Power System Technology
Volume 49, No. 1, 2025
ISSN: 1000-3673

A Novel Group-Interaction Contribution Model for Predicting the Auto-Ignition Temperature of Different Classes of Hydrocarbon Species Isomers

Khadra Mokadem
Kasdi Merbah Ouargla University, VPRS Laboratory, B.P. 511, 30000, Ouargla, Algeria.
Fatiha Chelgham
Kasdi Merbah Ouargla University, VPRS Laboratory, B.P. 511, 30000, Ouargla, Algeria.
Mohammed ELamine Messaoudi
Kasdi Merbah Ouargla University, VPRS Laboratory, B.P. 511, 30000, Ouargla, Algeria.
Zineb Ghiaba
Kasdi Merbah Ouargla University, VPRS Laboratory, B.P. 511, 30000, Ouargla, Algeria.
Mohamed Mokadem
Kasdi Merbah Ouargla University, VPRS Laboratory, B.P. 511, 30000, Ouargla, Algeria.
Abdulqader Saad Abed
Ministry of Water Resources, State Commission for the Operation of Irrigation and Drainage Projects, El Anbar, Iraq.

Abstract

Auto-ignition temperature (AIT) is among the most important physics properties, and this is an optimal candidate for studying and assessing hazards, safety, and environmental impact, especially for petroleum products. However, the lack of such data prevents this from happening. This is the temperature at which the compounds are ignited without the presence of any flammable source, such as a flame or other sources. In this study, a comprehensive set of experimental data for 280 hydrocarbons with different classes (alkanes, alkenes, alkanes, cyclic alkanes, cyclic alkenes, benzene, naphtha, and anthracene). The group-interaction contribution (GIC) method was accredited to estimate and predict the auto-ignition temperature (AIT). The statistical coefficients were obtained from the correlation coefficient (R^2) and the relative error (%AARD), 0.93 and 3.56 respectively.

Key Words: Group-Interaction Contribution, Hydrocarbons, Molecular Structure, Auto-ignition Temperature, Estimation.

1. Introduction

In one of these phenomena, however, there are a number of chemical substances, the most important of which are hydrocarbons, which can ignite spontaneously when they reach a certain temperature. where chemicals are present, most importantly hydrocarbons, which can ignite self-ignition when they reach a certain temperature, known as the auto-ignition temperature, which is the lowest temperature at which the substance ignites (hot flame in the air at a certain atmospheric pressure) without the aid of external energy sources such as sparks or flames. sparks or flames. It is one of the most important factors affecting the environment and has been classified as one of the main

causes of accidents that leave behind significant damage to humans and the environment in which they live. Predicting the Auto-ignition temperature (AIT) is one of the most important units of safety, prevention, and industrial security [1-2].

The importance of the auto-ignition temperature (AIT) lies in the transportation and storage of chemicals and hydrocarbons, as they are sensitive and may ignite or explode at any moment. The chemical composition of elements (the chemical structure of compounds) is the main reason for the change in the auto-ignition temperature of compounds, even though they have the same constituent atoms, namely carbon (C) and hydrogen (H). There are several factors, including chain length, the methyl and ethyl groups attached to the chain (alkyl radicals), unsaturation such as alkenes and alkynes, cyclic structures, and aromatic structures. Each type of chemical structure has a specific effect on the auto-ignition temperature [3].

Several factors can influence the experimental values of auto-ignition temperature (AIT), including the chemical and physical properties of the material, as well as the test pressure, oxygen concentration, and volume. Therefore, determining the auto-ignition temperature (AIT) experimentally is difficult and may even be impossible for some hazardous materials. For this reason, predicting the auto-ignition temperature of hydrocarbon compounds is the most effective solution to facilitate the process of avoiding chemical hazards [1,4].

There are several methods in the literature for estimating the auto-ignition temperature (AIT), the quantitative structure-property relationship (QSPR)[5-6] , and artificial neural networks (ANN) [7-8]. Despite the efforts made in these models, they are not sufficient due to the limited and insufficient availability of experimental information.

