

용액론에 근거한 표준끓는점과 인화점을 이용한 알코올류의 폭발한계 예측 Prediction of Explosion Limits Using Normal Boiling Points and Flash Points of Alcohols Based on a Solution Theory

하 동 명[†]

Dong-Myeong Ha[†]

세명대학교 안전공학과
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요 약

화학공정에서의 안전하고 최적화된 조작과 내재되어 있는 화재 및 폭발 위험성 평가를 위해서 연소 특 성치를 알아야 한다. 폭발한계는 가연성물질의 화재 및 폭발위험성을 결정하는데 주요한 특성치 가운데 하나이다. 본 연구에서, 알코올류의 폭발한계에 대해 용액론을 근거로 표준끓는점과 인화점을 이용하여 예측 하였다. 제시된 예측식에 의한 예측값은 문헌값과 적은 오차범위에서 일치하였다. 제시된 방법론을 사용하 여 다른 가연성 물질의 폭발한계 예측이 가능해졌다.

ABSTRACT

In order to evaluate the fire and explosion involved and to ensure the safe and optimized operation of chemical processes, it is necessary to know combustion properties. Explosion limit is one of the major combustion properties used to determine the fire and explosion hazards of the flammable substances. In this study, the explosion limits of alcohols were predicted by using the normal boiling points and the flash points based on a solution theory. The values calculated by the proposed equations agreed with literature data within a few percent. From the given results, using the proposed methodology, it is possible to predict the explosion limits of the other flammable substances.

Keywords : Combustion property, Fire and explosion hazard, Flammable substance, Alcohol, Explosion limit

1. Introduction

Flammable compounds are indispensable in domestic as well as in industrial fields as fuel, solvent and raw materials. The fire and explosion properties necessary for safe storage, transport, process design and operation of handling flammable substances are lower explosion limits(LEL), upper explosion limits(UEL), flash point, fire point, AIT(auto ignition temperature), MIE(minimum ignition energy), MOC(minimum oxygen concentration) and heats of combustion etc.¹⁾.

Explosion limit is one of the major physical properties used to determine the fire and explosion hazards of the flammable substances²⁾. Explosion limits are used to

classify flammable liquids according to their relative flammability. Such a classification is important for the safe handling of flammable liquids which constitute the solvent mixtures.

The research on the explosion limits is one of the fundamental fields of combustion process, and information on the explosion limits of mixture of fuel and oxidant, with or without additives, is very important for the prevention in industrial fire and explosion accidents. Therefore, the method to estimate the explosion limits of flammable materials have been of great concern of petroleum, paint, and other industries.

The UFL and LFL define the range of flammable concentrations for a substance in air at atmospheric pressure. The explosion limits may be used to specify operating, storage, and materials handling procedures

[†] E-mail: hadm@semyung.ac.kr(www.chollian.net/~hadm)

for a material. They are particularly useful in specifying ventilation requirements for operations involving flammable liquids and gases.

In this study, a new equation is proposed for predicting the lower explosion limits(LEL) of alcohol compounds on the basis of flash points, normal boiling points, statistics, and solution theories and for providing basic data to prevent fire and explosion.

2. Relationship between Explosion Limits, Flash Points and Normal Boiling Point

There are several properties of flammable materials that are frequently reported.

The flash point is defined by the National Fire Protection Association (NFPA)³⁾ as the lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface or within a vessel. The flash points are generally presented to values determined by two apparatus. The open cup (O.C.) flash points are generally somewhat higher than the closed cup(C.C.) flash points for same materials. Special precautions should be taken when the product has a low flash point. Materials having a low flash point have a greater fire hazard than materials having a high flash point.

The explosion limits in air are usually reported as the upper and lower limits (in volume percent at a certain temperature, usually 25°C), and represent the concentration region that the vapor must be within to support combustion. Hydrocarbons have a fairly narrow range, whereas hydrogen has a wide range. All concentrations between LEL and UEL are in the flammable range, and special precautions are needed to prevent ignition or explosion⁴⁾.

The explosion limits exist have close relationships to the flash points and normal boiling point. Therefore, the prediction of the explosion limits by these is an interesting field.

3. Multiple Regression Analysis and Evaluation Criteria Used

3.1. Multiple Regression Analysis

Regression analysis is any statistical method where the mean of one or more random variables are predicted

conditioned based on the other (measured) random variables. Sometimes there are only two variables, one of which is called X and can be regarded as constant, i.e., non-random, because it can be measured without substantial error and its values can even be chosen at will. For this reason it is called the independent or controlled variable. The other variable called Y, is a random variable called the dependent variable, because its values depend on X. In regression we are interested in the variation of Y on X.

Multiple regression analysis can be regarded as an extension of straight-line regression analysis (which involves only one independent variable) to the situation where there is more than independent variable to be considered^{5,7)}.

