

# Liquid-liquid Equilibria for Quaternary System of Eugenol (1) + $\beta$ -Caryophyllene (2) + 1-Propanol (3) + Water (4) at Temperatures 303.15, 313.15, and 323.15 K

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**Abstract.** In this work, the experimental liquid-liquid equilibrium (LLE) data were measured for quaternary mixtures of eugenol(1) +  $\beta$ -caryophyllene(2) + 1-propanol(3) + water(4) at temperatures 303.15, 313.15, and 323.15 K and at atmospheric pressure. The equilibrium data were determined by using an equilibrium cell with temperature controlled. Quantitative analysis was performed by using gas chromatography (GC) equipped with thermal conductivity detector and capillary column Rtx-5. The experimental data were then correlated by using the NRTL and the UNIQUAC models. The reliability of these models were tested by compared with the experimental results using a root mean square deviation (RMSD). Based on the RMSD, the NRTL and the UNIQUAC models suited really well and give satisfactory result for the system of eugenol,  $\beta$ -caryophyllene, 1-propanol, and water with the average RMSD of the UNIQUAC and the NRTL models were 0.417% and 0.502%, respectively. Furthermore there was no significant effect of temperatures on the equilibrium composition for the system.

## 1 Introduction

Clove oil is one kind of essential oils that has many uses, in general, such as aromatherapy, botanical pesticides, additives in the food industry and the tobacco industry. Clove oil is a complex mixture of chemical compounds, the main component of clove oil is eugenol. The content of eugenol in clove oil is approximately 70% - 90% and the largest impurities is  $\beta$ -caryophyllene in the level of less than 10% [1]. Low purity of eugenol which is less than 70% can only be sold at US \$ 4.75 / kg, while high purity of eugenol which contain more than 98% can be sold at US \$ 7.80 / kg [2].

Extraction is a common process for separating eugenol from their impurities. In the extraction process, the choice of solvent should consider the nature and characteristics of solvent such as polarity, volatility, and toxicity [3]. Alcohol is commonly used as solvent because of the nature of polarity, relatively cheap, and low toxicity. Methanol is the simplest alcohol that can be used as a solvent, but methanol easily corrode to steel and toxic to the human body. Other alcohols such as ethanol is widely used, but ethanol has an azeotropic properties that make phenol and terpen compounds (such as  $\beta$ -caryophyllene) will not completely dissolve in ethanol. Because of that, it's important to find other types of alcohol as a solvent in the eugenol extraction process. One of the best solutions is 1-propanol. Eugenol

has high solubility in 1-propanol that is better than methanol and ethanol. Additionally 1-propanol is less toxic to humans and has a relatively high volatility [4].

Liquid-liquid equilibrium data are important in the modeling and design of extraction process for eugenol purification. In previous work, the Liquid-liquid equilibrium data of ternary eugenol-ethanol-water [5] and the quaternary eugenol- $\beta$ -caryophyllene-ethanol-water [6] at same temperatures 303.15, 313.15 and 323.15 K have been reported. The purpose of this work is to obtain Liquid-liquid equilibrium data for the quaternary system eugenol,  $\beta$ -caryophyllene, 1-propanol, water at temperatures 303.15, 313.15 and 323.15 K and correlating the results of the experiments with NRTL [7] and UNIQUAC [8] models to obtain the binary interaction parameters.

## 2 Experimental

### 2.1 Materials

Eugenol and  $\beta$ -caryophyllene were obtained from PT. Indesso Niagatama. with purity of 99.9 mole %, 1-Propanol was supplied by Merck Co. with 99.8 mole % purity. All of those chemicals were used without further purification. Aquabidestilata or double distilled water

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used throughout this experimental work was supplied by PT. Ikapharmindo Putramas.

## 2.2 Apparatus and procedure

The apparatus used in this work consists of an equilibrium cell with 40 cm<sup>3</sup> volume equipped with a

heating jacket to keep the temperature remain constant. A magnetic stirrer is used to make sure that the solution was completely mixed. The equilibrium cell is connected to a chiller (water bath). The chiller equipped with a controller and a thermocouple with a rate of accuracy about  $\pm 0.10^{\circ}\text{C}$ .