The Group-Interaction Contribution (GIC) method is the optimal method used to estimate the physical and chemical properties and their ability to differentiate between engineering compounds such as isomers [9-10].

The study aims to provide a simple model for estimating and predicting the auto-ignition temperature using the Group-Interaction Contribution (GIC) with high accuracy compared to experimental results. It also compares the models obtained with previous models in terms of accuracy, reliability, and predictive power. This modeling thus reflects the following benefits:

- The ability to predict the auto-ignition temperature (AIT) based on the formula for compounds that do not belong to the database used, without the need for any experiments or testing.
- More approaches that contribute to safety, prevention, and industrial security.

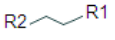
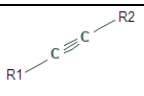
2. Materials and Method

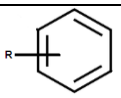
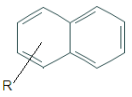
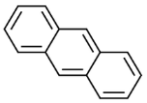
Data set

456 data points were prepared for this property as a database covering all types of hydrocarbon compounds. After sorting and verifying the data points, a total of 280 auto-ignition temperature values were obtained, as proposed by Kim et al. [11,] Mitchell and Jurs [12], Suzuki [13], Tetteh et al. [14], and Keshavarz et al. [15].

Through the database, in our study a significant number of geometric isomers were observed, estimated at 32 hydrocarbon compounds, divided into two types: 13 of the cis type and 19 trans compounds. To study this property, a database containing experimental chemical compounds was used, equivalent to 78 alkanes, 76 alkenes, 12 alkynes, 29 cycloalkanes, 7 cycloalkenes, 67 benzenes, 10 naphthenes, naphthacene, and anthracene, as shown in Table 1, Figure 1represents the molar mass of the hydrocarbon compounds used in the database.

Table 1: Types of Hydrocarbon Compounds

Type of Compound	Symbol	Number of Compounds	Percentage (%)	Carbon Atom Range	Molar Mass (g/mol)	Structural Formula
Alkanes	Alka	78	27.85	$C_2 – C_{29}$	16 – 408	
Alkenes	Alke	76	27.14	$C_2 – C_{20}$	28 – 280	
Alkynes	Alky	12	4.28	$C_3 – C_{10}$	26 – 128	

Cycloalkanes	C. Alka	29	10.35	$C_3 – C_{12}$	42 – 168	
Cycloalkenes	C. Alke	7	2.50	$C_6 – C_{12}$	82 – 166	
Benzene and Derivatives	Bez	67	23.92	$C_6 – C_{12}$	78 – 234	
Naphthalenes	Naph	10	3.57	$C_{10} – C_{14}$	128 – 184	
Anthracene	Anth	1	0.35	C_{14}	178	

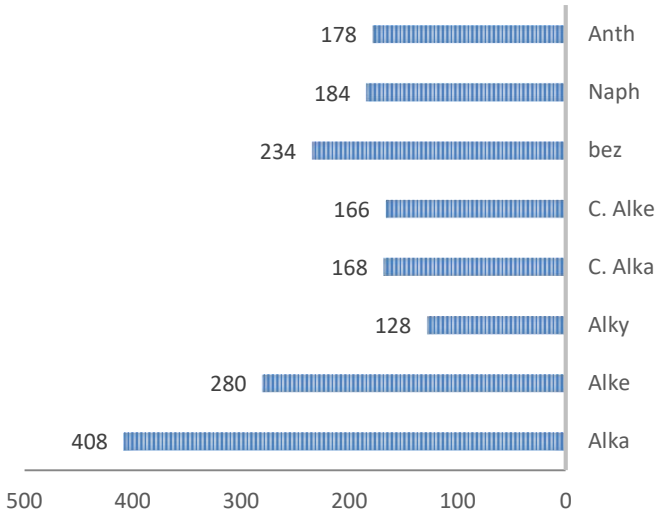


Figure 1:Molar Mass of Hydrocarbon Compounds Used in the Database

The principal criterion for selecting experimental values for the data set is the number and quality of the selected experimental values, given that the experimental values are found in several different references "replicates" and that there are similar values for the same compounds, which should be measured under the same conditions, taking into account the high accuracy of the results. In order to evaluate the model obtained, 80% of the database was used to obtain the model, and the rest was used to test its validity in most of the repeated data in the contribution of interaction groups.

