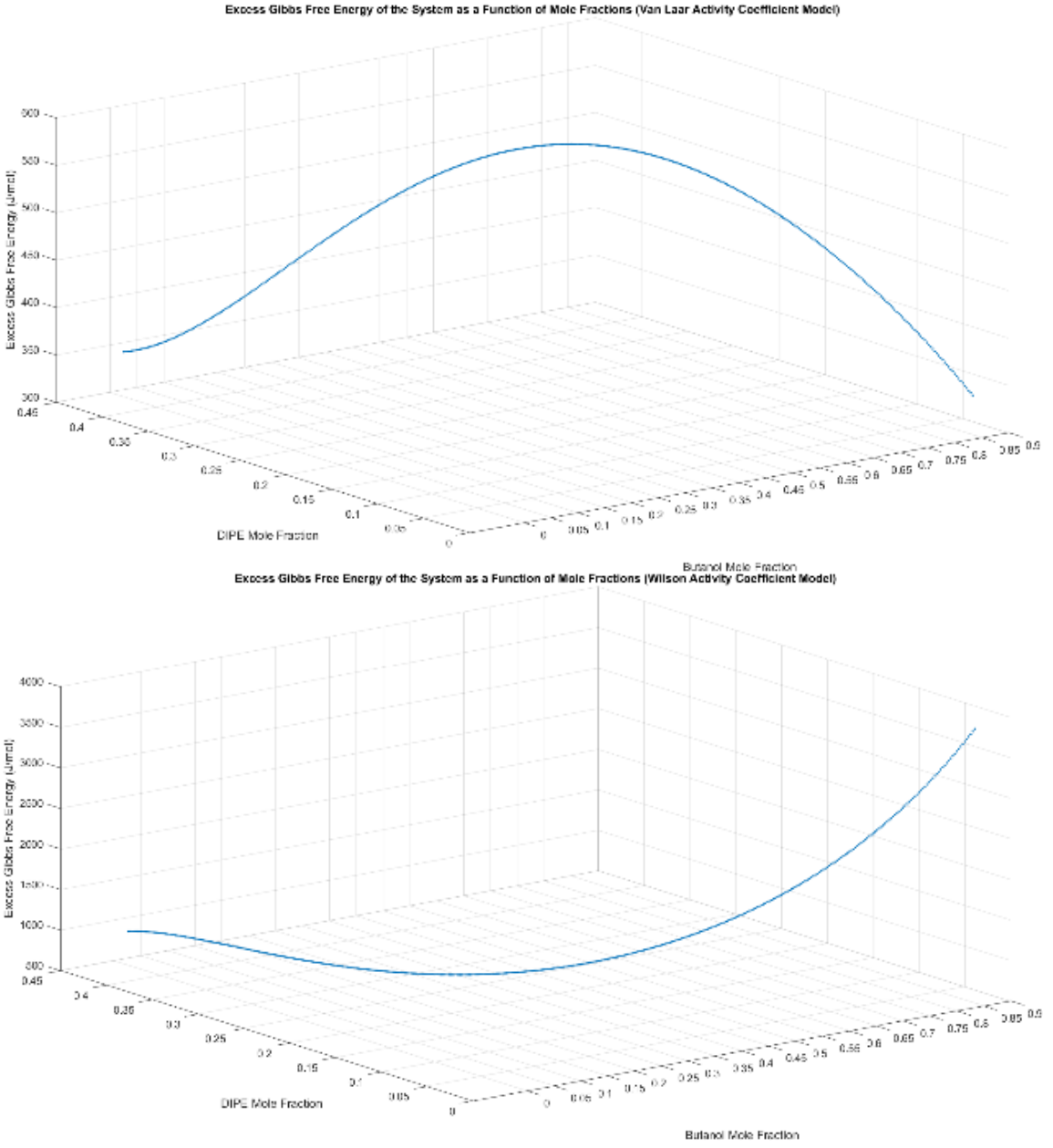

Figure 7. Excess Gibbs free energy as a function of butanol and DIPE mole fraction in the system butan-1-ol+DIPE+benzene ($T = 313.15\, K$) using van Laar (left) and Wilson (right) activity coefficient models.