**Table 1.** Experimental data for quaternary system of eugenol +  $\beta$ -caryophyllene + 1-propanol + water at 303.15 K

Organic Phase				Aqueous Phase			
$x_1^a$	$x_2^a$	$x_3^a$	$x_4^a$	$x_1^b$	$x_2^b$	$x_3^b$	$x_4^b$
0.0871	0.0850	0.3950	0.4329	0.0005	0.0005	0.0676	0.9314
0.1120	0.0971	0.4089	0.3820	0.0005	0.0005	0.0569	0.9421
0.1733	0.1593	0.3709	0.2965	0.0005	0.0005	0.0609	0.9381
0.1768	0.1815	0.3466	0.2951	0.0005	0.0005	0.0452	0.9538
0.0902	0.0917	0.3951	0.4229	0.0005	0.0005	0.0710	0.9280
0.3587	0.2391	0.2275	0.1748	0.0005	0.0005	0.0476	0.9514
0.1151	0.0165	0.3669	0.5016	0.0005	0.0005	0.0700	0.9290
0.1230	0.0237	0.3792	0.4740	0.0005	0.0005	0.0526	0.9464
0.5808	0.4192	0	0	0	0	0	1

**Table 2.** Experimental data for quaternary system of eugenol +  $\beta$ -caryophyllene + 1-propanol + water at 313.15 K

Organic Phase				Aqueous Phase			
$x_1^a$	$x_2^a$	$x_3^a$	$x_4^a$	$x_1^b$	$x_2^b$	$x_3^b$	$x_4^b$
0.1212	0.0763	0.3945	0.4079	0.0005	0.0005	0.0674	0.9316
0.1508	0.1545	0.3725	0.3222	0.0005	0.0005	0.0688	0.9302
0.1906	0.1729	0.3556	0.2809	0.0005	0.0005	0.0658	0.9332
0.1933	0.1347	0.3636	0.3084	0.0005	0.0005	0.0561	0.9429
0.1204	0.0547	0.3717	0.4533	0.0005	0.0005	0.0600	0.9390
0.2915	0.2765	0.2642	0.1678	0.0005	0.0005	0.0601	0.9389
0.1438	0.0145	0.3526	0.4891	0.0005	0.0005	0.0631	0.9359
0.1493	0.0231	0.3633	0.4643	0.0005	0.0005	0.0640	0.9350
0.5963	0.4037	0	0	0	0	0	1

**Table 3.** Experimental data for quaternary system of eugenol +  $\beta$ -caryophyllene + 1-propanol + water at 333.15 K

Organic Phase				Aqueous Phase			
$x_1^a$	$x_2^a$	$x_3^a$	$x_4^a$	$x_1^b$	$x_2^b$	$x_3^b$	$x_4^b$
0.1060	0.0674	0.4031	0.4234	0.0005	0.0005	0.0587	0.9403
0.1564	0.1259	0.3936	0.3241	0.0005	0.0005	0.0578	0.9412
0.1948	0.1832	0.3519	0.2702	0.0005	0.0005	0.0592	0.9398
0.1897	0.1672	0.3632	0.2800	0.0005	0.0005	0.0514	0.9476
0.1127	0.0848	0.4027	0.3999	0.0005	0.0005	0.0631	0.9359
0.3284	0.2056	0.2730	0.1930	0.0005	0.0005	0.0285	0.9705
0.1130	0.0205	0.3720	0.4946	0.0005	0.0005	0.0687	0.9303
0.1303	0.0173	0.3754	0.4771	0.0005	0.0005	0.0632	0.9358
0.5961	0.4039	0	0	0	0	0	1

To obtain the equilibrium data, the quaternary mixtures of components with known composition, were

mixed into the equilibrium cell equipped with a magnetic stirrer and jacket to circulate heating water according to

desired temperature. The quaternary mixtures were stirred at a constant temperature (303.15, 313.15, and 323.15 K) at atmospheric pressure for 4 hours, and then the mixture solution was left for 20 hours until the equilibrium was achieved. Once equilibrium was reached, the samples of each phase were taken for analysis by using gas chromatography (GC).

The type of Gas Chromatography used was Shimadzu 2010 with TCD detector using RTX-5 column 30m, 0.32mm ID, 0.25µm. Whereby helium was used as carrier gas with a flow rate of 3 ml / min. GC Analysis was done using temperature program method by setting the oven initial temperature at 343.15 K in 5 minutes hold time, and then temperature was raised until 473.15 K with an increment of 40°C / min in 8 minutes hold time, while the temperature of the detector and injector were 603.15 K. The resulting mole fraction from GC analysis was then used to find binary parameters using NRTL and UNIQUAC models.