One example of multiple regression model is given by any second- or higher-order polynomial. The addition of higher-order terms (e.g., an X² or X³ term) to the model can be considered as equivalent to the addition of new independent variables. Thus, if we rename X as X₁ and X², the second-order model is

$$Y = \beta_0 + \beta_1 X + \beta_2 X^2 + e \quad (1)$$

can be rewritten as

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + e \quad (2)$$

Of course, in polynomial regression we really have only one basic independent variable, the others being simple mathematical functions of this basic variable. In more general multiple regression problems, however, the number of basic independent variables may be greater than one. The general form of a regression model for k independent variables is given by

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_k X_k + e \quad (3)$$

where $\beta_0, \beta_1, \beta_2, \dots, \beta_k$ are the regression coefficient that need to be estimated. The independent variables X₁, X₂, ..., X_k, may all be separate basic variables, or some may be functions of a few basic variables.

In general, the least-square method is chosen as the best-fitting model which minimizes the sum of squares of the distances between the observed responses and those predicted by the fitted model^{12,13)}.

3.2 Evaluation Criteria Used

3.2.1 Average absolute percent errors(A.A.P.E.) and average absolute deviations (A.A.D.)

It is a non-dimensional quantity that permits an accurate quantitative comparison between the reported value and predicted one. The average absolute percent errors(A.A.P.E.)^{7,8)} is :

$$\text{A.A.P.E.} = \frac{\sum \left| \frac{\text{LEL}_i^{\text{cal}} - \text{LEL}_i^{\text{exp}}}{\text{LEL}_i^{\text{exp}}} \right|}{n} \times 100 \quad (4)$$

where the $\text{LEL}_i^{\text{exp}}$ is the experimental lower explosion limit, and $\text{LEL}_i^{\text{cal}}$ is the estimated lower explosion limit and n is the number of data.

It is another index, replacing the A.A.P.E. in the situation when an accurate quantitative comparison between the reported value and estimated value are attempted.

The average absolute deviations(A.A.D.) is:

$$\text{A.A.D.} = \sum \left| \frac{\text{LEL}_i^{\text{cal}} - \text{LEL}_i^{\text{exp}}}{n} \right| \quad (5)$$

where the A.A.D. is a measure of agreement between the experimental data and the calculated values.

3.3.2 The coefficient of determination (r^2), coefficient of correlation(r) and standard deviation

The determination of determination (r^2) and the coefficient of correlation (r) measure the proportion of the variation in the response around the mean that can be attributed to terms in the model rather than to random error and it is determined by^{5,6)}

$$r^2 = \frac{\text{SS}_r}{\text{SS}_{yy}} = 1 - \frac{\text{SS}_E}{\text{SS}_{yy}} \quad (6)$$

$$r = \pm \sqrt{r^2} \quad (7)$$

where SS_E is the sum of squares in the residual errors

($= \sum_{i=1}^n (y_i - Y_i)^2$) where Y_i is the predicted value by the

fitted model. SS_R is the sum of squares due to regression

($= \sum_{i=1}^n (Y_i - \bar{y})^2$) where \bar{y} is the overall average of y_i . SS_{yy}

is the total sum of squares about the mean given by

$$\text{SS}_y = \text{SS}_E + \text{SS}_R = \sum_{i=1}^n (y_i - \bar{y})^2 \quad (8)$$

The standard deviation(S) is :

$$S = \sqrt{\frac{\sum (y_i - \bar{y})^2}{n - 1}} \quad (9)$$

where n is the number of data.

4. Development of the Predictive Models in the Explosion Limits by the Flash Points and the Normal Boiling Points

4.1 Theory

For many liquids, the molecular specific entropy of vaporization is empirically found to be a universal constant, the consequence of the empirical invariance in the ratio of normal boiling point to critical temperature, so that

$$\Delta H_v = (90 \text{ J/molK}) T_b \quad (10)$$

$$\begin{aligned} \frac{\Delta H_v}{RT_b} &= \frac{90 \text{ J/molK}}{R} = \frac{90 \text{ J/molK}}{8.314 \text{ J/molK}} \\ &= 10.825 = \text{constant} \end{aligned} \quad (11)$$

which is useful for obtaining an approximate value of the vaporized heat of a liquid from a knowledge of its boiling point.

Known as Trouton's rule⁹⁾, this powerful relation enable one to estimate the enthalpy of vaporization $\Delta H_v/R$ from knowledge of the normal boiling point T_b and liquid molecular weight, M .

