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A SIMPLE METHOD FOR PREDICTION OF THE FLASH POINT OF MONOTERPENES

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ABSTRACT

The flash point(Fp) is very important physical property used to estimate the risk of fire and fire hazard of a flammable to avoid the occurrence of fire or explosion, Monoterpenes are a class of terpenes, They have relevance to the pharmaceutical, cosmetic, agricultural, food industries and product principle of compounds volatile, and cause augment ignition the fire .In this papier, a group contribution and a group-interaction contribution approach are proposed to predict the flash point(Fp) of Monoterpenes compounds, A comprehensive database of 259 composes type monoterpenes, The best performance was observed for group-interaction contribution approach, with an average absolute relative deviation of 1.43% and a correlation coefficient of 0.906 Results also show that both models represent simple and reliable approaches for the estimation of the flash point(Fp).

Keywords: Monoterpenes; Group-interaction contribution approach; Goup contribution; Flash point(Fp); Prediction

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1. INTRODUCTION

Forest fires are one of the most recurrent disturbances in the Mediterranean region, since some Mediterranean plants produce and emit volatiles substances and highly flammable [1].

Monoterpenes are the most important component of biogenic volatile organic compound (VOC) emissions [2-4] . The first value needed to indicated the flammability is the flash point(Fp) [5][6], But the experimental measurement of flash point of the most of monoterpenes presents a big obstacle for researchers in the field of environmental health and safety (EHS).

In this study, a. Altogether, the database comprised 259 monoterpenes, ranging from 298,72to 440,76K., all reported data for flash point were considered when developing the new model. the dataset was divided two sets training and test sets, 20% and 80% respectively. database of experimental measurements has been used to develop predictive models for the Flash point (Fp) of monoterpenes based on group–interaction contributions (GIC). A survey of the literature revealed no publication related to predictive methods exclusively devoted to the prediction of the Flash point (Fp) for monoterpenes,The present study is therefore the first account of the use of a group–interaction contributions (GIC) method for the estimation of the Flash point (Fp) of Monoterpenes,There is need for the development of predictive models for Monoterpenes properties as experiments are time-consuming. Furthermore, such models can easily be implemented in process simulators for the design of processes incorporating monoterpenes.

2. METHODOLOGY

2.1 Data set

A comprehensive database of the flash point of the monoterpenes, which were collected from reliable documentary sources [4, 11-15] , Their publication was used to gather a total of 259 monoterpenes. flash point(Fp)were in the range from 185.150 to 466.150 K. Since some monoterpenes were associated with more than one source of experimental data, No data selection was performed prior to the modelling process. We were aware that in so doing, large discrepancies between experimental and calculated or predicted values using model can be expected. However, in the absence of any recommended standard procedure for Fp

measurements, it is difficult to identify beyond any reasonable doubt, erroneous values that would be excluded from the database. Hence, all reported data for flash point(Fp) were considered when developing the new model. all reported data for flash point were considered when developing the new model. the dataset was divided two sets training and test sets, 20% and 80% respectively.

2.2 METHOD

The monoterpenes were broken down into groups whose interactions independently contributed to the flash point (Fp) which was the property of interest. Variables considered in the model consisted of the sub-structures (groups), their number of occurrences as well as their interactions for each investigated monoterpene.

The objective function used in this present study during regression analysis was as follows:

The deviations are represented by the average absolute relative deviation (Eq. (1)).

$$AARD = \frac{\sum_{i=1}^{n} \left| {Fp_i^{cal}}/{Fp_i^{exp}} - 1 \right|}{n} \times 100 \qquad (1)$$

Where n refers to the total number of data points of Fp (K)

The following objective function was used in this study during regression analysis:

$$F = \sum_{i=1}^{n} \left(Fp_{i\ i}^{cal\ Exp} - Fp_i^{cal} \right)^2 \qquad (2)$$

The average absolute deviation (AAD), the percent average relative deviation (%AARD) and the correlation coefficient (R2) were calculated as a means to assess the performance of the developed model, according to the following equation:

$$AAD = \frac{100}{n} \sum_{i=1}^{n} \left| Fp_i^{exp} - Fp_i^{cal} \right| \qquad (3)$$

$$\%AARD = \frac{100}{n} \sum_{i=1}^{n} \left| {Fp_i^{cal}}/{Fp_i^{exp}} - 1 \right| \qquad (4)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} \left| {Fp_i^{cal}}/{(Fp_i^{ext} - Fp_i^{exp})} \right|^2}{\sum_{i=1}^{n} \left| {Tm_i^{cal}}/{(Fp_i^{exp} - average(Fp_i^{exp}))} \right|^2} \qquad (5)$$

