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Flammability Limits, Flash Points, and Their Consanguinity: Critical Analysis, Experimental Exploration, and Prediction

Jeffrey R. Rowley
Brigham Young University - Provo

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Flammability Limits, Flash Points, and their Consanguinity: Critical Analysis, Experimental Exploration, and Prediction

Jef Rowley

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Doctor of Philosophy

W. Vincent Wilding, Chair
Richard L. Rowley
Larry L. Baxter
Thomas A. Knotts
David O. Lignell

Department of Chemical Engineering

Brigham Young University

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ABSTRACT

Flammability Limits, Flash Points, and their Consanguinity: Critical Analysis, Experimental Exploration, and Prediction

Jef Rowley

Department of Chemical Engineering

Doctor of Philosophy

Accurate flash point and flammability limit data are needed to design safe chemical processes. Unfortunately, improper data storage and reporting policies that disregard the temperature dependence of the flammability limit and the fundamental relationship between the flash point and the lower flammability limit have resulted in compilations filled with erroneous values. To establish a database of consistent flammability data, critical analysis of reported data, experimental investigation of the temperature dependence of the lower flammability limit, and theoretical and empirical exploration of the relationship between flash points and temperature limits are undertaken.

Lower flammability limit measurements in a 12-L ASHRAE style apparatus were performed at temperatures between 300 K and 500 K. Analysis of these measurements showed that the adiabatic flame temperature at the lower flammability limit is not constant as previously thought, rather decreases with increasing temperature. Consequently the well-known modified Burgess-Wheeler law underestimates the effect of initial temperature on the lower flammability limit.

Flash point and lower temperature limit measurements indicate that the flash point is greater than the lower temperature limit, the difference increasing with increasing lower temperature limit. Flash point values determined in a Pensky-Martens apparatus typically exceed values determined using a small-scale apparatus above 350 K.

Data stored in the DIPPR$^{®}$ 801 database and more than 3600 points found in the literature were critically reviewed and the most probable value recommended, creating a database of consistent flammability data. This dataset was then used to develop a method of estimating the lower flammability limit, including dependence on initial temperature, and the upper flammability limit. Three methods of estimating the flash point, with one based entirely on structural contributions, were also developed. The proposed lower flammability limit and flash point methods appear to predict close to, if not within, experimental error.

Keywords: flammability limit, flash point, DIPPR, flame propagation

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CHAPTER 1. INTRODUCTION

Knowledge of the combustion potential of a chemical is crucial when designing safe chemical processes. To prevent explosion, it is often simplest to keep a chemical outside of its flammable concentration range, as described by the flammability limits and flash point.

The flash point is an approximation of the lower temperature limit, the temperature at which a chemical evolves enough vapors to support combustion. Agencies such as the U.S. Department of Transportation, the National Fire Protection Agency, and the Occupational Safety and Health Administration classify flammable liquids for regulations and guidelines based on the flash point [1]. Consequently, the flash points of common chemicals are widely reported.

Flammability limits represent the concentrations of fuel in air that will just support flame propagation. The limits are better descriptors of a chemical's flammability, and more useful for safe process design because they are applicable to solids, liquids and gases. A substantial amount of flammability limit data has been published, though the temperature-dependence of the limits is nearly always neglected. For gases, data are frequently reported at 298 K. Flammability limit data for liquids and solids, however, are often reported at a single arbitrary temperature.

Differences in apparatuses and experimental methods can influence the measured flash point and flammability limits significantly. A common practice of reporting the widest range of flammability, i.e., the lowest flash point, has apparently been adopted by many compilations, as the values they report are often outliers and inconsistent with data for other related properties. These inconsistent data are then frequently used to regress parameters for estimation methods. The end result of reporting the widest flammability range instead of the most probable is unnecessary and costly restraints on chemical processes and inaccuracy in prediction methods developed from the reported data.

This dissertation describes a critical evaluation of published flammability data, undertaken to provide a database of recommended values. In addition, flammability data are determined experimentally for 29 organic compounds, chosen for measurment to further understanding of the interrelationship of flammability properties, quantify the effect of standardized experimental methods and apparatuses on flammability data, explore the effect of initial temperature on the lower flammability limit, and to supplement previously reported experimental data. Finally, this dissertation presents flammability limit and flash point estimation methods for the critically reviewed compounds.

CHAPTER 2. FLAMMABILITY LIMITS

ASTM defines the upper/lower flammability limits as “the [maximum/minimum] concentration of a combustible substance that is capable of propagating flame in a homogenous mixture of the combustible and a gaseous oxidizer under specified conditions of test” [2]. Many investigators have theorized why such limits exist [3-27], but currently the dominant view is that flame propagation fails when the heat loss rate exceeds the rate of enthalpy generation during the combustion reaction.

2.1 Experimental Determination

Though many methods of measuring the flammability limit have been developed [2, 28-39], only the three standardized methods for which a significant amount of data have been reported are considered here.

2.1.1 Bureau of Mines Tube Method

Data from the tube method developed by the U.S. Bureau of Mines were long considered the standard for flammability limits. Tests were performed in narrow tubes, 2 cm to 7.5 cm in diameter and at least 1 m high. A fuel-oxidizer mixture was considered flammable only if it could, in theory, support flame propagation along an infinite tube. Thus, flame propagation to the top of the tube was required for a mixture to be called flammable [3-4].

2.1.2 ASHRAE Method

The ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) method [2, 40-42] was developed specifically to accommodate halogenated compounds that may be difficult to ignite in smaller vessels. Though measurements are made in a spherical 12-L flask, the flame propagation criterion for this method was empirically designed to reproduce data measured in jumbo tubes with full flame propagation [43-45]. A mixture is considered flammable when a flame forms a continuous arc subtended by a 90^o angle, measured from the ignition source to the vessel walls (Figure 2.1).

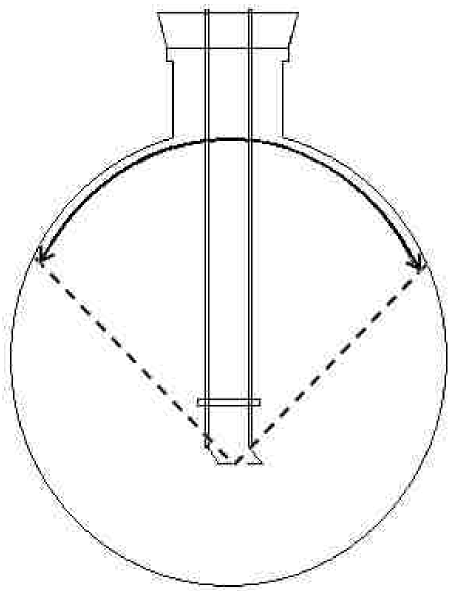

Figure 2.1. ASHRAE 90^o flame propagation criterion

2.1.3 EN 1839 Tube Method

Originally called DIN 51649, this European standard was developed with the reasoning that a fuel-oxidizer mixture supporting any ignition could result in potentially dangerous situations whether propagation is possible or not [5-6]. When the method was renamed EN 1839, the flammability criterion was changed to require flame detachment and at least 10 cm of flame propagation to account for localized heating introduced by the ignition source [7]. The standard test vessel is a vertical glass tube 150 cm long with a diameter of 5 cm.

2.1.4 Differences in Measurement Methods

Table 2.1 details the differences in the three flammability limit measurement methods described in this chapter. Several comparative studies have been published for these and other flammability apparatuses [44-48]. In general, it has been shown that data determined in the EN 1839 apparatus correspond to the widest fuel-concentration range over which a fuel-air mixture is considered flammable. The Bureau of Mines tube typically yields the narrowest range of fuel concentration, though data from the ASHRAE method are similar.

Table 2.1. Comparison of three widely-used standardized flammability apparatuses

	Bureau of Mines	**ASHRAE**	**EN 1839**
Vessel Shape	Vertical glass tube	Spherical glass flask	Vertical glass tube
Vessel Size	5 cm x 150 cm	12 L	8 cm x 30 cm
Ignition Source	Spark or flame, bottom of tube	Spark, below center of sphere	Spark, bottom of tube
Propagation Criterion	Full propagation to top of tube	Continuous flame arc subtending 90^o angle from ignition source	Flame detachment and 10 cm of propagation
Definition of Limit	Mean value of last ignition and non-ignition points	Mean value of last ignition and non-ignition points	Last non-ignition point

Many investigators have pointed to the discrepancies between flammability data determined using different methods as evidence that fundamental flammability limits may not exist [8-14]. On the other hand, much of the error between measurements may be a simple function of the flame propagation criteria and definition of the limit utilized in each study. However, the numerous other variables that affect the measured flammability limit make it difficult to show experimentally whether or not a fundamental flammability limit exists. A summary of these variables is provided in Appendix A. Because of the pertinence to this work, studies on the effect of temperature on the flammability limits will be summarized here.

2.2 Temperature Dependence of the Flammability Limit

Burgess and Wheeler [15] showed that the heat liberated by a mole of a lower limit mixture at ambient temperature and pressure is approximately constant for many compounds (Burgess-Wheeler law):

$$LFL \cdot (-\Delta H_{\mathrm{c}}) = k \,, \tag{2.1}$$

where LFL is the lower flammability limit and ΔH_{c} is the heat of combustion of the fuel.

Based on the findings of a constant adiabatic flame temperature with respect to the initial mixture temperature of the lower flammability limit, Zabetakis, Lambiris, and Scott [16-17] attempted to extend the law of Burgess and Wheeler to account for the temperature dependence of the lower flammability limit by adding the enthalpy required to raise a limit mixture from ambient temperature to the initial test temperature:

$$LFL \cdot (-\Delta H_{\mathrm{c}}) + \overline{C}_{p,\,\mathrm{fuel-air}} \cdot \Delta T = k\,, \tag{2.2}$$

where $\overline{C}_{p,\,\mathrm{fuel-air}}$ is the total specific heat of the fuel-air mixture, found by

$$\overline{C}_{p,\,\mathrm{fuel-air}} = LFL \cdot C_{p,\,\mathrm{f}} + (100 - LFL) \cdot C_{p,\,\mathrm{air}}\,, \tag{2.3}$$

and $C_{p,\,\mathrm{f}}$ and $C_{p,\,\mathrm{air}}$ are the molar heat capcities of the fuel and air, respectively. When the lower flammability limit is known at a given temperature, T_0, Equation 2.2 may be rewritten as

$$\frac{LFL(T)}{LFL(T_0)} = 1 - \frac{\overline{C}_{p,\,\mathrm{fuel-air}} \cdot 100}{LFL(T_0)\left(-\Delta H_{\mathrm{c}}\right)}\left(T - T_0\right). \tag{2.4}$$

For many hydrocarbons, this approximately corresponds to a 7 % decrease in the lower flammability limit per 100 K, relative to the value at 293 K.

Equation 2.4 is often expressed in the more general form

$$\frac{LFL(T_1)}{LFL(T_0)} = 1 - \frac{c}{100}\left(T_1 - T_0\right). \tag{2.5}$$

The parameter c represents the decrease relative to the lower flammability limit at T_0, typically 293 K, per 100 K increase, i.e., $c \sim 0.07\ \mathrm{K}^{-1}$ according to the modified Burgess-Wheeler law (Equation 2.4). Using a Bureau of Mines style apparatus with a 10 cm diameter, Hustad and Sønju [18] found c to be approximately $0.085\ \mathrm{K}^{-1}$ for hydrocarbons. Gibbon, Wainwright, and Rogers [19] showed c varied between $0.11\ \mathrm{K}^{-1}$ and $0.18\ \mathrm{K}^{-1}$ for common solvents in a 13-L closed sphere. Goethals et al. [20] and Brandes, Mitu, and Pawel [21] found c values between $0.13\ \mathrm{K}^{-1}$ and $0.23\ \mathrm{K}^{-1}$ in the DIN/EN tube apparatus for a wide range of compounds. A summary of studies on the effect of temperature on the upper flammability limit is included in Appendix A.

2.3 Flammability Limit Estimation Methods

Methods of predicting the lower flammability limit may be divided into two classifications: chemical equilibrium methods and empirical correlations.

2.3.1 Chemical Equilibrium Methods

Based on the findings of Zabetakis, Lambiris and Scott [17], chemical equilibrium methods assume that the adiabatic flame temperature at the flammability limit is approximately constant among different fuels. The adiabatic flame temperature (T_{ad}) is the theoretical temperature of the flame assuming no heat loss:

$$\sum_{\text{products}} H_i(T_{\mathrm{ad}}) = \sum_{\text{reactants}} H_i(T^{\circ}), \tag{2.6}$$

where T^{o} is the initial mixture temperature and H is the enthalpy of species i. The combustion products are typically estimated using a chemical equilibrium calculator.

Mashuga and Crowl [22] estimated the entire flammability envelope for methane and ethylene with satisfactory results by assuming a T_{ad} of 1200 K. Ervin et al. [23] also used an adiabatic flame temperature of 1200 K to predict the flammability limits of alkanes, carboxylic acids, and acetates. Shebeko et al. [24] and Vidal et al. [25] believed the temperature to be about 1600 K, while Melhelm [26] selected the conservative value of 1000 K.

Others have noted that the flame temperature is not constant at all, but rather it increases with the molecular weight of the fuel [27-29]. Zatsepin, Sorokin and Stepachev [30] developed a method to estimate the lower flammability limit from a T_{ad} calculated using structural contributions:

$$T_{\text{ad}} = \sum_i T_i x_i \, , \tag{2.7a}$$

where T_i is the contribution of bond-type i (Table 2.2), x_i is found by

$$x_i = \frac{k_i ng_i}{\sum_j k_j ng_j} \, , \tag{2.7b}$$

k_i is the multiplication factor of bond i (1.5 for aromatic bonds, 1 for all others), and ng_i is the number of occurrences of bond i.

Table 2.2. Group contributions for Zatsepin, Sorokin, and Stepachev [30] estimation method for lower flammability limits

i	**Bond**	T_i	*i*	**Bond**	T_i	*i*	**Bond**	T_i
1	C-H	1511	8	O-H	1487	14	$C{\approx}N^3$	2151
2	C-C	1910	9	C*-O	1832	15	$C\text{-}N^5$	1279
3	C≈C	1578	10	C=O*	1318	16	$C{\equiv}N^3$	1942
4	C=C	1720	11	C*=O	743	17	$N^5{=}O$	1652
5	C≡C	992	12	$C\text{-}N^3$	1892	18	C-Cl	1738
6	C-O	1571	13	$N^3\text{-}H$	1742	19	C-Br	7578
7	C=O	1345						

The symbol ≈ represents an aromatic bond, C* is a carbon atom not bonded to another carbon atom, O* is an oxygen atom from a carbonyl group of an aldehyde, and N^3 and N^5 are three and five valence nitrogen atoms, respectively.

Once T_{ad} has been calculated, the lower flammability limit may be estimated from

$$LFL = \frac{100}{(1+\nu)}, \tag{2.7c}$$

where

$$\nu = \frac{H_{\mathrm{f}}(T^{\mathrm{o}}) - \sum_{\mathrm{products}} n_j H_j(T_{\mathrm{ad}}) + \beta H_{\mathrm{O_2}}(T_{\mathrm{ad}})}{H_{\mathrm{air}}(T_{\mathrm{ad}}) - H_{\mathrm{air}}(T^{\mathrm{o}})}, \tag{2.7d}$$

and H_{f}, H_j, $H_{\mathrm{O_2}}$, and H_{air} are the enthalpies of the fuel, jth combustion product, oxygen, and air, respectively. The parameter n_j is the moles of the jth combustion product assuming complete combustion,

$$\mathrm{C_xH_yO_zN_wS_vX_u} \rightarrow \mathrm{xCO_2} + \frac{\mathrm{y-u}}{2}\mathrm{H_2O} + \frac{\mathrm{w}}{2}\mathrm{N_2} + \mathrm{vSO_2} + \mathrm{uHX}, \tag{2.8}$$

where X represents the halogens typically found in halogenated organic compounds, i.e. F, Cl, Br, or I, and β is the moles of oxygen required for stoichiometric combustion, found by

$$\beta = \mathrm{x} + \mathrm{v} + \frac{\mathrm{y-u}}{4} - \frac{\mathrm{z}}{2}. \tag{2.9}$$

2.3.2 Empirical Correlations

Empirical correlations have the advantage over chemical equilibrium methods because they don't require the use of chemical equilibrium calculators. While numerous methods for estimating the flammability limits at a single temperature point exist (Table 2.3), only three methods of estimating the temperature-dependent lower flammability limit were found. Only those methods are considered here. The reader is directed to Appendix B.1 for further details on the single-point methods.

