

CORRELATION AND PREDICTION OF AUTOIGNITION TEMPERATURES OF HYDROCARBONS USING MOLECULAR PROPERTIES

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Key Words: Autoignition Temperature, Flammability, Flash Point, Multivariate Analysis, Property Estimation

Introduction

For the assessment of the flammability and combustibility of substances, particularly fuels and hydrocarbons, information on the flash point and/or the autoignition temperature (*AIT*) is of great importance in production processes. In our previous papers^{1,12)}, an estimation scheme for the flash point of organic compounds from molecular structures was presented. The *AIT* is defined as the temperature at which a material in contact with air undergoes oxidation at a sufficiently high rate to initiate combustion without an external ignition source²⁾. This

definition, while descriptive, does not relate the *AIT* to any other physical properties. The interrelationship between the *AIT* and other physical properties is still poorly documented. Although a linear relation between the *AIT* and the flash point was presented by Shimy¹⁰⁾, it is limited to a homologous series of hydrocarbons and alcohols.

This paper is an attempt to derive a predictive model for the *AIT* of hydrocarbons using various molecular descriptors. As an alternative to the use of mathematical models based on theoretical equations, quantitative structure-property relationship (QSPR) techniques are used in this study.

* Received March 27, 1992. Correspondence concerning this article should be addressed to T. Suzuki.

1. Materials and Methods

1.1 AIT Data

Experimentally determined values of the *AIT* are dependent on the method (including ignition-delay times) and apparatus employed for their determination. Since the values of the *AIT* used for fire-protection purposes are normally the lowest reported, the lowest values determined in glass apparatus^{5,15} were used.

1.2 QSPR model for AIT

The molecular structure of a compound strongly influences its physical properties. Many physical properties are related to a large number of other physical properties. This connection between a physical property (including biological property) and the molecular descriptors (structural and/or other physical and chemical properties) defines the QSPR or quantitative structure-activity relations (QSAR).

The relationship between lowest experimental *AIT* and molecular descriptors is assumed to have the following multilinear form:

$$AIT = a_1 D_1 + a_2 D_2 + \dots + a_n D_n + a_0 \quad (1)$$

where n is the total number of descriptors (D), a_j are their coefficients, and a_0 is constant. Various candidates for the descriptors were entered into a model correlation equation (Eq. (1)), and the individual terms were screened for inclusion in a final regression equation using a standard stepwise multivariate linear regression analysis. All possible combinations of descriptor pairs were examined to identify those pairs which were highly correlated.

1.3 Descriptor variables

A set of 50 hydrocarbons (for which lowest experimental *AIT*s are available), ranging in type from saturated to polycyclic aromatic in molecular weights in the range of 58–180 daltons, was used to examine the correlation with molecular descriptors. The following representative descriptors were used, based in part on their perceived usefulness and in part on the availability of data: (1) flash point (T_f); (2) normal boiling point (T_b); (3) critical temperature (T_c); (4) critical pressure (P_c); (5) molecular weight (MW); (6) liquid-state molar volume (MV); (7) molecular surface area (A_w)¹¹; (8) first-order molecular connectivity index (1X)⁶; (9) zero-th order molecular connectivity index (0X)⁶; (10) molar refraction (MR); (11) parachor (PA); (12) enthalpy of vaporization at normal boiling point (H_v); (13) cohesive energy density (ϵ_{coh})¹³; (14) acentric factor (ω)⁸; (15) molar magnetic susceptibility (X_M); (16) Fujita's inorganicity/organicity value (I/O)⁴.

The values of experimental descriptors (T_f , T_b , T_c , P_c , MW , MV , MR , PA , H_v , ω , X_M) have been taken from the literature^{3,9,14}. Missing values

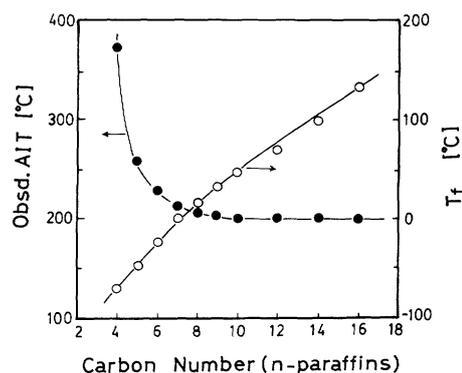


Fig. 1. Plot of lowest autoignition temperature and flash point against number of carbon atoms

were estimated from a variety of reliable estimation methods by referring to several monographs^{7,9,13}. The remaining five descriptors (A_w , 1X , 0X , ϵ_{coh} , I/O) were computed on the basis of methods in the literature denoted by superscripts.

2. Results and Discussion

The lowest reported values of *AIT* and the flash point data for a homologous series of hydrocarbons, the n -paraffins, are plotted in Fig. 1. They suggest that the *AIT* is not a simple function of the flash point. The linear relationship between the *AIT* and the flash point¹⁰ may be only valid for a limited set of the homologous hydrocarbons.

Simple correlation of the descriptors with observed *AIT* values was examined in the first step. There were no significant linear relationships between *AIT* and the descriptors. Even the highest correlation coefficient for the relationship between *AIT* and I/O was 0.519. These results require the QSPR approach to the *AIT* problem.

