

에스테르화합물에 대한 표준끓는점과 인화점을 이용한 폭발하한계 추산

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Estimation of the Lower Explosion Limits Using the Normal Boiling Points and the Flash Points for the Ester Compounds

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Abstract : The lower explosion limit(LEL) is one of the major combustion properties used to determine the fire and explosion hazards of the combustible substances. In this study, the lower explosion limits of the ester compounds were predicted by using the normal boiling points and the flash points based on the liquid thermodynamic theory. As a results, the A.A.P.E.(average absolute percent error) and the A.A.D.(average absolute deviation) of the reported and the calculated the LEL for the ester are 8.80 vol%and 0.18 vol%, respectively and the coefficient of correlation was 0.965. From a given results, by the use of the proposed methodology, it is possible to predict the lower explosion limits of the other flammable materials.

초록 : 폭발하한계는 가연성물질의 화재 및 폭발 위험성을 결정하는데 사용되는 중요한 연소특성치의 하나이다. 본 연구에서 에스테르 화합물에 대한 폭발하한계는 액체 열역학이론을 근거로 표준끓는점과 인화점을 이용하여 예측하였다. 그 결과, 문헌값과 예측값의 A.A.P.E.(average absolute percent error)는 8.80vol%이고, A.A.D.(average absolute deviation)는 0.18vol% 그리고 상관계수는 0.965로써 문헌값과 예측값은 일치하였다. 제시된 방법론 사용에 의해 다른 가연성물질의 폭발하한계 예측이 가능하다.

Key Words : lower explosion limit(LEL), combustion properties, combustible substance, ester compounds

1. Introduction

The flammable gases and vapors are frequently encountered in the working places and the chemical processes. In order to evaluate the fire and explosion involved and to ensure safe and optimal condition of the working places and the chemical processes, it is necessary to know their fire and explosion properties. The fire and combustible 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 concen-

tration), heats of combustion and flame temperature¹⁾.

Explosion limit is one of the major physical properties used to determine the fire and explosion hazards of the flammable substances²⁾. The research on the explosion limits is one of 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. A fuel-air mixture is flammable when combustion can be started by an ignition source. The main fact is the proportions or composition of the fuel-air mixture. A mixture that has less

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than a critical amount of fuel, known as the LEL, or greater than a critical amount of fuel, known as the UEL, will not be flammable. The LEL and UEL 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 for a material. They are particularly useful in specifying ventilation requirements for operations involving flammable liquids and gases.

In this study, the new equation for predicting the LEL of the ester compounds by using the flash points and the normal boiling points based on the liquid thermodynamic theory and the mathematical method is proposed and to provide basic data to prevent the explosion in the industrial field.

2. Relationship between explosion limit and combustible properties

Many manufacturing processes involve flammable chemicals, therefore flash points and explosion limits are essential to maximize safety in process design and operational procedures.

The flash point is the most common measure of flammability today, especially in transportation of chemicals, mainly because most regulations use the flash point to define different classes of flammable liquids. The flash point of a liquid is the lowest temperature at which sufficient vapor is evolved to form a flammable mixture in air at standard atmospheric pressure. The flash point provides a simple, convenient index for assessing the flammability of a wide variety of materials³⁾. The flash points are generally presented to values determined by tow 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 are a greater fire hazard than materials having a high flash point.

The explosion limits give the proportion of combustible gases in a mixture, between which limits this mixture is flammable Gas mixtures consisting of combustible, oxidizing, and inert gases are only flam-

mable under certain conditions. The LEL describes the leanest mixture that is still flammable, i.e. the mixture with the smallest fraction of combustible gas, while the UEL gives the richest flammable mixture. Increasing the fraction of inert gases in a mixture raises the LEL and decreases the UEL. The explosion limits may be used to specify operating, storage, and materials handling procedures for a material. They are particularly useful in specifying ventilation requirements for operations involving flammable liquids and gases.

The lower explosion limits are related directly to the normal boiling point and the flash point. Therefore, the prediction of the lower explosion limits by using the normal boiling points and the flash points is an interesting field in the chemical process industrial.

3. Prediction models of lower explosion limit

When measured and reported data are not available, various methods have been proposed for predicting explosion limits. There is no best prediction method. Therefore, estimating method will depend totally on the user's needs and the information that is already available or can be obtainable.

