

# Isobaric Vapor-Liquid Equilibrium of Methyl Salicylate + Ethyl Salicylate and Methyl Salicylate + $\alpha$ -Pinene Binary Systems at 20.0 and 50.0 kPa

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**Abstract.** Gandapura oil, also called wintergreen oil in international trade, is evaluated based on the purity of its methyl salicylate content. Gandapura oil has several impurities including mainly ethyl salicylate and  $\alpha$ -pinene, which can lower its quality and price. Indonesian local farmer's gandapura oil has a low methyl salicylate content of only 82.23%, and appears in a dark red colour instead of clear. The low grade product may have been caused by thermal degradation of compounds within gandapura oil by constant heating during atmospheric distillation at temperature above its thermal threshold. The determination of their vapor-liquid equilibrium data can provide basic data for the separation and purification of methyl salicylate towards its two main impurities in gandapura oil. The vacuum pressure condition was selected to lower the distillation temperature, aiming to reduce the chance of thermal decomposition. The vapor-liquid equilibrium under isobaric conditions in the binary systems of methyl salicylate + ethyl salicylate and methyl salicylate +  $\alpha$ -Pinene at 20.0 and 50.0 kPa were measured experimentally using modified Glass Othmer-Still. Gas Chromatography (GC) was utilized to analyze the composition of both the liquid and vapor phases in the samples. The thermodynamic consistency of experimental data was confirmed through the *L-W* Wisniak method. The experimental results were successfully correlated with Wilson, NRTL, and UNIQUAC models. The average absolute deviations of temperature (AAD T) and vapor phase composition (AAD  $y$ ) between experimental data and models are less than 0.8058 and 0.0196, respectively for all systems. In terms of quality, all samples collected post-experiment maintained a clear color, suggesting that vacuum pressure distillation effectively prevents the thermal decomposition of compounds in gandapura oil.

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## 1 Introduction

Indonesia's rich biodiversity makes it a prime candidate for plant-based product development, such as essential oils. Essential oils are liquid products resulting from water vapor distillation from certain parts of plants which contain alkaloid compounds with a distinctive aroma as special chemical substances that form flavors or aromas [1]. Essential oils are in great demand by consumers around the world due to the shift in interest from products based on synthetic compounds to natural products derived from plants, including products of chemical base compounds contained in essential oils [2]. Indonesia produces 40 of the 80 globally traded essential oil varieties, experiencing an annual demand increase of 8-10% [3]. Among these, gandapura essential oil, also known as wintergreen oil, stands out. Despite its lively and growth in Indonesia's mountainous regions, gandapura oil remains underdeveloped economically [4].

Gandapura essential oil contains several compounds, including three main components namely methyl salicylate, ethyl salicylate,  $\alpha$ -pinene, along with other compounds in small percentages [5]. The main and most important component of gandapura essential oil is methyl salicylate. Methyl salicylate finds diverse applications across industries, including pharmaceuticals, perfumery, cosmetics, and food processing, as well as being a key component in derivative compound synthesis. [6].

In 2003, Ma'mun's research found that gandapura oil distilled locally by the Gandapura Farmers Group in Dieng, Wonosobo had 82.23% purity of methyl salicylate. This falls short of Indonesia's standard (SNI) of 95% purity, affecting international market competitiveness. Synthetic methyl salicylate, synthesized from methanol and salicylic acid using concentrated  $H_2SO_4$  catalyst, achieves 99% purity [7]. Due to this, Indonesia imported an average of 2,372.5 tons of methyl salicylate annually from 2014-2019 [8]. Comparisons between the local refining of farmer groups in Wonosobo, imported synthetic oil, and the Indonesian National Standard (SNI) are tabulated in Table 1.

**Table 1.** Comparison of wintergreen oils [9]

Characteristic	Local's Gandapura Oil	Imported Synthetic Oil	SNI
Color	Dark red	Clear	Clear
Specific Gravity	1.1517	1.1797	1.176 - 1.185
Methyl Salicylate Content	82.23 %	Up to 99%	Min. 95%

In addition, oil from local's farmer also shown a dark red color, which also does not comply with the clear or light yellow-reddish color as the standardized suggest [10]. This indicates that there is a possibility that the local distillation results are not suitable in terms of temperature and pressure, causing the compounds contained in the leaves of the gandapura plant to decompose. The decomposition temperature of methyl salicylate is not known based on the literatures and the MSDS listed on the product, but it is a general knowledge that methyl salicylate is a thermally sensitive compound [11]. Thus, it can be assumed that the local distillation results are carried out at temperatures that are too high which can decompose the compounds in the gandapura plant extract and reduce the purity of methyl salicylate. This is also the basis for the option of purification solutions through vacuum distillation to lower the dew point and bubble point of separation and avoid the risk of thermal decomposition. Vapor-liquid equilibrium (VLE) information is essential for the purification of a system through vacuum distillation. This data serves as a reference for designing and operating the distillation equipment. There was a study by Cheng et al. in 1999 [12] that examined the vapor-liquid equilibrium for binary systems, one of which was the methyl salicylate +  $CO_2$  system under isothermal conditions in the high pressure range 1.4 MPa – 13 MPa, and produced experimental data that met the thermodynamic consistency test. Besides that, Hu and Cheng in 2017 [13] measured the vapor-liquid equilibrium binary methanol + methyl