### 3 Results and discussion

The experimental liquid-liquid equilibrium data for quaternary system eugenol(1) + β-caryophyllene(2) + 1-propanol(3) + water(4) at temperatures 303.15, 313.15, and 323.15 K are shown in Tables 1-3 and Figs.1-6.

**Table 4.** Binary interaction parameters and the RMSD values for the NRTL model.

T(K)	Comp. (ij)	NRTL Parameters		RMSD (%)	
		α	a <sub>ij</sub> (J/mol)		a <sub>ji</sub> (J/mol)
303.15	1-2	0.2	3817.37	4530.55	0.484
	1-3		-3313.96	1069.65	
	1-4		7045.09	3548.73	
	2-3		-2368.44	2416.38	
	2-4		3928.50	2865.81	
	3-4		-1200.03	862.55	
	313.15		1-2	0.2	
1-3		4993.55	4892.45		
1-4		17687.32	32020.01		
2-3		349.78	4808.39		
2-4		10907.27	2643.04		
3-4		7173.45	1701.00		
323.15		1-2	0.2		4920.82
	1-3	-2332.28		1349.87	
	1-4	13904.6		4154.15	
	2-3	10042.0		24188.8	
	2-4	1737.70		1774.12	
	3-4	2143.57		-1821.3	

The experimental data obtained were correlated using NRTL and UNIQUAC models. Those models are used since they can be applied for binary or multi-component systems of liquid liquid equilibrium. The binary interaction parameter pairs can be determined by minimizing the following objective function (OF) :

$$OF = \sum_k^n \sum_j^n \sum_i^n (x_{ijk}^{exp} - x_{ijk}^{cal})^2 \quad (1)$$

Where  $x_{ij}^{exp}$  and  $x_{ij}^{cal}$  are the experiment and calculated mol fraction, respectively.  $k = 1$  to  $n$  is number of tie-line, subscription  $i = 1-4$  is the number of components, and subscription  $j = I-II$  denotes the phase (organic and aqueous)[9].

**Table 5.** Binary interaction parameters and the RMSD values for the UNIQUAC model.

T(K)	Comp. (ij)	UNIQUAC Parameters		RMSD %
		u <sub>nit</sub> (J/mol)	u <sub>nit</sub> (J/mol)	
303.15	1-2	364.08	283.15	0.345
	1-3	203.33	123.86	
	1-4	737.41	397.08	
	2-3	147.36	227.94	
	2-4	541.88	296.23	
	3-4	76.64	244.30	
	313.15	1-2	537.56	
1-3		260.93	178.02	
1-4		8490.29	411.17	
2-3		170.68	203.07	
2-4		480.21	334.02	
3-4		-71.17	256.97	
323.15		1-2	507.95	240.26
	1-3	76.67	-20.89	
	1-4	850.43	357.40	
	2-3	145.98	163.85	
	2-4	601.63	336.66	
	3-4	33.10	236.62	

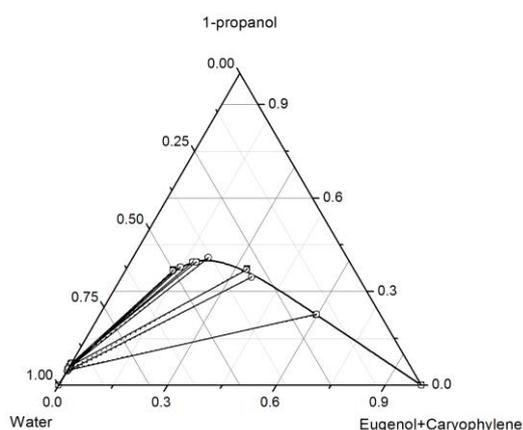
Based on this work the binary parameters for NRTL and UNIQUAC models along with root mean square deviation (RMSD) are given in Tables 4-5. Using those parameters, the experimental data were correlated then compared with the result of calculations by using RMSD in composition of both phase. The RMSD deviation model was defined as :

$$RMSD = 100\% \times \sqrt{\frac{\sum_k^n \sum_j^n \sum_i^n (x_{ijk}^{exp} - x_{ijk}^{cal})^2}{2nN}} \quad (2)$$

