



Estimation of Critical Properties of Eucalyptol, Alpha-Terpineol, Limonene, and Caryophyllene in Eucalyptus Oil (*Melaleuca leucadendra*) Using the Group Contribution Method

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Abstract

Critical property estimation of compounds in eucalyptus oil has been conducted using the Group Contribution method to improve the accuracy of calculations of critical temperature (T_c), critical volume (V_c), critical pressure (P_c), and normal boiling point (T_b). This study updates the previous research by adding a comparative analysis of estimation errors between methods. Eucalyptus oil was extracted using microwave hydrodistillation followed by vacuum distillation to determine experimental data, then estimated using the Joback, Constantinou-Gani (C&G), Wilson-Japerson (W&J), and Marrero-Pardillo (M&P) methods. The results show that the Wilson-Japerson method provides the most accurate P_c estimation with %AAE of 12.7819%, the Marrero-Pardillo method is best for V_c with %AAE of 5.3393%, the Marrero-Pardillo method provides the most accurate T_c estimation with %AAE of 2.7143%. The Joback method is most suitable for T_b with a %AAE of 20.0828%. The application of the results of this study in the essential oil industry is crucial in optimizing the extraction and distillation process, increasing the efficiency of separation units, developing refining technology, and formulating essential oil-based products. The method with the best accuracy can be used in the design of distillation equipment and thermodynamic reactors, thereby improving production efficiency and product quality in the pharmaceutical, cosmetic, and natural chemical industries.

Keywords: Estimation, critical properties, essential oil, eucalyptus oil

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1. Introduction

Eucalyptol is a naturally occurring compound found in plants such as eucalyptus and rosemary. Recent studies suggest its potential applications in treating Alzheimer's disease, neuropathic pain, and cancer (Hoch, 2023). Alpha-terpineol is commonly present in essential oils of eucalyptus, cardamom, and cypress and is widely used in the food, cosmetic, perfume, and hygiene industries (Sales, 2020). Limonene is a key terpene compound in the flavor and fragrance industry and serves as an alternative solvent to benzene, toluene, ethylbenzene, and xylene in oil and gas production (Jongedijk, 2016). Caryophyllene, found in essential oils, has demonstrated therapeutic effects on obesity, liver disease, diabetes, and nervous system disorders (Scandiffio, 2020).

In addition to their wide-ranging uses, eucalyptol, alpha-terpineol, limonene, and caryophyllene have physicochemical characteristics that are important to understand, especially in the context of their application in various industrial processes. Each compound has unique properties that affect its thermodynamic behavior in separation and processing. Therefore, further study of the pure properties of each compound, including critical properties, is an important first step before entering the process design and simulation stage.

Understanding the physicochemical properties of pure compounds such as eucalyptol, alpha-terpineol, limonene, and caryophyllene is fundamental for designing efficient industrial processes. These properties determine how compounds behave

under various process conditions, including heating, cooling, and separation. In the chemical industry, mastering critical properties is essential for process design, simulation, and optimization (Leon, 2022). Parameters such as vapor pressure, density, heat of vaporization, and heat capacity are required for building accurate process models. However, limited experimental data in the literature often presents a challenge, necessitating the use of estimation methods for process development (Tahami, 2019).

These problems can be overcome by the Group Contribution method, which is a commonly used approach for estimating critical property data from molecular structures through functional groups (Gani, 2019). In its development, several methods have emerged, including Joback, who utilizes basic structural information of chemical molecules; Constantinou and Gani, who use data from UNIFAC groups; Wilson and Japerson, who incorporate atomic contributions and the number of rings; and Marrero and Pardillo, who apply bond contribution data (Poling, 2001).

Previous studies have successfully applied Group Contribution methods to estimate the critical properties of hydrocarbons and simple alcohols (Chen, 2019; Leon, 2022; Tahami, 2019). However, terpenoid compounds, such as those in eucalyptus oil, exhibit complex molecular structures and unique intermolecular interactions, requiring further investigation. This study extends the application of Group Contribution methods to eucalyptol, alpha-terpineol, limonene, and caryophyllene, providing a comparative analysis of four estimation techniques to determine their accuracy and applicability in predicting critical properties of volatile compounds. By evaluating the advantages and limitations of each method, this study aims to determine the most suitable Group Contribution method for obtaining reliable property data. The findings contribute to the broader thermodynamic study of terpenoid compounds and support applications in

pharmaceutical, cosmetic, and essential oil industries, facilitating process optimization and industrial applications.