Bureau of Mines Method

The Bureau of Mines method estimates the lower flammability limit in two stages. First, prediction of the lower flammability limit at a single temperature point, assumed to be 293 K, by the method of Jones [31-32]:

$$LFL(T_0) = 0.55 C_{\mathrm{st}}, \tag{2.10}$$

where C_{st} is the fuel concentration required for stoichiometric combustion, typically found using

$$C_{\mathrm{st}} = \frac{100}{1 + 4.773\beta}. \tag{2.11}$$

Second, temperature dependence is added, using the modified Burgess-Wheeler law (Equation 2.4),

$$\frac{LFL(T)}{LFL(T_0)} = 1 - \frac{C_{p,\,\mathrm{fuel-air}} \cdot 100}{LFL(T_0)\left(-\Delta H_{\mathrm{c}}\right)}\left(T - T_0\right). \tag{2.4}$$

Method of Britton

The method of Britton and Frurip [33-34] follows a similar format. First the lower flammability is predicted at 298 K using data for a reference fuel:

Table 2.3. Single point prediction methods for lower and upper flammability limits

Lower Flammability Limit		**Upper Flammability Limit**	
Reference	**Parameters**	**Reference**	**Parameters**
Affens - Approximation [35]	Number of carbon atoms; hydrocarbons only	Affens [35]	Number of carbon atoms; hydrocarbons only
Shimy [36]	Number of carbon atoms	Shimy [36]	Number of carbon and hydrogen atoms
Solovev-Baratov [37]	Number of carbon atoms	High-Danner [38]	Structural contributions
Shebeko [39]	Atomic contributions	Nuzhda [40]	Structural contributions
Seaton [41]	Structural contributions	Seaton [41]	Structural contributions
Pintar [42]	Structural contributions	Pintar [42]	Structural contributions
Albahri [43]	Structural contributions; hydrocarbons only	Albahri [43]	Structural contributions; hydrocarbons only
Kondo [40, 78-79]	Structural contributions, C_{st}	Kondo [42-44]	Structural contributions, C_{st}
Jones [31-32]	C_{st}	Jones [31-32]	C_{st}
Zatsepin [44]	Structural contributions, C_{st}	Hilado [45]	C_{st}
Pintar – Approximation [42]	C_{st}	Pintar – Approximation [42]	C_{st}
Hilado [45]	C_{st}	Thornton [46]	β
Möller [47]	C_{st}	Monakhov [39, 48]	β
Oehley [49]	β	Miloshev [50]	Normal boiling point
Monakhov [39, 48]	β	Hanley [51]	Heat of combustion
Thornton [46]	β	Hshieh [52]	Heat of combustion
Britton [33-34]	β	Suzuki-Koide [53]	Gross heat of combustion
Funk [54]	β	Affens from LFL [35]	Lower flammability limit
Britton [33-34]	β, heat of combustion	Spakowski [55]	Lower flammability limit
Suzuki-Ishida [56]	Gross heat of combustion, critical temperature, critical pressure or Neural network	Suzuki-Ishida [56]	Gross heat of combustion, diffusion coefficient or Neural network
Spakowski [55]	Heat of combustion	Gharagheizi [57]	Molecular descriptors
Affens [35]	Heat of combustion	Pan [58]	Molecular descriptors
Hanley [51]	Heat of combustion		
Goto [59-60]	Heat of combustion		
Dalmazzone [61]	Heat of combustion; developed for hydrocarbons		
Suzuki [62]	Gross heat of combustion		
Hshieh [63-64]	Heat of combustion		
Miloshev [50]	Normal boiling point		
Gharagheizi [65]	Molecular descriptors		

$$LFL(T_0) = F \cdot LFL_{\mathrm{ref}}(T_0) \frac{\Delta H_{\mathrm{c,ref}}}{\Delta H_{\mathrm{c}}} \cdot \frac{\Delta H_{\mathrm{c,ref}} / \beta_{\mathrm{ref}}}{\Delta H_{\mathrm{c}} / \beta} . \tag{2.12}$$

When methane is used as the reference fuel, the empirical constant F is equal to 1.00 for hydrocarbons and 1.12 for other fuels. Equation 2.12 then becomes

$$LFL(T_0) = \Phi \cdot \frac{\beta}{\Delta H_{\mathrm{c}}^{\ 2}}, \tag{2.13}$$

where Φ equals 9.216 x 10^4 $(\mathrm{kcal \cdot mol^{-1}})^2$ for hydrocarbons and 1.032 x 10^5 $(\mathrm{kcal \cdot mol^{-1}})^2$ for other $C_xH_yO_zN_w$ fuels.

Based on the findings of White [16] and Zabetakis, Lambiris, and Scott [17], Britton assumed that the adiabatic flame temperature is constant with regards to the initial temperature of the fuel-air mixture. Thus, the temperature dependence can be written as

$$LFL(T) = LFL(T_0) \cdot \frac{T_{\mathrm{ad}} - T}{T_{\mathrm{ad}} - T_0}. \tag{2.14}$$

Britton also provided correlations for estimating T_{ad} (K):

$$T_{\mathrm{ad}} = 2181 - 7.4613 \cdot \frac{-\Delta H_{\mathrm{c}}}{\beta} \text{ for hydrocarbons,} \tag{2.15a}$$

$$T_{\mathrm{ad}} = 2290 - 7.6944 \cdot \frac{-\Delta H_{\mathrm{c}}}{\beta} \text{ for organo-chlorides,} \tag{2.15b}$$

$$T_{\mathrm{ad}} = 2427 - 8.3846 \cdot \frac{-\Delta H_{\mathrm{c}}}{\beta} \text{ for other CHON fuels} \tag{2.15c}$$

where the heat of combustion is in $(\mathrm{kcal \cdot mol^{-1}})$.

Method of Catoire and Naudet

With data predominantly from International Chemical Safety Cards and Bureau of Mines compilations, Catoire and Naudet [66] found the lower flammability limit could be predicted at temperatures up to 673 K using

$$LFL(T) = 519.957 \cdot X^{0.70936} \cdot n_{\mathrm{C}}^{-0.197} \cdot T^{-0.51536}, \tag{2.16a}$$

where

$$X = \frac{1}{1 + 5n_{\mathrm{C}} + \frac{5}{4}n_{\mathrm{H}} - \frac{5}{2}n_{\mathrm{O}}}, \tag{2.16b}$$

and n_{C}, n_{H}, and n_{O} are the number of carbon, hydrogen, and oxygen atoms in the molecule, respectively. Unlike the other temperature-dependent flammability limit methods, this method predicts a nonlinear response in the lower flammability with respect to temperature.

CHAPTER 3. TEMPERATURE LIMITS AND FLASH POINTS

3.1 Flammability Temperature Limits

Kuchta [67] defined the flammability temperature limits as the "temperature range over which the liquid can form flammable vapor concentrations." In other words, upper and lower flammability temperature limits are the temperatures at which a solid or liquid will produce enough vapor to form the upper and lower flammability concentration limits.

3.1.1 Flammability Temperature Limits: Experimental Determination

ASTM E 1232 is currently the only standardized method for determining temperature limits [68]. The apparatus proscribed by ASTM E 1232 is identical to the ASTM apparatus to determine flammability limits [2]. Although no European standardized method exists, Brandes, Mitu and Pawel [69-70] measured the lower temperature limit of several compounds using the EN 1839 tube apparatus. There is currently no standardized method of determining the upper temperature limit.

3.1.2 Flammability Temperature Limits: Estimation

No prediction methods have been developed explicitly for flammability temperature limits for two reasons: 1. Most researchers assume that the lower flammability temperature limit is essentially the same value as the flash point [106-108]. 2. The temperature limit can be obtained from a predicted flammability concentration limit and the vapor pressure curve assuming the partial pressure at the temperature limit equals the flammability limit. A few researchers have attempted to find a correlation between the flash point and lower temperature limit; however these will be discussed in Section 3.3.

3.2 Flash Point

Similar to the lower flammability temperature limit, the flash point is defined as the “lowest temperature, corrected to 101.3 kPa, at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of a test” [71]. The terms “flash point” and “lower temperature limit” have often been used interchangeably. Although they are similar in theory, in practice the lower temperature limit may be up to tens of degrees Celsius lower than the flash point [72]. According to Kuchta [67] and Zabetakis [32], this difference results from the less ideal conditions under which the flash point is determined (e.g., downward flame propagation and non-uniform mixtures).

3.2.1 Flash Point: Experimental Determination

In 1913 Redwood [73] described nearly 50 different flash point apparatuses. Since then, many attempts have been made to standardize flash point testers and today there are five main apparatuses used internationally (Table 3.1). ASTM has defined eight different test methods using four of these apparatuses (Table 3.2), and developed another method (ASTM E 502) that experimentalists may use to determine which ASTM test method is appropriate for any given situation.

In general, flash points are classified as either open- or closed-cup. As the names suggest, an open-cup apparatus contains no lid, and vapors are free to diffuse into the surrounding atmosphere. A closed-cup apparatus has a cover to contain vapors and produce equilibrium conditions. Closed-cup values are generally lower than open-cup values, though not always.

Table 3.1. Five main flash point apparatuses currently used

Apparatus	Temperature Uniformity	Sample Volume	Primary Use
Tagliabue (Tag)	Liquid Bath	50 mL	Less viscous compounds
Pensky-Martens	Stirred; Metal shell	75 mL	Viscous compounds
Cleveland	Metal plate across cup base	70 mL	Open-cup tests
Small-Scale (Setaflash)	Preheated to fixed temperature	2 or 4 mL	Small scale and flash/no-flash tests
Abel	Water bath and air gap	79 mL	European tests

Table 3.2. ASTM standardized method of measuring the flash point

Method	Apparatus	Open/Closed	Heating Rate	Range (^{o}C)
D 56	Tag	Closed	(1 to 3) (^{o}C$\cdot$min^{-1})	< 93
D 92	Cleveland	Open	(5 to 6) (^{o}C$\cdot$min^{-1})	79 to 400
D 93	Pensky-Martens	Closed	(4 to 5) (^{o}C$\cdot$min^{-1})	40 to 370
D 1310	Tag	Open	1 (^{o}C$\cdot$min^{-1})	-18 to 165
D 3278	Small-scale	Closed	Fixed temperature	0 to 110
D 3828	Small-scale	Closed	Fixed temperature	-20 to 300
D 3941	Tag or Pensky-Martens	Closed	Fixed temperature	0 to 110
D 3941	Tag or Pensky-Martens	Closed	0.5 (^{o}C$\cdot$min^{-1})	< 93 or 40 to 370

Several researchers have tried to quantify the effect of flash point apparatus on the measured value. Babrauskas [48] and Burgoyne [74] examined the differences between open-and closed-cup values, but as Meyerheim and Frank [75] reported, the open-cup value depends upon the distance of the ignition source from the fuel. Probst [76] found linear relationships between values measured in the Tag and Pensky-Martens apparatuses, and the Tag and Cleveland apparatuses. Montemayor [77] found no statistical difference between values determined in automated and manual apparatuses for Pensky-Martens, Tag, and Cleveland apparatuses, despite the ASTM policy that manual measurements are accepted over automated.

The effect of sample viscosity on measured flash points was studied by Kamarchik [78] and Montemayor [79]. Both investigators determined that at higher viscosities, lower flash points will be observed unless the heating rate is decreased or the stirring rate is increased.

3.2.2 Flash Point: Estimation

The published prediction methods for the flash point are listed in Table 3.3. The majority of the methods are based on the normal boiling point, with many calculating the flash point from a linear function of the boiling point, the coefficients varying by chemical class. The method proposed by Catoire and Naudet [80] is a unique, nonlinear boiling-point method where coefficients are independent of chemical class:

$$FP = 1.477 T_b^{0.797} \Delta H_{vp}^{\circ\ 0.168} n_C^{-0.059}, \tag{3.1}$$

where ΔH_{vp}° is the enthalpy of vaporization (kJ·mol^{-1}) at 298.15 K, and T_b is the normal boiling point (K).

Leslie and Geniesse [81] observed that at the flash point the vapor pressure was approximately constant:

Table 3.3. Published methods of estimating the flash point

Reference	Applicable Chemical Class	Parameters
Modified Thornton [82]	Organic compounds	Vapor pressure, β
Fujii-Hermann [83]	Organic compounds	Vapor pressure
Leslie-Geniesse [81]	Organic compounds	Vapor Pressure, β
Li-Moore [84]	Organic compounds	Normal boiling point
Hshieh [85]	Organic compounds	Normal boiling point
Möller [47]	Organic compounds	Normal boiling point
Satyanarayana-Rao [86]	Organic compounds	Normal boiling point
Wang-Sun [87]	Organic compounds	Normal boiling point
Satyanarayana-Kakati [88]	Hydrocarbons	Normal boiling point
Butler et al. [89]	Hydrocarbons	Normal boiling point
Bodhurtha [90]	Hydrocarbons	Normal boiling point
Riazi-Daubert [91]	Hydrocarbons	Normal boiling point
Akhmetzhanov [92]	Hydrocarbons, alcohols, Acids	Normal boiling point
Patil [93]	Acids, alcohols, aldehydes	Normal boiling point
Satyanarayana-Krishna [94]	Silanes	Normal boiling point
Ishiuchi [95]	Organic compounds	Normal boiling point, β
Oehley [49]	Organic compounds	Normal boiling point, atomic contributions
Affens [35]	*n*-Alkanes	Normal boiling point or vapor pressure
Blinov [96]	Organic compounds	Normal boiling point, vapor pressure, β
Prugh [97]	Organic compounds	Normal boiling point, C_{st}
Korol'chenko [96]	Organic compounds	Normal boiling point, structural groups
Shebeko [96]	Organic compounds	Normal boiling point, heat of combustion
Catoire-Naudet [80]	Organic compounds	Normal boiling point, heat of vaporization
Metcalfe [98]	Organic compounds	Normal boiling point, specific gravity
Modified Satyanarayana-Kakati [99]	Organic compounds	Normal boiling point, specific gravity
Katritzky [100-101]	Hydrocarbons	Normal boiling point, molecular descriptors
Suzuki [102]	Organic compounds	Structural groups, molecular descriptors
Tetteh [103]	Organic compounds	Neural networks
Zhokhova [104]	Organic compounds	Neural networks
Albahri [43]	Hydrcoarbons	Structural groups
Pan [105]	Alkanes	Structural groups

$$\frac{P^*(FP)}{101.3\ \text{kPa}} = \frac{1}{8\beta}. \tag{3.2}$$

Figure 3.1 shows the vapor pressure plotted against β for over 500 organic compounds. Though there is significant scatter about the fit proposed by Leslie and Geniesse, large errors in the vapor pressure correspond to small flash point errors.