Method proposed

In this study, the contribution of interaction groups was used, based on the approach of Pardillo-Fontdevila and Gonzalez-Rubio [16], Marrero-Morejon and Pardillo-Fontdevila [17], and Mokadem et al. [18], where the molecular structure of the compound was considered to be two levels: first-order contribution and second-order correction contribution. To determine the contribution of interaction groups, as in Figure 2, rely on:

1. A property related to the structural factors of the compound. Therefore, the frequency of the contribution of interaction groups is determined based on the principle used in previous studies as simple contributions, where the interaction groups are one or more carbon atoms, such as C-C, and vary according to the number of hydrogen atoms present, such as CH_3, CH_2, CH, C. These groups allow for a large number of hydrocarbon compounds, up to 37 simple groups.

2. The second level represents the correction factor group, which distinguishes between optical isomers (cis and trans), which are molecules with the same chemical formula and often the same type of bonds between atoms, but they differ in the arrangement of the different functional groups that make up these compounds. As can be seen in the compound shown in Figure 3 for the compound cis-2-Butene and Trans-2-Butene, the correction factors fTrans and fCis are introduced. The purpose of introducing the correction factor is to include the largest number of compounds, including complexes, in the model, in order to distinguish the largest number of isomers and their indirect effects.

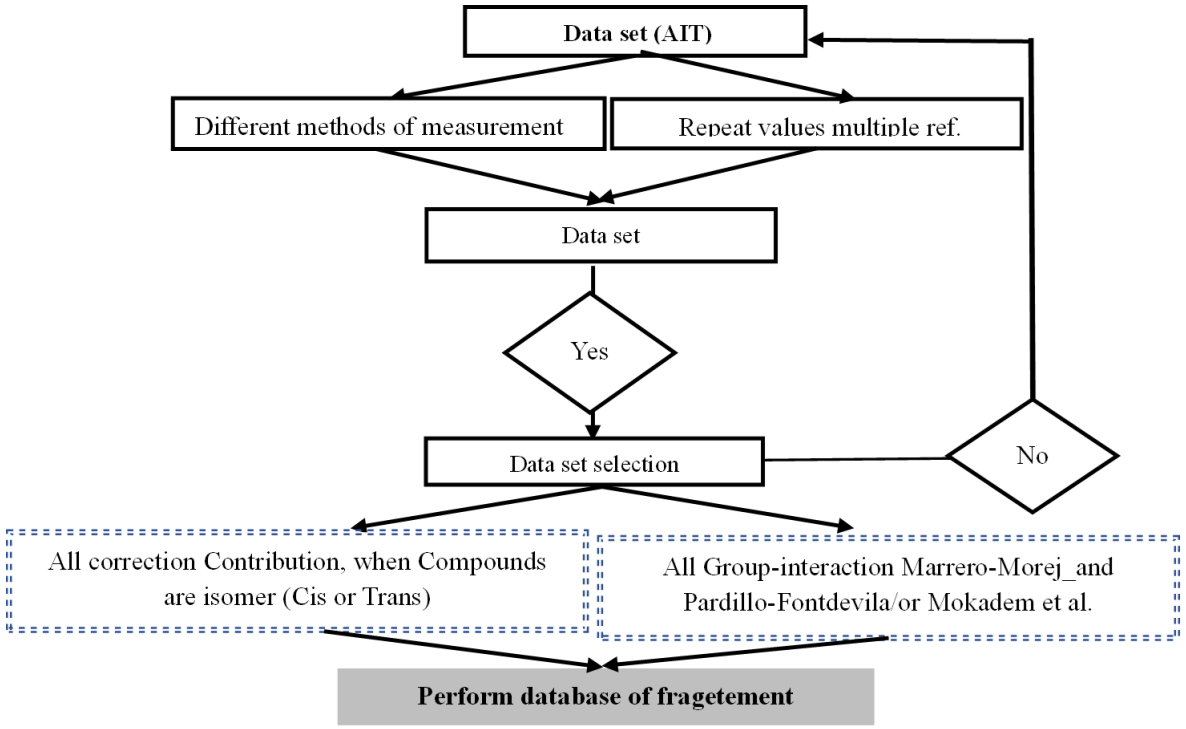


Figure2: Description of the interaction within groups.