2. Methodology

2.1. Materials

The materials used in this research include fresh eucalyptus leaves from Malang City. The process begins with extracting essential oil from eucalyptus leaf pieces using microwave radiation, followed by the separation of the condensate through a separating funnel.

The extracted oil was then vacuum distilled to study the critical properties of the compounds to be estimated, which was done three times to get accurate results. Furthermore, analysis using the Group Contribution method was carried out to determine the critical properties and evaluate the accuracy of the estimation method.

2.2. Content of Eucalyptus Oil

There are many components contained in eucalyptus oil with different percentages. In this study, the components used that have the highest percentage content are 1,8 cineol, alpha terpineol, limonene, and caryophyllene. The critical property data of the eucalyptus oil components were obtained from three independent experimental repetitions. Table 1 presents the experimental data for the critical properties of 1,8 cineol and alpha terpineol, including their respective critical temperature (T_c), critical pressure (P_c), and critical volume (V_c). Similarly, Table 2 details the experimental data for the critical properties of limonene and caryophyllene.

Since the variations between repetitions were insignificant, the final values presented in the manuscript, including the averages shown in both tables, are based on the averaged results.

Table 1. Experimental data on critical properties of 1,8 cineol & alpha terpineol

No.	Experiment							
	1,8 Cineol				Alpha Terpineol			
	T_b	T_c	V_c	P_c	T_b	T_c	V_c	P_c
1	448.0000	695.4000	507	30.1896	485.7930	733.5108	520	29.49
2	450.4500	695.6000	510	30.4915	495.6070	748.3292	524	29.5244
3	449.0000	695.5000	510	29.8877	490.7000	740.9200	522	29.5000
Average	449.1500	695.5000	509	30.1896	490.7000	740.9200	522	29.5048

Table 2. Experimental data on critical properties of limonene & caryophyllene

No.	Experiment							
	Limonene				Caryophyllene			
	T _b	T _c	V _c	P _c	T _b	T _c	V _c	P _c
1	448.0000	656.0000	494	27.4000	525.0000	800.0000	715	20.0000
2	452.0200	658.4800	498	27.7000	528.2000	805.0000	719	20.6169
3	451.000	657.0000	496	27.5668	526.0000	801.1800	717	20.2000
Average	450.3400	657.1600	496	27.5556	526.4000	802.0600	717	20.2723

This ensures the reliability and consistency of the data used for mathematical estimation and simulation.

2.3. Effect of Molecular Structure on Estimation Accuracy

The studied compounds—eucalyptol, α -terpineol, limonene, and caryophyllene—are terpenoids with distinct molecular structures that influence the accuracy of critical property estimation using the group contribution method. Eucalyptol (1,8-cineole) is a cyclic monoterpenoid with an ether group, increasing polarity and affecting boiling point and vapor pressure estimations (Almas, 2021). α -Terpineol, a monoterpenoid with a hydroxyl (-OH) group, forms hydrogen bonds, impacting water solubility and boiling point accuracy (Koyama, 2020). Limonene, a non-polar cyclic monoterpene, requires methods that account for its high volatility and solubility in organic solvents (Koyama, 2020). Caryophyllene (β -caryophyllene), a sesquiterpene with a complex cyclic structure, affects molecular flexibility and thermodynamic properties, demanding specialized estimation approaches (Lowe, 2024). Understanding these structural characteristics is crucial for improving estimation accuracy and selecting appropriate methods.

2.4. Analyze Group Contributions

Joback's method is an extension of Lydersen's method, and there are groups, formulas, and parameters for all three properties (critical temperature, critical pressure, and critical volume) supported by Lydersen. Joback has expanded the range of supported properties, created new parameters, and slightly changed the expression of the old Lydersen method. The Joback method is a cluster contribution method that uses basic structural information of chemical molecules, such as a simple list of functional groups, adds parameters to the functional groups and calculates

thermophysical and transport properties as a function of the number of cluster parameters (Poling, 2001).