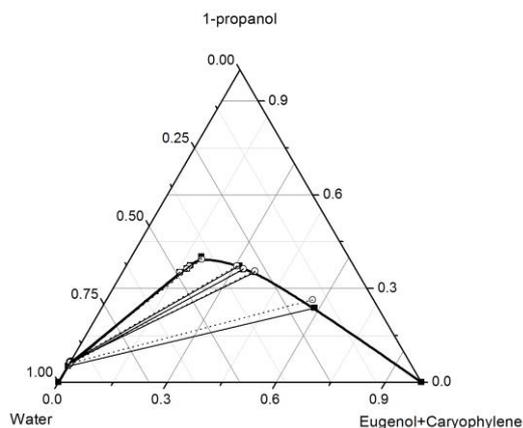
Where  $\theta$  is the number of components and  $N$  is number of tie-line [10]

The experimental and calculated data of this system were then plotted in pseudoternary diagram as shown in Fig.2-7, with average RMSD for NRTL and UNIQUAC models are 0,502% and 0,417%, respectively. The result of both models are less than 10%, it was good enough to represent the equilibrium data of this system [11].

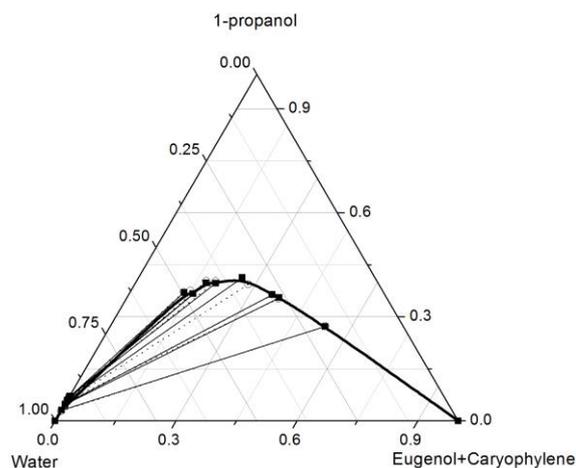
Furthermore, from Fig. 1-3 and Fig. 4-6 it can be observed that the temperature has no significant effect on the equilibrium composition, indicated by the large area under the dome (two phase area) that look almost the same for each temperatures.



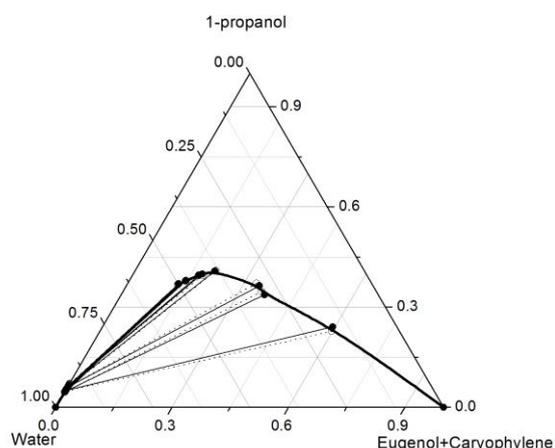
**Fig. 1.** LLE diagram for eugenol +  $\beta$ -caryophyllene + 1-propanol + water system at 303.15 K. (○) experimental data, (■) calculated data (NRTL), (⋯) experimental tie-lines, (—) correlated tie-lines using NRTL model.



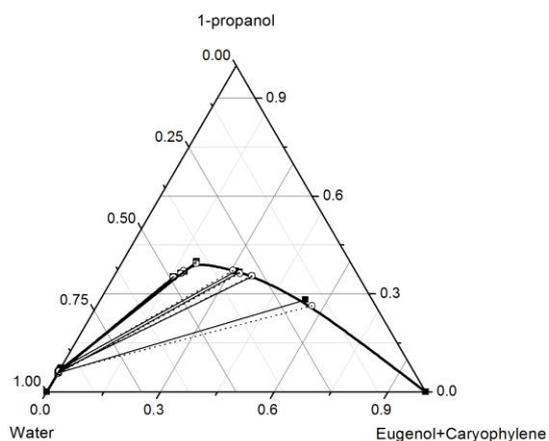
**Fig. 2.** LLE diagram for eugenol +  $\beta$ -caryophyllene + 1-propanol + water system at 313.15 K. (○) experimental data, (■) calculated data (NRTL), (⋯) experimental tie-lines, (—) correlated tie-lines using NRTL model.



