Vapor – Liquid Equilibrium of Linalool + β-Caryophyllene and α-Pinene + Linalool at Pressures of 30 and 60 kPa

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***Abstract*—** This research aims to obtain equilibrium data from essential oils, namely lavender oil. Lavender flowers are composed of several ingredients, such as essential oils (1-3%), alpha-pinene (0.22%), camphene (0.06%), beta-myrcene (5.33%), cymene (0.30%), limonene (1.06%), cineol (0.51%), linalool (26.12%), borneol (1.21%), terpinine-4-ol (4.64%), linalyl acetate (26.32%), geranyl acetate (2.14%), and caryophyllene (7.55%). This research focuses on determining vapor-liquid equilibrium (VLE) data for the binary systems Linalool + β-Caryophyllene and α-Pinene + Linalool at vacuum pressure of 30 kPa and 60 kPa. Research was conducted to support the equilibrium data for distillation process in the essential oil industry, by exploring the characteristics of VLE which is an important parameter in distillation column design. Experiments used a modified Othmer type ebulliometer and composition measurements were carried out using Gas Chromatography-Mass Spectrometry (GC-MS). The equilibrium data were correlated using Wilson, NRTL, and UNIQUAC model equations. The thermodynamic consistency tests have been performed using Wisniak Method. The research results showed that the VLE values obtained are thermodynamically consistent and the model used can correlate equilibrium with satisfactory accuracy. It was obtained from experimental data that for the Linalool + β-Caryophyllene system had the largest average absolute deviation in temperature (AAD T) value of 0.74% and for the Alpha Pinene + Linalool system had the largest AAD T with a value of 0.28% for both pressures.

Keywords — Vapor-Liquid Equilibrium, Wilson, NRTL, UNIQUAC, UNIFAC

I. INTRODUCTION

Indonesia is a tropical country which is rich in natural resources, such as spices as well as its essential oils. The pharmaceutical industry utilizes the compounds that make up essential oils and their derivatives as ingredients for cosmetics, fragrance oils, medicines, and food. Essential oils are also known as etheric oils or volatile oils. Essential oils are compounds that are generally in the form of liquids obtained from plant parts such as roots, skin, stems, leaves, fruit, seeds, or flowers by distillation using steam. Essential oils are volatile at room temperature without undergoing decomposition, have a bitter taste (pungent taste), and smell fragrant according to the producing plant. Essential oils can be soluble inorganic solvents. The need for essential oils have been increasing every year along with the increasing development of modern industries such as perfume, cosmetics, food, pharmaceutical, aroma therapy, and medicine industries [1].

One of the essential oils is lavender oil which comes from lavender flowers (Lavandula angustifolia). Lavender flowers have a mauve color and a distinctive and soft smell. Lavender is widely cultivated in various parts of the world. It is known that lavender flowers have anti-inflammatory, antiseptic, antibacterial, antifungal, and antidepressant, and can reduce acne [2]. Lavender flowers are composed of several ingredients, such as essential oils, alpha-pinene, camphene, beta-myrcene, cymene, limonene, cineol, linalool, borneol, terpinine-4-ol, linalyl acetate, geranyl acetate, and caryophyllene [3]. To obtain these components, the process starts with the extraction of oil from lavender flowers, followed by purification through fractional distillation techniques or other suitable separation methods. In this context, fractional distillation is particularly beneficial as it allows the separation of components based on their boiling point differences. After purification, vapor-liquid equilibrium (VLE) data of the binary system on some of these components is required to determine the best operational conditions to separate the components with high purity at specific operating pressures, such as 30 and 60 kPa.

The vapor liquid equilibrium (VLE) studies involving essential oil components - especially linalool, α-pinene, and β-caryophyllene- have been conducted by researchers. The isobaric VLE data related to bitter orange aroma compounds of α-pinene/ linalool has been investigated within water and ethanol mixture at atmospheric pressure [4]. The isothermal VLE data for various systems involving components of Litsea cubeba oil, namely citral + linalool/α-pinene and linalool + α-pinene at temperatures of 60 °C, 90 °C, and 130 °C have been investigated using headspace gas chromatography. Based on the positive deviations in Gibbs free energy, the system behaved non-ideally [5]. In addition, the VLE data of binary systems of β-caryophyllene/α-pinene + dipentene and the ternary system of β-caryophyllene, dipentene, and α-pinene have been studied using using modified Ellis still at 100.7 kPa. The Wilson model was able to predict ternary VLE data accurately with deviation less than 0.50 °C [6]. In another research, the VLE experiment of binary systems of α-pinene + longifolene/abietic acid and a ternary system of α-pinene + longifolene + abietic acid have been carried out using headspace gas chromatography at temperatures of 40 °C, 50 °C, and 60 °C. Its vapor pressure increased with

temperature and that no azeotropic behavior was observed in the systems studied [7]. Regarding lavender essential oil components, the isothermal VLE systems included linalool + linalyl acetate/α-terpineol and α-terpineol + linalyl acetate have been measured using headspace gas chromatography at temperatures of 90 ºC, 105 ºC, and 120 ºC. The Wilson, NRTL, and UNIQUAC models well correlated the experimental data with maximum absolute average deviation values of 0.80% [8]. However, the isobaric VLE data of linalool + β-Caryophyllene and α-Pinene + linalool at vacuum pressure have not been found in the literatures.