$$T_b = 198 + \sum_k N_k(tbk) \quad (1)$$

$$T_c(K) = T_b \left[\frac{0.584 + 0.965 \left\{ \sum_k N_k(tc1k) \right\}^{-1}}{- \left\{ \sum_k N_k(tc2j) \right\}^2} \right] \quad (2)$$

$$P_c(\text{bar}) = \left[\frac{0.113 + 0.0032N_{\text{atoms}}}{- \sum_k N_k(pck)} \right]^{-2} \quad (3)$$

$$V_c(\text{cm}^3 \text{mol}^{-1}) = 17.5 + \sum_k N_k(vck) \quad (4)$$

Remark:

T_b = boiling point
 N_k = molecule
 T_{bk} = Group Contributions T_b for Joback
 T_c = Critical temperature
 T_b = Boiling point
 T_{ck} = Group Contributions T_c for Joback
 P_c = Critical pressure
 N_{atoms} = Atomic number in the molecule
 P_{ck} = Group Contributions P_c for Joback
 V_c = Critical volume
 V_{ck} = Group Contributions V_c for Joback

Constantinou and Gani (1994) developed an advanced group contribution method based on UNIFAC groups. However, this method provides a more sophisticated approach to property flexibility by incorporating Second Order temporary correlations, partially overcoming the limitations of UNIFAC, which cannot distinguish special configurations such as isomers, multiple adjacent groups, and resonance structures in First Order (Poling, 2001).

$$T_b = 204.359 \times \ln \sum_k N_k(tb1) \quad (5)$$

$$T_c(K) = 181,128 \ln \left[\frac{\sum_k N_k(tc1k)}{\sum_j M_j(tc2j)} \right] \quad (6)$$

$$P_c(\text{bar}) = \left[\frac{\sum_k N_k (pc1k) + W \sum_j M_j (pc2j) + 0.10022}{+ 1.3705} \right]^{-2} \quad (7)$$

$$V_c(\text{cm}^3 \text{mol}^{-1}) = -0.00435 + \left[\frac{\sum_k N_k (vc1k) + W \sum_j M_j (vc2j)}{+ 1.3705} \right] \quad (8)$$

Remark:

- T_c = critical temperature
 N_k = first-order group molecules
 $Tc1k$ = first-order group distribution T_c for Constantinou Gani
 N_j = second-order group molecules
 $Tc2j$ = second-order group distribution T_c for Constantinou Gani
 P_c = critical pressure
 $Pc1k$ = first-order group distribution for P_c of Constantinou Gani
 W = weight second-order group distribution for Constantinou Gani
 $Pc2j$ = second-order group distribution for P_c for Constantinou Gani
 V_c = critical volume
 $Vc1k$ = first-order group distribution V_c for Constantinou Gani
 $Vc2j$ = second-order group distribution V_c for Constantinou Gani

Wilson and Jasperson (1996) reported three methods for estimating T_c and P_c that apply to organic and inorganic species. The mole-order method employs factor analysis using boiling point, liquid density, and molecular weight as descriptors. In the first-order method, atomic contributions are used along with boiling point and the number of rings, while the second-order method also incorporates group contributions. The zero-order method has not been tested in this study; it is iterative, and the authors report that it is less accurate by a factor of two or three compared to other methods, especially for P_c . The first-order and second-order methods use the following equations (Poling, 2001).

$$T_c(K) = \frac{T_b}{\left[0.048271 - 0.019846 N_r + \sum_k N_k (\Delta tck) + \sum_j N_j (\Delta tcj) \right]} \quad (9)$$

$$P_c(\text{bar}) = \frac{0.0186233 T_c}{\left[-0.96601 + \exp(Y) \right]} \quad (10)$$

$$Y = -0.00922295 - 0.0290403 N_r + 0.041 \left(\sum_k N_k (\Delta pck) + \sum_j M_j (\Delta pcj) \right) \quad (11)$$

Remark:

- T_c = critical temperature
 T_b = boiling point
 N_r = number of rings in the compound

- N_k = number of First-Order group atoms
 Tck = first-Order atomic contribution T_c for Wilson Japerson
 N_j = number of atoms of second-order group
 Tcj = second-order atomic contribution T_c for Wilson Japerson
 P_c = critical pressure
 T_c = critical temperature
 Pck = atomic contribution P_c for Wilson Japerson
 M_j = number of atoms in group contribution
 Pcj = group contribution P_c for Wilson Japerson