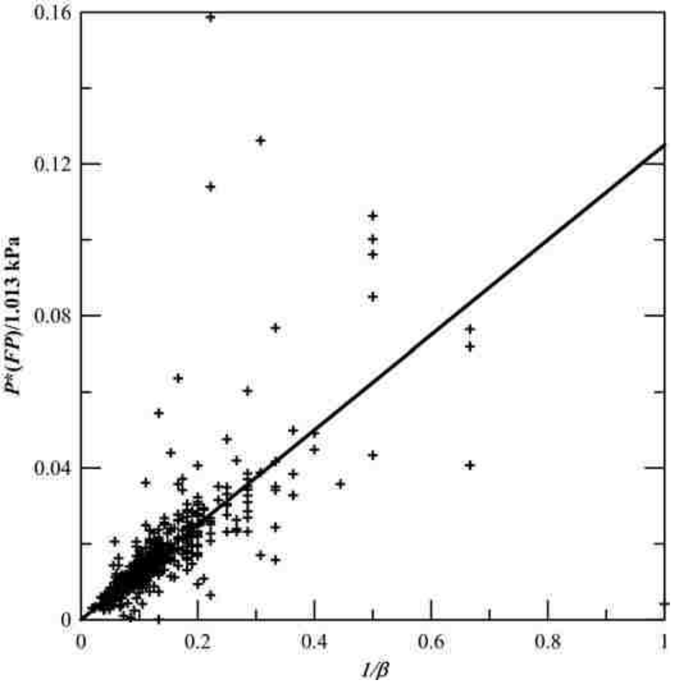

Figure 3.1. Vapor pressure at the flash point against the inverse of the moles of oxygen required for stoichiometric combustion. The solid line is the fit proposed by Leslie and Geniesse

Suzuki [102] proposed a method to calculate the flash point of organic chemicals solely from molecular structure:

$$FP = 25.57\,{}^{1}\chi + \sum_{i} ng_{i} h_{i} - 86.0\,, \tag{3.3}$$

where *ng* is the number of the i^{th} contribution with value *h* (given in Appendix B), and ${}^{1}\chi$ is the first-order Kier-Hall connectivity index,

$${}^{1}\chi = \sum (\delta_{i}\delta_{j})^{-1/2}\,. \tag{3.4}$$

The sum in Equation 3.4 is over all bonds between atoms *i* and *j*, excluding bonds to hydrogen atoms. δ_i is the valence of atom *i* minus the number of hydrogen atoms bonded to that atom.

Pan [105] and Albahri [43] also proposed structural contribution methods, however these methods apply to only alkanes and hydrocarbons, respectively. The reader is directed to Appendix B.2 for a summary of the other methods listed in Table 3.3.

3.3 Interrelation of Fire-Hazard Properties

Figure 3.2 depicts a typical flammability diagram and the relation of the individual fire-safety properties to each other. The only obvious relationship is between the temperature limits, T_L and T_U and flammability limits, *LFL* and *UFL*, which are related directly through the vapor pressure when the flammability limits are known at saturation, i.e.,

$$\frac{P^*(T_\mathrm{L})}{101.3\ \mathrm{kPa}} \times 100 = \frac{LFL\ (T_\mathrm{L})}{\mathrm{vol\%}}, \tag{3.5a}$$

$$\frac{P^*(T_\mathrm{U})}{101.3\ \mathrm{kPa}} \times 100 = \frac{UFL\ (T_\mathrm{U})}{\mathrm{vol\%}}. \tag{3.5b}$$

Flammability limits, however, are typically determined at some temperature above the boiling point and not at the temperature limit [106]. Because flammability limits widen with increasing temperature, using Equation 3.5a to calculate a lower flammability limit from an experimental temperature limit may result in a flammability limit that is higher than reported data. Conversely, calculating a lower temperature limit from an experimental flammability limit without accounting for the effect of increased temperature will result in values that are lower than experimental data.

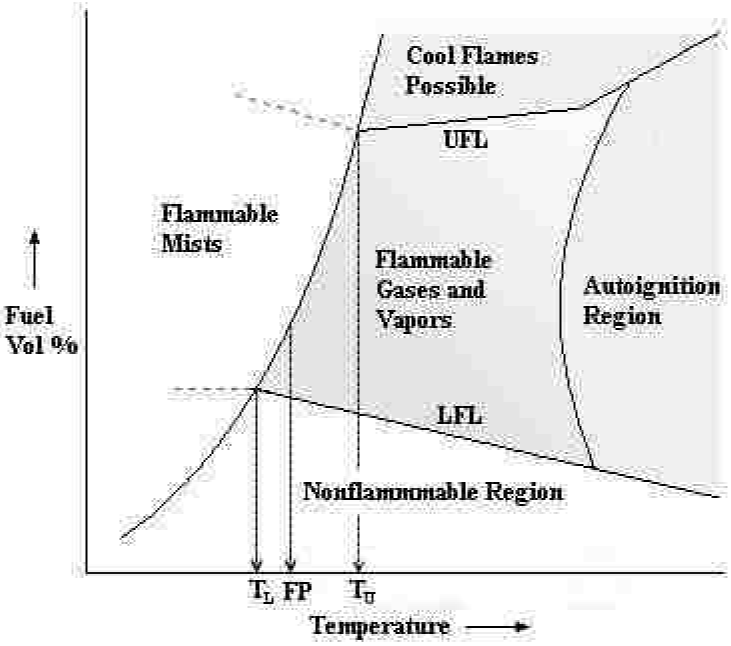

Figure 3.2. Flammability diagram illustrating the relationship between the flammability limits (LFL/UFL), flash point (FP), and temperature limits (T_L/T_U)

As mentioned above, the lower temperature limit in Equation 3.5a is often assumed to be the same as flash point. Because the experimental flash point is typically higher than the lower temperature limit, and becaue the vapor pressure curve rises steeply with temperature, calculation of the lower flammability limit from the flash point can result in large errors. This also means, however, that the lower temperature limit and even flash point may be approximated from an experimental lower flammability limit with reasonable accuracy.

Many empirical relationships have been developed to describe the relationship between the flash point, temperature limits, and flammability limits. Evlanov [107] correlated the open-cup flash point, $T_{FP,\,\mathrm{OC}}$, and the lower temperature limit, T_L:

$$\frac{1}{T_L} - \frac{1}{T_{FP,\mathrm{OC}}} = \frac{0.412\mathrm{R}}{\Delta H_{vp}}, \tag{3.6}$$

where R is the ideal gas constant, ΔH_{vp} is the heat of vaporization at the normal boiling point, and the temperatures are in ^{o}C. In another work, Evlanov [108] found a simple correlation between closed-cup flash points, T_{FP}, and the lower temperature limit:

$$T_{FP} - T_L = 0.04 T_{FP} - 2 . \tag{3.7}$$

Again, the temperatures are given in ^{o}C. Equation 3.7 indicates that the difference between the flash point and lower temperature limit increases linearly with increasing temperature. Shebeko et al. [96] and Pintar (as cited by Babrauskas) [48] both found the difference between the flash point and the lower temperature limit to be a constant of 1.9 K and 3 K, respectively.

Hasegawa and Kashiki [109] attempted to correlate the upper flash point determined by a small scale apparatus with the upper temperature limit; however, as few upper flash point data are available, this correlation has limited use.

Kueffer and Donaldson [110] correlated the lower flammability limit to the closed-cup flash point through the vapor pressure,

$$P^*(T_{FP}) = 1.15\, LFL(T_0) + 0.00198 , \tag{3.8}$$

while Oehley [49] claimed that the flash point and lower flammability limit were related by

$$LFL(T_0) = \frac{14400}{\left(T_b - T_{FP}\right)^2} . \tag{3.9}$$

Kanury [111-112] took a more theoretical approach and derived an expression relating the lower flammability limit and the flash point from the Clausius-Clapeyron equation:

$$\ln\left(\frac{1}{LFL(T_0)}\right)=\frac{\Delta H_{vp}}{\mathrm{R}\,T_b}\left(\frac{T_b}{T_{FP}}-1\right)+\ln(K)\,. \tag{3.10}$$

In this equation, K is a constant that accounts for fuel vapor dispersion and mass transfer in the apparatus, and the variability of the location of the ignition source. Kanury states that if the vapor is accumulated without convective and diffusive dissipation into the atmosphere and the mixture composition is uniform above the liquid, then K is unity. If, however, dispersion of the vapor is permitted, such as with an open-cup apparatus, K would be larger than unity.

Affens [35] reported a method for estimating the upper flammability limit, *UFL*, from the lower flammability limit at 293 K:

$$\frac{1}{UFL(T_0)}=0.0993\left(\frac{1}{LFL(T_0)}\right)+0.0472\,. \tag{3.11}$$

Spakowski [55] also found a correlation between the flammability limits:

$$UFL(T_0)=7.1\,LFL(T_0)^{0.56}\,. \tag{3.12}$$

Aside from Equation 3.5, the correlations presented in this section are empirically based and the values of the parameters surely depend on the measurement apparatuses employed to obtain the data. The predictive power of several of these correlations will be examined in a later chapter.

CHAPTER 4. EXPERIMENTAL METHOD

Measurements were performed to further understanding of how initial temperature affects the lower flammability limit in large-diameter vessels, and explore the relationship between the flash point and lower temperature limit. This chapter outlines the experimental technique used for this work.

4.1 Selection of Measurement Compounds

Measurement candidates were selected based on the value the flash point or lower flammability limit data would add to the DIPPR® 801 database. The potential value of the experimental data was judged by the number of similar compounds missing experimental data, or if existing data were suspected to be erroneous. The candidates were then reduced to 29 compounds based on measurement cost and safety considerations. Several compounds from the *n*-alcohol family were included to compare experimental results with previously reported values, and to illustrate how the experimental data vary within a chemical series. Table 4.1 lists the chemical phase, source, and chemical purity of the selected compounds.

Table 4.1. Compounds for which experimental work was performed

Compound	CAS Number	Phase	Purity	Source
1-Hexyne	693-02-7	L	>98 %	Alfa Aesar
4-*iso*Propyl-*m*-cresol	3228-02-2	S	99 %	Aldrich
1-Octanol	111-87-5	L	99 %	Aldrich
2-Methyl-1,3-propanediol	2163-42-0	L	99 %	Aldrich
2-Nonanone	821-55-6	L	99 %	Aldrich
4-Methyl-2-pentanol	108-11-2	L	99 %	Acros Organics
5-*o*-Tolyl-2-pentene	6047-69-4	L	98 %	Aldrich
Adamantane	281-23-2	S	99 %	Aldrich
α-Pinene	80-56-8	L	98 %	Aldrich
Anthraquinone	84-65-1	S	98 %	Aldrich
Butanol	71-36-3	L	99.90 %	Aldrich
Dibutylamine	111-92-2	L	>99.5 %	Aldrich
Diisobutyl Phthalate	84-69-5	L	99 %	Aldrich
Dodecanoic Acid	143-07-7	S	99 %	Aldrich
Ethyl Lactate	97-64-3	L	>98 %	Aldrich
Hexadecanol	36653-82-4	S	99 %	Aldrich
Hexyl Formate	629-33-4	L	>98.5 %	Vigon International
Isopropyl Myristate	110-27-0	L	98 %	Alfa Aesar
Methanol	67-56-1	L	99.80 %	Mallinckrodt
Methyl Benzoate	93-58-3	L	99 %	Sigma Aldrich
Decyl Acetate	112-17-4	L	98 %	Alfa Aesar
Niacin	59-67-6	S	99 %	Fluka
Octyl Formate	112-32-3	L	>98 %	Vigon International
p-Cumylphenol	599-64-4	S	99 %	Aldrich
Phenetole	103-73-1	L	99 %	Aldrich
Succinic Anhydride	108-30-5	S	>99 %	Aldrich
Trimellitic Anhydride	552-30-7	S	98 %	Fluka
Trioctylamine	1116-76-3	L	>99 %	Fluka
Urea	57-13-6	S	>99.5 %	Sigma

4.2 Lower Flammability Limit

An ASHRAE-style apparatus was constructed, as set forth in Appendix A of ASTM E 681 [2] (Figure 1). Apparatus specifications may be found in Appendix C. Lower flammability limit measurements were made at temperatures between 300 K and 500 K for 18 of the 19 liquids listed in Table 4.1 using the method described in ASTM E 681. Measurement of the lower flammability limit was attempted at 450 K for the 19th liquid, trioctylamine, but no flame

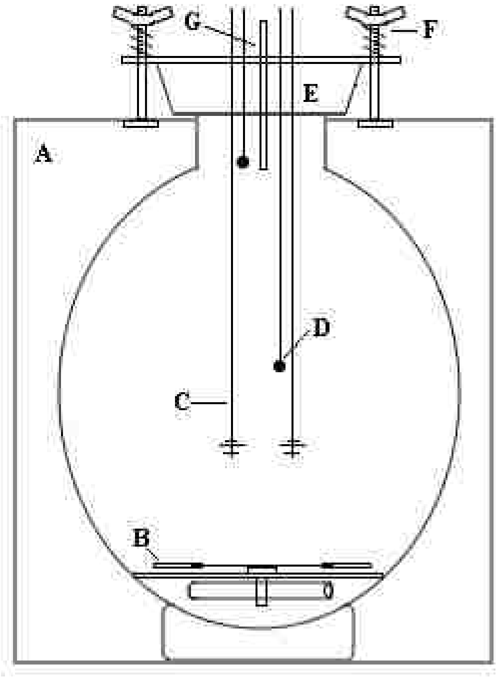

Figure 4.1. Schematic for 12 L flammability apparatus; A. Oven, B. Magnetic stir mechanism, C. Electrode, D. RTD, E. Silicon stopper, F. Spring-loaded cover clamp, G. Air/fuel inlet

could be induced, even with sample volumes corresponding to three times the estimated value based on earlier flash point measurements.

The lower flammability limits of the 18 liquids were determined by heating a spherical 12 L flask to the test temperature in an oven that regulated the temperature within the flask within ± 2 K. The flask was evacuated below 2.7 kPa, and a specified volume of liquid sample was injected through a rubber septum over the fuel-inlet tube. Once the sample was completely evaporated, air was slowly introduced through the inlet until the flask reached atmospheric pressure, sweeping any sample droplets from the inlet into the flask. The mixture was agitated for at least 7 min while the glassware above the oven was heated to avoid condensation. Two thermocouples, one positioned just below the neck of the flask and the other near the center, were used to verify achievement of thermal equilibrium within the flask.

Shortly before ignition, the stirring mechanism was shut off and the mixture was allowed to rest for 30 sec to eliminate turbulence. The barometric pressure was recorded, and the clamps on the flask cover were released to allow venting during ignition. Ignition of the mixture was attempted by a 15 kV (30 mA) power supply attached to tungsten electrodes 6.4 mm apart, 1/3 of the flask's height from the bottom, with a spark duration limited to 0.4 s. The ASHRAE 90^{o} flame propagation criterion discussed in Section 2.1 was utilized to distinguish between a flammable and nonflammable mixture.

This process was repeated, varying the sample injection volume by $(5 \pm 2)\ \mathrm{mm}^3$, until consecutive trials resulted in both a flame that fulfilled the flame propagation criterion (commonly called a "go" trial) and one that did not (commonly called a "no go" trial). The lower limit was calculated from the average injection volume of these two tests, $\overline{V}_{\mathrm{inj}}$, assuming ideal gas behavior:

$$LFL = \frac{\rho \cdot \overline{V}_{\mathrm{inj}} \cdot \mathrm{R} \cdot T^{\mathrm{o}}}{P \cdot V_{\mathrm{vessel}}} \times 100\,, \tag{4.1}$$

where P is the ambient pressure, ρ is the liquid density calculated from correlations given in the DIPPR® 801 database at the temperature of the lab, T^{o} is the average temperature measured by the two RTDs, and V_{vessel} is the calibrated volume of the flask. Between runs the vessel was flushed with air and evacuated below 2.7 kPa at least 6 times to remove any remaining fuel and combustion products.

4.3 Lower Temperature Limit

The lower temperature limit was determined using the ASHRAE apparatus described in Section 4.2 for 18 of the compounds listed in Table 4.1. The experimental method outlined in ASTM E 1232 [68] was followed.

At least 50 mL of sample was added to the flask, and the system was heated to the trial temperature. Once thermal equilibrium was achieved, as verified by the two RTDs shown in Figure 4.1, the sample was agitated for at least 15 minutes.

Shortly before ignition, the stirring mechanism was shut off and the mixture was allowed to rest for 30 sec to eliminate turbulence. The barometric pressure was recorded, and the clamps on the flask cover were released to allow venting during ignition. The ignition source described in 4.2 was engaged, and any flame propagation was recorded. The ASHRAE 90^o flame propagation criterion discussed in Section 2.1 was utilized to distinguish between a flammable and nonflammable mixture.

Between runs the flask was evacuated until the liquid sample boiled, 6 times to ensure all combustion products were removed, and the oven was set to a new trial temperature. For safety reasons, the temperature was adjusted by no more than 5 ^oC, final determinations having a step-size no larger than 0.5 ^oC. All final determinations were performed in a clean vessel with a fresh sample.

Because lower temperature limits are defined at 101.3 kPa, the measured lower temperature limit was adjusted for barometric pressure using the vapor pressure curve, as detailed in Appendix C.