A good understanding of vapor-liquid equilibrium (VLE) is a key factor in the processing industry of essential oils such as lavender oil, where the determination of composition and temperature in the vapor and liquid phases is essential. In particular, VLE data in the form of temperature and composition (T-x-y) is crucial for effective separation and refining processes. Using T-x-y data, it can be determined at which temperature and composition the essential oil or its components, such as linalool and β-Caryophyllene, will be optimally separated in the distillation process.

Considering Indonesia as one of the leading essential oil producers, T-x-y vapor-liquid equilibrium research for lavender oil becomes relevant to optimize the utilization of this natural resource. This research does not only contribute towards improving the quality of the final product but also guides energy efficiency for distillation equipment design. Therefore, research on vapor-liquid equilibrium in T-x-y form for the binary systems linalool + β-caryophyllene and linalool+α-pinene, both of which are the main components of lavender oil, becomes very substantial to maximize the yield of essential oil distillation. The quality standards for lavender oil based on the Indonesian National Standard (SNI) can be seen in Table 1.

TABLE 1. LAVENDER OIL QUALITY STANDARD BASED ON SNI

Characteristic	SNI Standard
Color	Bright yellow
Odor	Lavender
Specific Gravity	0.876 – 0.892
Refractive index (20ºC)	1.458 – 1.464
Solubility in 70% alcohol at 20°C	Clear Solution in volume ratio of 1-10 parts

The Indonesian National Standard (SNI) for lavender oil specifies certain quality criteria that must be met, including color, odor, specific gravity, refractive index, and solubility in alcohol. These criteria are highly relevant to the vapor-liquid equilibrium research of the binary systems Linalool + β-Caryophyllene and Alpha-Pinene + Linalool, as the successful separation of these components significantly affects the fulfillment of these standards.

The vapor-liquid equilibrium study provided the necessary data to optimize the distillation process, ensuring that linalool, as the main component of lavender oil, as well as β-Caryophyllene and Alpha-pinene can be separated with high efficiency, preventing degradation or loss of important components during distillation. This has a direct impact on achieving SNI standards, especially in the aspects of solubility and refractive index, which can be indicated as parameters to evaluate the purity and concentration of active components in the oil. For example, high solubility in alcohol and refractive index by the SNI range indicate that volatile components, such as linalool, have been appropriately separated and conserved during the distillation process. Moreover, vapor liquid equilibrium data also presents on how obtaining the pure component of α-Pinene and β-Caryophyllene from linalool mixtures. Pure components are required in the pharmaceutical formulation for consistent manufacturing and performance [9]. The α-Pinene has multiple important pharmacological, therapeutic, and industrial functions. The α-Pinene has antioxidant, antibacterial, and anti-inflammatory qualities. Because of its distinctive pine-like scent, it is widely utilized in the flavor and fragrance industries. It is also used as a chemical intermediary to create chemicals like camphene, geraniol, and linalool [10]. Likewise, β-Caryophyllene has numerous significant biological and therapeutic properties, including antioxidant and neuroprotective properties, anti-inflammatory and pain relieving properties, and metabolic and cardiovascular advantages [11,12].

II. METHOD

A. Experiment Scheme

The experimental setup consists of a modified Othmer Still Distillation system used to determine vapor-liquid equilibrium (VLE) data for binary systems, it is shown in Figure 1 below. The setup includes an ebulliometer chamber with a flat-bottom base and a magnetic stirrer to ensure homogeneous mixing. The ebulliometer cell is equipped with a heater (TDGC) connected to a heating cable to regulate the temperature of the sample solution. The vapor produced is condensed using a co-current cooling water system connected to a condenser. The system operates under vacuum conditions, maintained using a vacuum pump with a needle valve to adjust pressure, monitored by a pressure sensor. The equilibrium state is determined when the temperatures of both the liquid and vapor phases stabilize, measured using thermocouples connected to temperature indicators. The apparatus allows for precise control and measurement of pressure and temperature, facilitating accurate VLE data collection for the binary mixtures

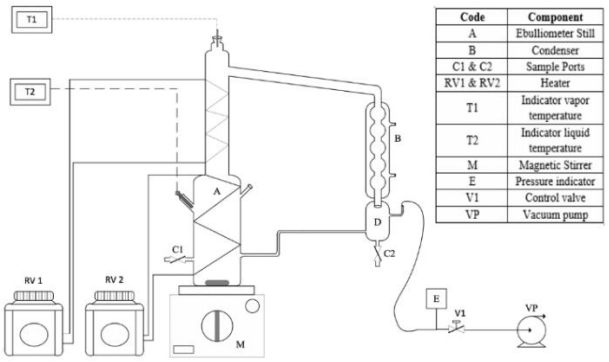


Figure 1. Experimental Apparatus

The experiment utilizes an equilibrium cell that features a heating jacket to maintain a constant temperature and a magnetic stirrer to stir the solution effectively. Figure 1 depicts that the equilibrium cell is furnished with a PID controller and Pt100 RTD to regulate the temperature of the circulating water.

B. Materials

Data on pure materials from the system used can be seen in Table 2.