Numerous method have been published for estimating the LEL of flammable substances. Suzuki⁴⁾ reported that the LEL of 123 organic compounds containing only C, H, O atoms can be correlated with the gross heat of combustion. He proposed an empirical equation to estimate the LEL of 123 organic compounds.

$$LEL(\text{Vol}\%) = -3.42\Delta H_c^{-1} + 0.596\Delta H_c + 0.0538\Delta H_c^2 + 180 \quad (1)$$

where ΔH_c is the heat of combustion.

Hshieh⁵⁾ extended the scheme to include compound containing halogen and Si atoms. He proposed an empirical equation to estimate the LEL by using the heats of combustion for 220 organic and organosilicon compounds.

$$LEL(\text{Vol}\%) = 1154.2246\Delta H_c^{-0.7972} - 0.3822 \quad (2)$$

Pintar⁶⁾ proposed an equation containing the flash point and the total pressure to predict the LEL.

$$LEL(\text{Vol}\%) = 100 \times \frac{P(T_f - 3)}{p} \quad (3)$$

where $P(T_f - 3)$ is vapor pressure at a temperature 3 °C lower than the flash point, P is total pressure.

Ha⁷⁾ suggested that the LEL for alcohols can be estimated by using the normal boiling points and the flash points based on a solution theory. Statistical analysis of these 23 compounds resulted in best-fit empirical equation for predicting the lower explosion limits of alcohol compounds. Empirical equation is as follow :

$$\frac{1}{LEL}(\text{Vol}\%) = -16.95703 + 22.24219\left[\frac{T_b - T_f}{T_f}\right] - 6.66211\left[\frac{T_b - T_f}{T_f}\right]^2 \quad (4)$$

where T_b is the normal boiling point.

4. Evaluation criteria used

4.1. 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 value. The average absolute percent errors(A.A.P.E.)⁸⁾ is :

$$A.A.P.E. = \frac{\sum \left| \frac{LEL_i^{cal} - LEL_i^{exp}}{LEL_i^{exp}} \right|}{n} \times 100 \quad (5)$$

where the LEL_i^{exp} is the experimental lower explosive limit, and LEL_i^{cal} is the estimated lower explosive limit and n is the number of data.

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

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

$$A.A.D. = \sum \frac{|LEL_i^{cal} - LEL_i^{exp}|}{n} \quad (6)$$

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

4.2. The coefficient of correlation(r) and standard deviation

The coefficients of determination(r^2) and 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 by⁹⁾

$$r^2 = \frac{SS_r}{SS_{yy}} = 1 - \frac{SS_E}{SS_{yy}} \quad (7)$$

$$r = \pm \sqrt{r^2} \quad (8)$$

where SS_E is the sum of squares of 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 (= $\sum_{i=1}^n (Y_i - y)^2$) where y is the overall average of y_i . SS_{yy} is the total sum of squares about the mean given by

$$SS_{yy} = SS_E + SS_R = \sum_{i=1}^n (y_i - y)^2 \quad (9)$$

The standard deviation(S) is :

$$S = \sqrt{\frac{\sum (y_i - Y_i)^2}{n - 1}} \quad (10)$$

where n is the number of data.

5. Estimations of the lower explosion limits by using the normal boiling points and the flash points

5.1. Theory

When the pressure of the vapor in equilibrium with a liquid reaches 1 atm, the liquid boils and is completely converted to vapor absorption of enthalpy of vaporization(ΔH_v) at the normal boiling point(T_b).

For many nonpolar liquids, the molecular specific entropy of vaporization is empirically found to be a

universal constant, a consequence of the empirical invariance of the ratio of the normal boiling point to critical temperature, so that

$$\Delta H_v = (90 \text{ J/molK}) T_b \quad (11)$$

$$\frac{\Delta H_v}{RT_b} = \frac{90 \text{ J/molK}}{R} = \frac{90 \text{ J/molK}}{8.314 \text{ J/molK}} = 10.825 = \text{constant} \quad (12)$$

Known as Trouton's rule¹⁰⁾, this powerful relation enable one to estimate the enthalpy of vaporization ($\frac{\Delta H_v}{R}$) 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 explosive limits exists through the dependence of vapor pressure on temperature, given by Clausius-Clapeyron equation¹¹⁾.

$$\ln\left(\frac{P_v}{P_T}\right) = \frac{\Delta H_v}{R} \left[\frac{1}{T_b} - \frac{1}{T} \right] \quad (13)$$

