Group contribution method for the estimation of flammability proprieties

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***Abstract*-This Work presents a new group contribution method development for estimation of flash point of organic compounds values while it is one of the important variables used for review the fire and explosion hazard. The proposed method is based on the molecular structure of organic compound, and the development of experimental data set base including 1685 organic compound. The result are discussed and compared with precedent works. This model shows a very low average relative error of 2, 43 % and an average absolute error of 9.22 K.**

***Keywords*— flash point, group contribution.**

Introduction

The flash point is one of the most important properties in chemical process safety. It is used to evaluate the flammability and combustibility of combustible material and also to characterize the fire and explosion hazard. The flash point gives the knowledge needed for the handling, storing and transporting of any combustible material- solid, liquid or gas. The flash point is the lowest temperature at which a liquid gives off sufficient vapor to form an ignitable mixture with air near the surface of the liquid or within the vessel used[1]. A compound with a higher flash point is less flammable or dangerous than one with a lower flash point.

The experimental determination of flash point can be made generally by the open cup and the closed cup methods [2]. It is one of the ways to have accurate and reliable data. However, the experimental determination of flash point can be expensive and very difficult especially if the compound concerned is metastabl, toxic, or has other hazardous properties. Moreover, the large gap between the number of compounds registered and the available experimental values of flash points of compounds is constantly increasing. Thus, a model that can provide reliable estimates of FP for a wide range of compounds is needed.

Different approaches have been presented in the literature for the prediction of FP of pure compounds. A good review on flash point estimation has been already published [3, 4, 5]. Tree major approaches which include the group contribution (GC)strategy, the quantitative structure–property relationship(QSPR) approach and empirical correlations have been developed for the estimation of the FP. Table 1 summarizes these previous works. It must be note that it is difficult to provide a comprehensive comparison between these previous works. This is due to several factors such as accuracy of the model, simplicity of the model, range of applicability covering a large number of compounds with different chemical compounds.

TABLE I
DIFFERENT APPROACHES FOR THE PREDICTIVE VALUE OF AVAILABLE FP PREDICTION METHODS FOR PURE COMPOUNDS, AS CHARACTERIZED BY AVERAGE ABSOLUTE ERRORS (AAE), AVERAGE RELATIVE ERRORS (ARE) AND R2

Ref	year	Dat set	method	AAE	ARE	R²
[6]	2014	1170	GC	13.3	3.5	/
[7]	2011	1471	Correlation	/	2.4	0.97
[8]	2008	1030	QSPR	10.2	/	0.96
[9]	2008	1378	ANN	8.1	/	0.97
[10]	2011	1062	Correlation	4.65	1.32	/

Based on both simplicity of the model and accuracy of the model, the group contribution approach is more convincing than the others approaches. This approach which is widely used to estimate and predict thermodynamic and other properties of pure organic compounds and mixtures [11 ,12], needs mainly tabulated groups (molecular fragments) where it is assumed that the property value of the molecule is a function of the contribution of all the groups and that a property value of any group has the same contribution in all molecules. The group contribution approach does not need any other physical properties, does not require specialized software to implement (simple procedure of calculation of group from SMILES of chemical structure) and has the advantage of quick predictions without requiring significant computing power.

In this study we developed a simple straightforward method for the estimation of the flash point of organic compounds using the third order of group contribution method with two models one based on only the molecular structure and the second base on molecular structure.

Materials and methods:

Data base: The quality of a predictive method depends on a variety factors such as quality of data set used in its development and validation. In order to provide this fact, a wide variety of classes of organic compounds containing hydrocarbons, halogenated hydrocarbons and compounds

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contain O, N and S atoms were selected in data set base. The description of this data-set based on various classes of organic compounds is given in Figure1.

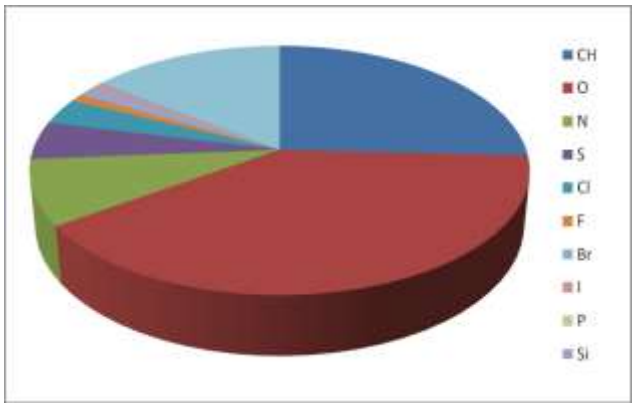

Fig. 1: class wise description of data sets base.

The data set base involves reliable experimental FP temperature of 1685 pure compounds have been employed for developing and testing an accurate group contribution model, 80% of the main data set are selected for training set (1348 compounds) and 20% are used for the test set (337 compounds). The first one is used to develop the model and the second to evaluate the predictive power of the model. In addition, ebullition temperature TB is given for each compound in Kelvin (K) to facilitate the comparison.