The regression approach leading to the best model performance in terms of low AARD and high R2 was selected as the most appropriate for the studied property. As part of this study,

the validation set comprised 208 data points used to test the developed model. Although the correlation and the validation sets were selected randomly, care was taken to ensure that during the modelling process, molecules were decomposed into fragments with all the groups found to have adequate frequency in the selected monoterpenes.

3. RESULTS, DISCUSSION AND EXEMEPLES

In the present study, the molecular structure dependence of the flash point (Fp) of monoterpenes is based on principles outlined in previous works owed to Marrero and Pardillo [16] as well as mokadem et al. [17,18]. Because the group-interaction contribution approach gave the best results for the studied property[17,18]. However, the statistical parameters reflecting the performance of the group contribution approach were close to those of the group-interaction contribution method, both models are proposed for the estimation of the flash point (Fp) of Monoterpenes. After computing group interaction parameters from the experimental data using the computational scheme shown literatures [17,19], the following equations were obtained:

$$Fp(K)_{GC} = 249{,}418 + \sum_j n_j \Delta C_j \qquad (6)$$

$$Fp(K)_{GIC} = 281{,}977 + \sum_j n_j \Delta C_j \qquad (7)$$

where n_j is the number groups of type *j* in the molecule respectively.All group group-interaction contribution parameters and group contribution parameters are reported in Table 1 and 2 respectively.

Table 1. Contributions of Simple Groups

	Interactions	Contribution		Interactions	Contribution
1	CH_3	00,4864	13	-OH (alcohol)	35,0895
2	$-CH_2-$	08,8164	14	-O-	11,8923
3	>CH-	11,3896	15	-CO-	39,5746

Table 1. Continued

	Interactions	Contribution		Interactions	Contribution
4	>C<	18,1484	16	-CHO-	33,5620
5	-CH=	12,4930	17	-COOH	34,2517
6	>C=	18,0339	18	-COO-	39,9049
7	H2C=	-3,7129	19	-OH (phenol)	28,8663
8	-CH2- r	07,8705	20	-O- r	12,5637
9	>CH- r	11,8916	21	-CO- r	42,9479
10	>C< r	07,3330	22	-SH	22,0912
11	-CH= r	10,2393	23	=S	21,7086
12	>C= r	14,3069			

Table 2. Contributions of Group Interaction

	Interactions	Contribution		Interactions	Contribution
1	CH_3 &-CH_2-	-8,3075	29	>C< &>C=	2,5550
2	CH_3 & >CH-	-2,5818	30	>C< &-CO-	14,5672
3	CH_3 & >C<	-1,1339	31	>C< &-CO_2-	42,7811
4	CH_3 &-CH=	0,2443	32	>C< &-O-	6,0630
5	CH_3 & >C=	0,2038	33	>C< & -S-	40,3599
6	CH_3 & -CO-	22,4127	34	>C< &Bz	31,3931
7	CH_3 &-CO_2-	10,2858	35	H2C= &-CH=	4,1231
8	CH_3 &-O-	14,7259	36	H2C= & >C=	-0,2269
9	CH_3 & Bz	19,0818	37	-HC= & -HC=	7,8206
10	CH_2- &-CH_2-	7,2229	38	-HC= & >C=	8,5040
11	CH_2- & >CH-	5,2331	39	-HC= &-CO-	30,2924
12	CH_2- & >C<	5,6829	40	-HC= &-CO_2	36,5273
13	CH_2- &-CH=	8,6601	41	-HC= & -O-	-23,5929
14	CH_2- & >C=	4,2004	42	-HC= et Bz	51,6775
15	CH_2- &-CO-	22,4073	43	>C= &> C=	10,4362
16	CH_2- & -CO_2-	30,6433	44	>C= & -CO-	28,5117
17	CH_2- & -O-	13,1198	45	>C= & -CO_2	40,0412
18	CH2- & Bz	39,6962	46	>C= & -O-	40,6198
19	>CH- & >CH-	4,9824	47	>C= & =S	0,0000
20	>CH- & >C<	1,6438	48	H-&-S-	0,0000
21	>CH- & -HC=	7,8176	49	H- &-O-	33,0221
22	>CH- & >C=	3,4135	50	H- &-CO-	10,4524
23	>CH- & -CO-	21,5313	51	H &-CO_2-	7,1807
24	>CH- &-CO_2-	32,2919	52	BZ &-O-	0,1745