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,

$$X_v = \frac{n_v}{n_T} = \frac{P_v V/RT}{P_T V/RT} = \frac{P_v}{P_T} \quad (14)$$

so that Eqn. (14) gives the mole fraction of the flammable fuel vapor in the space above the vaporizing liquid. The flammable fuel x_v has to exceed the lower explosive limit(L).

$$\ln\left(\frac{1}{LEL}\right) = \frac{\Delta H_v}{RT_b} \left[\frac{T_b}{T_f} - 1 \right] + \alpha \quad (15)$$

5.2. Various possible prediction models

Multiple regression analysis^{8,9)} are applied to obtain

the correlation for estimation of the lower explosion limits by using the normal boiling points and the flash points.

For the estimation of the lower explosive limits, the predicted equation which used Trouton's rule and various possible prediction models are as follows :

$$\ln\left(\frac{1}{LEL}\right) = \frac{\Delta H_v}{RT_b} \left[\frac{T_b - T_f}{T_f} \right] \quad (16)$$

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

$$\frac{1}{LEL} = a + b \left[\frac{T_b - T_f}{T_f} \right] + c \left[\frac{T_b - T_f}{T_f} \right]^2 \quad (18)$$

5.3. Selection of data and calculation of enthalpy of vaporization

All the lower explosion limits and the flash point of the ester compounds were obtained from NFPA 325M "Fire Hazard Properties of Flammable Liquid, Gases, and Volatile Solids"¹²⁾. The greater part of the heats of vaporization for the ester compounds were obtained from CRC Handbook¹³⁾ and Lange's Handbook of Chemistry¹⁴⁾. If there were not the heats of vaporization of ester compounds in these books, we were obtained from using the entropy values estimated by Vetere's equation¹⁵⁾.

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

Table 1. Vetere 's modification of the Kistiakowsky equation

Type of compounds	Correlations
Alcohols, Acids, Methylamine	$\Delta S_{vb} = 81.119 + 13.083 \log T_b - 25.769 \frac{T_b}{M} + 0.146528 \frac{T_b^2}{M} - 2.1362 \times 10^{-4} \frac{T_b^3}{M}$
Other polar compounds	$\Delta S_{vb} = 44.367 + 15.331 \log T_b + 0.39137 \frac{T_b}{M} + 4.330 \times 10^{-3} \frac{T_b^2}{M} - 5.627 \times 10^{-6} \frac{T_b^3}{M}$
Hydrocarbons	$\Delta S_{vb} = 58.20 + 13.7 \log M + 6.49 \frac{\{T_b - (263M)^{0.581}\}^{1.017}}{M}$

The ester compounds involved the other polar compounds. Therefore, the enthalpy of vaporization for alcohol compounds were predicted by the use of the entropy of vaporization calculated by Vetere's modification of the Kistiakowsky equation. Vetere's equation is as follow:

$$\Delta S_{vb} = 44.367 + 15.33 \log T_b + 0.39137 \frac{T_b}{M} + 4.330 \times 10^{-3} \frac{T_b^2}{M} - 5.627 \times 10^{-6} \frac{T_b^3}{M} \quad (19)$$

$$\Delta H_{vb} = \Delta S_{vb} T_b \quad (20)$$

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 i-butyl formate, sec-butyl acetate, i-butyl acetate and i-amylacetate were predicted by the use of the entropy of vaporization calculated by Vetere's method.

6. Comparison between reported and predicted lower explosion limits

Statistical analysis of these 16 ester compounds re-

sulted in best-fit empirical equation for predicting the lower explosion limits of the ester compounds.

Empirical equation is as follows :

$$\frac{1}{LEL} (Vol\%) = -0.52466 + 1.22656 \left[\frac{T_b - T_f}{T_f} \right] + 6.96680 \left[\frac{T_b - T_f}{T_f} \right]^2 \quad (21)$$

The reported LEL, the predicted LEL based on Trouton's rule and the predicted LEL of the empirical equation developed in this paper for 16 ester compounds are listed in Table 2. Also, Figure 1 shows the comparison between the reported lower explosion limits and the predicted LEL 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 (21) is in agreement with the predicted LEL values of 16 ester compounds, the A.A.P.E(average absolute percent error) is 8.80 vol%, the A.A.D. (average absolute deviation) is 0.18 vol% and the coefficient of correlation(r) is 0.965. The estimated values by the proposed equation were agreement with the reported values.