TABLE 2. CHEMICAL PROPERTIES

Material	CASRN	Material Properties *			
		Purity (%)	MW (g/mol)	Tn (K)	Density (g/cm^3)
Linalool[a]	78-70-6	99%	154.25	467.15	0.858
β-Caryophyllene[b]	87-44-5	99%	204.35	529.15	0.907
α-Pinene[c]	80-56-8	97%	136.23	430	0.850

[a] Xi'an International Healthcare Factory Co., Ltd
[b]PT.Indesso Aroma
[c] PT.Syailendra Bumi Investama
*Obtained from *Certificate of Analysis (CoA)* of each company

III. RESULT AND DISCUSSION

A. Ebulliometer Apparatus Validation

Before conducting experiments with the Ebulliometer in this vapor-liquid equilibrium study, the device was validated first to determine the feasibility of the apparatus, as generally conducted in VLE study [13]. The validation test uses the ethanol component with data in the form of vapor temperature (T_{exp}) at a predetermined pressure and then compared with the calculated vapor pressure (T_{cal}) using the Antoine equation and the Wagner equation, by reviewing the deviation between these values in the form of AD (absolute deviation) and %AAD (absolute average deviation) between T_{exp} and T_{cal} at various pressures. The equation AD and %AAD are shown in the equations 1 and 2, respectively.

$$AD = [T_i \text{ exp-} T_i \text{ calc}] \quad (1)$$

$$\%AAD = \frac{1}{n}\sum_{i-1}^{n}\left|\frac{Tcal-Texp}{Texp}\right| \times 100\% \quad (2)$$

The constant parameters used for the correlation of Ethanol compounds are shown in Table 3.

TABLE 3. PARAMETER CONSTANTS ON ETHANOL COMPONENTS

Parameters	A	B	C	D
[(a)]Antoine	8.12875	1660.8713	238.131	-
[(b)]Wagner	-8.976664	2.193165	-6.637628	5.085084

[(a)] $\log 10\, P^{sat}(mmHg) = A - B/(T_{cal} + C)$

[(b)] $\ln\left(\frac{P_{sat}}{P_c}\right) = \frac{A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^5}{1-\tau}$; $\tau = 1 - \frac{T}{T_c}$

The use of ethanol (alcohol) for validation testing because it is extensively researched thus it can be compared with correlations, in this case the Antoine equation and the Wagner equation. The results of the validation of the ethanol component using Antoine and Wagner parameters can be seen in Table 4.

TABLE 4. RESULTS OF VALIDATION OF ETHANOL COMPONENTS WITH ANTOINE AND WAGNER PARAMETERS

P_{exp} (kPa)	T_{exp} (K)	Antoine		Wagner	
		T (K)	% AAD T	T (K)	% AAD T
92.9	348.4	349.2	0.256	349.3	0.269
80.5	344.5	345.6	0.330	345.7	0.374
70.8	341.7	342.4	0.214	342.7	0.303
66.1	340.0	340.7	0.215	341.0	0.320
49.6	334.5	333.8	0.183	334.5	0.001
40.5	331.2	329.2	0.596	330.0	0.355
29.7	323.3	322.3	0.287	323.4	0.041
26.0	320.1	319.5	0.178	320.6	0.186
17.7	312.5	311.6	0.282	313.0	0.185
15.8	310.4	309.3	0.323	310.9	0.162
Average %AAD T		-	0.286	-	0.220

Through the data in Table 4, a graph of the relationship between vapor pressure (P_{exp}) and the experimental temperature of the Ethanol component (T_{exp}) can be obtained, as well as the relationship between P_{exp} and $T_{Antoine}$ and T_{Wagner} which can be seen in Figure 2.

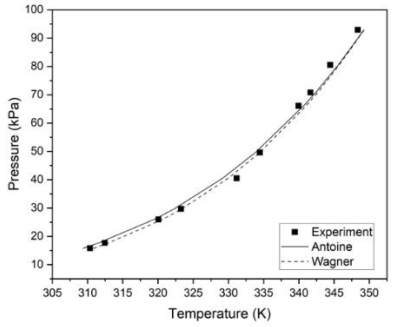


Figure 2. Graph of Apparatus Validation Results on Ethanol Components

Figure 2 above shows a small difference between the experimental results and the calculation of the Antoine and Wagner equations. In addition, based on Table 4, it can be seen that the results of the validation experiment using ethanol with the Antoine and Wagner equation method show that the average value of %AAD T is less than 0.5%. The average value of %AAD T validation of pure ethanol components based on the Antoine and Wagner equations is 0.286% and 0.220% respectively. This small value of %AAD T indicates

that this ebulliometer is reliable for vapor-liquid equilibrium experiments.