Method development:

The group contribution method is base on the molecular structure of a compound. Is considered to be divided on three categories of groups: first, second and third order groups. The first one is used to describe a variety of organic compounds while the second and the third categories are to prove more precise structures information about the fragments of the compounds. After finishing the data set base of FP defined by the collection of structural groups. And the fragmentation of the molecular structure was performed by an automatic program using Marrero and Gani [13]. In this work the data set was divided into two sub-data sets using semi randomly choice. Indeed if a compound is selected and if this compound is described by one of the irrelevant groups: group having their contribution value generated by less than three compound , this compound is removed from the test set , this is important to avoid the lack of some necessary data for training step and to allow better regression of same model parameters.

In this work a simple practical multivariable nonlinear model is proposed. In fact, in a several mathematical functions were tested to represent the FP model. From many researches in the literature and a variety functions tests, two of the best forms to be a simple nonlinear and more practical ones. The first model is based only on the group's contribution of the molecular structures. It is as follows:

$$Fp = k1\left(\frac{k2\ A}{1 + k2A}\right) + k3$$

A: is obtained with the addition of group contributions for each molecule compositions:

$A=\sum_i NiCi$

Ni : frequency of occurrences of n group in a molecule

Ci : contribution of n group

K1 =546,65 ; K2 =-0,179 ; K3=226,66.

50 group contributions are defined corresponding to each group. For readability of the display the last are not displayed.

Results and discussion

The Performance of this model for the prediction of FP values of organic compounds was evaluated, analyzed and discussed. Generally, in the case of large data set it is necessary to estimate the detail results of the proposed model.

The statistical performance indicators used in this work are coefficient of determination (R2) standard deviation (SD) average deviation (AAD) and the average relative deviation (ARE) for this model based on molecular structure is shown in Table 3.

TABLE 2
RESULTS OF THE PREDICTED MODEL OF FP, AS CHARACTERIZED BY AVERAGE ABSOLUTE ERRORS (AAE), AVERAGE RELATIVE ERRORS (ARE) AND R2 AND STANDARD DEVIATION SD

Total compound	*N°*	**ARE(%)**	**AAD*K*)**	**SD (*K*)**	*Dmax*(*K*)	R^2
Training	1328	2,34	8,29	8,87	81,30	0,9877
Test	332	3,02	10,75	12,89	113,30	0,9757
Total	1660	2,68	9,52	10,88	97,30	0,9817

The prediction deviations according to their experimental values are displayed in the figure 1. It is noted that the prediction error does not exceed 12, 4 K, these results confirm the credibility of our model over the results of the methods found in literature

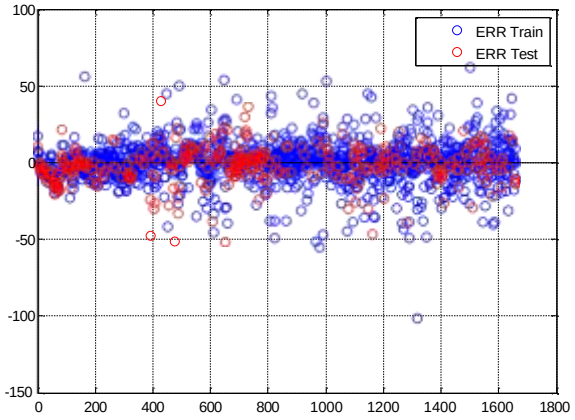

Fig 2: plot the error test and training

The following figure Fig2 shows the dispersion of the average relative deviation in the four intervals. So it is seems

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that over 70% of the values of flash point are predicted with an instrumental precision 2,5% .This means that our objective is achieved.

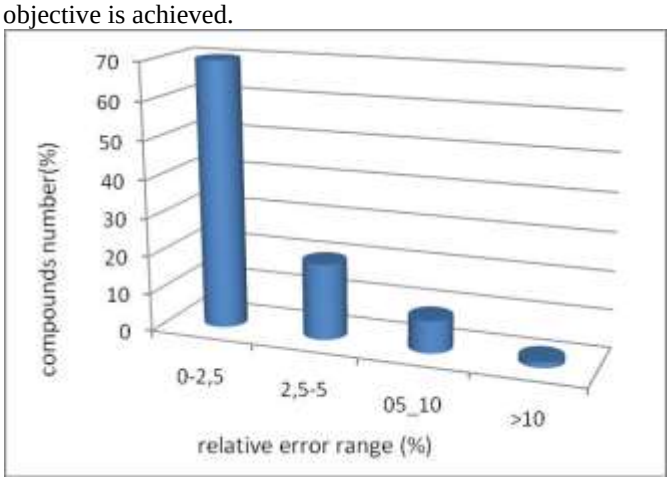

Fig 3: Percentages relative error range for FP

CONCLUSIONS

A new method has been developed for simple and reliable predictions of flash point of organic compounds by GC model. This model is based only on molecular structure of the compounds

The reliability of the methodology presented here is relatively good compared to the using the training test data sets of 1348 compounds and was tested using test data set of 337 compounds. This method produces an average relative error (ARE) 2,68 %, coefficient of determination (R^2 0,9817) standard deviation (SD) 10,88 K and the average deviation (AAD) 9,52 K Investigation of the capability of the proposed method for evaluated of the flash point of various compounds demonstrates its wide range of applicability compared with the available method in the literature.

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