salicylate and dimethyl carbonate + methyl salicylate under isobaric conditions in the temperature range of 85°C – 227°C, and produced experimental data that met the thermodynamic consistency test. Then Zheng et al., in 2020 [14] examined the vapor-liquid equilibrium under isothermal conditions for the citral +  $\alpha$ -pinene and linalool +  $\alpha$ -pinene systems using Headspace Gas Chromatography (HS-GC), and a P-x-y equilibrium curve was produced that corresponds to the correlation and satisfies thermodynamic consistency test. Furthermore, Wei et al. in 2023 [15] conducted experiments using HS-GC in measuring the vapor-liquid equilibrium of the Linalool +  $\alpha$ -Pinene and  $\alpha$ -Pinene +  $\beta$ -Pinene binary systems at temperatures of 312.2 K, 323.2 K, and 333.2 K, and produced appropriate equilibrium data and meets correlation as well as thermodynamic consistency tests.

Considering previous research, there was a notable scarcity of experimental vapor-liquid equilibrium (VLE) data for methyl salicylate, ethyl salicylate, and  $\alpha$ -pinene systems under vacuum conditions. Therefore, it was imperative to conduct a study to gather VLE data for a binary system under vacuum pressure, which could serve as a foundational reference for designing distillation columns. This research specifically focused on measuring VLE data for two binary systems: methyl salicylate + ethyl salicylate and methyl salicylate +  $\alpha$ -pinene, at pressures of 20.0 and 50.0 kPa. The acquired experimental data were then subjected to correlation using the Wilson [16], nonrandom two-liquid (NRTL) [17], and universal quasichemical (UNIQUAC) [18] models.

## 2 Experimental Section

### 2.1 Materials

The experiment utilized materials provided by different suppliers. These included methyl salicylate from Lansida (Indonesia), ethyl salicylate from Zhishang Shandong in (China), and  $\alpha$ -pinene from Jianxi Senhai (China). None of the materials underwent additional processing before use. The basic properties are shown in **Table 2**.

**Table 2.** Properties of pure components

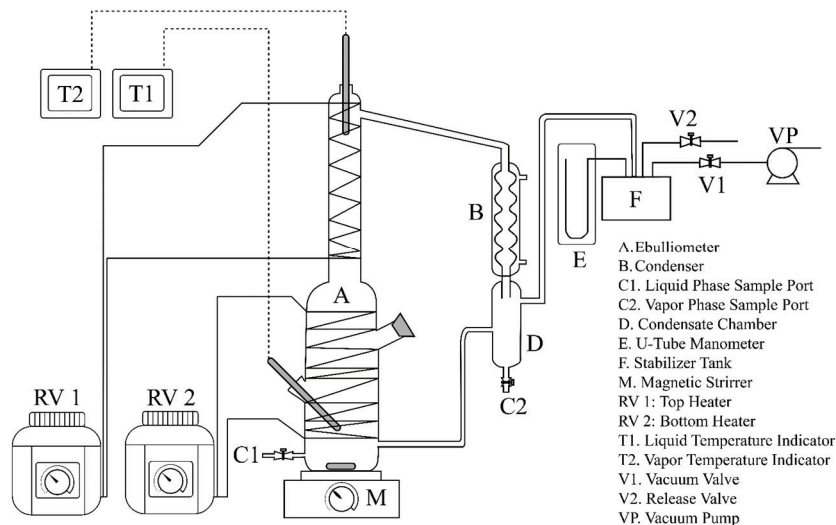
Component*	Source	CASRN	Purity (%)	MW (g/mol)	T <sub>boiling</sub> (K)	Density (g/cm <sup>3</sup> )
Methyl Salicylate [19]	Lansida	119-36-8	99	152.14	495	1.174
Ethyl Salicylate [20]	Zhishang Shandong	118-61-6	99	166.17	505	1.13
$\alpha$ -Pinene [21]	Jianxi Senhai	80-56-8	95	136.24	430	0.858

\*Obtained from Certificate of Analysis (CoA) of each company

### 2.2 Apparatus and Procedures

Binary system vapor-liquid equilibrium experimental data was acquired using a customized glass Othmer still, as depicted in **Fig. 1**. The setup consisted of an ebulliometer chamber with a 200 mL capacity, outfitted with a heating regulation mechanism, a magnetic stirring device, a condenser, two temperature gauges (Autonics TC4S and Autonics TC4Y), a vacuum pump capable of achieving a maximum vacuum pressure of 5 Pa absolute, and a U-shaped mercury manometer used to precisely gauge equilibrium pressure to within 0.5 mmHg. Temperature readings were taken using an RTD Pt100 temperature sensor, with an accuracy of  $\pm 0.1$  K. There were two temperature sensors, namely T1 and T2. T1 was used to measure equilibrium temperature and located at the bottom of still, while T2 was measuring the vapor temperature

at the top of still. The still was designed with two distinct sections for sampling, which includes the liquid and vapor phase samples.