25	>CH- &-O-	10,1047	53	BZ &-CO-	37,2572
26	>CH- & Bz	23,6340	54	BZ &-CO_2-	53,5455
27	>C< & >C<	-5,8529	55	-O- &-O-	3,3994
28	>C< & -HC=	5,0056			

A comparison between experimental and calculated the flash point temperatures are made in Figures 1 and 2 for the group-interaction contribution and the group contribution models respectively. It can be seen that most of the points of the plot are close to the bisector. This indicates consistency between predicted or calculated and experimental data.

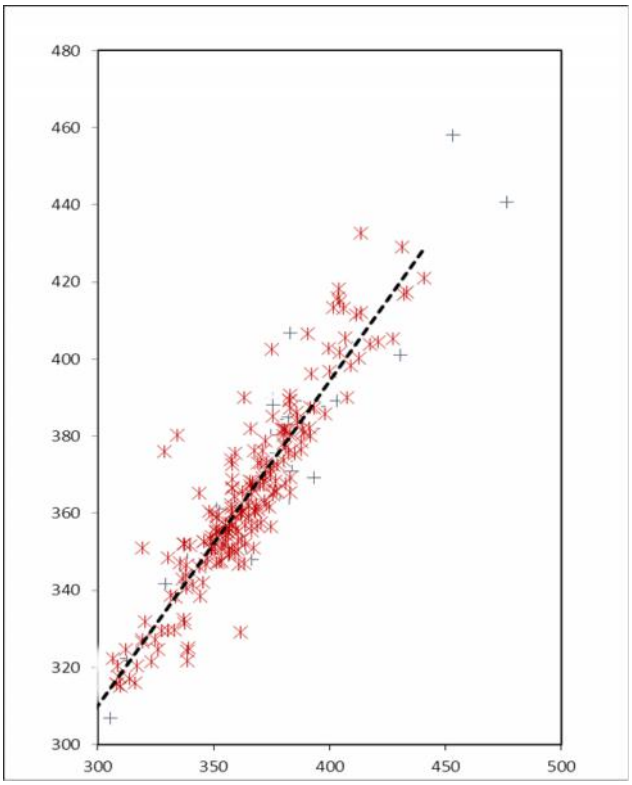


Fig.1. Comparison between experimental and predicted Fp using the group contribution method

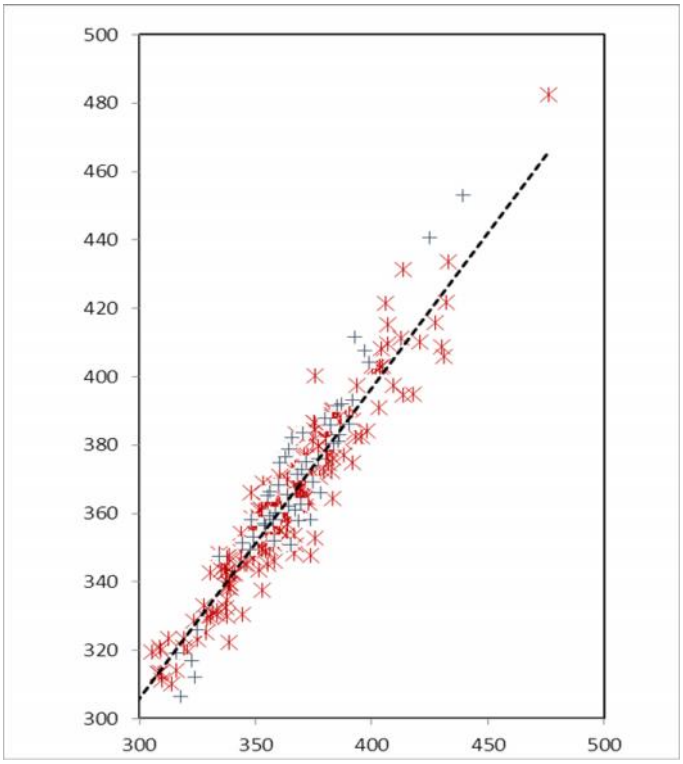


Fig. 2. Comparison between experimental and predicted Fp using the group-interaction contribution method