Marrero-Marejón and Pardillo-Fontdevila (1999) described a method for estimating T_c , P_c , and V_c , which they called the group interaction contribution technique or, effectively, the bond contribution method. They provided equations that use values from pairs of atoms only, such as C & -N, or with bound hydrogens, such as CH_3 - & $-\text{NH}_2$. The basic equation is based on the number of atoms in the compound (N_{atom}) and the number of k-type atoms (N_k), which contribute to $tcbk$, $pcbk$, and $vcbk$. It should be noted that T_c requires T_b , but Marrero and Pardillo provide an estimation method for T_b (Poling, 2001).

$$T_c(K) = \frac{T_b}{\left[0.5851 - 0.9286 \left(\frac{\sum_k N_k (tcbk)}{(\sum_k N_k (tcbk)) - (\sum_k N_k (tcbk))^2} \right) \right]} \quad (12)$$

$$T_b(K) = Mr^{-0.404} \sum_k N_k (tbbk) + 156.00 \quad (13)$$

$$P_c(\text{bar}) = \left[(0.1285 - 0.0059 N_{\text{atom}} - \sum_k N_k (pcbk)) \right]^{-2} \quad (14)$$

$$V_c(\text{cm}^3 \text{mol}^{-1}) = 25.1 + \sum_k N_k (vcbk) \quad (15)$$

Remark:

- T_c = critical temperature
 N_k = number of atoms in the molecule
 $Tcbk$ = group contribution T_c for Marrero/Pardillo method
 T_b = boiling point
 Mr = molecular formula
 $Tbbk$ = group contribution T_b for Marrero/Pardillo method
 P_c = critical pressure
 N_{atom} = number of atoms in the compound
 $Pcbk$ = group contribution P_c for Marrero/Pardillo method
 V_c = critical volume
 $Tcbk$ = group contribution T_c for the Marrero/Pardillo method

2.5. Statistical Analysis

Accuracy and estimates for critical properties are evaluated which are compared with

experimental data using the following percentage relative deviations as accuracy criteria (Tahami, 2019). In this case, AAE is the average relative error to measure the deviation of the estimated property values from the data. ARE is the average relative error to measure the average value of the relative error concerning the experimental data values (Hukkerikar, 2012).

$$AAE = \frac{1}{N} \sum_j |(X_j^{exp} - X_j^{est})| \quad (16)$$

$$AAE\% = \frac{1}{N} \sum_j \frac{|(X_j - X_j^{exp})|}{X_j} \times 100\% \quad (17)$$

Remark:

AAE = absolute average error

N = total number of data or compounds

X_j^{exp} = experimental value of compound

property

X_j = estimated value of the property based on

the method

3. Results and Discussion

3.1. Critical Pressure Estimation

Critical pressure (P_c) is a key value in designing industrial processes, including for essential oils. This study estimated the P_c of four eucalyptus oil compounds—1,8-cineole, alpha-terpineol, limonene, and caryophyllene—using four different methods: Joback, C&G, W&J, and M&P. Table 3 shows the experimental and estimated values, which were compared to assess each method's accuracy. The accuracy of each method was assessed by comparing the estimated values with the experimental data.

Table 4 presents the percentage error for the critical pressure estimation of each compound using the four methods, as well as the overall Percentage Absolute Average

Error (%AAE) for each method. The %AAE was calculated to determine accuracy. The W&J method exhibited the lowest %AAE value (12.7819%), making it the most accurate for estimating the critical pressure of eucalyptus oil compounds, as shown in Table 4. The Joback method followed closely with a %AAE of 12.8115%, while the C&G method had a higher error of 16.3617%. In contrast, the M&P method showed the largest estimation error, with a %AAE of 45.8300%, indicating poor accuracy.

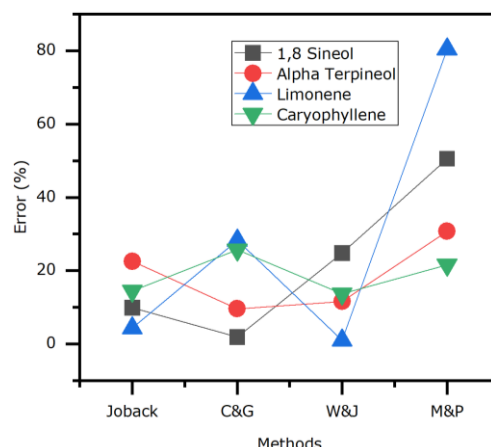


Figure 1. Percentage error of critical pressure (P_c) estimation for each compound with different group contribution methods

Figure 1 shows the estimation errors, where the M&P method has the largest deviations, especially for 1,8-cineole and limonene. In contrast, the W&J method gives more consistent and smaller errors, making it more reliable for estimating the critical pressure of eucalyptus oil compounds. This method is more accurate because it considers molecular structure, not just functional groups, which helps in predicting values for cyclic compounds like limonene and caryophyllene.