**Fig. 1.** Schematic diagram of the apparatus.

## 2.3 Analytical Method

Analysis of the solution composition for the binary system of methyl salicylate (1) + ethyl salicylate (2) and  $\alpha$ -Pinene (1) + methyl salicylate (2) was done using Gas Chromatography (GC). The specifications for the GC device used are the Thermofischer brand (TRACE 1310) with an FID detector using a fused silica column. Hydrogen gas is used as a carrier gas with a flow rate (make up) of 50 mL/minute, combustion flow (H<sub>2</sub>) of 35.0 mL/min, and combustion (air flow) of 350.0 mL/min. The analysis was carried out by setting the isothermal oven temperature (column temperature) with an initial temperature of 125 °C (for 2 minutes) to a temperature of 230 °C with a total time (oven program time) for 9 minutes. Split ratio of 50:1, with detector and vaporization chamber temperatures of 250 °C. By making a calibration curve, the results for the composition of each sample can be obtained.

## 3 Results and Discussion

### 3.1 Reliability Test of The Apparatus

The first phase of this experiment involved evaluating the reliability of the apparatus. The apparatus used in this study has successfully conducted several research papers in the topic of essential oil VLE, including most recently the isobaric vapor–liquid equilibrium of citronellal + geraniol and citronellal + citronellol binary systems experiments at 16.0 and 32.0 kPa by Aulia et al. in 2023 [23], and vapor-liquid equilibrium measurement of limonene +  $\beta$ -citronellol and citronellal +  $\beta$ -citronellol binary systems in kaffir lime essential oil at vacuum pressures by Devianda and Kuswandi in 2023 [24].

To ensure the reliability of the apparatus for the VLE (Vapor-Liquid Equilibrium) experiment, a vapor pressure test was conducted using pure ethanol. The observed results

were compared with the values obtained from the Wagner equation (1) sourced from Poling et al. [22],

$$\ln(P_{Wagner}) = \ln(P_C) + \left(\frac{T_C}{T}\right) (A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^5) \quad (1)$$

with  $\tau = (1 - T/T_C)$ . The Wagner parameters for pure ethanol is outlined in Table 3.

**Table 3.** Parameters of Wagner equation of pure ethanol

Equation	A	B	C	D	T <sub>c</sub> (K)	P <sub>c</sub> (bar)
Wagner	-8.686	1.178	-4.876	1.588	513.92	61.32

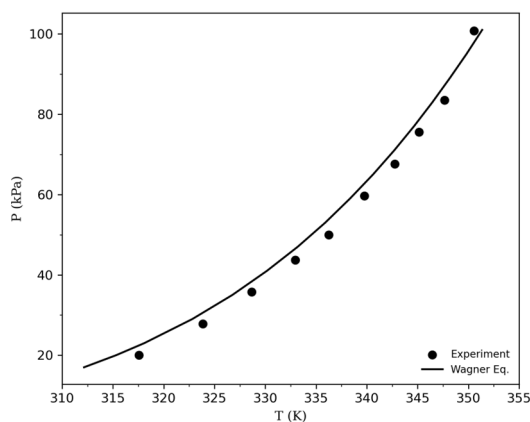
The experimental data's compatibility with established vapor pressure data of pure ethanol was confirmed by calculating the absolute deviation (AD) through equation (2) between the experimental temperature and Wagner's equation [23]. This calculation was averaged across the tested pressure points to obtain the absolute average deviation (AAD) through equation (3)[24]. The comparison of experimental and calculated data is presented in Table 4 and Fig 2, alongside with their deviations.

$$AD T = |T_{i_{exp}} - T_{i_{calc}}| \quad (2)$$

$$AAD T = \frac{1}{n} \sum_{i=1}^n |T_{i_{exp}} - T_{i_{calc}}| \quad (3)$$

**Table 4.** Measured and calculated vapor pressure data of pure ethanol

P <sub>exp</sub> (bar)	T <sub>exp</sub> (K)	T <sub>wagner</sub> (K)	AD T (K)
1.01	350.55	351.44	0.89
0.84	347.65	346.77	0.88
0.76	345.15	344.36	0.79
0.68	342.75	341.72	1.03
0.60	339.75	338.79	0.96
0.52	336.25	335.54	0.71
0.44	332.95	331.84	1.11
0.36	328.65	327.52	1.13
0.28	323.85	322.30	1.55
0.2	317.55	315.31	2.24
<b>Overall AAD T (K)</b>			<b>1.13</b>



**Fig. 2.** Ethanol vapor pressure data.

The findings demonstrate a strong concurrence between the data, yielding a temperature average absolute deviation (AAD T) of 1.13 K. The consistent results obtained from this reliability test led to the conclusion that the apparatus is suitable for use in VLE research.

