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Empirical Method for Representing the Flash-Point Temperature of Pure Compounds

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Ⓢ *Supporting Information*

ABSTRACT: Flash point temperature is one of the most-widely used physical properties for the evaluation of the flammability hazard of combustible liquids. In this communication, an empirical method involving normal boiling-point temperature and number of carbon atoms of the pure compounds is presented for accurate representation of the flash-point temperature of pure substances. A total of 1471 pure compounds belonging to 77 chemical families were used to develop a general correlation. The global absolute average deviation of the model results from experimental values is 2.4%. A successful comparison is finally made with respect to some of the methods proposed in the literature, which apply a similar approach for calculation of the flash-point temperature of pure compounds.

1. INTRODUCTION

Flash-point (FP) temperature is defined as the lowest temperature at which a liquid produces enough vapor to ignite in air at atmospheric pressure when an ignition source such as an external flame, for instance, is applied under specified test conditions. The FP is important characteristic of liquid fuels, but is also used to describe other liquids. Above the FP temperature, a liquid is capable of producing enough vapor to form a flammable mixture with air.[1,2] FP values are important information for the safe transportation, storage, and use of combustible liquids, and their accurate knowledge is drastic for the design and construction of chemical processes and plants.[1,2]

Experimental measurement of flash-point temperature is costly and may contain high experimental uncertainties.[3] Calculation of the flash point of pure chemical compounds has therefore been the subject of many theoretical investigations. A preliminary study shows that the proposed methods may fall into three main categories: "empirical correlations", "quantitative structure—property relationship (QSPR)-based" methods, and "group contribution (GC)" methods. Good reviews of these methods are available in the articles of Catoire and Naudet,[4] Vidal et al.,[5] and Liu and Liu.[6]

The first group of methods contains the empirical correlations which need some physical properties such as normal boiling point temperature (NBP), density, vapor pressure, critical properties, and enthalpy of vaporization, *etc*. We can refer to the empirical correlations presented by Prugh,[7] Fujii and Herman,[8] Patil,[9] Suzuki et al.,[10] Satyarayana and Kakati,[11] Satyarayana and Rao,[12] Metcalfe and Metcalfe,[13] Hshieh,[14] and Catoire and Naudet.[4] Accuracy of these kinds of empirical correlations is directly dependent on the accuracy of the measured physical properties and the empirical methods used for their estimation. The empirical correlations may include some drawbacks.[2] For instance, if only one of the aforementioned properties is not available, it is not possible to estimate the FP property.[2]

Category 2 includes the QSPR methodology, in which molecular-based parameters that are called "molecular descriptors" are used.[1,15−23] Molecular descriptors are numeric characteristics of a pure compound directly calculated from its molecular structure with special algorithms. Several molecular descriptors (normally less than 10 molecular descriptors)[1,2] are selected to correlate the desired property of pure compounds. Several QSPR methods have been proposed in the literature to calculate the FP of pure compounds: Tetteh et al.,[24] Katritzky et al.,[25,26] and Gharagheizi and Alamdari.[1] The most important disadvantage of these kinds of methods is the complex procedure of calculation of some molecular descriptors from the chemical structure. As a result, these correlations are not generally simple to develop.[1,2]

The last group of methods contains the group contribution methodology. Application of these methods for calculation of the FP property of pure compounds is limited to the works of Albahri,[27] Pan et al.,[28] and Gharagheizi and co-workers.[2] Albahri[27] applied the *GC* methodology to predict the FP of about 287 pure hydrocarbon compounds. Additionally, the *FP* of 92 pure alkanes was calculated by Pan et al.[28] using the same approach. Although this technique results in good calculation/prediction of the flash points of the pure compounds, its application is generally limited to a particular group of materials.[1,2]

Comparison between these three groups of methods is pretty difficult, because of the fact that there are several factors to be considered in such a comparative study, for instance, simplicity and accuracy of the model, simplicity of the parameters, and comprehensiveness of the method for covering a wider range of

investigated chemical compounds. On the basis of the simplicity of the method, the first category seems to be more convincing than the others. In addition, on the basis of the accuracy and comprehensiveness of model, the third group appears to be more convincing than the others.[2] In a recent comparative study, it has been concluded that the group contribution methods are applicable to a wider range of chemical species, whereas QSPR methods are occasionally specific to a particular class of chemical compounds.[29]

In this work, a simple, accurate, and comprehensive empirical method belonging to the first category using two physicochemical parameters including the normal boiling point and the number of carbon atoms of pure compounds is presented for accurate and successful representation of the flash point temperatures of 1471 pure compounds form 77 various chemical categories.

