EVALUATION OF SOME GC METHODS TO PREDICT THE CRITICAL PROPERTIES OF AROMA COMPOUNDS

Manuel G. Cerpa *
C & C E.I.R.L.
Urb. María Auxiliadora Mz "E", Lt. 11, Lima29, Lima, Perú.
Fax: +5113-302850, E-mail: cercman@ec-red.com

ABSTRACT

In this work, it presents a evaluation of the latest and well-know Group-Contribution Methods in order to predict the normal boiling temperature of some aroma compounds. The elected Methods were: Joback-Reid, Joback-Marrero-Pardillo, Constantinou-Gani, Marrero-Gani and Marrero-Pardillo, with their last modifications. Eight compounds were selected for this work: α-pinene, d-limonene, 1,8-cineole, anethole, menthone, thymol, isoamyl acetate and eugenol, in agreement to available information of some recognized databases. From this evaluation, it selected the methods with the best accuracy to predict the critical properties (T_c, P_c) of elected compounds. The acentric factor and critical compressibility factor were also calculated using these critical values and their experimental data of vapor pressure. With these data, it publicities an actualized and consistent compilation of critical properties for these compounds. Finally, it recommends using the Marrero-Gani GC Method to predict the critical properties of any sesquiterpene or terpene presents in a essential oil. Because, it demonstrated its better accuracy and large diversity of chemical groups required for the representation of chemical structure of elected compounds.

KEYWORDS

Critical properties, Group-Contribution Methods, Joback-Reid, Marrero-Pardilla, Constantinou-Gani, Marrero-Gani, normal boiling temperature, terpenes, oxygenated sesquiterpenes.

INTRODUCTION

When it makes the design of classic or new extraction or refination operations of essential oils, some critical properties are necessaries to calculate the parameters of a Cubic Equation of State or a predictive equation of viscosity or any other physical property [1, 4, 10, 11]. There are various databases with these experimental critical values, [3, 4, 5] but the data of main compounds have not been determined. Because, these compounds suffer a thermal degradation when the saturation temperature is up it normal boiling point. For that reason, its necessary to use efficient methods in order to predict their critical properties [12]. In this work, it testes five Group Contribution Methods to know their accuracy and flexibility in order to calculate the normal boiling

temperature of 8 aroma compounds. The better Methods will be elected to calculate the critical properties (P_c, T_c), the acentric factor and the critical compressibility factor. The substances have been elected in agreement to the available information and their importance in some essential oils. So, the ***a-pinene*** and ***d-limonene*** are present in the essential oils of citric fruits, *ocimum basilicum*, *coriandum sativum* and *pinus caribea*. The ***anethole*** is in the fennel, *pimpinella* and *star anisum* oils. The ***1,8-cineole*** presents in the *eucalytus globulus* oil, the ***thymol*** is in the *origanum*, *thymus* and *satureja panicera* oils. The ***isoamyl acetate*** presents in the *banana* and the ***menthone*** is in the *mentha spicata, piperita* and *arvensis* oils. The ***eugenol*** presents in the clove leaf and cinnamon leaf oil.

I. THEORY

Actually, there are numerous GC Methods to predict the critical properties of much compounds [3, 4, 7, 8]. However, some methods are not design to work with complex chemical structure compounds like are the terpenes and sesquiterpenes. We have revised the above mentioned GC Methods and we have elected only five for next reasons:

a. These methods are actualised and easy to work. In addition, they need only the stereo-chemical structure of compound.
b. These methods have a wide variety of chemical groups that they can represent the complex structures of aroma compounds.
c. These methods have been tested to much compounds of different chemical nature with very good results.

The selected GC Methods are:

1. Joback (**J**) [4].
2. Marrero and Pardillo have recently revised the Joback Method and publicized the actualised values of the group contributions for this method [7]. We used the two formulas to calculate T_b. (**JMP-1**, **JMP-2**)
3. Constantinou and Gani [4]: We used the two levels. The “First Order” is (**CG-1**) and with the “Second Order” is (**CG-2**).
4. Marrero and Pardillo [4, 7] (**MP**).
5. Marrero and Gani [8]: We used the two levels. The “First Order” is (**MG-1**) and with the “Second Order” is (**MG-2**).