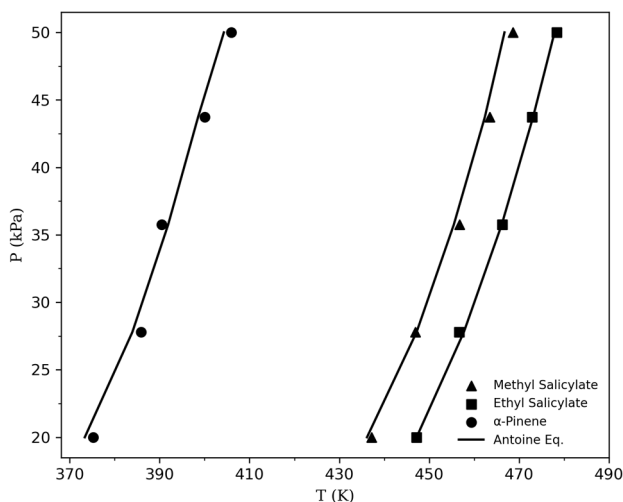
### 3.2 The Vapor Pressures of Pure Components

In this study, vapor pressure measurements were conducted for pure methyl salicylate, ethyl salicylate, and  $\alpha$ -pinene. The Antoine constants (A, B, and C) employed for these three individual compounds are outlined in Table 5. A comparison between the experimentally determined vapor pressure of each pure compound (methyl salicylate, ethyl salicylate, and  $\alpha$ -pinene) and the calculated values using the Antoine equation is illustrated in Fig. 3, while the specific pressure and temperature data are provided in Table 6.

**Table 5.** Parameters of Antoine equation of pure methyl salicylate, ethyl salicylate, and  $\alpha$ -pinene

Component	A	B	C
Methyl Salicylate <sup>a</sup> [25]	21.751	4323.800	-71.190
Ethyl Salicylate <sup>b</sup> [26]	6.983	2315.827	-39.595
$\alpha$ -Pinene <sup>c</sup> [26]	7.061	1621.220	231.645

<sup>a</sup>ln (Psat) = A - B / ( T + C ) [Psat (Pa); T (K)]  
<sup>b</sup>log (Psat) = A - B / ( T + C ) [Psat (kPa); T (K)]  
<sup>c</sup>log (Psat) = A - B / ( T + C ) [Psat (mmHg); T (C)]



**Fig. 3.** Methyl salicylate, ethyl salicylate,  $\alpha$ -pinene vapor pressure data.

**Table 6.** Measurement vapor pressure data of pure methyl salicylate, ethyl salicylate, and  $\alpha$ -pinene

Methyl Salicylate		Ethyl Salicylate		$\alpha$ -Pinene	
P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)
50.0	466.65	50.0	478.35	50.0	405.95
43.7	463.45	43.7	472.85	43.7	400.05
35.8	456.75	35.8	466.25	35.8	390.45
27.7	446.95	27.7	456.65	27.7	385.85
20.0	437.15	20.0	447.15	20.0	375.25

The graph in Fig. 3 shows a consistent relationship with minimal deviation regarding vapor pressure between the components utilized in this study and the Antoine equation found in the literature. Therefore, all three components are deemed suitable for the upcoming binary

system vapor-liquid equilibrium experiment. This test further reveals that the highest temperature for the VLE binary system test is in the 50.0 kPa system involving ethyl salicylate, which is around  $\pm 478.35$  K. This marks a significant decrease from the standard boiling point of ethyl salicylate at 505 K under atmospheric pressure.

### 3.3 Binary System Measurement Results

This research involved vapor-liquid equilibrium measurements for two binary systems: methyl salicylate + ethyl salicylate and methyl salicylate +  $\alpha$ -pinene. The study was conducted under two vacuum pressure conditions, 20.0 and 50.0 kPa, using a simple ebulliometer. Data acquired included temperature (T) at constant pressure, liquid mole fraction (x), and vapor mole fraction (y) which were determined through GC analysis of equilibrium samples. Tables 7 and 8 display provisional results, presenting equilibrium temperature (T), liquid mole fraction (x), and vapor fraction (y) variations ranging from 0.0 to 1.0 for the binary systems methyl salicylate + ethyl salicylate and methyl salicylate +  $\alpha$ -pinene at 20.0 kPa and 50.0 kPa.