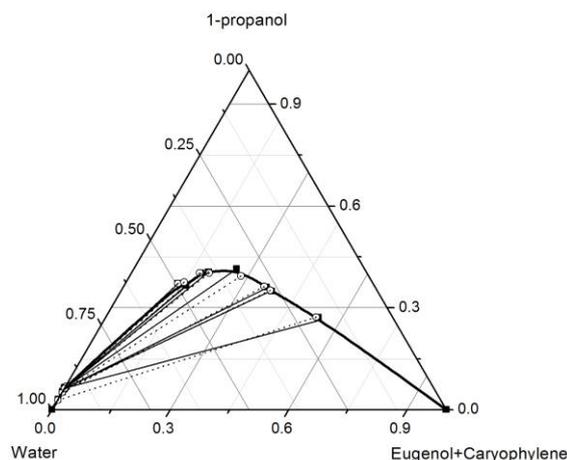
**Fig. 3.** LLE diagram for eugenol +  $\beta$ -caryophyllene + 1-propanol + water system at 323.15 K. (○) experimental data, (■) calculated data (NRTL), (⋯) experimental tie-lines, (—) correlated tie-lines using NRTL model.



**Fig. 4.** LLE diagram for eugenol +  $\beta$ -caryophyllene + 1-propanol + water system at 303.15 K. (○) experimental data, (■) calculated data (UNIQUAC), (⋯) experimental tie-lines, (—) correlated tie-lines using UNIQUAC model.



**Fig. 5.** LLE diagram for eugenol +  $\beta$ -caryophyllene + 1-propanol + water system at 313.15 K. (○) experimental data, (■) calculated data (UNIQUAC), (⋯) experimental tie-lines, (—) correlated tie-lines using UNIQUAC model.



**Fig. 6.** LLE diagram for eugenol +  $\beta$ -caryophyllene + 1-propanol + water system at 323.15 K. (○) experimental data, (■) calculated data (UNIQUAC), (⋯) experimental tie-lines, (—) correlated tie-lines using UNIQUAC model.

## 4 Conclusion

In this study, the liquid-liquid equilibria of quaternary system of the eugenol +  $\beta$ -caryophyllene + 1-propanol + water at temperatures of 303.15, 313.15, and 323.15 K have been measured accurately. Experimental data were well correlated using the NRTL and the UNIQUAC models. The results are satisfactory, with the average RMSD of the NRTL and the UNIQUAC models 0.502% and 0.417%, respectively. In the range of the temperatures studied, it showed that the temperatures are no significant effect to the equilibrium composition.

This research was supported by PT. Indesso Niagatama and the Thermodynamics Laboratory, Chemical Engineering Department, Institut Teknologi Sepuluh Nopember.

## References

1. E. Gunther, *Minyak Atsiri Jilid 1*. (1987)
2. J. Towaha. *Indones. Res. Inst. Ind. Beverage Crop.* **11**, 1412-8004 (2012)
3. A. Cháfer, J. de la Torre, R. Muñoz, M. C. Burguet, *Fluid Phase Equilib.* **238**, 72–76 (2005)
4. Y. -K. Kim, D. -W. Park, *J. Ind. Eng. Chem.* **14**, 602–607 (2008)
5. K. Kuswandi, E. Naryono, *Int. Rev. Chem. Eng (IReChE)*. **3**, 663–667 (2011)
6. R. Fitriani, K. Kuswandi, *int prosiding seminar nasional pasxasarjana XIII (SNPs)* (2013)
7. H. Renon, J. M. Prausnitz, *AIChE J.* **14**, 135–144 (1968)
8. D. S. Abrams, J. M. Prausnitz, *AIChE J.* **21**, 116–128 (1975)
9. I. C. Hwang, S. J. Park, J.S. Choi, *Fluid Phase Equilib.* **269**, 1–5 (2008)

10. C. Stoicescu, O. Iulian, R. Isopescu, *Rev. Roum. Chim.* **56**, 3214–3221 (2011)
11. J.M. Smith, H .C. Van Ness, M. M. Abbot, *Chemical Engineering Thermodynamics 6th edition*. (2001)