2. MATERIALS

DIPPR 801[30] database was found useful for applications in developing new methods for representation or prediction of physical properties because it contains a large number of pure compounds with their evaluated physical properties. This database was used here to provide a data set for representation of flash points. A total of 1471 pure compounds from 77 different chemical groups are investigated, and the related values of the NBP and number of carbon atoms are considered for the calculations. These compounds are presented as Supporting Information.

3. RESULTS AND DISCUSSION

In several previously proposed methods for estimation of the FP property,[4,7–9,11–14,31] normal boiling point (which provides a convenient way to account for the tendency of the fluid to evaporate[32]) plays a key role. Therefore, we consider this property as the basic parameter of the proposed empirical correlation. From a theoretical point of view, FP is a flammability characteristic of a substance, which is related to the burning process. It is consequently easy to conclude that the parameters which relate burning chemical reaction to the flash-point temperature may improve the accuracy of the FP estimation methods. It should be noted that we tried several parameters of this kind as the parameters of the empirical correlation including number of halogen, sulfur, and oxygen atoms, number of non-H bonds, and number of three-membered and eight-membered rings. (The results of these calculations are freely available upon request to the authors.) As a result, number of carbon atoms (n_C) was found to be more appropriate parameter than the others (the addition of six aforementioned parameters to the empirical correlation slightly improves R^2 from the value of 0.979 to 0.983, but considering n_C as a parameter of the empirical correlation changes the value of R^2 from 0.953 to 0.979). It should be noted that correlating the flash-point temperature of n-alcohols with n_C has also been already proposed by Rowley et al.[33] n_C is somehow a measure of flammability capacity of a compound. Hence, this parameter is applied as well as NBP to correlate the model. The following empirical correlation has been obtained from regression of the calculated results over the experimental flash-point temperature values:

$$FP = -18.44 + 0.8493 \times NBP - 3.723 \times n_C \quad (1)$$

where n_C is the number of carbon atoms as pointed out earlier, and FP and NBP are the flash-point and normal boiling point temperatures of a desired pure compound in K, respectively. The statistical parameters of the model are shown in Table 1.

Table 1. Statistical Parameters of the Presented Empirical Correlation

statistical parameter	value
square correlation coefficient R^2	0.979
absolute average deviation[a]	2.4%
absolute average error[b]	8.1 (K)
standard deviation error	7.39
root mean square error	10.6
N^c	1471

[a] %AAD = $(100/N)\Sigma_i^N(|\text{calcd}(i) - \text{expt}(i)|)/\text{expt}(i)$ [b] %AAE = $(100/N)\Sigma_i^N|\text{calcd}(i) - \text{expt}(i)|$ [c] Number of pure compounds.

The absolute average deviations (AAD (in percent)) and absolute average errors (AAE (K)) of the results of flash-point temperature calculations for each group of pure chemical substances are reported in the Supporting Information. This information also compares the obtained deviation values with the results of three similar methods proposed by Catoire and Naudet,[4] Patil,[9] and Hshieh.[14] The average absolute deviation of the presented empirical corelation results from the experimental values is the lowest one among the other three. It should be noted that the method proposed by Catoire and Naudet[4] has the drawback that it results in an infinite value for the compounds without the carbon atoms; that is, it can be only used for the compounds containing carbon atoms in the chemical structure. Hence, the total absolute average deviations/errors of this method results have been obtained eliminating these kinds of compounds. The calculated values along with absolute deviation (%)/error (K) of the flash-point temperatures from experimental data using the preceding four methods for all of the 1471 compounds in the database are presented as Supporting Information. Also, the chemical structures of all of the investigated compounds have been sketched and reported as Supporting Information.

For a more general comparison, the calculated values of the FP property have been compared with the results of other approaches[1,2,10,24–26] in a table in the Supporting Information. This table compares the obtained deviation values with similar models proposed by Gharagheizi and Alamdari[1] and Gharagheizi et al.[2] To the best of our knowledge, there are no such detailed reported deviations for each chemical family in the literature. As can be seen, the average absolute deviations of the presented method results from the experimental values[30] are lower than those from other methods although it is a simple tool which only uses two physical properties of the pure compounds including the normal boiling point temperature and number of carbon atoms, as mentioned earlier. It should be noted that other properties such as density, vapor pressure, critical properties, enthalpy of vaporization, or molecular descriptors of the components are not required as the proposed model parameters. This fact results in much simplicity of the application of the proposed empirical correlation compared with most of the existing methods in the literature.[1–14,24–29,33] Moreover, a comprehensive comparison of different correlations corresponding to flash-point temperature values can also be found in the work of Rowley et al.[33]