**Table 7.** VLE experimental data methyl salicylate (1) + ethyl salicylate (2) at 20.0 and 50.0 kPa

P = 20.0 kPa			P = 50.0 kPa		
T <sub>exp</sub> (K)	Mole Fraction		T <sub>exp</sub> (K)	Mole Fraction	
	x <sub>1 exp</sub>	y <sub>1 exp</sub>		x <sub>1 exp</sub>	y <sub>1 exp</sub>
447.15	0.0000	0.0000	477.85	0.0000	0.0000
445.45	0.1343	0.1910	476.15	0.1238	0.1730
443.65	0.2714	0.3580	474.25	0.2587	0.3210
442.45	0.3692	0.4510	473.05	0.3578	0.4330
441.15	0.4816	0.5726	471.35	0.5094	0.5827
439.75	0.6088	0.6887	470.15	0.6182	0.6788
438.75	0.7134	0.7572	469.05	0.7372	0.7778
437.85	0.8035	0.8378	468.35	0.8134	0.8465
437.35	0.8627	0.8836	468.05	0.8456	0.8774
437.05	0.8991	0.9183	467.55	0.8975	0.9149
436.65	0.9340	0.9475	467.25	0.9277	0.9427
436.55	0.9507	0.9612	467.15	0.9435	0.9560
436.45	0.9550	0.9637	466.95	0.9618	0.9720
436.05	1.0000	1.0000	466.65	1.0000	1.0000

**Table 8.** VLE experimental data  $\alpha$ -pinene (1) + methyl salicylate (2) at 20.0 and 50.0 kPa

P = 20.0 kPa			P = 50.0 kPa		
T <sub>exp</sub> (K)	Mole Fraction		T <sub>exp</sub> (K)	Mole Fraction	
	x <sub>1 exp</sub>	y <sub>1 exp</sub>		x <sub>1 exp</sub>	y <sub>1 exp</sub>
436.15	0.0000	0.0000	466.75	0.0000	0.0000
427.15	0.0642	0.3241	455.65	0.0919	0.3533
416.45	0.1751	0.6038	444.65	0.1992	0.5714
407.15	0.2986	0.7626	435.45	0.3085	0.7395
399.85	0.3994	0.8535	429.35	0.3890	0.8085
393.95	0.4903	0.9084	423.55	0.4883	0.8619
394.55	0.4737	0.9053	424.55	0.4784	0.8596
388.25	0.6155	0.9474	416.95	0.6200	0.9196
384.15	0.7178	0.9601	412.15	0.7286	0.9502
379.55	0.8388	0.9745	408.05	0.8372	0.9749
373.35	1.0000	1.0000	402.75	1.0000	1.0000

The samples collected from both liquid and vapor phases across all tested pressures displayed no discoloration even after continuous heating. This suggests that vacuum pressure distillation effectively prevents the thermal decomposition of compounds in gandapura oil. The data obtained from the experiments will undergo verification via thermodynamic consistency tests and local composition models.

### 3.3.1 Thermodynamic Consistency Tests

The experimental data's consistency towards thermodynamic principles was verified using Wisniak's L-W point-to-point test technique [27]. This approach involves conducting a trend line analysis on the Redlich-Kister expansion, arranged to optimally align with or represents the  $G^E/RT$  distribution data as depicted in equation (3). Wisniak's formulation, as expressed in equation (4), describes deviations from the Gibbs-Duhem equation, where a D value of less than 5 indicates thermodynamic consistency, and the L and W values were obtained from equation (5).

$$G^E = RT \sum x_i \ln \frac{y_i}{x_i} + \sum x_i \Delta S_i^{sat} (T_i^{sat} - T) \quad (4)$$

$$D = 100 \left| \frac{L - W}{L + W} \right| \quad (5)$$

$$L_i = \left[ \sum x_i \frac{\Delta S_i^{sat}}{\Delta S} T_i^{sat} - T \right] = \left[ \frac{g^E}{\Delta S} - \frac{RT}{\Delta S} \omega \right] = w_i \quad (6)$$

With  $\Delta S = \sum x_i \Delta S_i^{sat}$  and  $\omega = \sum x_i \ln \frac{y_i}{x_i}$ . In this approach, the vaporization entropy was employed to examine the L and W parameters. Once these parameters were acquired, the deviation could be calculated, affirming the thermodynamic consistency of the data. The thermodynamic consistency test results are show in Table 9.

**Table 9.** Thermodynamic consistency test results using the L-W test

System	Pressure (kPa)	L/W	D	Consistency
Methyl Salicylate + Ethyl Salicylate	20.0	1.037	1.846	Consistent
	50.0	0.999	0.065	Consistent
Methyl Salicylate + $\alpha$ -Pinene	20.0	0.998	0.118	Consistent
	50.0	1.010	0.504	Consistent

Based on the experimental results, it can be concluded that all systems across all tested pressures are thermodynamically consistent. This is apparent through the fulfilment of the conditions  $0.92 < Li/Wi < 1.08$  and D value of less than 5 [27]. Hence, the data can be utilized for subsequent determination of the correlation parameters for Wilson, NRTL, and UNIQUAC models.