B. Antoine Constant Measurements of Linalool, β – Caryophyllene and α – Pinene

The determination of the equilibrium model used (Wilson, NRTL, and UNIQUAC) depends on the calculation of the saturated condition, so it is necessary to calculate the condition of the compound in the saturated state. In this study, the compounds β-Caryophyllene, α-Pinene, and Linalool were analyzed under pure conditions to obtain the value of Antoine parameters. The calculation of the Antoine constant from the experimental data is necessary to ensure that the prediction of vapor pressure is in accordance with the specific conditions of the study, thereby increasing the validity and reliability of the research results [14]. The calculation of Antoine parameters is based on the linearization of the Antoine equation as in the following explanation.

$$\ln(P)=A-\frac{B}{T+C} \quad (3)$$

$$T \times \ln(P)+ C \times \ln(P) =A \times T+A\times C-B \quad (4)$$

$$\ln(P) =A+\frac{A \times C-B}{T}-\frac{C\times \ln(P)}{T} \quad (5)$$

An example is made with,

$$y = \ln(P) \quad (6)$$

$$x_1 = \frac{1}{T} \quad (7)$$

$$x_2=\frac{\ln(P)}{T} \quad (8)$$

So that, equation (5) will be,

$$y=a_0+a_1.x_1+a_2.x_2 \quad (9)$$

Therefore, experimental data in the form of pressure (P) in kPa and temperature (T) in Kelvin (K) can be depicted in a graph and the values of a_0, a_1, and a_2 can be known, which will later be processed into values A, B, and C. The results of the pressure and temperature experiments carried out can be seen in Table 5.

TABLE 5. RESULTS OF PRESSURE (P) AND TEMPERATURE (T) EXPERIMENTS FOR 3 COMPONENTS

Linalool		β - Caryophyllene		α – Pinene	
P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)
72.8	459.25	71.1	511.55	76.0	417.35
59.8	452.35	65.8	509.75	57.0	406.15
49.6	446.95	55.9	503.55	47.1	400.35
41.6	440.85	48.8	497.95	38.4	393.85
29.8	430.55	30.9	478.95	31.2	385.85
18.6	416.95	21.0	466.45	19.6	371.35
11.0	402.75	10.8	443.65	10.7	352.95
AADT%	0.030	-	0.153	-	0.097

Antoine parameters of the three components used in this study can be seen in Table 6.

TABLE 6. ANTOINE PARAMETER FITTING RESULTS ON EACH COMPONENT

Component	A	B	C
Linalool	16.669	5291.428	-31.949
β - Caryophyllene	12.718	3202.096	-134.444
α – Pinene	17.164	6234.957	68.330

From the results of the Antoine parameter fitting, then depiction can be carried out using equation (3) to confirm the results of the parameters obtained. A comparison between the results of the Antoine parameter fitting with the experimental can be seen in Figure 3.

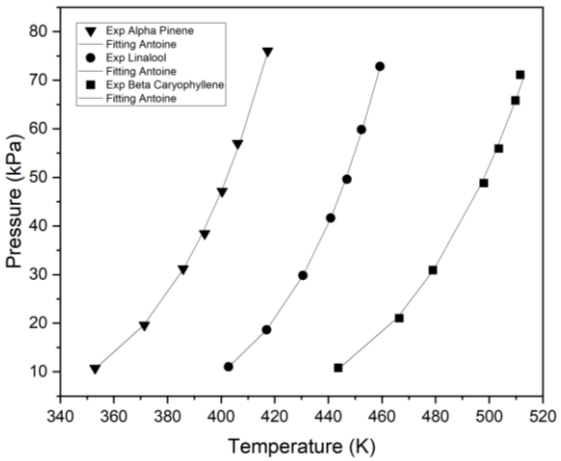


Figure 3. P-T Chart of Linalool, Beta-caryophyllene and Alpha-Pinene

The graph above shows that there is no significant difference between the experimental results and Antoine's calculation results, and based on calculations with Antoine's fitting parameters, the %AAD T values of 0.030, 0.153, 0.097 for Linalool, β-Caryophyllene, and Alpha-pinene components are obtained respectively. The selection of 30 and 60 kPa pressure is also based on the results which show that the data is stable and the color of the solution does not change or no decomposition occurs. The AAD T value which is small shows that the solution used has good agreement with the results of the calculation of Antoine parameters.

C. Thermodynamics Consistency Test of Experimental Data

In the Vapor liquid Equilibrium study, a consistency test is needed using the L-W Wisniak method which makes a plot between the experimental GE/RT (excess Gibbs energy per gas constant and temperature) and the liquid composition (xi), according to Wisniak the Redlich – Kister expansion trend line is arranged according to which it already represents the experimental GE/RT distribution data. According to the provisions, the experimental data must meet the requirements, namely the L and W values have a deviation value of less than 5 so that it can be said to be consistent. Tables 7 and 8 show the experimental data of liquid vapor equilibrium, while the Redlich- Kister constant values used can be seen in Table 9. In the

Wisniak model, a solver in the Microsoft Excel is applied by setting the objective to the average value of objective function of GE/RT and adjusting the changing cells for the Redlich-Kister constants (B, C, D, E, F, G). This method yields the exact values of the Redlich-Kister constants as shown in Table 9. Using this solver, the ratio of the liquid phase inconsistency (L) to the vapor phase inconsistency (W), which provides a comparative measure of deviation between the liquid and vapor phases and overall deviation (D) values are obtained to match the parameters B, C, D, E, F, and G, as listed in Table 9.