II. CALCULUS

First, it tabulates the critical and physical properties of each compound in agreement to available information (**Table 1**). Then, it shows the values of T_b for each compound with the five methods and their modifications (**Table 2**). The results in bold letter have been elected for their minimum error and they serve to select the better GC Methods. (**Table 3**) Finally, it tabulates a new and recommend databases of critical properties for these compounds. (**Table 4**) The acentric factor was calculated using the available experimental data of vapour pressure together with the Ledanois equation [13]. The critical compressibility factor was calculated using the Soave equation [14] for non-polar compounds.

Table 1: Critical and physical properties of pure compounds.

Compounds	CAS N°	T_b	MW	Source
Anethole	104-46-1	508.45	148.2	[5]
α-pinene	7785-70-8	429.29	136.2	[5]
Menthone	14073-97-3	483.15	154.2	[3]
Eugenol	97-53-0	526.30	164.2	[3]
D-limonene	5989-27-5	450.8	136.2	[6]
1,8-cineole	470-82-6	449.55	154.2	[3]
Isoamyl acetate	123-92-2	415.15	130.2	[6]
Thymol	89-83-8	505.22	150.2	[3]

Table 2: Values of T_b calculate with the elected Methods

CAS N°	J	JMP-1	JMP-2	CG-1	CG-2	MP	MG-1	MG-2
7785-70-8	445.66	466.37	469.79	419.86	**428.99**	NE	422.46	427.79
104-46-1	486.44	492.10	485.02	507.00	503.67	477.32	**508.44**	511.54
14073-97-3	475.83	477.80	453.19	462.56	**476.71**	NE	498.14	498.58
97-53-0	559.58	539.89	553.78	550.67	545.07	544.65	528.19	**525.30**
5989-27-5	**448.41**	435.04	441.81	NE	NE	NE	444.75	443.90
470-82-6	472.98	491.40	477.38	NE	NE	NE	**449.50**	455.81
89-83-8	513.31	546.56	538.10	519.09	517.21	575.16	511.53	**508.86**
123-92-2	417.34	412.86	413.52	421.43	418.40	**416.69**	417.98	417.86

NE = The method can not evaluate this compound

Table 3: Relative errors (%) in the prediction of T_b with the elected Methods

CAS N°	J	JMP-1	JMP-2	CG-1	CG-2	MP	MG-1	MG-2
7785-70-8	3.813	8.638	9.434	-2.197	**-0.07**	NE	-1.591	-0.349
104-46-1	-4.329	-3.216	-4.608	-0.285	-0.94	-6.123	**-0.002**	0.608
14073-97-3	-1.515	-1.107	-6.201	-4.262	**-1.333**	NE	3.103	3.194
97-53-0	6.323	2.582	5.221	4.630	3.566	3.487	0.359	**-0.190**
5989-27-5	**-0.530**	-3.496	-1.994	NE	NE	NE	-1.342	-1.531
470-82-6	5.212	9.309	6.191	NE	NE	NE	**-0.011**	1.393
89-83-8	1.601	8.183	6.508	2.745	2.373	13.843	1.249	**0.720**
123-92-2	0.528	-0.552	-0.393	1.513	0.783	**0.371**	0.682	0.653

NE = The method can not evaluate this compound

III. DISCUSSION OF RESULTS

It observes in the **Tables 2 and 3,** that the better results are obtained with the Marrero-Gani GC Method (anethole, eugenol, 1,8-cineole and thymol). For other compounds, the alternative Methods give better results that the MG.

The Marrero-Pardillo GC Method has available the chemical groups to represent some elected compounds. We can see that it is a problem to use it with other same substances. In addition, this Method demonstrates to be very good for non-cyclic compounds, but it produces high errors for complex compounds.

The Constantinou-Gani GC Method has not available the chemical groups in order to represent the d-limonene and 1,8-cineole. However, the new Marrero-Gani Method, based in the CG, has all groups in the two levels. The CG offers better results when it uses the "Second Order" level, because it takes in count more bond to bond interactions.

The revised Joback Method not offers better results that the original Method for these compounds. Only, the original Joback Method is very efficient to d-limonene. An hypothesis to explain this behaviour could be that the Joback Method was not designed to represent the interaction of special bonds, like aromatic carbon – oxygen, cyclic cetone or cyclic oxygen, present in the sesquiterpenes.