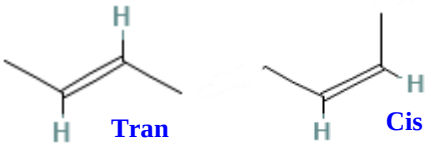


Figure 3: The geometric structures of cis-2-Butene and Trans-2-Butene

The statistical parameters for evaluating the performance of this process are the absolute average deviation (AAD), the relative average deviation (%AARD), and the correlation coefficient (R^2). These are tools that give an idea of the reliability of the developed model and are calculated according to the following equations:

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

$$\%AARD = \frac{100}{n}\sum_{i=1}^{n}\left|{p_i^{cal}}/{p_i^{exp}} - 1\right| \qquad (2)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}\left|{p_i^{cal}}/{\left(p_i^{ext} - p_i^{exp}\right)}\right|^2}{\sum_{i=1}^{n}\left|{p_i^{cal}}/{\left(p_i^{exp} - average\left(p_i^{exp}\right)\right)}\right|^2} \qquad (3)$$

Where P_i^{Exp} and P_i^{cal} are the experimental and calculated values, respectively, i represents the corresponding compound, n is the number of data points in the database studied.

The test validation is the method used to estimate the true performance of the model. Mainly, the selection of compounds for the validation test is based on the random selection of 56 compounds, with the percentage of points involved in this test equal to 20% with the highest R^2 compatibility, Most hydrocarbon groups are included in the test.

Through this study, little we've found in the literature on predicting the auto-ignition temperature of hydrocarbon compounds is pretty limited, and the experimental values are all over the place. Nevertheless, a simplified study on this subject was attempted, relying on a database consisting of 280 compounds from various hydrocarbons (alkanes, alkenes, alkynes, cyclic alkanes, cycloalkenes, benzene, naphtha, anthracene), highlighting the differences between them in terms of the number of compounds, symbol, ratio, number of carbon atoms, and molar mass. in addition to the chemical formula and and chemical structure of each compound. In order to use the overlapping group contribution method, the algorithm was used to calculate each property, starting with the molecular property (GIC) using the compound division method, while determining the accuracy and verifying the validity of the results.

3. Results and Discussion

In this study, a very simple linear model was obtained to estimate the auto-ignition temperature (AIT) of hydrocarbon compounds with the formula (C_xH_Y) (such as can, alkanes, alkenes, etc.). The AIT value can be expressed by the following equation:

$$AIT=565{,}11+\sum_j n_j\Delta C_j +10{,}94\times f_{Trans}+16{,}29\times f_{cis} \qquad (4)$$

nj: the number of overlapping groups of type j in the molecule, ΔCj: the contribution of the interaction group to the molecule. Table 2 gives the values obtained according to the above equation. f_{cis}, f_{Trans} the correction coefficient for geometric interaction respectively.

Table 2: Contribution of interaction group

No	Interactions	ΔCj/K
1	CH_3 & -CH_3	222.886
2	CH_3 & H	302.886
3	CH_3 & >CH-	9.454
4	CH_3 & >C<	21.014
5	CH_3 & =CH-	-19.233
6	CH_3 & -CH_2	-18.098
7	CH_3 & >C=	44.459
8	CH_2- & -CH_2-	-3.109
9	CH_2- & >CH-	-1.356
10	CH_2- & >C<	21.542
11	CH_2- & -CH=	-12.035
12	CH_2- & >C=	35.495
13	>CH- & >CH-	25.150
14	>CH- & >C<	54.277
15	>CH- &-HC=	30.405
16	>CH- & >C=	7.748
17	>C< & >C<	29.368
18	>C< & -HC=	-150.376