TABLE 7. EXPERIMENTAL DATA OF LINALOOL (1) + BETA-CARYOPHYLLENE (2) SYSTEM

T_{exp} (K)	P = 30 kPa		T_{exp} (K)	P = 60 kPa	
	x_1	y_1		x_1	y_1
478.1	0.0000	0.0000	505.8	0.0000	0.0000
468.9	0.1158	0.3396	496.4	0.0800	0.2307
462.6	0.1962	0.5005	487.3	0.1903	0.4305
452.6	0.3485	0.6744	478.5	0.3062	0.6250
441.5	0.6051	0.8469	475.1	0.4021	0.7174
433.7	0.7950	0.9382	471.4	0.5015	0.7508
430.8	1.0000	1.0000	465.7	0.6051	0.8354
-	-	-	462.5	0.7113	0.8681
-	-	-	458.7	0.8151	0.9312
-	-	-	455.7	0.8880	0.9640
-	-	-	452.8	1.0000	1.0000

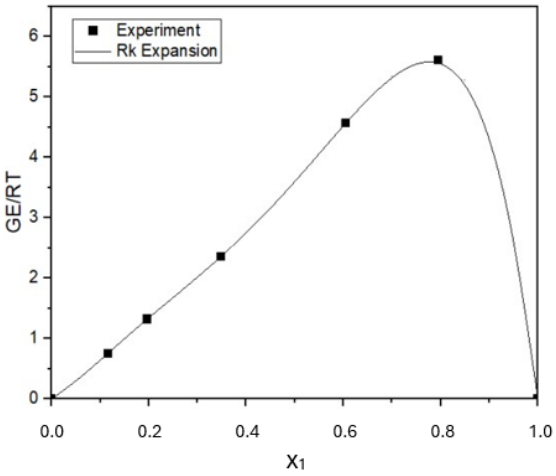
TABLE 8. EXPERIMENTAL DATA OF ALPHA-PINENE (1) + LINALOOL (2) SYSTEM

T_{exp} (K)	P = 30 kPa		T_{exp} (K)	P = 60 kPa	
	x_1	y_1		x_1	y_1
430.8	0.0000	0.0000	452.8	0.0000	0.0000
419.7	0.1154	0.3487	444.5	0.1236	0.2996
415.3	0.2150	0.5451	440.9	0.2190	0.4657
410.7	0.2818	0.6331	435.4	0.3105	0.5898
405.8	0.3893	0.7423	430.8	0.3810	0.6581
401.3	0.4958	0.8007	425.9	0.4671	0.7583
398.0	0.6292	0.8755	421.9	0.6149	0.8518
393.5	0.7131	0.9169	419.4	0.6933	0.8841
391.3	0.7857	0.9364	416.4	0.7973	0.9237
390.4	0.8818	0.9560	414.5	0.8561	0.9551
387.4	1.0000	1.0000	408.8	1.0000	1.0000

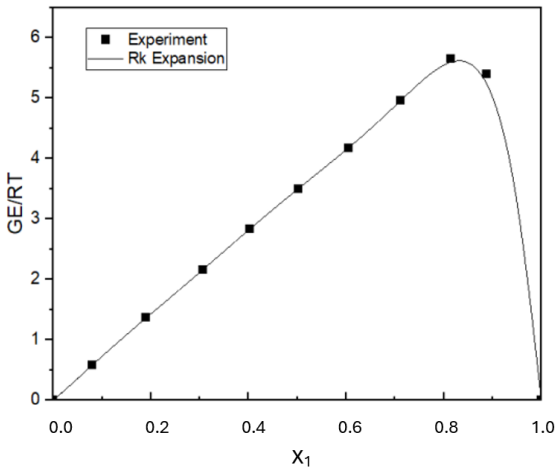
TABLE 9. REDLICH-KISTER CONSTANT FOR CONSISTENCY TEST

P (kPa)	B	C	D	E	F	G	OF G^E/RT
Linalool + Beta-Caryophyllene							
30	14.3812	18.1605	18.8721	9.1484	4.1862	5.5624	0.0594
60	13.9590	13.0515	12.3470	18.2887	27.1600	15.4175	0.0791
Alpha Pinene + Linalool							
30	18.1811	17.4805	14.7426	4.6094	7.8252	2.0010	0.5279
60	17.6688	9.2593	22.2836	14.9581	15.6752	3.6425	0.1387

The G^E/RT plot curves from the Redlich-Kister equation and experiment can be seen in Figure 4 for the binary system Linalool + β-Caryophyllene, in Figure 5 for the binary system α-Pinene + Linalool.

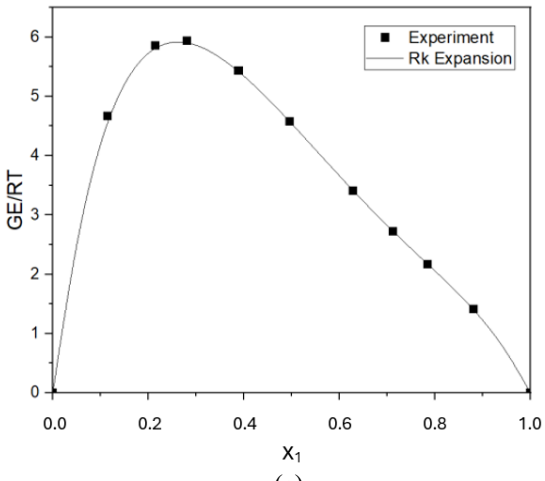


(a)