4.4 Flash Point

The flash point was measured for 25 of the compounds listed in Table 4.1 using a Pensky-Martens apparatus (Koehler K16200), and for 27 of the compounds using a small-scale apparatus (ERDCO Rapid Test RT-1).

4.4.1 Pensky-Martens Procedure

The flash point was determined in the Pensky-Martens apparatus as outlined in ASTM D 93 [113]. 75 mL of a fresh liquid sample was placed in the test cup. If the sample was solid, the cup was loosely filled to the 75 mL mark on the cup.

The stirrer was engaged, and the thermostat adjusted until the sample temperature increased by about 4 ($^{o}C \cdot min^{-1}$). Starting about 5 ^{o}C below the expected flash point, ignition trials were attempted by lowering the pilot flame into the cup for about 0.5 sec, repeated every 2 ^{o}C. The flash point was recorded as the temperature at which a flash was seen. For subsequent runs, the ignition trial increment was reduced to every 1 ^{o}C to refine the measured flash point. The sample cup and lid were cleaned between runs.

The measured flash point was adjusted for differences in atmospheric pressure from 101.3 kPa using the vapor pressure curve, as outlined in Appendix C.

4.4.2 Small-Scale Procedure

The flash point was determined in the small-scale apparatus as outlined in ASTM D 3828 [114]. The apparatus was set to the test temperature and allowed to reach thermal equilibrium. If the sample was liquid, 2 mL was injected into the cup when the test temperature was 100 ^{o}C or less, and 4 mL was injected when the test temperature was above 100 ^oC. The equivalent volume of the sample was packed into the cup if the sample was solid.

The sample was allowed to heat in the cup for 1 min when the test temperature was 100 ^oC or below, 2 min when the test temperature was above 100 ^oC, and 6 min when the sample was solid. The pilot flame was ignited and ignition was attempted by lowering the flame into the cup for about 0.5 sec. The results of the test were recorded as a “go” if a flash was observed and a “no go” if no flash was seen. The sample was removed from the cup and the cup and lid were cleaned between runs. The test was repeated, varying the cup temperature until the flash point was known within 0.5 ^oC. The flash point was recorded as the average of the lowest “go” and highest “no go” trials. This value was then adjusted to 101.3 kPa using the vapor pressure curve as outlined in Appendix C.

4.4.3 Additional Measurements

Additional measurements were made in both the Pensky-Martens and small-scale apparatuses to explore the effect of the individual apparatus parameters on the measured flash point. To test the assumption of thermal and chemical equilibrium in the Pensky-Martens cup, the ramping rate was reduced to about 1 $^oC\cdot min^{-1}$ instead of 4 $^oC\cdot min^{-1}$. To test the assumption of thermal and chemical equilibrium within the small-scale cup, the wait time was extended to 6 min, regardless of the injection volume. The effect of vapor space on the small-scale flash point was also tested by measuring the flash point using both 2 mL and 4 mL of sample for several components.

CHAPTER 5. EXPERIMENTAL RESULTS

5.1 Lower Flammability Limit as a Function of Temperature

5.1.1 Experimental Data

Table 5.1 lists the experimental results for the 18 compounds for which lower flammability limit measurements were made, including the 95 % confidence intervals. Raw data are provided in Appendix D.

As reported by Zabetakis [32], the lower flammability limit decreased linearly with increasing temperature for most compounds. There were three notable exceptions to this rule as seen in Figure 5.1. Lower flammability limit data for 2-nonanone and decyl acetate became nonlinear at temperatures exceeding 450 K and 470 K, respectively. This change in behavior at elevated temperatures was thought to indicate the onset of slow auto-oxidation. Subsequent trials for decyl acetate at 492 K confirmed that a longer mixing time raised the experimental lower flammability limit, consistent with this hypothesis. Extending the mixing time had no measurable effect, however, on the lower flammability limit of 2-nonanone at 472 K. It is possible that at some temperature between 450 K and 480 K 2-nonanone decomposes into a mixture of flammable gases, and thus exhibits a different flammability limit at higher temperatures. However, no decomposition temperature has been reported for 2-nonanone.

Table 5.1. Experimental lower flammability limit data and 95 % confidence intervals at temperatures between 300 K and 500 K

Material	***T*/K**	***LFL*/vol%**	**Material**	***T*/K**	***LFL*/vol%**
1-Hexyne	342	0.945 ± 0.007	5-*o*-Tolyl-2-pentene	375	0.644 ± 0.009
	365	0.92 ± 0.01		423	0.537 ± 0.009
	448	0.786 ± 0.009		447	0.51 ± 0.01
	472	0.754 ± 0.009		471	0.48 ± 0.02
Phenetole	355	0.949 ± 0.006	Isopropyl Myristate	450	0.377 ± 0.007
	379	0.888 ± 0.007		446	0.389 ± 0.004
	453	0.754 ± 0.009		471	0.426 ± 0.005
	481	0.717 ± 0.009		496	0.383 ± 0.005
4-Methyl-2-pentanol	345	1.13 ± 0.01	Methanol	301	7.03 ± 0.07
	374	1.06 ± 0.01		333	6.79 ± 0.04
	422	0.99 ± 0.01		372	6.43 ± 0.04
	471	0.91 ± 0.01		420	6.08 ± 0.05
2-Methyl-1,3-propanediol	422	1.64 ± 0.02	Butanol	328	1.67 ± 0.01
	447	1.56 ± 0.02		372	1.57 ± 0.02
	471	1.50 ± 0.01		422	1.48 ± 0.01
	496	1.43 ± 0.02		470	1.35 ± 0.02
Dibutylamine	341	0.803 ± 0.007	1-Octanol	375	0.82 ± 0.01
	365	0.731 ± 0.008		398	0.77 ± 0.01
	448	0.608 ± 0.008		470	0.68 ± 0.01
	472	0.580 ± 0.008		490	0.65 ± 0.02
α-Pinene	351	0.680 ± 0.007	*n*-Hexyl Formate	352	1.03 ± 0.01
	374	0.644 ± 0.007		376	0.98 ± 0.01
	423	0.58 ± 0.01		423	0.89 ± 0.01
	472	0.52 ± 0.01		472	0.82 ± 0.01
2-Nonanone	376	0.767 ± 0.008	*n*-Octyl Formate	376	0.777 ± 0.009
	400	0.713 ± 0.007		423	0.698 ± 0.009
	448	0.656 ± 0.008		474	0.62 ± 0.01
	473	0.68 ± 0.01	Diisobutyl Phthalate	452	0.496 ± 0.007
	483	0.686 ± 0.007		473	0.440 ± 0.005
	493	0.68 ± 0.02		493	0.414 ± 0.007
Methyl Benzoate	374	1.04 ± 0.01	Ethyl Lactate	352	1.64 ± 0.02
	399	0.97 ± 0.01		374	1.55 ± 0.01
	451	0.86 ± 0.01		447	1.37 ± 0.01
	472	0.82 ± 0.01		471	1.30 ± 0.02
Decyl Acetate	400	0.598 ± 0.006			
	424	0.556 ± 0.009			
	447	0.516 ± 0.007			
	472	0.502 ± 0.007			
	491	0.533 ± 0.009			

The lower flammability limit of isopropyl myristate exhibited a unique relationship with temperature. At the two points below 470 K, the difference between a “go” and a “no go” run was less distinct than with other compounds, and the mixing time appeared to have a small effect on the measured values. Above 470 K, however, the distinction between a “go” and “no go” run became larger than with any of the other compounds, and the lower flammability limit was no longer affected by differences in mixing time. This sudden shift in flame behavior may be explained by the slow decomposition of isopropyl myristate below 470 K. Above 470 K, the decomposition reaction is complete and the limits become independent of mixing time. Bonhorst, Althouse, and Triebold [115] reported a decomposition temperature for isopropyl myristate between 465 and 473 K.

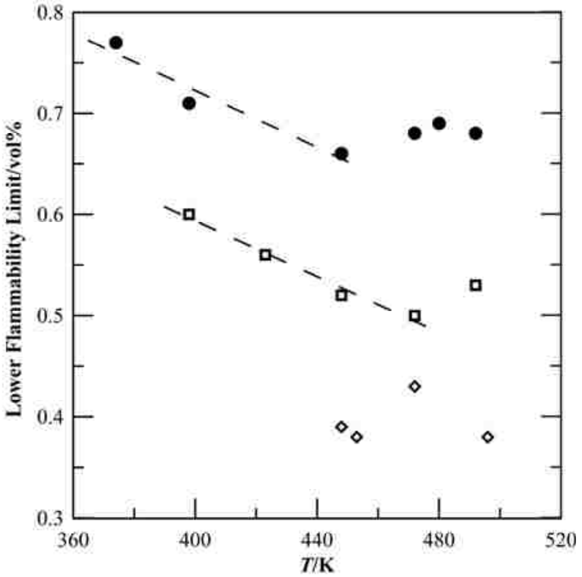

Figure 5.1. Lower flammability limit data versus temperature for: 2-nonanone (●); decyl acetate (□); isopropyl myristate (◇). Linear fits are given by dashed lines

5.1.2 Adiabatic Flame Temperature Analysis

The adiabatic flame temperature was calculated from the measured lower flammability limit at each temperature point using Equation 2.6. Complete combustion (no disassociation) was assumed, as per Equation 2.8. Thus, when Equation 2.6 is expanded, it becomes

$$\begin{aligned} & LFL\left(H_{\mathrm{f}}^{\mathrm{o}} + \int_{298\ \mathrm{K}}^{T^{\mathrm{o}}} C_{\mathrm{p,\,f}}\mathrm{d}T \right) + (100 - LFL)\int_{298\ \mathrm{K}}^{T^{\mathrm{o}}} C_{\mathrm{p,\,air}}\mathrm{d}T = LFL \cdot \sum_{\mathrm{products}} n_i \left(H_i^{\mathrm{o}} + \int_{298\ \mathrm{K}}^{T_{\mathrm{ad}}} C_{\mathrm{p},\,i}\mathrm{d}T \right) \\ & + 0.79(100 - LFL)\int_{298\ \mathrm{K}}^{T_{\mathrm{ad}}} C_{\mathrm{p,\,N_2}}\mathrm{d}T + \left[0.21(100 - LFL) - \beta \cdot LFL\right]\int_{298\ \mathrm{K}}^{T_{\mathrm{ad}}} C_{\mathrm{p,\,O_2}}\mathrm{d}T \end{aligned} \quad . \qquad (5.1)$$

To test the validity of the assumption of combustion with no disassociation, the adiabatic flame temperature was calculated for the reported values of several compounds using Equation 5.1 and thermodynamic data from the DIPPR 801® database [116]. These results, shown in Table 5.2, were nearly identical to T_{ad} values calculated using CEA, a free chemical equilibrium calculator, as well as values calculated by other researchers.

Table 5.2. Comparison of reported calculated adiabatic flame temperatures (K) with values found using CEA, a chemical equilibrium calculator, and Equation 5.1

Compound	**LFL**	**Reported T_{ad}**	**CEA T_{ad}**	**Equation 5.1**	**Compound**	**LFL**	**Reported T_{ad}**	**CEA T_{ad}**	**Equation 5.1**
Methane	4.85	1450 [22]	1453	1452	Ethylene	2.62	1343 [22]	1345	1343
Methane	5	1482 [25]	1484	1483	Ethylene	2.7	1369 [25]	1372	1371
Methane	5	1481 [26]	1484	1483	Ethylene	2.7	1370 [26]	1372	1371
Methane	5	1480 [28]	1484	1483	Ethylene	2.4	1271 [29]	1267	1265
Methane	4.4	1366 [29]	1360	1358	Propylene	2.4	1621 [25]	1624	1625
Ethane	3	1534 [25]	1536	1536	Propylene	2	1431 [26]	1434	1433
Ethane	3	1534 [26]	1536	1536	Propylene	1.8	1341 [29]	1335	1334
Ethane	3	1530 [28]	1536	1536	1-Butene	1.7	1572 [25]	1544	1543
Ethane	2.4	1327 [29]	1322	1320	1-Butene	1.6	1479 [26]	1481	1481
Propane	2.1	1530 [25]	1531	1531	1-Butene	1.2	1226 [29]	1222	1220
Propane	2.1	1540 [28]	1531	1531	Acetylene	2.5	1268 [26]	1272	1270
Propane	1.7	1335 [29]	1329	1327	Acetylene	2.1	1130 [29]	1130	1128
n-Butane	1.8	1640 [25]	1643	1644	Ethanol	3.3	1492 [26]	1494	1494
n-Butane	1.8	1640 [28]	1643	1644	Ethanol	3.3	1490 [28]	1494	1494
n-Butane	1.4	1396 [29]	1389	1387	Ethanol	3.1	1407 [29]	1439	1433
n-Butane	1.2	1608 [25]	1612	1612	Propanol	2.2	1490 [28]	1483	1483
n-Hexane	1.2	1610 [28]	1612	1612	Propanol	2.1	1446 [29]	1439	1438
n-Hexane	1	1434 [29]	1427	1426					

Figure 5.2 shows T_{ad} as a function of initial mixture temperature for the alcohols studied in this work. Contrary to the findings of [16] and [17], T_{ad} is not independent of the initial mixture temperature, but decreases significantly with increasing initial temperature. This is true

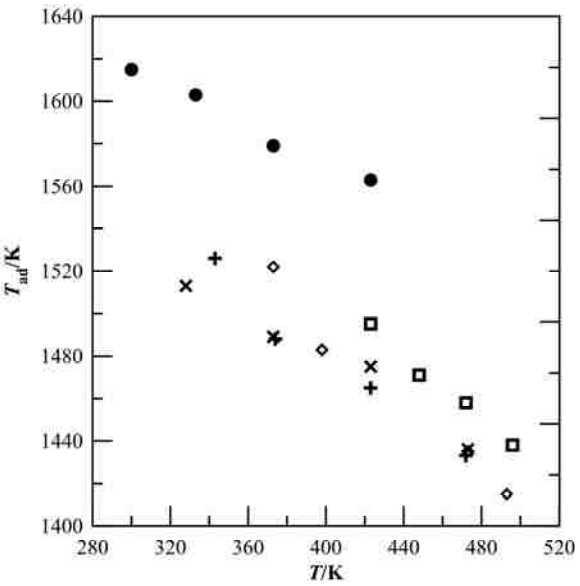

Figure 5.2. Calculated adiabatic flame temperature, T_{ad}, from experimental lower limit data as a function of initial mixture temperature: methanol (●); butanol (◇); 4-methyl-2-pentanol (+); 1-octanol (x); 2-methyl-1,3-propanediol (□)

for all compounds studied, though the magnitude of the effect of initial temperature varies by chemical. The majority of published data also correspond to flame temperatures that decrease with increasing initial temperature (Table 5.3). Exceptions to this rule were determined preponderantly in vessels with diameters less than 6 cm or in bomb-style apparatuses.