Table 2. Comparison between the predicted LEL by Trouton rule and this study for ester compounds

No.	Components	Molecular formula	T _b [K]	T _f [K]	H _v [KJ/mol K]	H _v /RT _b	LEL exp.	Trouton rule	This work
1	Methyl formate	C ₂ H ₄ O ₂	304	245	27.9	10.93	4.5	6.29	4.31
2	Ethyl formate	C ₃ H ₆ O ₂	326	254	29.9	11.03	2.8	4.39	2.61
3	n-Prpyl formate	C ₄ H ₈ O ₂	354	269	33.6	11.42	2.3	2.71	1.79
4	n-Butyl formate	C ₅ H ₁₀ O ₂	380	287	36.3	11.58	1.7	2.35	1.65
5	i-Butyl formate	C ₅ H ₁₀ O ₂	372	283	32.8**	10.60	1.7	3.57	1.82
6	Methylacetate	C ₃ H ₆ O ₂	333	264	30.3	11.01	3.2	6.12	3.68
7	Ethylacetate	C ₄ H ₈ O ₂	350	270	31.9	10.96	2.2	3.89	2.22
8	n-Propylacetate	C ₅ H ₁₀ O ₂	375	286	33.9*	10.87	1.7	3.40	1.87
9	i-Propylacetate	C ₅ H ₁₀ O ₂	362	275	32.9*	10.93	1.78	3.07	1.74
10	n-Butylacetate	C ₆ H ₁₂ O ₂	398	295	36.3*	10.97	1.4	2.17	1.33
11	sec-Butylacetate	C ₆ H ₁₂ O ₂	385	289	33.9**	10.59	1.7	2.97	1.54
12	i-Butylacetate	C ₆ H ₁₂ O ₂	391	294	34.5**	10.31	1.3	3.40	1.57
13	n-Amylacetate	C ₇ H ₁₄ O ₂	422	297	41.0*	11.68	1.1	1.47	1.231
14	i-Amylacetate	C ₇ H ₁₄ O ₂	415	298	36.7**	10.64	1.0	1.53	0.97
15	Methyl propionate	C ₄ H ₈ O ₂	352	271	32.2*	11.00	2.4	3.59	2.06
16	Ethyl propionate	C ₅ H ₁₀ O ₂	372	285	33.9*	10.96	1.85	3.63	2.00
A.A.P.E.								71.79	8.80
A.A.D.								1.39	0.18

* Lange's Handbook of Chemistry

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

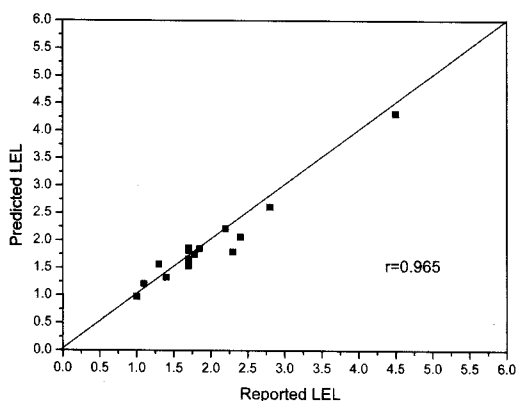


Fig. 1. Comparison between reported and predicted lower explosion limits for ester compounds.

By using the proposed equations, it is possible to predict the other properties. It is hoped eventually that this method will permit the estimation of the explosion limits of alcohol with improved accuracy and the broader application for other compounds.

7. Conclusions

The new equation for predicting the lower explosion limits(LEL) by using the flash points, and the normal boiling points based on the liquid thermodynamic theory and the mathematical method for ester compounds is proposed.

The lower explosion limits are correlated as a function of the normal boiling points and the flash points. The equation proposed is superior to the Trouton's rule. The predictive LEL by the empirical equation is in agreement with the reported LEL values of 16 ester compounds. As a results, the A.A.P.E. (average absolute percent error) is 8.80vol%, the A.A.D.(average absolute deviation) is 0.18vol%, and the coefficient of correlation(r) is 0.965.

The prediction results of this model can thus be applied to incorporate inherently safer design for chemical processes, such as the determination of the safe storage and handling conditions for the other ester compounds. Also, empirical correlation found serve as an estimation method for the LEL of the other compounds.

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