Table 3: The statistical parameters for the developed methods

		group contribution method	group-interaction contribution method
Training set	**R2**	0.841	0.906
	%AARD	1.66	5.05
	Standard Deviation	6.148	5.48
	No of data points	208	208
Validation set	**R2**	0.894	0,908
	%AARD	1.894	5.57
	Standard Deviation	6.665	6.07
	No of data points	51	51
Overall set	**R2**	0.841	0.906
	%AARD	1.73	1.43
	Standard Deviation	6.223	5.14
	No of data points	259	259

Relative deviations between experimental and calculated data are further presented in Figures 1 and 2. As explained previously, no action was taken to exclude ‘doubtful’ or presumably

inaccurate experimental data. For this reason, high deviations could be observed for some Monoterpenes. Nevertheless, for the the group-interaction contribution, there are only 8 data points with an absolute relative deviation greater than 10 %, i.e 3.09% (see table 4) of the total number of Monoterpenes in the database. The same applies to the group-interaction contribution. More details on the discrepancies between calculated and experimental values for each and every Monoterpenes contained in the database are available in the supplementary materials appended to this article.

Table 4 . Distribution of fitting errors in percentage among compounds

	GC	**GIC**
Monoterpenes	259	259
AARD% (%)	1,73	1,43
Δ Fp min (%)	0,00	0,00
Δ Fp max (%)	14,35	6,97
$\lvert \Delta Fp \rvert$ (%) < 5	227	251
$\lvert \Delta Fp \rvert$ (%) [5 – 10]	12	8
$\lvert \Delta Fp \rvert$ (%) > 10	2	0

The regression approach (i.e. group-interaction contribution or group contribution approach) leading to the best model performance in terms of low AARD and high R2 is generally selected as the most appropriate for the studied property. The training set used for developing the models of this present study consisted of 208 monoterpenes. The validation set comprised 51data points used to test the predictive ability of developed model. The correlation and the validation sets were selected randomly and care was taken to ensure a fair representation of all substructures in the selected monoterpenes. A different approach to the estimation of flash point(Fp) using a GC method and CIG ,It is worth emphasising that as compared to conventional group contribution methods, group-interaction contribution (GIC) models have the advantage of differentiating between values related to isomers. Considering the large database used, the obtained results (R2 =0.841 and 0.906 as well as % AARD=1.73and 1.43%) suggest that the newly developed models are generally reliable as predictive tools for the flash point (Fp) of Monoterpenes.

The performance of the developed models can also be evaluated through statistical parameters provided in Tables 4. Due to the lack of similar work in the open literature, no comparison

could be made between the presented models and any other method.

A closer examination of these two models leads to the following observations: i) the group-interaction contribution model exhibit the highest coefficient correlation and the highest average absolute relative deviation ii) R2 and AARD values for the two models are very close to each other; iii) both models are generally consistent with experimental data.

Examples of application of the proposed model in illustrated for 4 compounds of monoterpenes method in Table (5)

Table 5. Worked example for Fp prediction using the developed GIC model

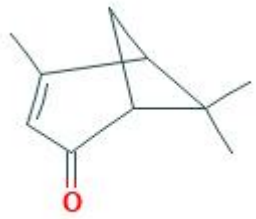
Compounds	**Fp^{exp} (°C)**	**Interactions**	**Frequency**	**Contribution**
 Verbenone (4,6,6-trimethylbicyclo[3.1.1] hept-3-en-2-one)	358,16	CH3 & >C<	2	-1,1339
		CH3 & >C=	1	0,2038
		CH2- &>CH-	2	5,2331
		>CH- & >C<	1	1,6438
		>CH- &-HC=	1	7,8176
		>CH- & >C=	1	3,4135
		>CH- & -CO-	1	21,5313
		-HC= & >C=	1	8,5040
		-HC= &-CO-	1	30,2924
		Fp_{GIC}^{cal} (°C) = 357,40 AARD%=0,21		
		CH3	3	0,4864
		-CH2- r	1	7,8705
		>C< r	1	7,3330
		>CH- r	2	11,8916
		-CH= r	1	10,2393
		>C= r	1	14,3069
		-CO-r	1	42,9479
		Fp_{GC}^{cal} (°C) =368.705 AARD%=2.95		