The vapor pressure of a liquid increases as the temperature is elevated. A relationship of flash point to the lower explosion limits exists through the dependence of vapor pressure on the temperature, given by Clausius-Clapeyron equation¹⁰⁾.

$$\ln\left(\frac{P_v}{P_T}\right) = \frac{\Delta H_v}{R} \left[\frac{1}{T_b} - \frac{1}{T} \right] \quad (12)$$

where ΔH_v is the enthalpy of vaporization of the liquid, P_v is the vapor pressure, P_T is the total pressure, T_b is the normal boiling point, R is the gas constant, and T is the Kelvin temperature.

Turning now to the mole fraction of the flammable fuel x_v , with ideal gas approximation,

$$x_v = \frac{n_v}{n_T} = \frac{P_v V/RT}{P_T V/RT} = \frac{P_v}{P_T} \quad (13)$$

so that Eqn. (13) gives the mole fraction of the flammable fuel vapor in the space above the vaporized liquid. The flammable fuel x_v has to exceed the lower explosion limit (L).

$$\ln\left(\frac{1}{L}\right) = \frac{\Delta H_v}{RT_B} \left[\frac{T_b}{T_f} - 1 \right] + \alpha \quad (14)$$

4.2 Various Possible Prediction Models

Multiple regression analyses^{5,6)} are applied to obtain the correlation for estimation of the lower explosion limits by using the flash points and the normal boiling points.

For the estimation of the lower explosion limits, the predicted equation which used Trouton’s rule and various possible prediction models based on Trouton’s rule are as follows :

$$\ln\left(\frac{1}{L}\right) = \frac{\Delta H_v}{RT_B} \left[\frac{T_b}{T_f} - 1 \right] \quad (15)$$

$$\frac{1}{L} = a + b \left[\frac{T_b - T_f}{T_f} \right] \quad (16)$$

$$\frac{1}{L} = a + b \left[\frac{T_b - T_f}{T_f} \right] + c \left[\frac{T_b - T_f}{T_f} \right]^2 \quad (17)$$

where L is the lower explosion limit, T_b is the normal boiling point and T_f is the flash point.

4.3 Selection of the Data of the Lower Explosion Limits and the Prediction of Enthalpy of Vaporization

All the explosion limits and the flash point data for

this study were obtained from NFPA 325M “Fire Hazard Properties of Flammable Liquid, Gases, and Volatile solids”¹¹⁾. The greater parts of the vaporized heats for alcohols were obtained from CRC Handbook¹²⁾ and Lange’s Handbook of Chemistry¹³⁾. If there were not the vaporized heats of alcohol compounds in these books, we obtained them from using the entropy values estimated by Vetere’s equation¹⁴⁾.

Vetere proposed a form wherein ΔS_{vb} is correlated as a function of T_b and M, his relation are given in Table 1.

The enthalpy of vaporization for alcohol compounds was predicted by the use of the entropy of vaporization calculated by Vetere’s modification of the Kistiakowsky equation. Vetere’s equation is as follow:

$$\Delta S_{vb} = 81.119 + 13.083 \log T_b - 25.769 \frac{T_b}{M} + 0.14652 \frac{T_b^2}{M} - 2.1362 \times 10^{-4} \frac{T_b^3}{M} \quad (18)$$

$$\Delta H_{vb} = \Delta S_{vb} T_b \quad (19)$$

where ΔH_{vb} is the enthalpy of vaporization, ΔS_{vb} is the entropy of vaporization and M is molecular weight.

In this study, the enthalpies of vaporization of 3-propanol, 2-octanol and 1-decanol were predicted by the use of the entropy of vaporization calculated by Vetere’s method.

5. Comparison with Reported and Estimated Values

Statistical analysis of these 23 compounds resulted in best-fit empirical equation for predicting the lower

Table 1. Vetere’s modification of the Kistiakowsky equation

Type of compounds	Correlations
Alcohols, Acids, Methylamine	$\Delta S_{vb} = 81.119 + 13.083 \log T_b - 25.769 \frac{T_b}{M} + 0.14652 \frac{T_b^2}{M} - 2.1362 \times 10^{-4} \frac{T_b^3}{M}$
Other polar compounds	$\Delta S_{vb} = 44.367 + 15.33 \log T_b + 0.39137 \frac{T_b}{M} + 4.330 \times 10^{-3} \frac{T_b^2}{M} - 5.627 \times 10^{-6} \frac{T_b^3}{M}$
Hydrocarbons	$\Delta S_{vb} = 58.20 + 13.7 \log M + 6.49 \frac{\{T_b - (263M)\}^{0.581}}{M}^{1.017}$

explosion limits of alcohol compounds.

Empirical equation is as follows :

$$\frac{1}{L} = -16.95703 + 22.24219 \left[\frac{T_b - T_f}{T_f} \right] - 0.66211 \left[\frac{T_b - T_f}{T_f} \right]^2 \quad (20)$$

The reported lower explosion limits and the predicted lower explosion limits based on Trouton's rule and the empirical equation developed in this paper for 23 alcohol compounds are listed in Table 2. Also, Fig. 1 shows the comparison between the reported lower explosion limits and the predicted lower explosion

limits based on the empirical equation.