The effect of apparatus diameter on the slope of T_{ad} is easily explained by the relationship between the slopes of the lower flammability limit and T_{ad} versus temperature curves. A decrease in the lower flammability limit results in an increase of excess oxygen and nitrogen present during combustion, and accordingly an increase in the total specific heat of the products. Consequently, the slope of the T_{ad}-temperature curve is directly related to the slope of the lower flammability limit, which, as White [16] observed, becomes more negative with increasing vessel diameter until a critical diameter is reached. From lower limit measurements at 298 K, Jones [31] found the diameter affected the limit up until about 5 cm. According to Table 5.3a,

Table 5.3a. The effect of initial temperature, *T*, on calculated adiabatic flame temperatures, T_{ad}, for reported lower flammability limit data

Name	**Reference**	**Vessel**	**Vessel diameter/cm**	***T* range/K**	**Direction of calculated T_{ad} with increasing *T***
Methanol	[117]	A	9	200	Decreasing
	[118]	A	9	150	Decreasing
	[119]	B	7.5	150	Decreasing
	[21]	C	8	160	Decreasing
	[120]	D		275	Increasing
Ethanol	[117]	A	9	200	Decreasing
	[118]	A	9	150	Decreasing
	[19]	E		200	Constant
Propanol	[19]	E		200	Decreasing
Butanol	[118]	A	9	150	Decreasing
	[21]	C	8	80	Decreasing
1-Octanol	[21]	C	8	60	Decreasing
Acetone	[118]	A	9	150	Decreasing
2-Butanone	[121]	F	5	185	Constant
	[122]	G	7.6	100	Decreasing
Methane	[123]	H	2	680	Constant
	[16]	I	2.5	430	Constant
Pentane	[16]	I	2.5	280	Constant
Isopentane	[118]	A	9	150	Decreasing
Hexane	[124]	J	5.7	175	Increasing
Heptane	[124]	J	5.7	175	Constant
Octane	[124]	J	5.7	175	Constant
2,2,4-Trimethylpentane	[124]	J	5.7	175	Constant
Nonane	[124]	J	5.7	160	Decreasing
Decane	[124]	J	5.7	150	Constant
Cyclohexane	[125]	A	9	150	Decreasing
Cyclohexene	[125]	A	9	150	Decreasing
Benzene	[126]	B	7.5	230	Decreasing
	[125]	A	9	150	Decreasing
Toluene	[125]	A	9	150	Decreasing
	[121]	F	5	170	Weakly decreasing
	[126]	B	7.5	230	Decreasing
	[20]	K	6	200	Decreasing
	[4]	A	9	100	Decreasing
	[4]	L	10.2	175	Constant
	[4]	M	30.6	200	Decreasing
o-Xylene	[126]	B	7.5	200	Decreasing
Tetrahydrofuran	[121]	F	5	185	Constant
Ethylene	[16]	I	2.5	380	Constant
Acetylene	[16]	I	2.5	280	Constant
Hydrogen	[16]	I	2.5	380	Increasing
	[16]	N	25	380	Increasing
Ammonia	[127]	N	25	580	Constant
Carbon Monoxide	[16]	I	2.5	380	Decreasing
Difluoromethane	[128]	O		70	Decreasing
1,1-Difluoroethane	[128]	O		70	Weakly decreasing

Table 5.3b. Apparatus styles listed in Table 5.3a

Apparatus	Dimensions
A	9 cm x 45 cm cylinder; downward flame propagation
B	7.5 cm x 150 cm tube
C	EN 1839 (T); 8cm x 30 cm tube
D	7.5 L spherical bomb; determined at 150 kPa
E	13 L spherical bomb
F	5 cm x 150 cm tube
G	7.6 cm x 180 cm steel tube
H	2 cm x 15 cm closed tube; downward flame propagation
I	2.5 cm x 150 cm tube; downward flame propagation
J	5.7 cm x 122 cm tube.
K	DIN 51649; 6 cm x 30 cm tube
L	10.2 cm x 96 cm closed tube
M	30.6 cm x 39 cm tube
N	25 cm x 25.7 cm closed tube
O	ASTM E 681; 5 L sphere

the vessel diameter affects the measured temperature-dependence of the lower flammability limit at least up to 6 cm, though the value surely depends on the selected flame-propagation criterion, with criteria requiring stronger flames also requiring larger diameters. Because the modified Burgess-Wheeler law is based on a constant T_{ad} with respect to initial mixture temperature, Equation 2.4 underestimates the effect of temperature on the lower flammability limit for large-diameter apparatuses (Figure 5.3).

5.1.3 Flame Temperatures and the Theory of Flammability Limits

The combustion reaction is typically divided into two stages. In the first stage, most or all of the fuel rapidly converts into intermediate products, including CO. During the second stage, carbon monoxide oxidizes into CO_2. Shebeko et al. [24] and Mashuga and Crowl [22] contended that the largely exothermic oxidation of CO in the second stage was the controlling reaction that determined whether a fuel-air mixture was flammable.

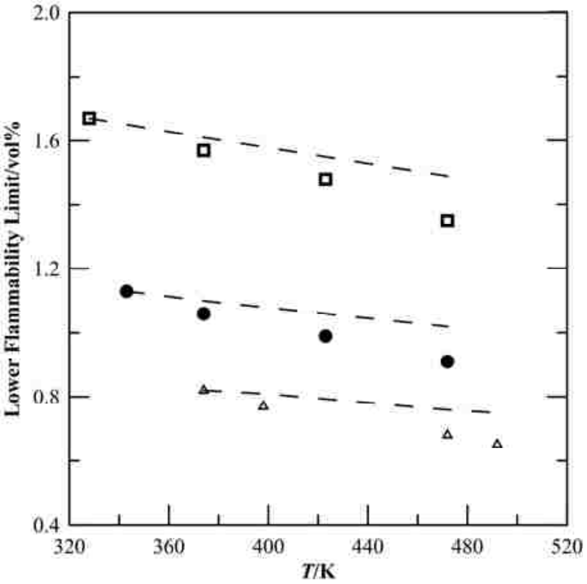

Figure 5.3. The effect of temperature on the lower flammability limit calculated by the modified Burgess-Wheeler law (- - -), compared with experimental data for: 4-methyl-2-pentanol (●); butanol (□); 1-octanol (Δ)

Assuming CO oxidation occurs primarily through the reaction

$$OH + CO \rightarrow CO_2 + H, \tag{5.2}$$

the rate of oxidation will be limited by the concentration of OH radicals. This is consistent with the theory of Law and Egolfopoulos [129-130]. They found through numerical studies that

$$H + O_2 \rightarrow OH + O \tag{5.3}$$

is the dominant branching reaction. The rate of this reaction is significantly retarded with decreasing temperature, approaching the rate of the dominant termination reaction,

$$H + O_2 + M \rightarrow HO_2 + M \tag{5.4}$$

at the lower flammability limit.

Using the rate coefficients of [131], Shebeko et al. showed that OH termination becomes dominant over branching mechanisms around 1000 K. A plot of $T_{ad, CO}$, the calculated adiabatic flame temperature assuming complete fuel conversion to water and CO, shows that the experimental data in this work support this theory (Figure 5.4). The scatter shown in Figure 5.4 is relatively narrow, and likely a result of experimental error, error associated with the thermodynamic data used to calculate the flame temperatures, and the empirical nature of the flame propagation criterion used to determine the flammability limits.

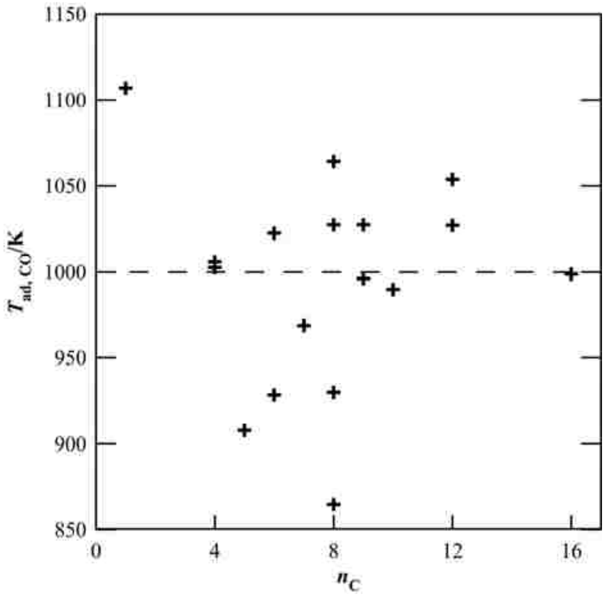

Figure 5.4. Adiabatic flame temperatures assuming CO formation ($T_{ad, CO}$) at the lower temperature limit; OH termination becomes dominant over branching below about 1000 K, shown by the dashed line

Thus, the existence of the lower flammability limit may be explained by the flame temperature becoming too low to support OH radical production. The interdependence of the OH branching reactions on the enthalpy obtained from the exothermic CO oxidation reaction also explains why flammability limits appear more as a continuous band over which a wide range of partial propagation is possible, rather than a discrete value below which ignition fails.

Within this range, an ignition source initially creates enough radicals at a sufficient temperature to initiate flame development. As the flame begins to spread throughout the relatively cool fuel-air mixture, the temperature of the flame front must remain high enough for OH branching to be dominant over terminating reactions. If the flame front temperature drops, the concentration of OH radicals decreases. A reduction in OH radical concentration decreases the rate of the exothermic CO oxidation reaction, and consequently the flame temperature and OH concentration decrease further. This continues until the flame temperature can no longer support radical production, at which point the flame extinguishes. Therefore, the rate of flame extinction depends on the proximity of the fuel concentration to the critical concentration that sustains a flame front around 1000 K, i.e., the lower flammability limit.

CO and CO_2 concentrations in extinguishing flames appear to support this theory (Figure 5.5). Concentrations were determined from combustion products of fuel-air mixtures that supported various magnitudes of flame propagation using a Horiba PG-250 portable gas analyzer. Definitions for the extent of flame propagation used in Figure 5.5 are given in Table 5.4. Although the observed degrees of flame propagation were approximate, the percent of CO oxidized to CO_2 clearly decreases with diminishing flame propagation, and decreases most significantly below the empirically based ASHRAE flammability limit criterion.

This theory is also supported by the slopes (γ) of the adiabatic flame temperature, $T_{\text{ad, CO}}$, for the experimental data reported in this work. If the existence of the flammability limit is related to a critical radical concentration prior to CO oxidation, the calculated flame temperature at the lower flammability limit should be independent of initial temperature. As shown in Figure 5.6, this is true for compounds with less than 7 or 8 carbon atoms. The slope of the adiabatic

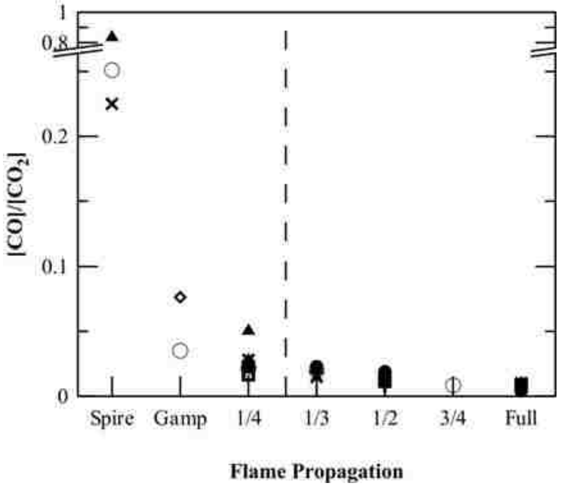

Figure 5.5. Ratio of CO and CO_2 concentrations from product gases of flames that propagated to different extents: methanol at 100 ^{o}C (△) and 150 ^{o}C (▲), butanol at 150 ^{o}C (◇), 1-octanol at 100 ^{o}C (□) and 150 ^{o}C (■), decyl acetate at 150 ^{o}C (○) and 200 ^{o}C (●), dibutyl amine at 100 ^{o}C (x),and diisobutyl phthalate at 200 ^{o}C (+); 90^{o} ASHRAE propagation criterion is given by dashed line, and definitions of the flame propagation are given in Table 5.4

Table 5.4. Definitions of flame propagation listed in Figure 5.5

Flame Propagation	Definition
Spire	Flame forms a spire nearly reaching the top of the flask
Gamp	Spire reaches top of flask and just begins downward propagation
1/4	Flame reaches top of flask and propagates downward 1/4 of the flask height
1/3	Flame reaches top of flask and propagates downward 1/3 of the flask height
1/2	Flame reaches top of flask and propagates downward 1/2 of the flask height
3/4	Flame reaches top of flask and propagates downward 3/4 of the flask height
Full	Flame reaches top of flask and propagates downward to the flask bottom

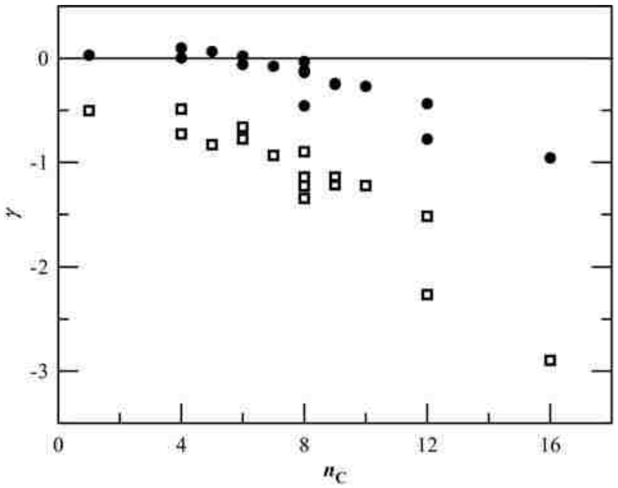

Figure 5.6. The slope of the adiabatic flame temperature with respect to initial mixture temperature assuming CO_2 (□) and CO (●) as the main carbon product

flame temperature of larger molecules, however, becomes increasingly negative with increasing carbon number. This phenomenon is likely a result of thermal decomposition. Whereas smaller molecules rely predominantly on radicals generated during the oxidation reaction, larger molecules may also form radicals by thermal decomposition. Thus, the flame temperature of a large molecule-air mixture may drop below the 1000 K threshold, and still sustain a flame.

5.1.4 Comparison with Reported Data

The lower flammability limit data were fitted with a linear function of temperature,

$$LFL(T) = aT + b\,. \tag{5.5}$$

To preserve the normal distribution of errors, as stated in the central limit theorem, the coefficients were first fit using injection volume data, $\overline{V}_{\text{inj}}$,

$$\overline{V}_{\text{inj}} = a' + \frac{b'}{T}, \tag{5.6}$$

and then Equation 5.6 was transformed to Equation 5.5:

$$\left(\frac{\rho \mathrm{R} T}{P V_{\text{vessel}}}\right) \cdot \overline{V}_{\text{inj}} = \left(a' + \frac{b'}{T}\right)\left(\frac{\rho \mathrm{R} T}{P V_{\text{vessel}}}\right). \tag{5.7}$$

Regression was constrained to the linear regions for decyl acetate and 2-nonanone. No fit was possible for isopropyl myristate due to the nonlinear and irregular behavior of the lower flammability limit. Table 5.5 summarizes the regressed slopes and intercepts for all other compounds.

Table 5.5. Regressed slopes and intercepts from experimental lower flammability limit data

Compound	Slope x 10^3	Intercept
Phenetole	-1.84	1.59
Dibutylamine	-1.67	1.36
1-Hexyne	-1.55	1.48
2-nonanone	-1.50	1.33
Octanol	-1.43	1.35
Methyl Benzoate	-2.16	1.84
5-o-Tolyl-2-Pentene	-1.86	1.34
α-pinene	-1.38	1.16
n-Decyl Acetate	-1.41	1.16
Diisobutyl Phthalate	-2.00	1.39
Butanol	-2.14	2.37
Octyl Formate	-1.62	1.39
4-Methyl-2-Pentanol	-1.77	1.74
2-Methyl-1-3-propanediol	-2.81	2.82
Hexyl Formate	-1.82	1.67
Methanol	-8.19	9.50
Ethyl Lactate	-2.74	2.59

Figure 5.7 is fairly representative of the confidence regions of parameters *a* and *b* for each compound. The small size of the confidence region shows that the parameters in Equation 5.5 are fairly precisely determined, and exclusion of zero from both the slope and intercept intervals shows that they are statistically different from zero. Appendix D summarizes confidence regions for the other compounds measured in this work.