Table 4: Recommend Databank of critical properties:

CAS N°	Tc (K)	Pc (Bar)	w	Zc	Method
7785-70-8	631.26	29.940	0.3172	0.2634	CG-2
104-46-1	712.67	29.396	0.5659	0.2476	MG-1
14073-97-3	668.61	25.043	0.5492	0.2424	CG-2
97-53-0	747.34	40.107	0.6345	0.2441	MG-2
5989-27-5	660.6	27.550	0.3146	0.2636	J
470-82-6	643.16	27.000	0.4190	0.2563	MG-1
89-83-8	740.69	33.472	0.3700	0.2596	MG-2
123-92-2	592.33	27.700	0.4428	0.2548	MP

It observes in the **Table 4**, that the critical properties and acentric factor are consistent with other values of analogous compounds (heavy alcohols, cetones and ethers). The critical volume was not calculate using the GC Methods, because it is well-know that they offer poor predictive values. For that reason, we use the Soave equation [14] to calculate directly the Z_c. If it is necessary to determinate the V_c with a high accuracy, it recommends to use the available experimental data of saturated liquid density in order to calculate it with the Rackett equation and a non-lineal regression method [1].

IV. CONCLUSIONS

1. It recommends to use the Marrero-Gani GC Method for the prediction of critical properties and normal boiling temperature for aroma compounds. Because this method has all chemical groups need to represent the structure chemical of sesquiterpenes and terpenes.
2. In the case that the MG produces poor results, it recommends to use the Constantinou-Gani GC Method. But it should verify that all chemical groups of elected compound are available for the calculus.
3. If the mentioned Methods give poor results or have not available the chemical groups to reproduce the chemical configuration, it recommends to use the original Joback Method.

NOMENCLATURE

MW	Molecular weight (g/mol)
P	Pressure (Bar)
T	Absolute temperature (K)
Z	Compressibility factor

Greek letters:

ω	Acentric factor

Super/subscripts:

b	Conditions in normal boiling point
c	Critical conditions

VI. REFERENCES

[1] CERPA, M.G. Tecnol. Ciencia Ed. (IMIQ), 14 (1-2), **1999**, p.19.

[2] GÜENTHER, E. The Essential Oils. Vol 1, Krieger Publishing, U.S.A., **1948**.

[3] LILEY, P.E., THOMSON, G.H., FRIEND, D.G., DAUBERT, T.E., and BUCK, E. in Perry's Chemical Engineers's Handbook, Section 2, 7Th Ed., McGraw-Hill, **1997**.

[4] POLING, B.E. PRAUSNITZ, J.M. O´CONNELL, J. The Properties of Gases and Liquids. 5Th Edition, McGraw-Hill, USA, **2001**.

[5] YAWS, C. Chemical Properties Handbook. McGraw-Hill, USA, **1999**.

[6] ESPINOZA DIAZ, M.A. GUETACHEW, T. LANDY, P. JOSE, J. and VOILLEY, A. Fluid Phase Equilib., 157, **1999**, p. 257.

[7] MARRERO-MOREJON, J. and PARDILLO-FONTDEVILA, E. AIChE J., 45, **1999**, p. 615.

[8] MARRERO, J. GANI, R. Fluid Phase Equilib., 183-184, pp. 183-208, **2001**.

[9] BAUER, K. GARBE, D. SURBURG, H. Common Fragrance and Flavor Materials. 2nd Edition, VCH Publishers, **1990**.

[10] CERPA, M.G. Tecnol. Ciencia Ed. (IMIQ), 16 (1), **2001**, p. 42-48.

[11] CERPA, M.G. Ingeniería Química, Octubre **2002**, Año XXXIV, No. 394, Ed. Alción, p. 401 – 405.

[12] MOURA, L.S. CARVALHO, R.N. MEIRELES, M.A.A. ARAUJO, M.E. Selecao de Metodos Preditivos de Propiedades Físicas de Substancias Termosensiveis. In the Proceedings of XIX Interamerican Congress of Chemical Engineering. **2000**.

[13] LEDANOIS, J.M. COLINA, C.M. SANTOS, J.W. GONZÁLEZ-MENDIZABAL, D. AND OLIVERA-FUENTES, C. Ind. Eng. Chem. Res., 36, 2505-2508. (**1997**)

[14] SOAVE, G.S. Ind. Eng. Chem. Res. 34:3981 (**1995**)