Table 3. Calculation of P_c (bar) estimation in each method for essential oil constituents

No	Compound		Experiment P_c (Bar)	Calculation			
	Name	Formula		Joback	C & G	W & J	M & P
1	1,8 Sineol	$C_{10}H_{18}O$	30.1896	27.4690	29.6249	24.1926	20.0550
2	Alpha Terpineol	$C_{10}H_{18}O$	29.5048	24.0764	32.6504	26.4306	22.5681
3	Limonene	$C_{10}H_{16}$	27.5556	26.4067	38.3882	27.2688	141.0509
4	Caryophyllene	$C_{15}H_{24}$	20.2723	17.7136	27.2800	17.8365	16.6733

Table 4. Comparison of percentage error of P_c (bar) estimation calculation results in each method

No.	Name	% Error			
		Joback	C & G	W & J	M & P
1	1,8 Sineol	9.9042	1.9060	24.7885	50.5341
2	Alpha Terpineol	22.5465	9.6343	11.6311	30.7365
3	Limonene	4.3507	28.2186	1.0517	80.4641
4	Caryophyllene	14.4448	25.6880	13.6562	21.5852
Total		51.2462	65.4469	51.1276	183.3198
% AAE		12.8115	16.3617	12.7819	45.8300

Based on these findings, the W&J method is recommended for critical pressure estimation in eucalyptus oil-related processes. Its ability to provide estimates closer to experimental values aligns with previous studies, which highlight its effectiveness due to its systematic approach and computational efficiency (Soo, 2010).

3.2. Critical Temperature Estimation

Critical temperature (T_c) is a key thermodynamic parameter in industrial process design, including essential oil processing. This study estimated the T_c of four major eucalyptus oil compounds—1,8-cineole, alpha-terpineol, limonene, and caryophyllene—using the Joback, Constantinou & Gani (C&G), Wilson & Jasperson (W&J), and Marrero & Pardillo (M&P) methods. Table 5 displays the experimental critical temperature values alongside the estimated T_c values obtained from each of these four methods. The estimated values were then compared with experimental data to evaluate accuracy and determine the most suitable approach for T_c estimation in the essential oil industry.

Table 6 shows the percentage error for estimating the critical temperature of each compound using four methods, along with the overall %AAE for each. The W&J method had the lowest %AAE (2.71%), making it the most accurate. The C&G method followed with 6.33%, then the Joback method with 6.82%. The M&P method had the highest error (9.34%), making it the least accurate. Figure 2 visualizes the estimation errors, revealing that the Joback method has the largest error for alpha-terpineol, while the

M&P method shows significant deviation for limonene. Conversely, the W&J method demonstrates the most stable results with smaller deviations, while the C&G method exhibits a relatively uniform error trend across all compounds, albeit with some variations.

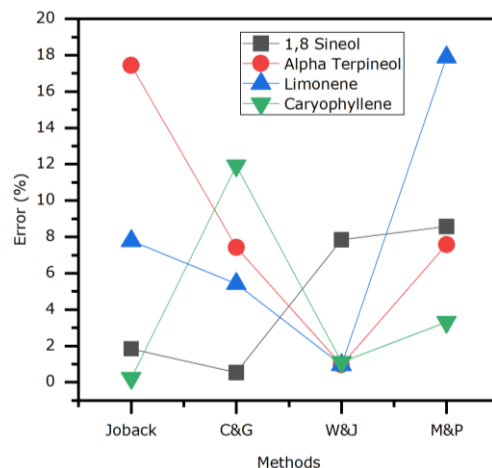


Figure 2. Percentage error value of critical temperature estimation (T_c) of each compound with different group contribution methods

These findings confirm that the W&J method provides the most accurate T_c estimation, making it a reliable choice for industrial applications involving eucalyptus oil. By incorporating these factors, the W&J method yields T_c estimates that closely align with experimental values. Similar results have been reported in previous studies, where the Wilson & Jasperson method consistently produced estimates with the lowest AAE error for various organic compounds (Martins, 2017).