A summary of the multiple-regression analysis based on Eq. (1) is presented in Table 1. The best model for *AIT* was found to be the following equation with five descriptors, T_c , P_c , PA , A_w , and 0X :

$$AIT = -1.52T_c + 7.67P_c - 2.64PA - 47.6A_w + 300.6{}^0X + 501.3 \quad (2)$$

$(n = 50, r = 0.941, s = 39.4)$

The average absolute error for the 50 compounds in the training set was 28.8°C. Although this model requires experimentally determined descriptors, T_c , P_c , and PA , these descriptors can be estimated accurately on the basis of molecular structure^{7,9}. Thus Eq. (2) allows the calculation of *AIT* from structural information alone.

The validity of Eq. (2) has been tested for calculating *AIT*s of a set of hydrocarbons not included in the original data set. The set includes 20 alkanes (C_2 – C_{16}), 11 alkenes (C_4 – C_{14}), 12 naphthenes (C_7 –

Table 1. Comparison of fitness of Eq. (1) using various combinations of descriptors

Descriptors	<i>r</i>	<i>s</i>
$T_c, P_c, A_w, {}^1X, {}^0X, MR, PA, X_M, I/O$	0.955	36.0
$T_c, P_c, A_w, {}^0X, MR, PA, X_M, I/O$	0.955	35.9
$T_c, P_c, A_w, {}^0X, PA, X_M, I/O$	0.952	36.5
$T_c, P_c, A_w, {}^0X, PA, I/O$	0.945	38.6
$T_c, P_c, A_w, {}^0X, PA$	0.941	39.4
$T_c, P_c, {}^0X, PA$	0.924	43.9
$T_c, A_w, {}^0X, PA$	0.919	45.3
$T_c, {}^0X, PA$	0.893	51.3
${}^0X, PA$	0.886	52.2

Table 2. Evaluation results in the calculation of *AIT*s of 112 hydrocarbons

Chemical class	No. of compounds	Data range	Eq. (2)	
			Av. error ^{a)}	Bias ^{b)}
Alkanes	35	C2–C16	28.2	16.8
Naphthenes	22	C5–C11	25.0	8.5
Alkenes	21	C5–C16	38.0	–36.0
Cycloolefins	3	C5–C6	39.3	–30.0
Aromatics	31	C6–C14	38.7	4.8
Total	112	C2–C16	32.6	0.7

^{a)} Av. error = $\sum |AIT(\text{obsd}) - AIT(\text{cald})| / \text{number of compounds}$
^{b)} Bias = $\sum (AIT(\text{obsd}) - AIT(\text{cald})) / \text{number of compounds}$

C₁₁), a cycloolefin (C₆), and 18 aromatics (C₈–C₁₄). Missing values of *T_c* and *P_c* were estimated by Lydersen's method^{3,7,9}. Eisenloh's method⁷) was applied to missing values of *PA*. Reasonable prediction results were confirmed (average absolute error for the 62 compounds was 35.4°C).

Statistical evaluation of the 112 hydrocarbons used as the original data set and the test data set are shown in **Table 2**. Average absolute and bias errors are shown for individual classes of hydrocarbons. The average absolute error of all compounds is 32.6°C. The accuracy of the present model is still quite reasonable because of the large experimental uncertainties of *AIT*. Additional work is necessary to expand the utility of this approach to other types of compounds.

Conclusion

A QSPR model for predicting approximate lowest *AIT* of hydrocarbons has been developed. It requires five molecular descriptors, the critical temperature, the critical pressure, the molecular surface area, the zero-th order molecular connectivity index, and the parachor. This model is especially useful for preliminary evaluation of actual measurement of *AIT*.

Supplementary material available

All data used in this study and a list of the observed and calculated *AIT*s for the compounds in the test set can be obtained from the authors on request.

Nomenclature

<i>AIT</i>	= autoignition temperature	[°C]
<i>A_w</i>	= molecular surface area	[10 ⁹ cm ² · mol ⁻¹]
<i>H_v</i>	= enthalpy of vaporization at normal boiling point	[kcal · mol ⁻¹]
<i>I</i>	= Fujita's inorganicity	[–]
<i>MR</i>	= molar refraction	[cm ³ · mol ⁻¹]
<i>MV</i>	= liquid-state molar volume at 20°C	[cm ³ · mol ⁻¹]
<i>MW</i>	= molecular weight	[g · mol ⁻¹]
<i>n</i>	= number of data points in set	[–]
<i>O</i>	= Fujita's organicity	[–]
<i>PA</i>	= parachor	[(cm ³ · mol ⁻¹)(dyn · cm ⁻¹) ^{1/4}]
<i>r</i>	= multiple correlation coefficient	[–]
<i>s</i>	= standard deviation	[°C]
<i>T_b</i>	= normal boiling point	[°C]
<i>T_c</i>	= critical temperature	[K]
<i>T_f</i>	= flash point	[°C]
<i>ε_{coh}</i>	= cohesive energy density	[kJ · cm ⁻³]
<i>ω</i>	= acentric factor	[–]
¹ <i>X</i>	= first-order molecular connectivity index	[–]
⁰ <i>X</i>	= zero-th order molecular connectivity index	[–]
<i>X_M</i>	= molar magnetic susceptibility	[10 ⁻⁶ cm ³ · mol ⁻¹]

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