(b)

Figure 4. Consistency Test Chart of Linalool (1) + Beta-caryophyllene (2) (a) at 30 kPa, (b) at 60 kPa



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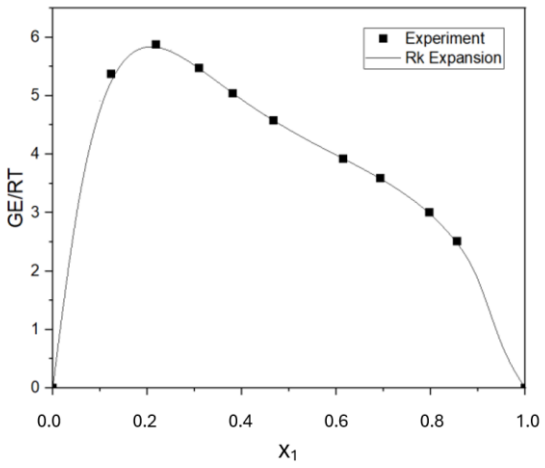

Figure 5. Consistency Test Chart of Alpha-pinene (1) + Linalool (2) (a) at 30 kPa, (b) at 60 kPa

Data is categorized as thermodynamically consistent if the Deviation (D) value is < 5. The D value of the experimental results is presented in Table 10.

TABLE 10. THERMODYNAMIC CONSISTENCY TEST RESULTS

System	Pressure (kPa)	L/W (0.92 – 1.08)	D	Consistency
Linalool + β- Caryophyllene	30	0.9815	0.9347	Consistent
	60	1.0013	0.0669	Consistent
Alpha – pinene + Linalool	30	1.0271	1.3386	Consistent
	60	1.0092	0.4565	Consistent

The GE/RT Redlich-Kister equation obtained based on the results of calculations carried out using a solver on Microsoft Excel is compared with experimental data, thus a GE/RT vs x_1 can be obtained. Where Gibbs energy is parameter in thermodynamics that can be used to calculate the maximum reversible work that can be done by thermodynamic systems at constant temperature and pressure under isobaric or isothermic conditions. On Figures 4 and 5, it can be observed that Gibbs Energy = 0 when $x_1 = 0$ and $x_2 = 0$, which indicates the ideal solution obeys Raoult's Law. The highest Gibbs energy value for the Linalool + Beta-caryophyllene system at pressures of 30 kPa and 60 kPa occurs at $x_1 \approx 0.8$, meanwhile for the Alpha-pinene + Linalool system at pressures of 30 kPa and 60 kPa occurs at $x_1 \approx 0.1$. These points indicate that the solution is non-ideal and does not obey Raoult's Law at these points, indicating the presence of significant molecular interactions between the components in the solution. These deviations from Raoult's Law indicate the presence of different intermolecular interactions between the components in the mixture, which are amplified by the effects of differencesin component volatility.

The L-W consistency test proposed by Wisniak, 1994, was chosen because this consistency test method is suitable for vapour-liquid equilibrium at low pressure. This method was chosen because other consistency test methods such as the Area test (Herington) require information about the heat of mixing, where heat of mixing data with temperature and composition of studied system are unavailable. As for the L-W Test method, consistency uses the boiling point approach of the mixture and does not require heat of mixing information. In addition, the L-W test method is suitable for application to binary and multicomponent systems [15]. Otherwise, From the experimental results, the data presented in Table 10 shows that all tested systems are thermodynamically consistent as the deviation (D) value is less than 5. The L/W value is also within the range of 0.92 to 1.08, indicating that the consistency of the experimental data is acceptable. Therefore, this data can be further processed to obtain correlation parameters for the Wilson, NRTL, and UNIQUAC models.

D. VLE Experimental Results with Wilson, NRTL, UNIQUAC and UNIFAC

The data that has been obtained and tested for consistency is then correlated using the Wilson, NRTL, and UNIQUAC equations to obtain the parameters of each model. The correlation parameters are calculated using the GRG Non-Linear solving method found in the Microsoft Excel programme, and the parameters obtained in this way are called independent parameters. Table 11 shows the binary parameters for system studied at 30 and 60 kPa. The following presents the parameters obtained from the correlation of experimental data along with the deviation of T and y_1 values.

Wilson, NRTL, and UNIQUAC equation models were chosen because they are suitable and have been widely used to correlate vapour-liquid equilibrium experimental data. These models effectively describe non-ideal liquid phase behavior through activity coefficients. They model molecular interactions and incorporate local composition concepts. In addition, these models provide adjustable binary interaction parameters that can be fitted to experimental data, allowing precise correlation of VLE data across a wide range of temperatures, pressures, and compositions [16.17]. From the correlation model used, optimal binary parameters will be obtained, where for the Wilson model there are 2 parameters to be optimised, namely a_{ij} and a_{ji}. For the NRTL model, there are 3 parameters to be optimised, namely b_{ij}, b_{ji}, and α. The value of α is determined in the range of values 0.2-0.42, which later selected the value that has the smallest AAD T against the experimental results. As for the UNIQUAC model, there are 2 parameters to be optimised, namely u_{ij} and u_{ji} [18].