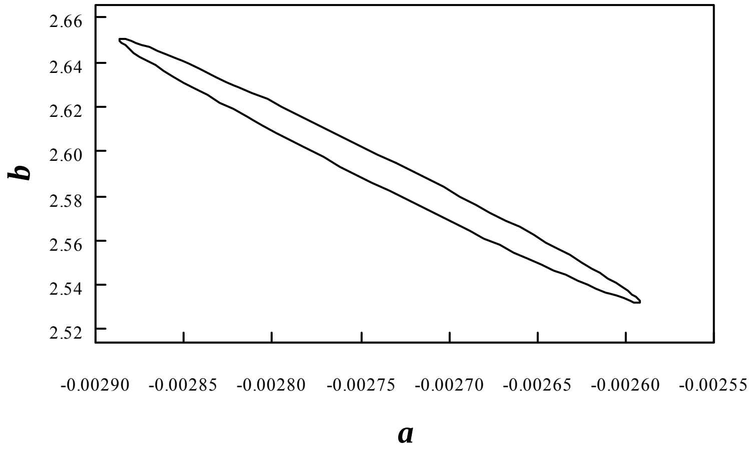

Figure 5.7. Confidence regions for the slope (*a*) and intercept (*b*) of the lower flammability limit as a function of temperature for ethyl lactate

The slope of the regression line is easily transformed to the parameter c of Equation 2.5, the decrease of the lower flammability limit relative to the lower flammability limit at T_0, 293 K, for direct comparison with reported values:

$$c = \frac{a}{a \cdot (298\ \text{K}) + b} \times 100\,. \tag{5.8}$$

Reported values of c range between 0.07 K^{-1} to 0.085 K^{-1} for the Bureau of Mines apparatus [32, 124], 0.11 K^{-1} to 0.18 K^{-1} for a 13-L closed sphere [19], and 0.13 K^{-1} to 0.23 K^{-1} for the DIN and EN tube apparatuses [20-21]. Data measured in this work correspond to c values between 0.12 K^{-1} and 0.25 K^{-1}, though a lack of previously reported data only permits a direct comparison of experimental data for methanol, butanol, and 1-octanol (Figures 5.8 and 5.9).

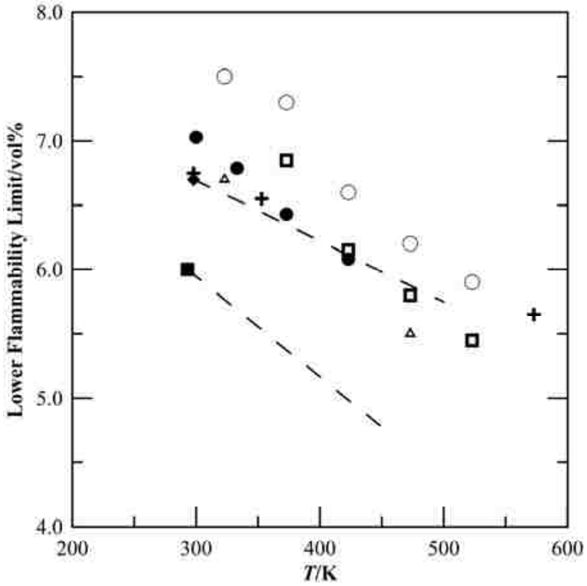

Figure 5.8. Experimental lower flammability limit data for methanol; [117] (○); [118, 125] (□); [119] (Δ); calculated from a single data point from ref [70] and reported slope from ref [21] (■- - -); data point from [32] with slope calculated using the modified Burgess-Wheeler law (♦- - -); this work (●)

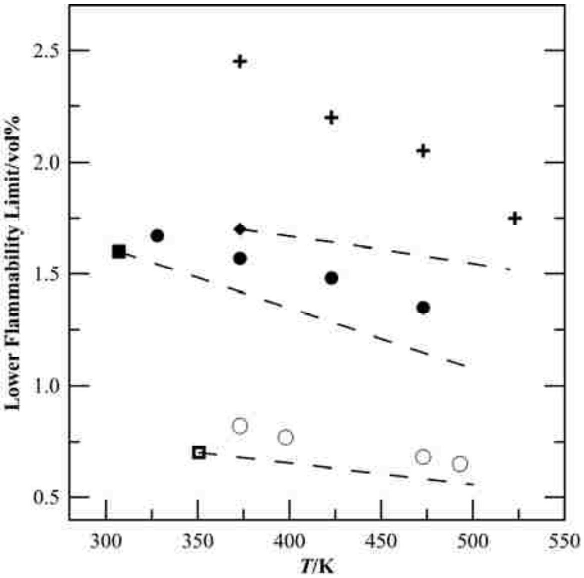

Figure 5.9. Experimental lower limit data for butanol (●■♦+) and 1-octanol (○□); calculated from a single data point from [70] and reported slope from [21] (■/□- - -); data point from [32] and slope calculated using the modified Burgess-Wheeler law (♦- - -); [118, 125] (+); this work (● ○)

Several striking similarities exist between reported and experimental data for methanol. The data reported by [118, 125] (apparatus type A) and [119] (apparatus type B) closely resemble the data measured in this work. These data also exhibit a similar slope with the data of [117] (apparatus type A) and the trend calculated from the data point and slope reported by Brandes et al. [21, 70] (apparatus type C). The apparatus types are defined in Table 5.3b. Data for butanol and 1-octanol also show similar slopes to those reported by Brandes et al.

That the work of [119] closely resembles the data reported in this work is not surprising, as the 90^o ASHRAE propagation criterion was specifically created to yield results equivalent with full flame propagation in large tubes. The EN 1839 method employed by Brandes et al. requires only flame detachment and minimal flame propagation for a fuel/air mixture to be considered flammable, and as expected, the lower flammability limit values are lower than those measured in this work. The lower flammability limit values of [117] are significantly higher than those reported in this work because downward flame propagation was used rather than the upward propagation used in the present work. The discrepancy between the results of [117] and [118, 125] is rather surprising. Both studies supposedly employed the same experimental method, yet the lower flammability limit values of [117] are significantly higher.

It appears likely that the offset between these data sets, for the most part, is merely a function of the propagation criteria utilized and the direction of flame travel. The fact that lower flammability limits obtained in different geometries remain parallel with increasing temperature is encouraging. If the apparatus and method of flammability limit determination only affects the magnitude of the data and not the slope once a critical diameter is reached, this could imply the existence of a fundamental flammability limit.

Comparison with literature lower flammability limit data reported at a single point is also possible for several compounds, though less instructive as most of the reported values lack documentation pertaining to the measurement temperature. Data are given in Table 5.6.

Table 5.6. Comparison of experimental lower flammability limit results with single-point literature values

Compound	LFL(298 K)/vol%	LFL(T_L)/vol%	Literature LFL/vol%
Dibutylamine	0.86	0.84	**0.63** (at 353 K)[132], **1.1** [133-135]
Ethyl Lactate	1.78	1.7	**1.55** [136], **1.5** [32, 134, 137-138]
Diisobutyl Phthalate	0.8	0.53	**0.4** [133-134], **0.43** [139]
4-Methyl-2-Pentanol	1.2	1.2	**1.0** [136, 138, 140]
2-Nonanone	0.88	0.82	**0.9** [133-134]

5.2 Lower Temperature Limit and Flash Point

5.2.1 Calculated vs. Experimental Lower Temperature Limit

Theoretical lower temperature limits were calculated for all compounds with lower flammability limit data (except isopropyl myristate) by finding the intersection of the lower flammability limit and vapor-pressure curves, as shown in Figure 5.10 for phenetole.

Uncertainties for the theoretical lower temperature limits were calculated from the 95 % prediction uncertainy bands and 84 % confidence intervals of the lower flammability limit correlations. The 84 % confidence intervals were included because, as detailed by Payton [141], inspection of 84 % confidence intervals for overlap results in similar conclusions as a rigorous F-test at a 95 % confidence level. A visual F-test for statistical difference between the theoretical and experimental lower temperature limits is shown in Figure 5.11.

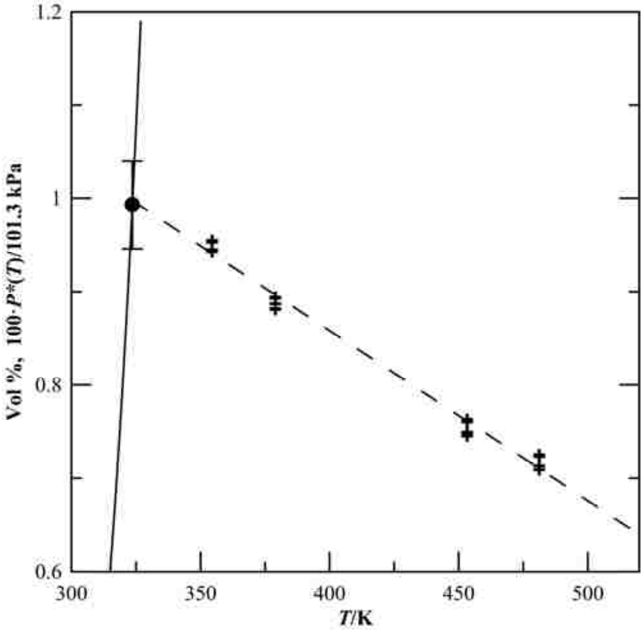

Figure 5.10. Calculation of lower temperature limit by finding the intersection of the vapor pressure curve (—) and the regressed lower flammability limit curve (- - -) from experimental data (+), illustrated here with the experimental lower temperature limit data (●) for phenetole

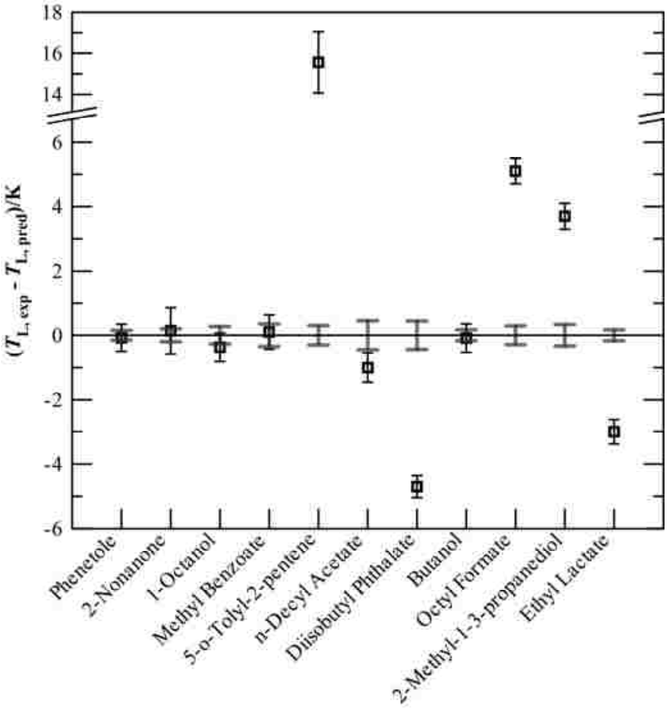

Figure 5.11. Visual F-test for statistical difference between calculated and experimental lower temperature limits; confidence intervals for experimental data are shown on the zero line

As indicated in Figure 5.11, the calculated and experimental lower temperature limits are inconsistent for more than half of the 11 compounds studied. This is not surprising for compounds like 5-*o*-tolyl-2-pentene and octyl formate which have little or no experimental vapor pressure data, because the accuracy of the calculated lower temperature depends on the accuracy of the vapor pressure curve. This may also explain the deviations between the calculated and experimental lower temperature limit values of 2-methyl-1,3,-propanediol and ethyl lactate. The regressed vapor pressure curves of these compounds deviate significantly from additional experimental vapor pressure data in the DIPPR database at temperatures near the experimental lower temperature limit. In fact, the discrepencies in Figure 5.11 can be resolved for all the compounds with experimental vapor pressure data by forcing the vapor pressure curve through a different set of reported data near the lower temperature limit (Figure 5.12). One interesting implication of this analysis is that flammability limit curves combined with experimental lower temperature limits may be used as a rough quality check for vapor pressure data.

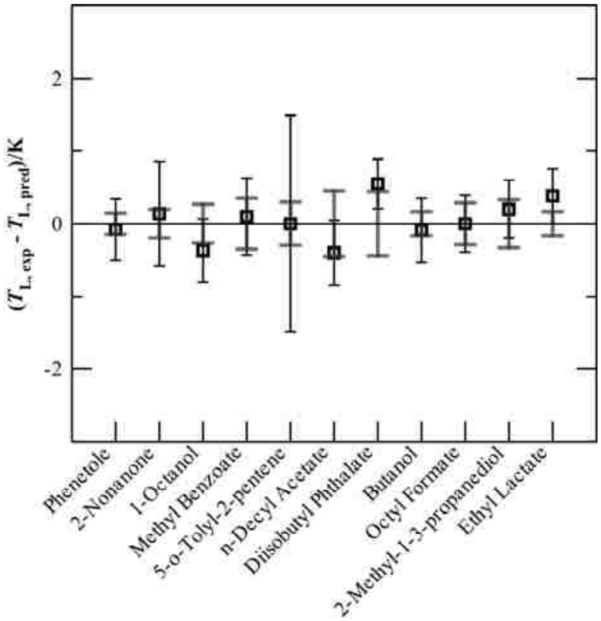

Figure 5.12. Deviations between calculated and experimental lower temperature limits following correction of vapor pressure curves

Lower temperature limits are listed in Table 5.7, including 95 % confidence intervals, with theoretical values shown for compounds for which an experimental value was not determined. Confidence intervals for theoretical values were estimated using the 95 % prediction bands of the regressed lower flammability curves at the theoretical lower temperature limit.

Table 5.7. Lower temperature limits, T_L

Chemical	T_L/K	Chemical	T_L/K
1-Hexyne$_{calc}$	248.4 ± 0.3	Dodecanoic Acid	429.6 ± 0.7
1-Octanol	353.4 ± 0.6	Ethyl Lactate	324.6 ± 0.5
2-Methyl-1,3-Propanediol	387.3 ± 0.6	Hexadecanol	420.5 ± 0.7
2-Nonanone	338.6 ± 1.0	Hexyl Formate$_{calc}$	316.3 ± 0.5
4-*iso*Propyl-*m*-cresol	393.5 ± 2.3	Isopropyl Myristate	412.0 ± 1.1
4-Methyl-2-Pentanol$_{calc}$	306.5 ± 0.2	Methyl Benzoate	347.0 ± 0.7
5-*o*-Tolyl-2-Pentene	354.0 ± 2.1	Decyl Acetate	376.4 ± 0.6
Adamantane^{S}	355.9 ± 0.7	Octyl Formate	342.4 ± 0.5
α-Pinene$_{calc}$	302.5 ± 0.2	*p*-Cumylphenol	440.0 ± 0.7
Butanol	307.5 ± 0.6	Phenetole	323.6 ± 0.6
Dibutylamine$_{calc}$	311.7 ± 0.4	Succinic Anhydride	418.9 ± 0.5
Diisobutyl Phthalate	433.0 ± 0.5		

calc: Calculated from the intersection of the vapor pressure and lower flammability limit curves
S: Solid state

5.2.2 Flash Point

The results of the standardized flash point measurements in the Pensky-Martens (PM) and small-scale (SS) apparatuses are shown in Table 5.8, including 95 % confidence intervals. Literature flash point data are compared with these results in Table 5.9. It should be noted that at the reported PM temperatures for urea and trimellitic anhydride, the respective compounds did not actually flash; rather at this temperature the off-gases ignited above the cup when the ignition source was applied.

Originally, the PM and SS values obtained for 5-*o*-tolyl-2-pentene were 340.6 ± 10.3 K and 357.1 ± 1.4 K, respectively. Such a large discrepancy, particularly with the SS flash point exceeding the PM value by so much, warranted further investigation. After first boiling samples of 5-*o*-tolyl-2-pentene to drive off volatile impurities, flash point values were re-measured in both apparatuses and the values in Table 5.8 were obtained.