No	Interactions	ΔCj/ K
19	>C< & >C=	-1.087
20	H_2C= & CH_3	0.000
21	H_2C= & H_2C=	157.886
22	H_2C= & -CH=	19.400
23	H_2C= & >C=	-16.669
24	-HC= & -HC=	31.063
25	-HC= & >C=	14.299
26	>C= & > C=	-24.413
27	CH_3 & ΞC	41.975
28	CH_3 & ΞCH	58.976
29	CH_2 & ΞC	26.238
30	>CH- & ΞC	49.183
31	HCΞ & ΞCH	12.886
32	ΞC- & ΞCH	-36.944
33	>C= & -CΞ	42.5100
34	HC= & -CΞ	-31.2420
35	CΞ &-CΞ	-53.247

A comparison between the experimental and calculated auto-ignition temperature (AIT) is shown in Figure 4. For the contribution of interaction groups, it can be observed that most points are close to the midpoint. This indicates the consistency between the predicted and the experimental data.

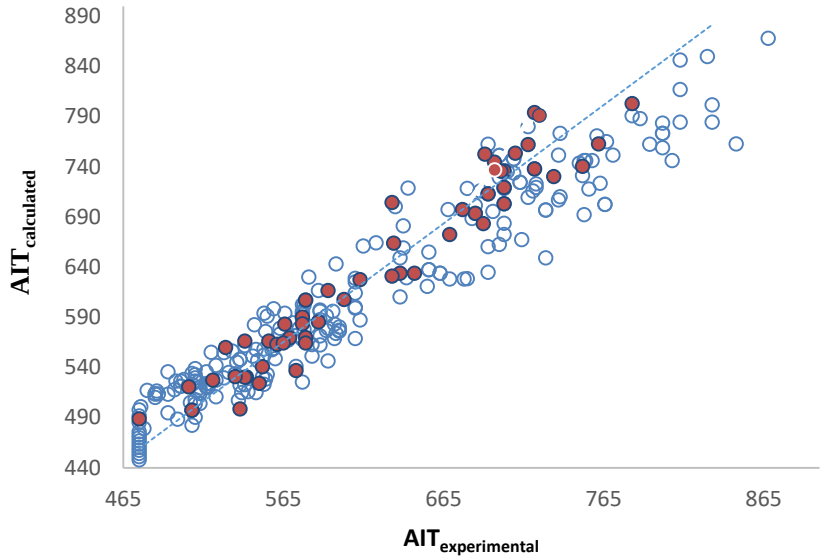


Figure 4. Comparison between experimental and calculated results for auto-ignition temperature (AIT), ( ), ( ) values used to obtain the model and to perform model validation, respectively.

The performance of the developed model can also be evaluated using the statistical criteria shown in Table3.

Table 3:Statistical results for the model proposed by the GIC method for auto-ignition temperature (AIT).

Training set	R^2	0,93
	%AARD	22,07
	Deviation Standard	3,56
	No of data points	224
Validation set	R^2	0,94
	%AARD	3,56
	Deviation Standard	22,67
	No of data points	56
Overall set	R^2	0,93
	%AARD	3,56
	Deviation Standard	22,19
	No of data points	280

The relative deviations between the experimental and calculated data are shown in Figure 4 As explained earlier, there was no effort to exclude " dubious" or presumably inaccurate experimental data. For this reason, high deviations can be observed for some monoterpenes. However, for the overlapping interaction contribution, there are only 13 data points with an absolute relative deviation greater than 10%, or 4.64% (see Table 4) of the total in the database.

Table 4: Relative error distribution and number of compounds

Number of compounds	**280**
AARD (%)	3,56
Δ AITmin (%)	0,00
Δ AIT max (%)	17,71
|ΔAIT| (%) < 5	209
|ΔAIT| (%) [5 – 10]	58
|ΔAIT| (%) > 10	13

A more detailed view of this modeling can be seen in Figure 5, which shows the relative error for the different categories contained in the database studied in this feature. It can be seen that despite the difference in the number of compounds and the variation in the number, the relative error is similar.