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Figure 7 shows the excess property plotted against the mole fraction of butan-1-ol and DIPE, in the butan-1-ol + DIPE + benzene system. In the van Laar model, the excess Gibbs free energy experienced a gradual rise and fall as the butan-1-ol mole fraction increased and the DIPE mole fraction decreased. In the Wilson model, the plot resulted in just a gradual rise. For the van Laar model, the peak of the plot occurred at $x_1 = 0.462$ and $x_2 = 0.204$ where $G^{ex} = 587.89\, J/mol$. For the Wilson model, the peak of the plot occurred at $x_1 = 0.850$ and $x_2 = 0.01$ where $G^{ex} = 3877.79\, J/mol$.

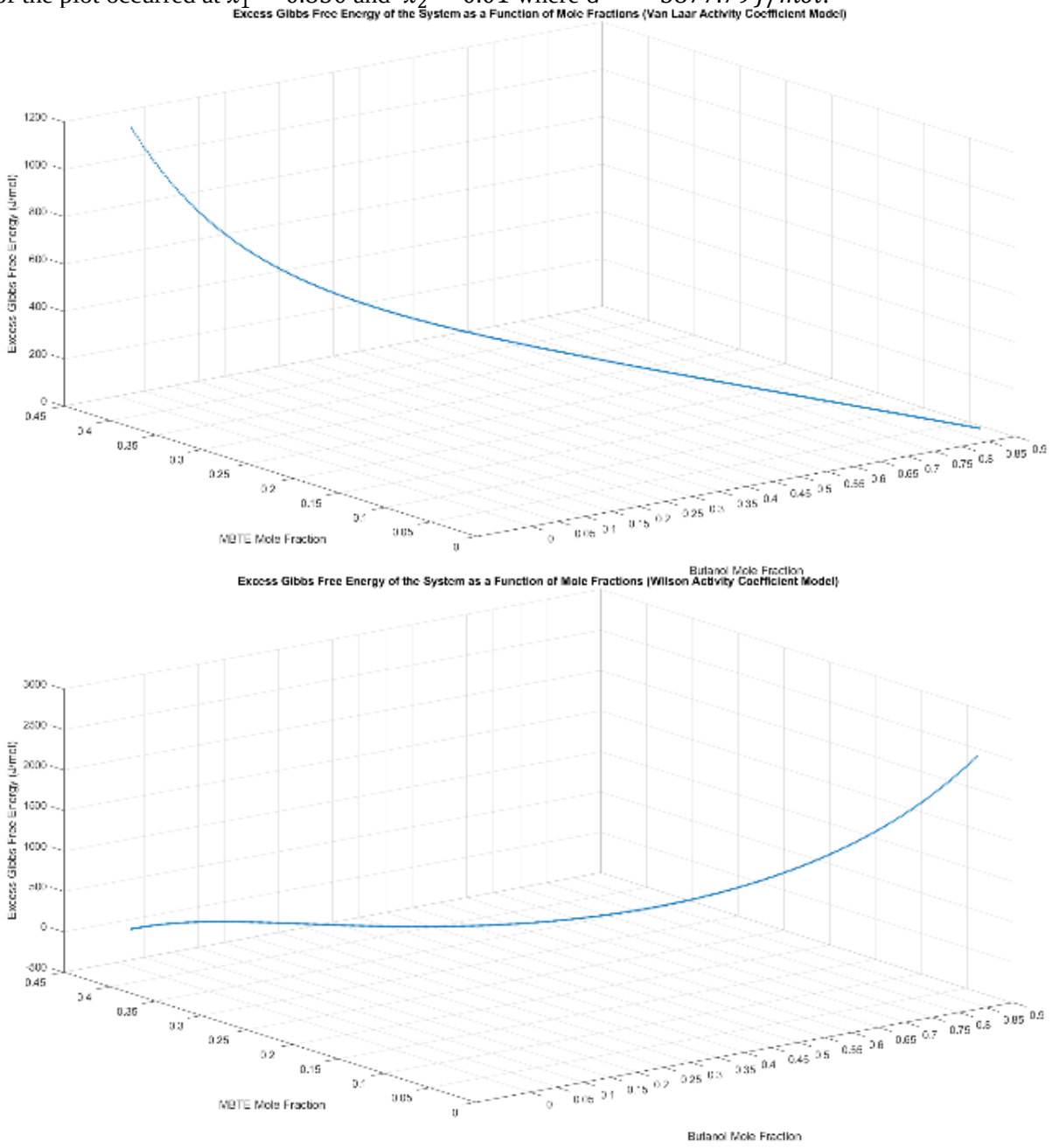

Figure 8. Excess Gibbs free energy as a function of butanol and MBTE mole fraction in the system butan-1-ol+MBTE+methanol ($T = 298.15\ K$) using van Laar (left) and Wilson (right) activity coefficient models.

Figure 8 shows the excess property plotted against the mole fraction of butan-1-ol and DIPE, in the butan-1-ol + MBTE + methanol system. In the van Laar model, the excess Gibbs free energy experienced

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a gradual fall as the butan-1-ol mole fraction increased and the DIPE mole fraction decreased. In the Wilson model, the plot resulted in just a gradual rise. For the van Laar model, the peak of the plot occurred at $x_1 = 0.002$ and $x_2 = 0.434$ where $G^{ex} = 1137.90\, J/mol$. For the Wilson model, the peak of the plot occurred at $x_1 = 0.850$ and $x_2 = 0.01$ where $G^{ex} = 2565.28\, J/mol$.

As a general rule, systems with a lower Gibbs free energy are more stable than those with higher ones. Since excess properties are deviations from the ideal mixture assumption, it follows that for a system, conditions that result to lower excess Gibbs free energy results to higher stability. Furthermore, Gibbs free energy can be used to calculate the maximum amount of work that may be performed. A lower excess Gibbs free energy then translates to a higher possible maximum amount of work, making the system more desirable. Since the value of this excess property differed depending on whether van Laar or Wilson models for activity coefficients were used, it would be reasonable