Table 5. Calculation of the estimated T_c (K) of each method for essential oil constituents

No.	Compound		Experiment T_c (K)	Calculation			
	Name	Formula		Joback	C & G	W & J	M & P
1	1,8 Sineol	$C_{10}H_{18}O$	695.5000	682.8946	679.2642	629.8804	688.9407
2	Alpha Terpineol	$C_{10}H_{18}O$	740.9200	630.9271	681.5537	688.1494	639.6868
3	Limonene	$C_{10}H_{16}$	657.1600	609.7573	644.7724	650.9856	792.8762
4	Caryophyllene	$C_{15}H_{24}$	802.0600	803.8164	718.2135	710.3704	734.6500

Table 6. Comparison of Percentage error of T_c (K) estimation calculation results in each method

No.	Name	% Error			
		Joback	C & G	W&J	M & P
1	1,8 Sineol	1.8459	0.5345	7.8402	8.5726
2	Alpha Terpineol	17.4335	7.4281	0.9585	7.5760
3	Limonene	7.7740	5.4306	0.9544	17.8957
4	Caryophyllene	0.2185	11.9189	1.1041	3.3049
Total		27.2719	25.3121	10.8572	37.3492
% AAE		6.8180	6.3280	2.7143	9.3373

3.3. Critical Volume Estimation

Critical volume (V_c) is a key thermodynamic parameter in determining fluid behavior and properties in various industrial applications, including essential oil processing. Accurate V_c estimation is crucial for process design and optimization. In this study, the critical volumes of four major eucalyptus oil compounds—1,8-cineole, α -terpineol, limonene, and caryophyllene—were estimated using the Joback, Constantinou & Gani (C&G), and Marrero & Pardillo (M&P) methods. Table 7 displays the experimental critical volume values alongside the estimated V_c values obtained from each of these three methods. The estimated values were compared with experimental data to assess accuracy and identify the most suitable approach for V_c estimation.

Table 8 presents the percentage error for the critical volume estimation of each compound using the three methods, as well as the overall Percentage Absolute Average Error (%AAE) for each method. The %AAE was calculated to evaluate accuracy. The M&P method exhibited the lowest %AAE value (5.3393%), making it the most accurate for estimating the critical volume of eucalyptus oil compounds, as detailed in Table 8. The C&G method ranked second with a %AAE of 8.2646%, followed by the Joback method, which showed the highest estimation error (%AAE = 9.4543%).

The superior accuracy of the W&J method is attributed to its empirical correlation-based approach, which integrates functional group contributions with broader experimental trends, resulting in more consistent estimates. Additionally, this method is

particularly effective for complex molecular structures such as α -terpineol and caryophyllene, which involve inter-group interactions and ring systems that can cause significant deviations if not properly accounted for.

Figure 3 visualizes the estimation errors, highlighting that the C&G method has the largest deviation, particularly for limonene, which exhibits the highest error. In contrast, the M&P method demonstrates more stable results, with the lowest deviation observed for caryophyllene.

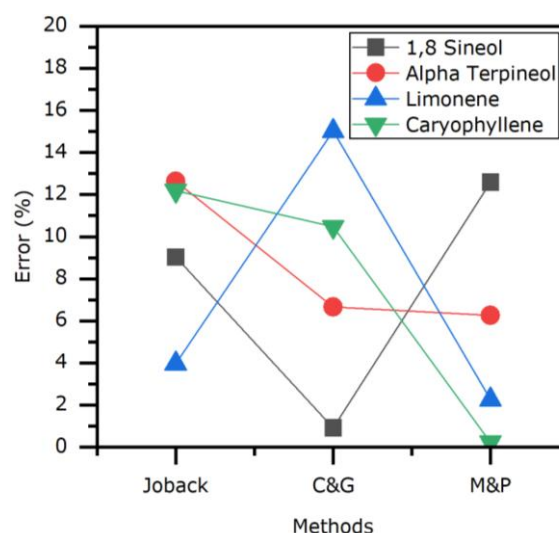


Figure 3. Percentage error value of critical volume estimation (V_c) of each compound with different group contribution methods

These findings confirm that the M&P method provides the most accurate V_c estimation, making it a reliable approach for industrial processes involving eucalyptus oil.