The uncertainties on the experimental flash-point data should be considered in order to estimate the uncertainties of calculated FP values. These uncertainties are not always reported along with the experimental data.[31] It is sometimes stated[4,29,30] that the maximum uncertainty on calculated FP values are generally ±3 K for organic liquids[4] or ±4.4 K for paraffins.[29] However, the experimental values
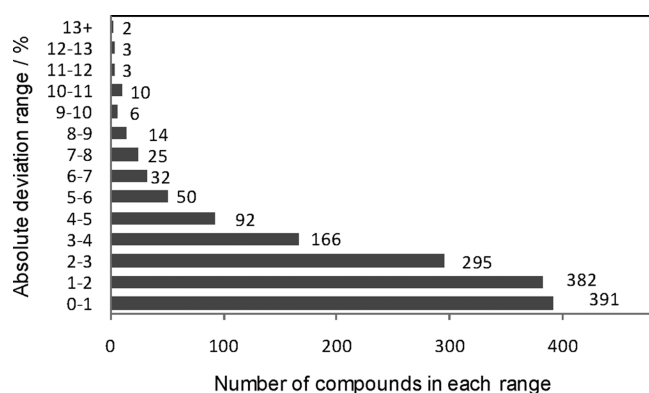
Figure 1. The absolute deviation ranges of the results obtained using the presented model versus the corresponding number of pure compounds in each range.

of DIPPR 801[30] database are generally reported to have uncertainties less than 10% in the case of availability.

Another element to consider is that the maximum absolute deviation of the calculated flash-point temperatures from experimental values[30] is approximately 16%, whereas it is much higher regarding some of previously reported methods[1–14,24–29] (see the Supporting Information), for instance, the maximum AD% of the results of the method proposed by Hshieh[14] from experimental values[29] is around 84%. The absolute deviation ranges of the results obtained using the presented empirical correlation and the corresponding number of pure compounds in each range are shown in Figure 1.

Another element that can be inferred from the results (see the Supporting Information) is that the calculated FP of methane as the first element of the *n*-alkane chemical family has a somewhat high deviation from the experimental value. However, this is true just for methane and not for any other root substances of other chemical families (e.g., ammonia).

An important point should not be omitted from our discussion. The presented empirical method is able to calculate the flash-point temperatures of the studied chemical families. It means that the experimental data of all of the investigated chemical families have been used to develop the empirical correlation. Because of this, use of the proposed empirical correlation to predict flash-point temperatures of other substances from the chemical families excluding those investigated may be conservative. This prediction is even hardly possible using the more complicated methods, for example, artificial neural network-group contribution (ANN-GC) or QSPR.[1,2]

4. CONCLUSION

Flash-point temperature is a key parameter for evaluation of the flammability hazard of combustible liquids. In this study, an accurate, and very simple empirical method for evaluation of the FP property of pure compounds was presented. The method requires only the normal boiling-point temperature and number of carbon atoms of a desired pure substance. The DIPPR 801[30] was considered as the experimental database. The proposed empirical correlation shows an average absolute deviation of 2.4% for the calculated results from the experimental values. Finally, a comparison was made between the presented empirical correlation results and the similar previously reported models in the literature.[4,9,14] It was inferred that the presented empirical

correlation brings about the least absolute average deviations of the results from experimental values. The simplicity and easy to use characteristics of the presented method along with acceptable accuracy of the results are among its advantages over the previously reported methods[1–14,24–29] for evaluation of the flash-point temperature of pure compounds. Therefore, one can use the benefits of the rapid calculation/estimation of the FP temperature of a desired compound, especially in urgent situations of the chemical processes.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Calculated flash-point temperature values accompanied with absolute deviations/errors of the proposed empirical correlation results and some of the previously presented models from the experimental values; structures of the investigated chemical species. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ NOMENCLATURE

AAD = absolute average deviation, (%)
AAE = absolute average error, (K)
AD = absolute deviation
ANN = artificial neural network
calcd = calculated value
expt = experimental value
FP = flash point temperature, (K)
GC = group contribution
i = ith pure compound
N = number of pure compounds in the database
NBP = normal boiling point temperature, (K)
n_C = number of carbon atoms
QSPR = quantitative structure-property relationship
R^2 = square correlation coefficient

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