to pick a model that best fits the system in terms of its prediction of other physical properties such as calculated deviations of pressure and vapor mole fractions. Otherwise, a compromise between the plots should be made. Though it is important to note that this alone should not be the only consideration in deciding specifications for a system, it is crucial that we know the extent of its effects.

4. Conclusion

In this study, excess Gibbs free energy of mixing has been predicted for binary biofuel systems (butan-1-ol + DIPE, butan-1-ol + MBTE) and ternary biofuel systems (butan-1-ol + DIPE + benzene, butan-1-ol + MBTE + methanol) using machine learning where data was based on isothermal VLE modelling established through Modified Raoult's Law. The interaction parameters of the multiple component systems are obtained by activity coefficient models, including Wilson and van Laar model. Through Neural Net Fitting, it was found that both activity coefficient models perfectly fit the data yielding a great linear relationship, and it was observed that Wilson model is a better fit as an activity coefficient model for all the biofuel systems. In examining bubble point pressure using Machine Learning, the rational quadratic GPR under the Regression Learner performed the best among the five algorithms used, producing the lowest RSME on most systems based on both activity coefficient models. The Fine Tree algorithm also performed well for some binary systems producing low RMSE values close to the values acquired from the rational quadratic GPR. Vapor mole compositions were also examined, where the binary system containing MBTE yielded the lowest RSME when based on the Wilson model; moreover, the van Laar model was found to be more suitable for the other three systems. High mole fraction resulted in high values excess Gibbs free energy of mixing. The values of the excess free energy varied based on different activity coefficient models, indicating that the best fitting VLE model for a system can be determined through other property predictions such as deviations of pressure and vapor mole fractions. Moreover, a more sophisticated and developed VLE model can be employed.

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