As can be seen from A.A.D in Table 2, the method proposed in this study is superior to the Trouton's rule. equation (20) is in agreement with the predicted LEL values of 23 alcohol compounds, average absolute percent error is 17.77, average absolute deviation is 0.315 vol% and the coefficient of correlation(r) is 0.962. Methanol and ethanol have a few deviation between the estimated and reported values. Therefore, the estimated values by the proposed equation were agreement with the reported values.

By using the proposed equations, it is possible to predict the other properties. We hoped eventually that

Table 2. Comparison with the predicted and estimated LEL values for alcohol compounds

No.	Components	T _b [K]	T _f [K]	H _v [KJ/mol K]	H _v / RT _b	LEL exp.	Trouton rule	This Work
1	Methanol	337	285	35.20	12.56	6.00	10.11	7.08
2	Ethanol	351	286	38.26	13.21	3.30	4.97	2.15
3	n-Propanol	370	296	41.44	13.47	2.20	2.16	1.62
4	i-Propanol	355	285	39.85	13.50	2.00	3.63	1.70
5	n-Butanol	390	302	43.29	13.35	1.70	2.04	1.14
6	i-Butanol	373	301	40.75	13.14	1.68	3.18	1.43
7	2-Methyl-1-propanol	380	310	41.52	13.14	1.70	5.15	2.20
8	2-Methyl-2-propanol	357	277	39.07	13.16	1.90	2.24	1.16
9	1-Pentanol	411	311	44.36	12.98	1.20	1.54	0.96
10	2-Pentanol	392	307	41.40	12.70	1.20	2.79	1.27
11	3-Pentanol	391	313	43.01**	13.23	1.20	3.70	1.63
12	2-Methyl-1-butanol	403	316	43.90*	13.10	1.20	2.71	1.28
13	2-Methyl-2-butanol	375	294	39.04	12.52	1.40	3.19	1.28
14	3-Methyl-1-butanol	403	319	44.07	13.15	1.20	3.14	1.42
15	3-Methyl-2-butanol	385	300	41.40*	12.93	1.20	2.56	1.21
16	1-Hexanol	430	333	41.40	12.45	1.20	2.66	1.13
17	3-Methyl-1-pentanol	423	332	46.30*	13.17	1.10	2.34	1.29
18	4-Methyl-2-pentanol	405	314	45.60*	13.45	1.20	1.98	1.15
19	1-Heptanol	449	347	48.10*	12.89	0.89	2.26	1.12
20	1-Octanol	469	354	46.90*	12.09	0.79	1.97	0.94
21	2-Octanol	452	344	47.34**	12.06	0.80	2.14	0.99
22	1-Nonanol	487	349	54.40*	13.44	-	0.49	-
23	1-Decanol	504	355	48.78**	11.88	0.7	0.76	0.68
A.A.P.E.							100.38	17.77
A.A.D.							1.43	0.315

*Lange's Handbook of Chemistry

**The predicted enthalpy of vaporization by the use of Vetere's method

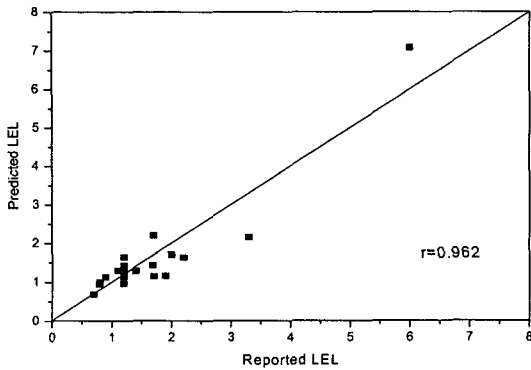


Fig. 1. Comparison between reported lower explosion limits and predicted lower explosion limits for alcohol compounds.

this method will permit the estimation of the explosion limits of alcohol with improved accuracy and the broader application for other compounds.

6. Conclusions

The new equation is proposed for predicting the lower explosion limits(LEL) of alcohol compounds on the basis of flash points, normal boiling points, solution theories, statistics, and mathematical method.

The relationship between the lower explosion limits, the normal boiling points, and the flash points was found. The lower explosion limit is correlated as a function of the normal boiling points and the flash points. The equation proposed is superior to the Trouton's rule. The empirical equation is in agreement with the predicted LEL values of 23 alcohol compounds, the A.A.P.E(average absolute percent error) is 17.77, the A.A.D.(average absolute deviation) is 0.315 vol%, and the coefficient of correlation (r) is 0.962. The prediction results of this model can thus be applied to incorporating inherently safer design for chemical processes, such as the determination of the safe storage and handling conditions for the other alcohol compounds.

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