Table 7. Calculation of estimated V_c (cm^3/mol) in each method for essential oil constituents

No.	Compound		Experiment V_c (cm^3/mol)	Calculation		
	Name	Formula		Joback	C & G	M & P
1	1,8 Sineol	$\text{C}_{10}\text{H}_{18}\text{O}$	509.0000	559.5000	513.7500	582.3000
2	Alpha Terpineol	$\text{C}_{10}\text{H}_{18}\text{O}$	522.0000	597.5000	489.4500	556.9000
3	Limonene	$\text{C}_{10}\text{H}_{16}$	496.0000	516.5000	431.2500	507.5000
4	Caryophyllene	$\text{C}_{15}\text{H}_{24}$	717.0000	816.5000	649.0500	718.7000

Table 8. Comparison of Percentage error of V_c (cm^3/mol) estimation calculation results in each method

No.	Name	% Error		
		Joback	C & G	M & P
1	1,8 Sineol	9.0259	0.9246	12.5880
2	Alpha Terpineol	12.6360	6.6503	6.2668
3	Limonene	3.9690	15.0145	2.2660
4	Caryophyllene	12.1862	10.4691	0.2365
Total		37.8171	33.0585	21.3574
% AAE		9.4543	8.2646	5.3393

The superior accuracy of the M&P method is attributed to its group-pair approach, which effectively accounts for molecular structure effects and inter-functional interactions. Consequently, the Marrero-Pardillo method is recommended for critical volume estimation of eucalyptus oil compounds. Similar findings have been reported in previous studies, further validating the reliability of this method (Hartanto, 2013).

3.4. Estimated boiling temperature

Boiling temperature (T_b) is an important thermodynamic property in many industrial processes, including essential oil production. Accurate T_b estimation helps understand a compound's volatility, which affects distillation and extraction efficiency. In this study, the boiling temperatures of four main eucalyptus oil compounds—1,8-cineole, alpha-terpineol, limonene, and caryophyllene—were estimated using the Joback, Constantinou & Gani (C&G), and Marrero & Pardillo (M&P) methods. Table 9 shows both the experimental and estimated T_b values. These results were compared to find the most accurate method for estimating boiling temperature.

Table 10 shows the percentage error for boiling temperature estimates of each compound and the overall %AAE for each method. The Joback method had the lowest %AAE (20.08%), making it the most accurate. The C&G and M&P methods had higher %AAE values (21.40% and 21.50%), showing they were less reliable for estimating the boiling temperature of eucalyptus oil compounds.

Figure 4 visualizes the estimation errors, highlighting that the C&G method exhibits the largest deviation, particularly for caryophyllene. In contrast, the Joback method demonstrates more stable results with smaller deviations, further confirming its accuracy and reliability in boiling temperature estimation.

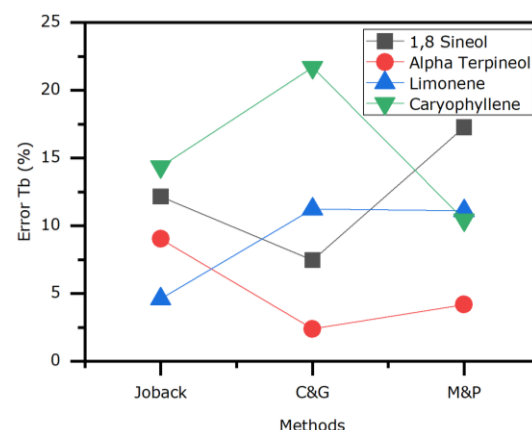


Figure 4. Percentage error value of boiling point estimation (T_b) of each compound with different group contribution methods

The superior performance of the Joback method can be attributed to its first-order group contribution approach, which directly considers functional group contributions rather than complex molecular structures. This makes the Joback method especially useful for predicting boiling points in essential oil compounds. It is recommended for industrial use with eucalyptus oil because it gives more accurate results and can improve production efficiency. Other studies also found that the Joback method gives the most accurate boiling point estimates, with the lowest %AAE (Aghezzi, 2021).