TABLE 11. INTERACTION PARAMETERS OF BINARY SYSTEM

Correlation Model	Parameter (cal/mol)		AAD T (%)	AAD Y (%)
Linalool (1) + Beta - caryophyllene (2) at 30 kPa				
Wilson	a12	-50.6734	0.18	1.47
	a21	-47.3673		

Correlation Model	Parameter	(cal/mol)	AAD T (%)	AAD Y (%)
NRTL (α = 0.42)	b_{12}	45.8793	0.19	1.35
	b_{21}	-112.8603		
UNIQUAC	u_{12}	9.9026	0.74	4.92
	u_{21}	10.1039		
Linalool (1) + Beta - caryophyllene (2) at 60 kPa				
Wilson	a_{12}	-412.7641	0.15	3.78
	a_{21}	450.9013		
NRTL (α = 0.42)	b_{12}	-8.5609	0.16	4.27
	b_{21}	-24.6454		
UNIQUAC	u_{12}	-17.7363	0.15	4.34
	u_{21}	-17.7339		
Alpha - Pinene (1) + Linalool (2) at 30 kPa				
Wilson	a_{12}	33.5408	0.23	1.03
	a_{21}	30.8959		
NRTL (α = 0.42)	b_{12}	12.7416	0.26	1.70
	b_{21}	30.7633		
UNIQUAC	u_{12}	-4.0324	0.24	1.24
	u_{21}	-3.9707		
Alpha - Pinene (1) + Linalool (2) at 60 kPa				
Wilson	a_{12}	-236.8916	0.17	1.23
	a_{21}	248.6644		
NRTL (α = 0.42)	b_{12}	-43.7012	0.22	1.60
	b_{21}	-48.0649		
UNIQUAC	u_{12}	-8.0324	0.28	3.07
	u_{21}	-6.9707		

After calculating the correlation using the Wilson, NRTL, and UNIQUAC methods for the binary systems Linalool + Beta-caryophyllene and Alpha-pinene + Linalool at vacuum pressures of 30 and 60 kPa, curves were madewith the y-axis in the form of temperature vs. the x-axis in the form of the mole fraction of the liquid phase (x_1) and also the mole fraction of the vapor phase (y_1) so as to obtain the T-x-y curve of the modelling results with the binary parameters of each method which can be seen in Figure 6 for Linalool + Beta - caryophyllene binary system at 30 kPa and 60 kPa pressure and in Figure 7 for Alpha Pinene + Linalool binary system at 30 and 60 kPa pressure.

These obtained binary parameters for both tested systems can be fitted. From the optimization results of the three correlation models used, the overall AAD T value is below 1%. However, in the AAD Y results, the maximum value was obtained at 4.92% in the UNIQUAC model in the Linalool (1) + Beta - caryophyllene (2) binary system at a pressure of 30 kPa, and the minimum was at 1.03% in the Wilson model in the Alpha - pinene (1) + Linalool (2) binary system at a pressure of 30 kPa. This indicates that the three correlation models namely Wilson, NRTL, and UNIQUAC can be used and are suitable for the two binary systems studied.

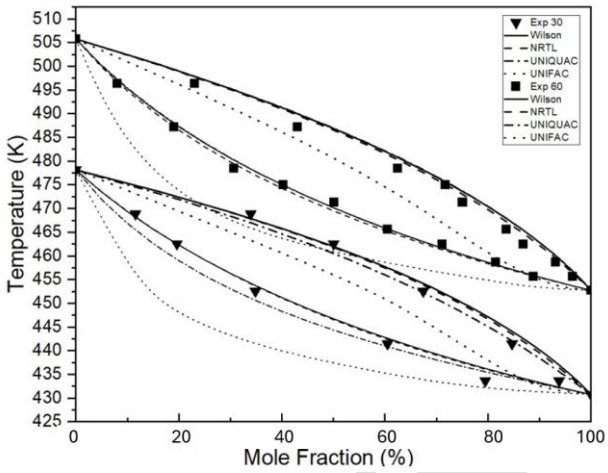

Figure 6. T-x-y Graphs of Binary System of Linalool (1) + Beta - caryophyllene (2) at Pressures of 30 and 60 kPa

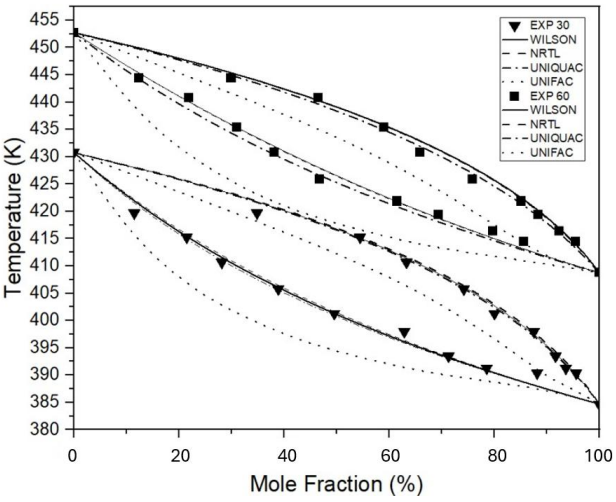

Figure 7. T-x-y Graphs of Binary System of Alpha-Pinene (1) + Linalool (2) at Pressures of 30 and 60 kPa

Based on the correlation results using the Wilson, NRTL, and UNIQUAC equations, there is no significant difference in the AAD T and AAD Y values of the three correlation methods. In addition to the AAD T and AAD y values which show that the experimental T and y_1 values can be correlated well with the T and y_1 values of Wilson, NRTL, and UNIQUAC modelling results, it can also be seen from Figures 6 and 7 which show the T-x-y curves of experimental results with correlation are quite close. This results are in line with literatures mentioning that activity coefficient model (Wilson, NRTL, UNIQUAC) well correlated the VLE data involving essential oil constituents [5-8].