Table 5. Contenued

Table 5. Continued

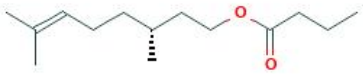
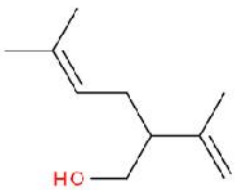
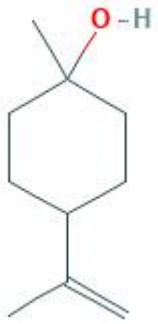
Compounds	Fp^{exp} (°C)	Interactions	Frequency	Contribution
Citronellyl butyrate (3,7-dimethyloct-6-enyl butanoate) 	385,94	CH3 & -CH2-	1	-8,3075
		CH3 & >CH-	1	-2,5818
		CH3 & >C=	2	0,2038
		CH2- &-CH2	3	7,2229
		CH2- & >CH-	2	5,2331
		CH2- &-CH=	1	8,6601
		CH2- &-CO	2	22,4073
		-HC= &>C=	1	7,8206
		Fp_{GIC}^{cal} (°C) = 382,08 AARD%=0,999		
		CH3	4	0,4864
		-CH2-	6	8,8164
		>CH-	1	11,3896
		-CH=	1	12,4930
		>C=	1	18,0339
		-COO-	1	39,9049
		Fp_{GC}^{cal} (°C) = =386,08 AARD%=0,038		
Lavandulol (5-methyl-2-prop-1-en-2-ylhex-4-en-1-ol) 	361,49	CH3 & >C=	3	0,2038
		CH2- & >CH-	2	5,2331
		CH2- &-CH=	1	8,6601
		CH2- & -O-	1	13,1198
		>CH- &>C=	1	7,8176
		H2C= & >C=	1	-0,2269
		H- &-O-	1	33,0221
		Fp_{GIC}^{cal} (°C) = 359,548 AARD% =0,54		
		CH3	3	0,4864
		-CH2-	2	8,8164
		>CH-	1	11,3896
		-CH=	1	12,4930
		>C=	2	18,0339
		H2C=	1	-3,7129
		-OH (alcohol)	1	35,0895
		Fp_{GC}^{cal} (°C) = = 357,123 AARD%=1.21		

Table5. Continued

Compounds	Fp^{exp} (°C)	Interactions	Frequency	Contribution
 beta--Terpineol (1-methyl-4-prop-1-en-2-ylcy clohexan-1-ol)	360,38	CH3 & >C<	1	-1,1339
		CH3 & >C=	1	0,2038
		CH2- &-CH2-	2	7,2229
		CH2- & >CH-	2	5,2331
		CH2- & >C<	2	5,6829
		>CH- &>C=	1	3,4135
		>C< &-O-	1	6,0630
		H2C= & >C=	1	-0,226
		H- &-O-	1	33,0221
		Fp_{GIC}^{cal} (°C) =359,59 AARD%=0,22		
		CH3	2	0,4864
		>C=	1	18,0339
		H2C=	1	-3,7129
		-CH2- r	4	7,8705
		>CH- r	1	10,2393
		>C< r	1	7,3330
		-OH (alcohol)	1	35,0895
		Fp_{GC}^{cal} (°C) = =350,50 AARD%=2.74		

4. CONCLUSION

A Two simple method are presented in this work for the estimation of the flash Point of monoterpenes; one is GC and the other CIG, This method Similar to the estimation of Tg, mokadem's [8] . A total of 259 monoterpenes . Its other merit is owed to diverse monoterpenes comprising the database, i.e. altogether 208 data points for 51 monoterpenes involved in the modelling process. The GC method was found slightly superior to the CIG method one. Acceptably low deviations between experimental values and those predicted in this study (AARD=1.73 and 1.43 %) coupled with correlation coefficients of 0.841And 0.906 suggest that the model is generally accurate and reliable.

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