Table 9. Calculation of T_b (K) estimation in each method for essential oil constituents

No.	Compound		Experiment T_b (K)	Calculation		
	Name	Formula		Joback	C & G	M & P
1	1,8 Sineol	$C_{10}H_{18}O$	449.1500	511.3800	485.3771	542.8979
2	Alpha Terpineol	$C_{10}H_{18}O$	490.7000	450.0500	479.2185	512.1791
3	Limonene	$C_{10}H_{16}$	450.3400	430.5600	404.8637	506.5763
4	Caryophyllene	$C_{15}H_{24}$	526.4000	614.7400	672.3315	587.8028

Table 10. Comparison of Percentage error of T_b (K) estimation calculation results in each method

No.	Name	% Error		
		Joback	C & G	M & P
1	1,8 Sineol	12.1690	7.4637	17.2680
2	Alpha Terpineol	9.0323	2.3959	4.1937
3	Limonene	4.5940	11.2325	11.1012
4	Caryophyllene	14.3703	21.7053	10.4462
Total		40.1657	42.7974	43.0091
% AAE		20.0828	21.3987	21.5046

3.5. Error Comparison of Each Method

Figure 5 compares the absolute average error (%AAE) values for critical pressure (P_c), critical volume (V_c), critical temperature (T_c), and boiling temperature (T_b) using four Group Contribution-based estimation methods: Joback, Constantinou & Gani (C&G), Marrero & Pardillo (M&P), and Wilson & Jasperson (W&J).

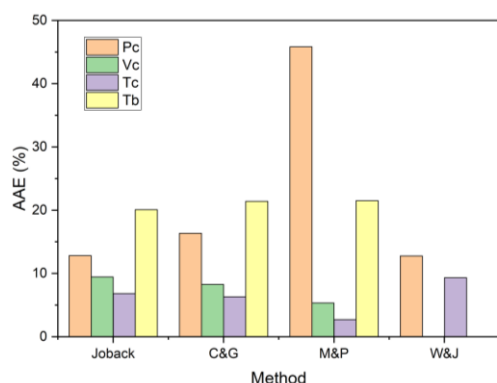


Figure 5. Comparison value of each group contribution method on the whole compound.

The results indicate that the M&P method provides the most accurate estimates for T_c and V_c , with %AAE values of 2.7143% and 5.3393%, respectively. This suggests that the M&P method effectively accounts for molecular complexity. Conversely, the Joback method demonstrates the highest accuracy in P_c estimation, with a %AAE of 12.8115%, outperforming the C&G and M&P methods. Additionally, the Joback method yields the lowest error for T_b estimation (%AAE = 20.0828%), whereas the C&G and M&P methods exhibit slightly higher errors of 21.3987% and 21.5046%, respectively.

The M&P method showed the highest error for P_c estimation (%AAE = 45.83%), making it less reliable for this parameter. However, it is recommended for T_c and V_c . The Joback method gives the best results for P_c , with W&J as a good alternative. Therefore, the choice of method should match the specific thermodynamic property and its required accuracy.

4. Conclusion

The thermodynamic properties of Eucalyptol, Alpha-Terpineol, Limonene, and Caryophyllene were successfully estimated using the Group Contribution method. Error analysis showed that the accuracy of each method depends on the property being predicted. The Wilson-Jasperson (W&J)

method gave the most accurate estimate for critical pressure (P_c) with a 12.81% error. The Marrero & Pardillo (M&P) method was most accurate for critical volume (V_c) and critical temperature (T_c), with errors of 5.34% and 2.71%. For boiling temperature (T_b), the Joback method had the lowest error at 20.08%. These results show that choosing the right method for each thermodynamic property is important for better accuracy. Some higher %AAE values suggest that certain methods may not fully reflect the molecular structure of essential oil compounds. This approach can also be used for other terpenoid compounds with similar structures. The findings can support essential oil processing, pharmaceutical product development, and thermodynamic modeling of volatile compounds. Overall, this study helps improve understanding of how terpenoid compounds behave in different industrial applications.

Author Contribution Statement

S.M.: Conceptualisation, writing – original draft. M.D.P.: Investigation, formal analysis. Writing – review and editing A.P.P.S.: Supervision, S.M.: Writing – original draft.

Data Availability Statement

The data presented in this work are included in the article.

Declaration of Competing Interest

The authors declare no conflict of interest.

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0758

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