Table 5.8. Pensky-Martens (PM) and small-scale (SS) flash point measurements; p-value based on two-sided t-test for statistical difference between experimental values

Chemical	PM/K	SS/K	P-value
1-Octanol	361.8 ± 0.5	359.7 ± 1.1	0.0008
2-Methyl-1,3-Propanediol	396.9 ± 1.8	393.8 ± 2.0	0.004
2-Nonanone	345.7 ± 6.7	345.4 ± 0.8	0.54
4-*iso*Propyl-*m*-cresol	-	392.0 ± 2.7	-
4-Methyl-2-Pentanol	316.2 ± 1.1	317.2 ± 0.8	0.38
5-*o*-Tolyl-2-Pentene	364.3 ± 1.1	360.8 ± 0.9	0.018
Adamantane[S]	345.3 ± 6.5	360.5 ± 1.5	< 0.0001
α-Pinene	304.9 ± 1.6	308.1 ± 0.5	0.004
Anthraquinone[S]	487.0 ± 4.2	469.5 ± 1.6	< 0.0001
Butanol	310.5 ± 0.6	313.1 ± 0.7	< 0.0001
Dibutylamine	315.0 ± 1.3	317.0 ± 0.6	0.008
Diisobutyl Phthalate	447.6 ± 2.1	444.6 ± 1.1	0.007
Dodecanoic Acid	440.9 ± 2.6	437.1 ± 0.4	0.016
Ethyl Lactate	332.3 ± 1.7	331.0 ± 1.1	0.14
Hexadecanol	446.7 ± 3.2	443.0 ± 0.7	0.03
Hexyl Formate	319.7 ± 0.7	320.3 ± 0.4	0.076
Isopropyl Myristate	432.3 ± 3.7	424.4 ± 0.8	0.005
Methanol	-	288.6 ± 1.4	-
Methyl Benzoate	353.7 ± 0.8	352.6 ± 1.0	0.025
Decyl Acetate	389.7 ± 2.7	386.3 ± 1.2	0.021
Niacin[S]	455.6 ± 4.3	448.2 ± 1.5	0.002
Octyl Formate	351.3 ± 2.6	349.5 ± 0.9	0.13
p-Cumylphenol	448.6 ± 6.3	444.2 ± 4.2	0.15
Phenetole	327.9 ± 0.8	330.0 ± 0.8	0.001
Succinic Anhydride	428.9 ± 7.6	424.6 ± 0.6	0.20
Trimellitic Anhydride	576.8 ± 5.2	522.5 ± 1.0	< 0.0001
Trioctylamine	-	444.3 ± 1.5	-
Urea[S]	395.4 ± 0.2	-	-

S: Flashes as a solid

Table 5.9. Comparison of experimental flash points with literature values

Compound	PM/K	SS/K	Literature/K
1-Octanol	361.8	359.7	**354**[135, 138, 140, 142-144]
2-Nonanone	345.7	345.4	**333**[145], **337**[133, 138, 146-147], **344.3**[148-149]
4-Methyl-2-Pentanol	316.2	317.2	**314**[136, 138, 140], **319**[150], **327**[151]
α-Pinene	304.9	308.1	**303**[133], **305**[152], **306**[67, 134, 138, 148, 153-154]
Anthraquinone	487.0	469.5	**458**[138, 142, 154-156]
Butanol	310.5	313.1	**302**[67, 140, 142, 157], **308**[138], **310**[134, 158]
Dibutylamine	315.0	317.0	**312**[133], **314**[159], **315**[138], **315.7**[160], **320**[134], **330**[151]
Diisobutyl Phthalate	447.6	444.6	**434**[133], **458**[134, 139]
Dodecanoic Acid	440.9	437.1	**428-438**[138]
Ethyl Lactate	332.3	331.0	**319**[67, 134, 137-138, 154, 161-162], **320**[150]
Hexadecanol	446.7	443.0	**383**[163], **408**[143], **427**[153]
Hexyl Formate	319.7	320.3	**313-318**[138]
Methanol	-	288.6	**280**[164], **284**[67, 138, 140, 165], **285.4**[142]
Methyl Benzoate	353.7	352.6	**355**[146], **356**[134, 151, 154, 156-157]
Decyl Acetate	389.7	386.3	**378-388**[138]
p-Cumylphenol	448.6	444.2	**433**[136]
Phenetole	327.9	330.0	**336**[134]

Evidently impurities lowered the PM flash point by about 24 ^{o}C and compromised the repeatability of the measurement. On the other hand, the presence of impurities only dropped the small-scale flash point by about 4 ^{o}C, and had very little effect on the repeatability of the measurement. The greater flash point sensitivity to impurtites in the PM apparatus is likely a result of the larger vapor space in the PM apparatus, which allows for increased concentration gradients as the less dense impurities settle near the top of the cup. This may also explain the irregular results for adamantane, but further tests were not possible because the entire sample was depleted during the first set of tests.

Figure 5.13 shows that the flash points obtained from the PM and SS apparatuses are highly correlated. Over the range of 300 K to 460 K, the relationship between the PM and SS flash points is well represented by a linear correlation:

$$\mathrm{PM} = 1.05\,\mathrm{SS} - 17.33 \tag{5.9}$$

(R^2 = 0.9992, excluding flash point of adamantane). The 95 % confidence region of the slope and intercept does not contain zero (Figure 5.14), and therefore indicates a statistical difference, in general, between flash-point values obtained in PM and SS apparatuses. Although the best estimate of the slope is near unity, its 95 % confidence region does not include unity, so there is both a constant offset and a trend in the difference. Two-sided t-tests confirmed that the difference between PM and SS values were statistically significant at a 95 % confidence level for 17 of the 24 possible comparisons in Table 5.8.

When the temperature range is extended to include all the flash points (expect for adamantane), a total range of 300 K to 580 K, the data are well represented by

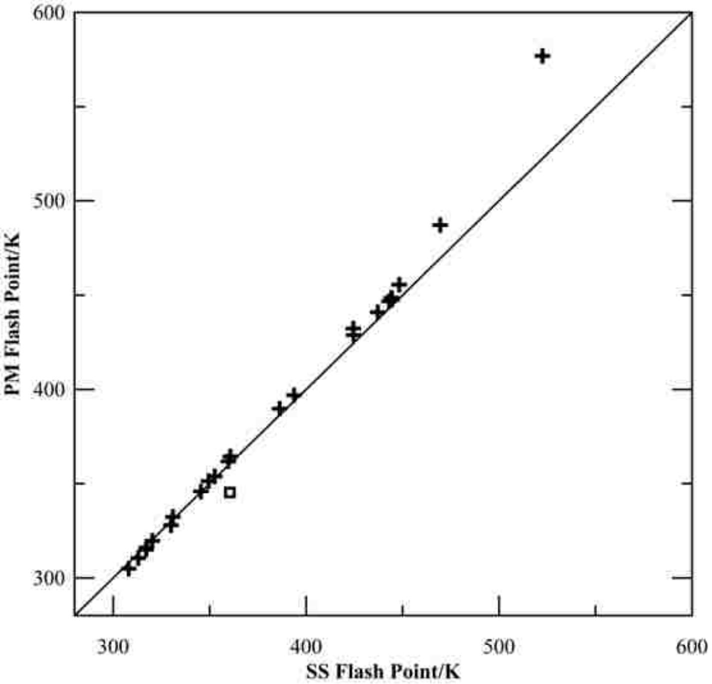

Figure 5.13. Pensky-Martens (PM) and small-scale (SS) flash point values; adamantane (□) appears to be an outlier

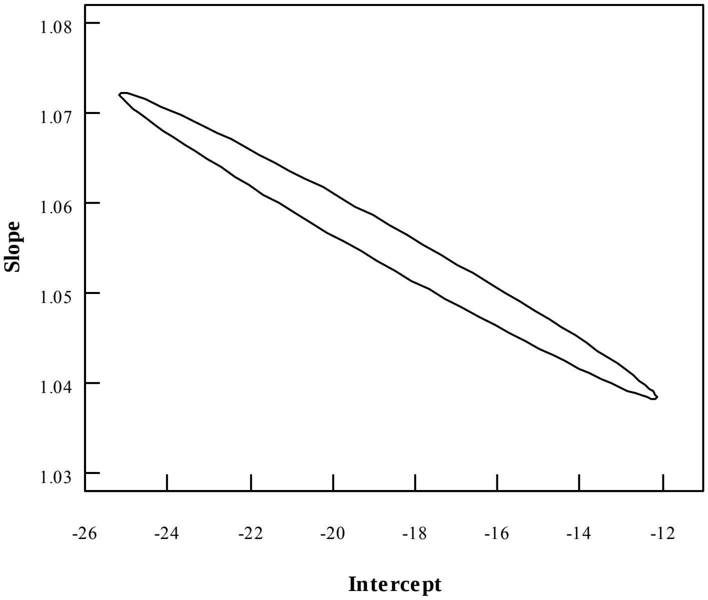

Figure 5.14. 95 % confidence region for the coefficients of Equation 5.9

$$\mathrm{PM} = -16200.2 + 3660.4\ln(\mathrm{SS}) - 18.5\,\mathrm{SS} + 0.013\,\mathrm{SS}^2 \tag{5.10}$$

(R^2 = 0.9993), though this extension only incorporates two more compounds than the linear correlation (trimellitic anhydride and anthraquinone). As mentioned earlier, trimellitic anhydride, the compound with the highest flash point in Figure 5.13, did not actually exhibit a flash point in the Pensky-Martens apparatus. Instead, at the reported temperature the off-gases ignited above the Pensky-Martens cup. Thus, the compound should probably be excluded from the analysis. In this case Equation 5.9 accurately describes all but one of the differences between the PM and SS flash points.

5.2.3 Effect of Measurement Parameters on the Flash Point

The effect of changing the ramping rate on the measured PM value, and the sample injection volume and wait-time on the measured SS flash point is shown in Table 5.10. Only those changes that were shown to be statistically significant using a two-sided t-test (α = 0.05) are listed.

The decrease in anthraquinone's flash point with decreased rate of temperature-ramping was expected, as the PM flash point of this compound does not follow the linear correlation with the small-scale value given in Equation 5.9. As shown in Figure 5.15, the flash point obtained using the slower ramping rate agrees well with Equation 5.9. Increasing the waiting time between sample injection and application of the ignition source, and decreasing the sample volume of isopropyl myristate also brought the SS values into agreement with Equation 5.9, though the change was much smaller. This indicates that at the reported SS value, the sample was likely not at thermal or chemical equilibrium.

Table 5.10. Effect of ramping rate, wait-time, and sample injection volume on the experimental flash point

Compound	Effect of Temperature Ramping Rate $(PM_{1dpm} - PM)/K$	Effect of Wait Time $(SS_{6min} - SS)/K$	Effect of Injection Volume $(SS_{4mL} - SS_{2mL})/K$
1-Octanol			
2-Methyl-1,3-Propanediol		▨	▨
4-Methyl-2-Pentanol			
5-*o*-Tolyl-2-Pentene			
Anthraquinone	-8.1	▨	-10.3 °C
Dibutylamine			
Diisobutyl Phthalate	▨		▨
Dodecanoic Acid			▨
Ethyl Lactate			
Hexadecanol	-15.0	▨	▨
Isopropyl Myristate		+3.6 °C	-4.9 °C
Decyl Acetate			
Niacin		▨	▨
Octyl Formate			▨
Phenetole			

The subscripts 1dpm, 6min, 4mL, and 2mL signify a thermal ramping rate in the Penksy-Martens apparatus of (1 $^{o}C \cdot min^{-1}$), a small-scale flash point measurement made with a 6 min wait time between sample injection and application of the ignition source, and small-scale measurements with a sample injection volume of 4 mL and 2 mL, respectively. Grey boxes indicate the test was not performed.

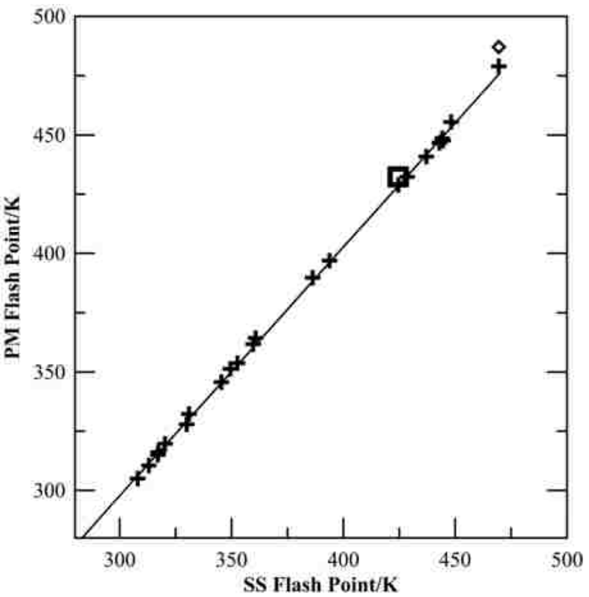

Figure 5.15. Calculated PM values using Equation 5.9 compared to experimental data; previously reported values of isopropyl myristate (□) and anthraquinone (◊) were affected by extending the waiting time between injection and ignition in the small-scale apparatus, and decreasing the thermal ramping rate of the Pensky-Martens appartus

During regular SS operation, the flash points of solids appeared to depend on the solid volume, though this was only quantified for anthraquinone. In general, using less solid raised the SS flash point. If thermal equilibrium considerations were the only reason for this phenomenon, the observed flash point would be expected to increase with larger volumes of solid given the same wait time before the ignition source is applied. It is possible that this phenomenon occurs because increasing the sample volume effectively decreases the vapor space in the cup, bringing the surface of the sample and dense fuel vapors closer to the ignition source. Thus the sample volume would only affect the flash point of fuels whose vapors are significantly denser than air.

5.2.4 Flash Point vs. Lower Temperature Limit

Figure 5.16 shows the relationship between experimental flash points and the measured lower temperature limit. Only two flash points were below the experimental lower temperature limit: the PM value for adamantane, which as discussed in the previous section is suspected of being influenced by impurities, and the SS value for 4-*iso*Propyl-*m*-cresol, which showed no statistical difference from the lower temperature limit. In fact, the SS value of 4-*iso*Propyl-*m*-cresol was the only flash point measurement that was not statistically different from the experimental lower temperature limit based on a Tukey-Kramer multiple comparison test ($\alpha = 0.05$).

The flash point is an increasingly poor representation of the lower temperature limit as the lower temperature limit increases, though the SS apparatus appears to yield closer results to the lower temperature limit than the PM apparatus. Linear correlations between individual flash point apparatuses and the lower temperature limit are given here:

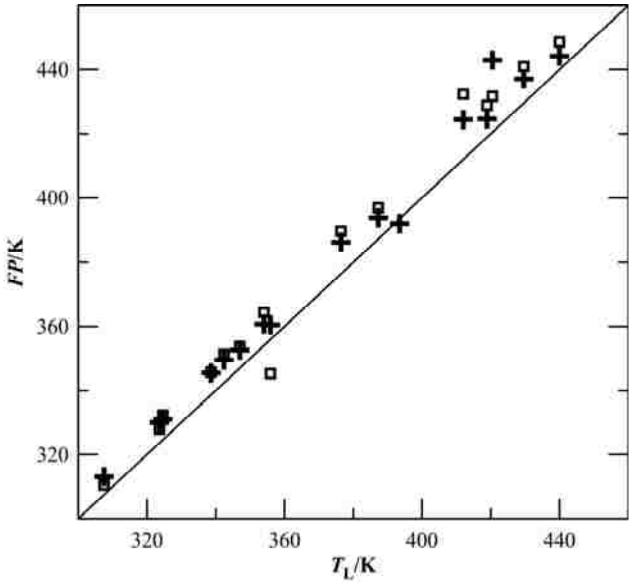

Figure 5.16. Flash point (*FP*) vs. lower temperature limit (T_L) for the Pensky-Martens (□) and small-scale (+) apparatuses

$$FP_{\mathrm{PM}} = 1.085T_{\mathrm{L}} - 21.27 \tag{5.11a}$$

($R^2 = 0.990$, excluding adamantane), and

$$FP_{\mathrm{SS}} = 1.030T_{\mathrm{L}} - 3.85 \tag{5.11b}$$

($R^2 = 0.988$). It should be noted, however, that the correlation error increases with increasing lower temperature limit for both equations.

The previous section discusses the significant decrease in the PM flash point of hexadecanol with slower thermal ramping-rate. If the lowered PM point is used, and it is assumed that extending the waiting time before the ignition attempt would have similarly affected the flash point in the small-scale apparatus, the relationships between the flash points and lower temperature limit become

$$FP_{\mathrm{PM}} = 1.065\,T_{\mathrm{L}} - 14.98\,, \tag{5.12a}$$

$$FP_{\mathrm{SS}} = 1.010\,T_{\mathrm{L}} - 3.046\,. \tag{5.12b}$$

A plot of the 95 % confidence regions for the coefficients of these equations shows that these correlations differ statistically (Figure 5.17). Additionally, the slope of 1.0 lies with the SS apparatus confidence region, which indicates that the findings of Pintar [48] and Shebeko et al. [96], that the difference between the flash point and lower temperature limit is a constant, are valid for the SS flash point. Figure 5.17 also shows that the coefficients proposed by Evlanov [108] are approximately the average of the coefficients in Equations 5.12a and 5.12b. Evlanov's dataset was likely a mixture of flash point data from similar apparatuses, if not the Pensky-Martens and small-scale apparatuses in particular.