### 3.3.2 Local Composition Models

The molecular thermodynamics of liquid-solution behavior models that will be use are based on the concept of local composition. In a liquid solution, it is assumed that local compositions, contribute to the short-range arrangement and specific molecular alignments arising from variations in molecular size and intermolecular forces [28]. The activity coefficient of each component was regressed with Wilson, NRTL, and UNIQUAC equations. The binary interaction parameters for each equation were established by minimizing the objective function (OF) stated in equation (6) [29].



$$OF = \sum_{i=1}^N \left( \frac{\gamma_1^{exp} - \gamma_1^{calc}}{\gamma_1^{exp}} \right)^2 + \left( \frac{\gamma_2^{exp} - \gamma_2^{calc}}{\gamma_2^{exp}} \right)^2 \quad (7)$$

The pure-species parameters for UNIQUAC [22] were derived by identifying the theoretical group within each compound, as outlined in Table 10.

**Table 10.** UNIQUAC group parameters<sup>a</sup>

Compound	Group Identification			V <sub>k</sub>	R <sub>k</sub>	Q <sub>k</sub>
	Group	Main	Secondary			
Methyl Salicylate	ACH	3	9	4	0.5313	0.400
	AC	3	10	1	0.3652	0.120
	ACOH	8	17	1	0.8952	0.680
	CH <sub>3</sub> COO	11	21	1	1.9031	1.728
	CH <sub>3</sub>	1	1	1	0.9011	0.848
Ethyl Salicylate	ACH	3	9	4	0.5313	0.400
	AC	3	10	1	0.3652	0.120
	ACOH	8	17	1	0.8952	0.680
	CH <sub>3</sub> COO	11	21	1	1.9031	1.728
α-Pinene	CH <sub>3</sub>	1	1	3	0.9011	0.848
	CH <sub>2</sub>	1	2	2	0.6744	0.540
	ACH	3	9	3	0.5313	0.400
	AC	3	10	2	0.3652	0.120

<sup>a</sup>Notes: V<sub>k</sub> = number of species belonging to the same group, R<sub>k</sub> = group volume parameter, and Q<sub>k</sub> = group area parameter.

The chosen  $\alpha$  value for the NRTL model is 0.47, which demonstrates the best fit concerning the AAD both temperature (T) and mole fraction (y) when compared against the other suggested discrete values of 0.2, 0.3, and 0.4 [17].

The fitted pairs of binary parameters in this study include AAD between experimental and calculated values, both in terms of temperatures (AAD T) through equation (2) and vapor phase compositions (AAD y) through equation (7) [23] for each model.

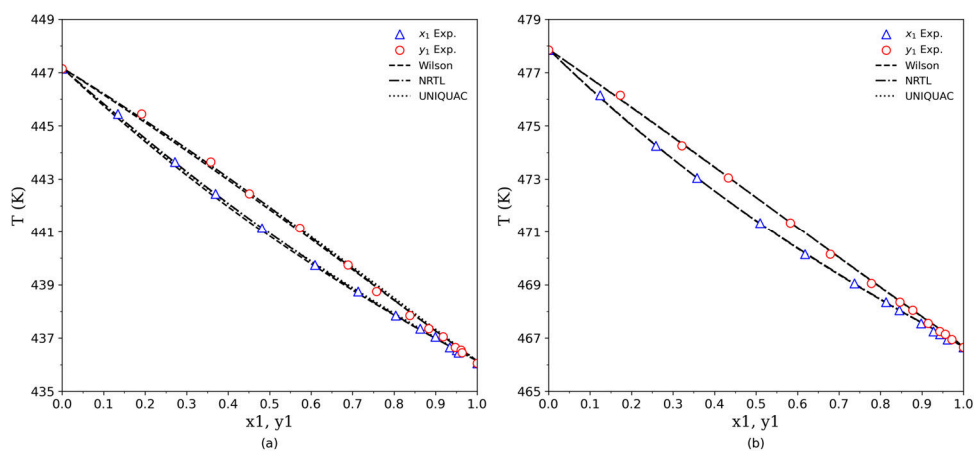
$$AAD\ y\ (\%) = \frac{1}{N_y} \sum_{i=1}^{N_y} |y_i^{exp} - y_i^{calc}| \quad (8)$$

The binary parameters are presented in Table 11.