Overall, the Wilson, NRTL, and UNIQUAC models showed variations in binary parameter values with changes in pressure. However, the Wilson model tends to give smaller AAD T and AAD Y values at some conditions, indicating a better fit. The selection of the most appropriate model depends on the specific system and operating conditions. The optimal binary parameters should be selected based on the AAD T and

AAD y values to ensure better accuracy in the prediction of molecular interactions within the system.

Comparisons were then made based on the use of two different vacuum pressures of 30 and 60 kPa as shown in Figure 6 for the Linalool + Beta-caryophyllene binary system and Figure 7 for the α-pinene + Linalool binary system. From Figure 6, it can be seen that the curves for both pressures are in the higher temperature range, which is between430 K to 510 K. Whereas in Figure 7, the curve is at a lower temperature range, which is between 380 K to 460 K. It indicates that this system has a lower volatility compared to the system in Figure 6. From both figures, it can also be seen that the size of the T-x-y curve for the Linalool + Beta-caryophyllene system does not show a significant difference with the curve for the Alpha-pinene + Linalool system. The volatility between the components in the two systems slightly differ. The stability of the intermolecular interactions in these systems explains why pressure changes do not have a significant effect on the liquid and vapor phase distributions. This is supported by the fact that the boiling point differences between Linalool and Beta-caryophyllene and Linalool and Alpha-pinene are not significant enough to produce large changes in the volatility of the mixture.

The experimental results were also compared with the vapor-liquid equilibrium predictions using the UNIFAC method equation for both binary systems. This comparison can be seen in Figures 6 and 7. The UNIFAC model is not accurate enough in describing the VLE results. This discrepancy is likely due to two mixtures Linalool + Beta Caryophyllene and Alpha Pinene + Linalool have quite complex constituent groups, which are more intricate in structure. Such complexity in the molecular structure can lead to a lack of accuracy in theUNIFAC predictions, as the model may not fully capture all the interactions between these groups.

IV. CONCLUSION

Vapor - Liquid equilibrium data of binary systems of Linalool + Beta caryophyllene and Alpha Pinene + Linaloolat pressures of 30 and 60 kPa have been obtained experimentally. The experimental data of the Linalool + Beta Caryophyllene and Alpha Pinene + Linalool binary systems have been thermodynamically consistent with the L-Wisniak consistency test method and have been correlated with the Wilson, NRTL, and UNIQUAC methods. Data from the experimental results of the two Linalool + Beta Caryophyllene binary systems of 30 and 60 kPa have the greatest AAD T value of 0.74% and the largest AAD Y of 4.92% of all correlations carried out by Wilson, NRTL, and UNIQUAC, also for the Alpha-pinene + Linalool system 30 and 60 kPa have the largest AAD T of 0.28% and the largest AAD Y of 3.07%. Whereas the prediction results using UNIFAC, produced results that were not accurate to the experimental results for both systems.

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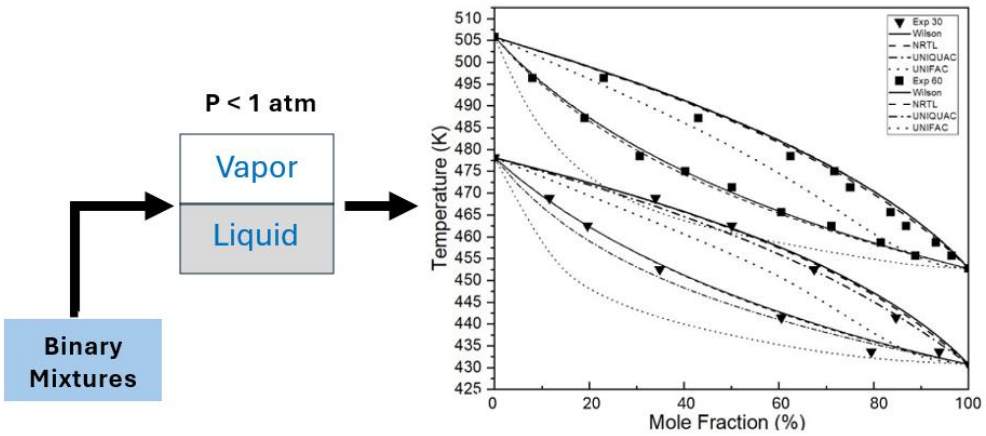
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Liquid
Binary Mixtures
Temperature (K)
Mole Fraction (%)
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Wilson
NRTL
UNIQUAC
UNIFAC
Exp 60
Wilson
NRTL
UNIQUAC
UNIFAC