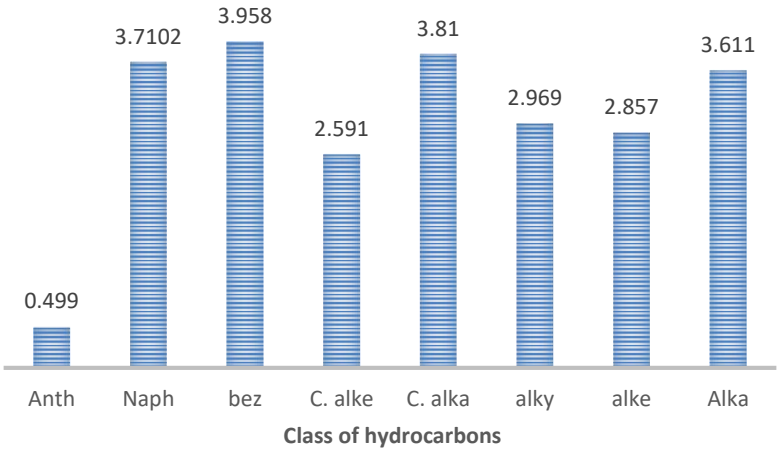


Figure 5: Detailed results for the categories used and the relative error using the GIC method for the auto-ignition temperature (AIT).

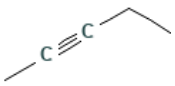
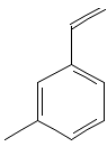
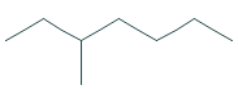
A careful examination of the model obtained and its comparison with the closest previous studies proposed by Keshavarz et al. [15] and as a simple comparison, the following observations can be made:

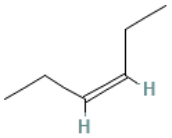
- The interaction model shows the same correlation coefficient and a lower mean relative deviation.
- The data set is convergent if it does not exceed 2% of the total number of data points.
- The model obtained can be used to estimate the characteristic of distinction between geometric combinations.

Examples

The below table provides some examples for the autoi-gnition temperature estimation.

Table 5: Some examples of estimating the auto-ignition temperature(AIT) of some hydrocarbon compounds.

Compounds	AIT $_{exp}$ **(K)**	**Interactions**	**Frequency**	**Contribution**
 2-Pentyne	575	CH_3- & CH_2<	1	-18.098
		CH_2 - & -CΞ	1	26.238
		CΞ & ΞC	1	-53.247
		CH_3- & -CΞ	1	41.975
		AIT_{cal} **(K)** =578,982, **A%ARD**=0,692		
 3-Vinyltoluene	762	CH_2= & =CH-	1	19.400
		CH_3- & -C=	1	44.459
		=CH- & -C=	3	7.7489
		CH= & =C-	2	14.299
		CH= & =CH	1	31.063
		=CH- & -CH=	1	30.405
		AIT_{cal}**(K) =** 762,595, **%AARD**=0,078		
 3-Methylheptane	518	CH_3- & -CH_2-	2	-18.098
		CH_2- & -CH_2-	2	-3.109
		CH_3- & -CH<	1	9.454
		CH_2- & -CH<	2	-1.356
		AIT_{cal}**(K) = 519, %AARD=0,383**		
	553	CH_3- & -CH_2-	2	-18.098

 cis-3-Hexene		CH_2- & -CH=	2	-12.035
		-CH=& =CH-	1	31.063
		AIT_{cal}**(K) =552,206, %AARD=0,143**		

4. Conclusion

A database consisting of 280 database values was used in this study, including 78 alkanes, 76 alkenes, 12 alkynes, 29 cycloalkanes, 7 cycloalkenes, 67 benzenes, 10 naphthenes, naphthacene, and anthracene. The results showed that this method is an excellent alternative to classical techniques, as we obtained a correlation coefficient (R^2) of 0.93 and an average relative error (%AARD) of 3.56. The latter gave value to this new model, as it is the best study and closest to the previous studies by Keshavarz [15]. The most important feature of this new model is that it distinguishes between isomers, which is not found in the traditional methods used in previous studies.

References

[1] Cheng, L., & Zhang, Y. (2019). Prediction of Auto-Ignition Temperature of Organic Compounds Using Machine Learning Methods. *Process Safety and Environmental Protection, 125*, 286–295.