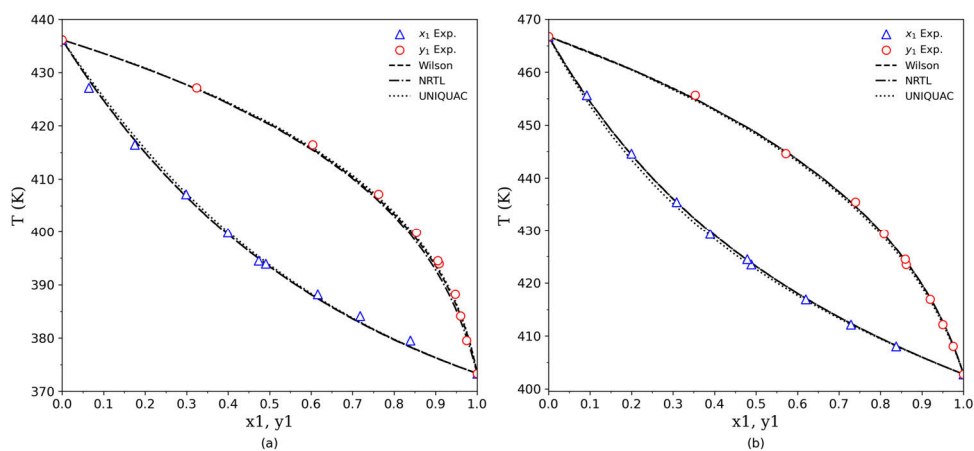
Based on the correlation results for all systems using the Wilson, NRTL, and UNIQUAC models, the value of AAD T < 0.8058 and AAD y < 0.0196 were obtained. These results suggest a well correlation between the experimental results' T and y<sub>i</sub> values and those obtained from the Wilson, NRTL, and UNIQUAC models. The comparison between the experimental T-x-y plots of the binary systems methyl salicylate + ethyl salicylate and methyl salicylate + α-pinene, obtained at 20.0 and 50.0 kPa, and the corresponding correlated model are presented in Fig. 4 and 5.

**Table 11.** Binary interaction parameters of Wilson, NRTL, and UNIQUAC models

Binary System	Model	Parameter (cal/mol)	AAD T	AAD y	
Methyl Salicylate (1) + Ethyl Salicylate (2) at P = 20.0 kPa	Wilson	$\Lambda_{12}$	41.7835	0.0763	0.0035
		$\Lambda_{21}$	31.9747		
	NRTL	$b_{12}$	53.1928	0.0298	0.0073
		$\alpha = 0.47$	$b_{12}$		
	UNIQUAC	$u_{12}$	3.5745	0.0440	0.0076
		$u_{21}$	3.5732		
Methyl Salicylate (1) + Ethyl Salicylate (2) at P = 50.0 kPa	Wilson	$\Lambda_{12}$	116.4913	0.0408	0.0043
		$\Lambda_{21}$	-44.2898		
	NRTL	$b_{12}$	55.2749	0.0399	0.0039
		$\alpha = 0.47$	$b_{12}$		
	UNIQUAC	$u_{12}$	6.3485	0.0407	0.0043
		$u_{21}$	6.3486		
$\alpha$ -Pinene (1) + Methyl Salicylate (2) at P = 20.0 kPa	Wilson	$\Lambda_{12}$	-78.7695	0.7359	0.0167
		$\Lambda_{21}$	-77.3125		
	NRTL	$b_{12}$	-12.9457	0.7552	0.0196
		$\alpha = 0.47$	$b_{12}$		
	UNIQUAC	$u_{12}$	-78.7803	0.8058	0.0105
		$u_{21}$	39.2511		
$\alpha$ -Pinene (1) + Methyl Salicylate (2) at P = 50.0 kPa	Wilson	$\Lambda_{12}$	4.9274	0.2016	0.0090
		$\Lambda_{21}$	5.2169		
	NRTL	$b_{12}$	6.5452	0.2184	0.0050
		$\alpha = 0.47$	$b_{12}$		
	UNIQUAC	$u_{12}$	8.3104	0.5338	0.0043
		$u_{21}$	8.2999		



**Fig. 4.** T-x-y graph of the binary system methyl salicylate (1) + ethyl salicylate (2) at 20.0 kPa (a) and 50.0 kPa (b)



**Fig. 5.** T-x-y graph of the binary system  $\alpha$ -pinene (1) + methyl salicylate (2) at 20.0 kPa (a) and 50.0 kPa (b)

The obtained results reveal that the T-x-y curve region for the  $\alpha$ -pinene + methyl salicylate binary system is notably broader when compared to the methyl salicylate + ethyl salicylate system. This signifies that the separation process of the  $\alpha$ -pinene + methyl salicylate system can be readily accomplished through distillation. Conversely, the separation of the methyl salicylate + ethyl salicylate binary system via distillation proves to be considerably challenging, even under low pressure or vacuum conditions. This complexity arises due to both methyl salicylate and ethyl salicylate belonging to the same salicylic compound family, derivatives of salicylic acid. These compounds exhibit closely aligned molecular weights and very similar boiling points. Given their closely matched chemical properties encompassing boiling point, melting point, and vapor pressure, these compounds together are characterized as a very ideal solution. Consequently, the blend of these compounds poses difficulty in separation using distillation. Therefore, future discussions and research on alternative separation techniques between methyl salicylate and ethyl salicylate within Gandapura oil are crucial to ensure the production of oil meeting quality standards.

## 4 Conclusions

In this study, experimental data for the isobaric liquid-vapor equilibrium of two binary systems, namely methyl salicylate + ethyl salicylate and methyl salicylate +  $\alpha$ -pinene, have been successfully obtained at pressures of 20.0 kPa and 50.0 kPa. The obtained experimental data for both binary systems underwent thermodynamic evaluation and physical examination. The thermodynamic evaluation exhibits consistency, confirmed through the L-W Wisniak consistency test method. These experimental results were also effectively correlated using the Wilson, NRTL, and UNIQUAC correlation models, resulting in the value of AAD T < 0.8058 and AAD y < 0.0196. As for the quality, all the samples collected from both liquid and vapor phases across every tested pressure displayed no discoloration, suggesting vacuum pressure distillation has effectively prevents the thermal decomposition of compounds in gandapura oil.

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## References

1. J. C. Adiwijaya and U. E. Malika, *J.Ilm.Inov.* **16**, (2017)
2. W. Wang, N. Li, M. Luo, Y. Zu, and T. Efferth, *Molecules* **17**, 2704 (2012)
3. P. S. Andila, I. P. A. H. Wibawa, T. Warseno, A. S. Li'aini, I. G. Tirta and T. M. Bangun, *Seri Koleksi Kebun Raya Eka Karya Bali Tanaman Berpotensi Penghasil Minyak Atsiri* (LIPI, Jakarta, 2020)
4. P. Kusumo, *JTI* **15**, 124 (2016)
5. W.-R. Liu, W.-L. Qiao, Z.-Z. Liu, X.-H. Wang, R. Jiang, S.-Y. Li, R.-B. Shi, and G.-M. She, *Molecules* **18**, 12071 (2013)
6. F. Le Grand, G. George, and S. Akoka, *J. Agric. Food Chem.* **53**, 5125 (2005)
7. S. Arctander, *Perfume and Flavor Chemicals: (aroma Chemicals)*. (University of Michigan, NJ, 1969)
8. Central Statistics Agency (BPS), (2023)
9. Ma'mun, *Bul. Pen. Tanaman Rempah dan Obat.* (2005)
10. U.S. Coast Guard, Commandant Instruction 16465.12C, (U.S. Government Printing Office, Washington, D.C., 1999)
11. I. Sunshine, *CRC Handbook of Analytical Toxicology* (The Chemical Rubber Co., Cleveland, 1969)
12. K.-W. Cheng, S.-J. Kuo, M. Tang, and Y.-P. Chen, *The Journal of Supercritical Fluids* **18**, 87 (2000)
13. C.-C. Hu and S.-H. Cheng, *Chemical Engineering Research and Design* **127**, 189 (2017)
14. P. Zheng, L. Wang, X. Chen, X. Wei, J. Liang, and J. Wu, *J. Chem. Eng. Data* **65**, 3593 (2020)
15. X. Wei, X. Chen, L. Wang, X. Wei, Y. Yang, J. Liang, and J. Liang, *Ind. Eng. Chem. Res.* **62**, 4122 (2023)
16. G. M. Wilson, *J. Am. Chem. Soc.* **86**, 127 (1964)
17. H. Renon and J. M. Prausnitz, *AIChE J.* **14**, 135 (1968)
18. D. S. Abrams and J. M. Prausnitz, *AIChE J.* **21**, 116 (1975)
19. Lansida, *Methyl Salicylate Certificate of Analysis (CoA)* (2023)
20. Zhishang Shandong, *Ethyl Salicylate Certificate of Analysis (CoA)* (2023)
21. Jianxi Senhai,  *$\alpha$ -Pinene Certificate of Analysis (CoA)* (2023)
22. B. E. Poling, J. M. Prausnitz, and J. O'Connell, *The properties of gases and liquids*, 5th ed. (McGraw-Hill Professional, New York, 2000)
23. A. F. Aulia, R. P. Anugraha, and K. Kuswandi, *J. Chem. Eng. Data* **68**, 1646 (2023)
24. P. A. Devianda and K. Kuswandi, *Vapor-liquid equilibrium measurement of limonene-citronellol and citronellal-citronellol binary systems in Kaffir lime essential oil at vacuum pressures*, (2023)
25. D. E. Tevault, *Vapor Pressure of Methyl Salicylate and n-Hexadecane* (Army Edgewood Chemical Biological Center APG MD, 2014)

26. R. M. Stephenson & S. Malanowski, *Handbook of the Thermodynamics of Organic Compounds*, (Elsevier, New York, 1987)
27. J. Wisniak, *Ind. Eng. Chem. Res.* **32**, 1531 (1993)
28. J. M. Smith, H. C. Van Ness, M. Abbott, and M. Swihart, *Introduction to chemical engineering thermodynamics*, 8th ed. (McGraw-Hill Education, Columbus, 2017)
29. M. A. Batutah, K. Kuswandi, and G. Wibawa, *J. Chem. Eng. Data* **65**, 3802 (2020)