[2] Zabetakis, M. G. (1965). *Flammability Characteristics of Combustible Gases and Vapors.* U.S. Bureau of Mines Bulletin 627.

[3] Lewis, B., & von Elbe, G. (1987). *Combustion, Flames and Explosions of Gases* (3rd ed.). Academic Press.

[4] Gmehling, J., & Rasmussen, P. (1993). Flash Points and Autoignition Temperatures of Organic Compounds. *Journal of Chemical & Engineering Data, 38*(3), 350–354.

[5] Yeong Suk Kim, Sung Kwang Lee, Jae Hyun Kim,Jung Sup Kimc and Kyoung Tai No(2002) , Prediction of autoignition temperatures (AITs) for hydrocarbons and compounds containing heteroatoms by the quantitative structure–property relationship,J. Chem. Soc., Perkin Trans. 2, 2087–20922

[6] Shijing Shen, Yong Pan , Xianke Ji, Yuqing Ni and Juncheng Jiang (2019), Prediction of the Auto-Ignition Temperatures of Binary Miscible Liquid Mixtures from Molecular Structures,Int. J. Mol. Sci., 20, 2084; doi:10.3390/ijms20092084

[7] Yong Pan, Juncheng Jiang , Rui Wang (2008), Hongyin Cao, Jinbo Zhao,Prediction of auto-ignition temperatures of hydrocarbons by neural network based on atom-type electrotopological-state indices,Journal of Hazardous Materials 157, 510–517

[8] Bingyu Guo , Zehui Cheng , Shuangqi Hu(2024) ,Neural network-based prediction of auto-ignition temperature of ternary mixed liquids,Heliyon, 10 e28713

[9] Mokadem K., Korichi M., Tumba K. (2016), A new group-interaction contribution method to predict the thermal decomposition temperature of ionic liquids,Chemometrics and Intelligent Laboratory Systems, 157, 15 October 2016, Pages 189-195

[10] Xiao-Jing Hou,Liu-Ying Yu,Yan-Xu Wang,Ke-Jun Wu,Chao-Hong He(2021),Comprehensive Prediction of Densities for Deep Eutectic Solvents: A New Bonding-Group Interaction Contribution Scheme, Ind. Eng. Chem. Res. , 60, 35, 13127–13139

[11] Kim Y. S., Lee S. K., Kim J. H., Kim J. S. and No K. T. (2002), Prediction of autoignition temperatures (AITs) for hydrocarbons and compounds containing heteroatoms by the quantitative structure-property relationship, J. Chem. Soc., Perkin Trans.2,2087–2092.

[12] Mitchell B. E. and Jurs P. C.(1997), Prediction of Autoignition Temperatures of Organic Compounds from Molecular Structure, J. Chem. Inf. Comput. Sci., 37, 538-547.

[13] Suzuki T(1994)., Quantitative Structure-Property Relationships for Auto-ignition Temperatures of Organic Compounds, FIRE AND MATERIALS, 18, 81-88 .

[14] Tetteh J., Metcalfe E. , Howells S. L.(1996), Optimisation of radial basis and backpropagation neural networks for modelling auto-ignition temperature by quantitative-structure property relationships, Chemometrics and Intelligent Laboratory Systems, 32 177-191.

[15] Keshavarz M. H. , Gharagheizi F., Ghanbarzadeh M.(2013), A simple correlation for prediction of autoignition temperature various classes of hydrocarbons, J. IRAN CHEM SOC, 10, 545–557.

[16] Marrero-Morej_on J., Pardillo-Fontdevila E.(1999), Estimation of pure compound properties using group-interaction contributions, AIChE J., 45 615-621.

[17] Pardillo-Fontdevila E., Gonz_alez-Rubio R.(1998), A group-interaction contribution approach. A new strategy for the estimation of physico-chemical properties of branched isomers, Chem. Eng. Commun. 163, 245-254.

[18] Mokadem K., Korichi M., Tumba K. (2016), An enhanced group-interaction contribution method for the prediction of glass transition temperature of ionic liquids", Original Research Article, Fluid Phase Equilibria, 425, 259-268.