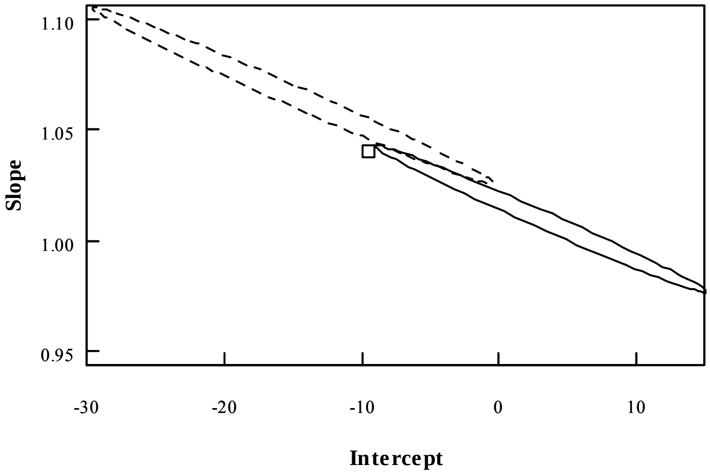

Figure 5.17. Confidence regions of the coefficients in Equations 5.12a (dashed line) and 5.12b (solid line) compared with the coefficients recommended by Evlanov (□)

5.2.5 Interrelationship of Flash Point and Lower Flammability Limit

The relationships between the flash point and the lower flammability limit discussed in Section 3.3 were evaluated for accuracy based on the experimental data from this work. Evaluation statistics are given in Table 5.11.

Table 5.11. Evaluation statistics of published relationships between the flash point and the lower flammability limit

Reference	Equation	Independent Variable	Average Deviation/%	Average Absolute Deviation/%	Max Absolute Deviation/%	Absolute Standard Deviation/%
Kueffer-Donaldson [110]	3.8	PM	-0.1	10.1	23.5	7.1
Kueffer-Donaldson [110]	3.8	SS	-1.8	8.8	25.0	5.3
Oehley [49]	3.9	PM	13.9	20.7	51.2	14.2
Oehley [49]	3.9	SS	11.4	21.5	55	13.3
Kanury [112]	3.10	PM	121.9	121.9	380.5	97.4
Kanuy [112]	3.10	SS	126.1	126.1	319.0	63.4

It is possible that the poor performance of these methods is because the data in the training sets differed significantly from the data found in this work. To evaluate the predictive power of the form of each equation, the coefficients were refit to the data from this work. Results are shown in Table 5.12.

Though several of the methods improved significantly, only the linear relationship between the flash point and lower flammability limit proposed by Kueffer and Donaldson shows predictive potential. The theoretically-based method of Kanury performs much worse than the empirically based methods, partially because it relies on the accuracy of the input thermodynamic data. The enthalpy of vaporization and boiling point used to estimate the lower

Table 5.12. Evaluation statistics of published relationships between the flash point and the lower flammability limit when parameters have been fit using the experimental data of this work

Reference	Equation	Independent Variable.	Average Deviation/%	Average Absolute Deviation/%	Max Absolute Deviation/%	Absolute Standard Deviation/%
Kueffer-Donaldson [110]	3.8	PM	-1.7	8.1	19.1	6.4
Kueffer-Donaldson [110]	3.8	SS	-0.9	5.0	13.3	3.9
Oehley [49]	3.9	PM	-5.3	14.8	29.2	10.5
Oehley [49]	3.9	SS	-2.3	16.7	35.9	10.8
Kanury [112]	3.10	PM	3.3	22.7	109.7	26.2
Kanuy [112]	3.10	SS	2.5	18.2	90.0	21.2

flammability limit of 5-*o*-tolyl-2-pentene were predicted values obtained from the DIPPR® 801 database. Use of these questionable property data produces an error in the predicted lower flammability limit of nearly 100 %. However, excluding this compound during the fit of the equation proposed by Kanury only reduces the absolute average deviation to 16.2 % when the Pensky-Martens flash point is used, and 13.1 % when the small-scale flash point is the dependent variable.

CHAPTER 6. CRITICAL REVIEW OF PREVIOUSLY REPORTED DATA

6.1 Flammability Data Compilations

Compilations of chemical property data can be excellent resources to researchers and engineers, eliminating hours of searching literature for a single value. However, data compilations, and compilations pertaining to flammability data in particular, have many flaws. The most significant weakness is often poor documentation. Compilations rarely have the infrastructure to provide detailed information pertaining to the source of each data point. The end result is data of unknown origins, which should consequently be used with caution.

Another flaw often seen in flammability data compilations is the overly-used policy of reporting the “conservative” value, or in other words the lowest reported flash point and lower flammability limit, and highest reported upper flammability limit. This is the stated policy of at least the National Fire Protection Association’s (NFPA) compilations [134], and Lange’s Handbook of Chemistry [161], though many other compilations are suspected to have adopted this policy as well. Adoption of the lowest reported value makes the database susceptible to inaccurate and erroneous values from outliers, data with sources of large experimental error, and typographical errors. Although such a policy was surely instituted for safety purposes, it ignores the fundamental relationships between properties, and may lead to the imposition of unnecessary and costly restrictions on chemical processes.

The errors introduced by accepting the most conservative values are further exacerbated by circular referencing among compilations, illustrated in Figure 6.1. As compilations are prone to unit conversion and typographical errors, it is not hard to imagine how, over time, data will creep away from their original values. Specific examples of recurring errors of this nature seen throughout compilations are outlined here.

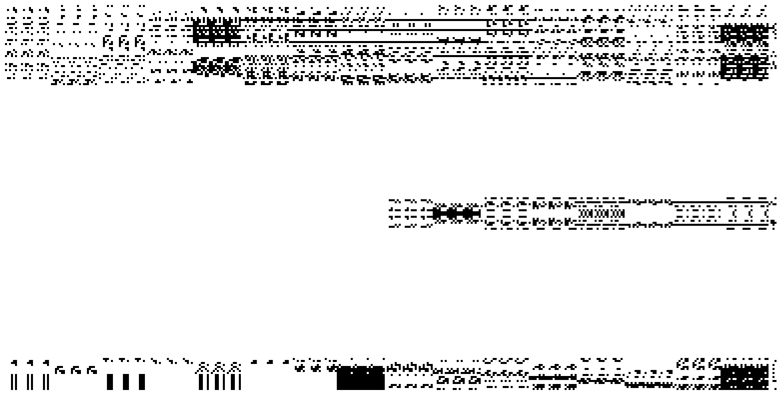

Figure 6.1. Illustration of documented circular referencing among compilations

Typographical Errors

Certain flash point values appear repeatedly in fire-hazard data compilations such that the following values should always be considered suspect: 110 °C (230 °F), 100 °C (212 °F), 0 °C (32 °F), and -20 °C (-4 °F). These values are actually extrema of the expected flash point, i.e., >110 °C or <-20 °C, but unfortunately the inequality sign is often absent. The most frequent of these values is 110 °C, which is the upper range of the ASTM 9C thermometer, commonly used in flash point experiments.

Generalized Statements

Because the measured flash point may depend significantly on the apparatus, information pertaining to measurement method/apparatus is crucial in evaluating flash-point data. Unfortunately, compilations often make general statements pertaining to the measurement method that are inaccurate for many of the reported values. For example, the *Aldrich Handbook of Fine Chemicals* [166] states that the reported flash points are "determined with the 'Setaflash' apparatus recommended by the DOT using ASTM Procedure D3278." Personal communication with Aldrich confirmed the validity of this statement for flash points actually measured by Aldrich. Unfortunately, the data measured by Aldrich with the Setaflash apparatus are not differentiated from the the other values in the Handbook that are predicted, cited, or measured prior to the standardization of the Setaflash apparatus.

Rather than specify a specific apparatus, most compilations generalize by stating that measurements are "closed-cup unless otherwise noted." It does not take long to find inconsistencies among the compilations with regard to this statement. For example, DIPPR cites several compilations reporting the flash point of 1-pentene as 255 K. Two compilations claim this value was determined in an open-cup [67, 140], three references make no statement pertaining to the apparatus [149, 161, 167], and one specifically lists the value as being determined in a closed-cup apparatus [168].

Unit Conversions

Unit conversion is a perpetual problem in data compilations, and flammability-property data are not expempt from this problem. Compilations often neglect to convert flash points reported in ^{o}C to ^{o}F and vice versa.

Flammability Limits at Elevated Temperatures

The temperatures of reported flammability limits are rarely reported in compilations. For gases, it is normally assumed that the data were determined at 298 K. However, for liquids, no standardized temperature exists. Because the lower flammability limit decreases with increasing temperature, omitting the measurement temperature leads to apparent scatter in data that would otherwise be consistent.

6.2 DIPPR® 801 Database

The DIPPR® 801 database serves as a good foundation for a comprehensive review of flammability data for several reasons:

- It already represents a large collection of flash point and flammability limit data
- The compounds in the DIPPR database have been selected as “industrially important chemicals” [169]

- Unlike many other compilations of flammability data, it also contains critically evaluated data for other thermophysical properties
- The relational structure of the database provides some inherent quality control, permits multiple points to be reported for a single property of each compound, and is capable of storing detailed documentation of the data source
- It has a commercially available graphical user-interface (DIADEM™) designed specifically for data evaluation, creation and maintenance of a user database, side-by-side comparison of multiple databases, and automated data prediction

This is not to say that the DIPPR® 801 database is impervious to the weaknesses shared by compilations mentioned in the previous section. In fact, the current DIPPR policy is to accept the "lowest reasonable value" of the reported flash points and lower flammability limits, with the term "reasonable" left undefined. Nor does the database provide a clear way to report flammability limits at various temperatures. It should be noted that these weaknesses are common to all or nearly all databases and compilations that report flammability data.

6.3 Review Methodology

Flammability limit and flash point data in the DIPPR® 801 database were supplemented with over 3600 data points found from a comprehensive literature search for this disseration. The combined data were manually evaluated for accuracy to determine the most probable value, and this value was then "accepted" as DIPPR's recommended value. This section presents the criteria used to select the most probable value.

6.3.1 Measurement Method

When available, information pertaining to the experimental method was taken into account in the following manner:

Chemical Purity

The purity of the sample was rarely noted. In the rare instances when it was, preference was typically given to samples of higher purity.

Experimental Apparatus

As already discussed, the measurement apparatus may result in significant differences in measured values. In general, closed-cup flash points were trusted over open-cup values. Although a specific closed-cup flash point apparatus was not preferred, knowledge of how the flash points differed between apparatuses was helpful in spotting irregularities in reported data. For example, PM flash points are typically lower than SS flash points at low temperatures, but may be significantly higher above 350 K. The fact that the PM flash point is sensitive to impurities, as detailed in Section 5.2.2, also helped explain several apparent outliers.

Since the Bureau of Mines data represent the largest set of consistent flammability data requiring full flame propagation, preference was given to upper and lower flammability limits consistent with these data. Data representing full flame propagation were desired because of the theoretical significance, and because such data are more widely used in the US. When values determined in an ASHRAE 12-L sphere were available, these values were given preference as they represent large-scale flammability determinations.

Knowledge of the flammability apparatus used in the measurements was often used to verify the accuracy of the data by comparison of points from other apparatuses. Typically, limits from European standards are wider than those determined using ASTM E 681, which are wider than those determined in the ASHAE 12-L apparatus, which in turn often approximate the Bureau of Mines values near ambient temperature. Data from the Nabert, Schön, and Redeker compilation [138, 151] were assumed to have been determined using EN 1839.

Experimental Conditions

Preference was given to values determined in air at 101.3 kPa. Lower flammability measurements were assumed to have been determined at 298 K when the T_L calculated from Equation 3.5a was less than 298 K, and at the lower temperature limit when the calculated T_L was greater than 298 K, unless otherwise documented. The temperature dependence of the flammability limits was assumed to follow the modified Burgess-Wheeler law (Equation 2.4) because this represents the median between assuming temperature-independent flammability limits and the temperature dependence discussed in Section 5.1.

6.3.2 Interrelation of Properties

The most fundamental interrelationship between hazard properties is that involving flammability limits, the temperature limits, and the vapor pressure curve. As detailed in Section 3.3,

$$\frac{P^*(T_\mathrm{L})}{101.3\ \mathrm{kPa}} \times 100 = \frac{LFL\ (T_\mathrm{L})}{\mathrm{vol\%}}, \tag{3.5a}$$

$$\frac{P^*(T_\mathrm{U})}{101.3\ \mathrm{kPa}} \times 100 = \frac{UFL\ (T_\mathrm{U})}{\mathrm{vol\%}}. \tag{3.5b}$$

Since the temperature limits are typically unknown, these equations represent a method of estimating T_L and T_U when the measurement temperature of the reported flammability limits are assumed (298 K if the estimated temperature limits are less than 298 K, and at saturation otherwise).

Given that flash point measurements are made in small vessels using downward propagation, the flash point should theoretically be higher than the lower temperature limit. This was shown to be true experimentally in Section 5.2.4. Thus, the first step in evaluating the flash point was to ensure

$$FP + \varepsilon \geq T_\mathrm{L}, \tag{6.1}$$

where ε is a positive tolerance that takes into account the experimental error of the flash point and lower temperature limit. When the lower temperature limit is estimated from a lower flammability limit, ε also accounts for errors associated with the assumed temperature dependence of the flammability limit (for gases), and the vapor pressure curve. In both cases, ε was assumed to be about 2 K, though preference was given to the lowest flash point that satisfied Equation 6.1 when ε equaled 0 K. It was also assumed that the difference between flash point and lower temperature limit increased slightly with increasing flash point, consistent with Equation 5.12a.

When the flash point of a chemical was well-defined it was used to evaluate lower flammability limit data in a similar manner:

$$\frac{P^*(FP)}{101.3\ \text{kPa}}\times 100 > \frac{LFL(T)}{\text{vol\%}}\,. \tag{6.2}$$

Note that this guideline is true for gases regardless of the measurement temperature of the lower flammability limit because the lower flammability limit decreases with increasing temperature. For solids and liquids, when the temperature is assumed to be T_L, Equation 6.2 is still valid because in reality the lower flammability limit is measured at some unknown temperature above saturation.

Several other basic guidelines for simultaneously evaluating flash points and flammability limits are often over-looked. For example, the general relation between the flash point and the upper temperature limit:

$$FP < T_U\,, \tag{6.3}$$

and accordingly,

$$\frac{P^*(FP)}{101.3\ \text{kPa}}\times 100 < \frac{UFL(T)}{\text{vol\%}}\,. \tag{6.4}$$

The reported flammability limits were also compared with the concentration required for stoichiometric combustion, C_{st}, calculated from Equation 2.11:

$$LFL < C_{st} < UFL\,. \tag{6.5}$$

Experimental autoignition temperature data, though scattered, provided an upper-threshold for questionable temperature data. Autoignition occurs when the compound spontaneously combusts in air, free of any external ignition source. Thus, the temperatures related to forced ignition should be lower than the autoignition temperature (*AIT*):

$$FP, T_{\mathrm{L}}, T_{\mathrm{U}} < AIT\ . \tag{6.6}$$

However, when data from a reputable source exceeded experimental AIT data, the flash point and flammability data were accepted over the AIT value.

Based on the observation of Leslie and Geniesse [81] described in Section 3.2.2, the flash point was expected to agree with the value estimated using Equation 3.2:

$$\frac{P^*(FP)}{101.3\ \mathrm{kPa}} = \frac{1}{8\beta}\,. \tag{3.2}$$

This was not a strict rule, rather when flash point data disagreed by more than approximately 3 %, the points were examined more closely for possible errors.

6.3.3 Chemical Series Trends

Plots of homologous series (e.g., *n*-alcohols, 1-alkenes, alkylbenzenes) were used to check for irregularities in data trends with respect to carbon number. Figures 6.2 and 6.3 depict typical behaviors of the flash point, temperature limits, and flammability limits with increasing carbon number. Values could be estimated from these plots, but were only accepted over experimental data when the experimental data deviated significantly from the expected trend, as shown in Figure 6.2.

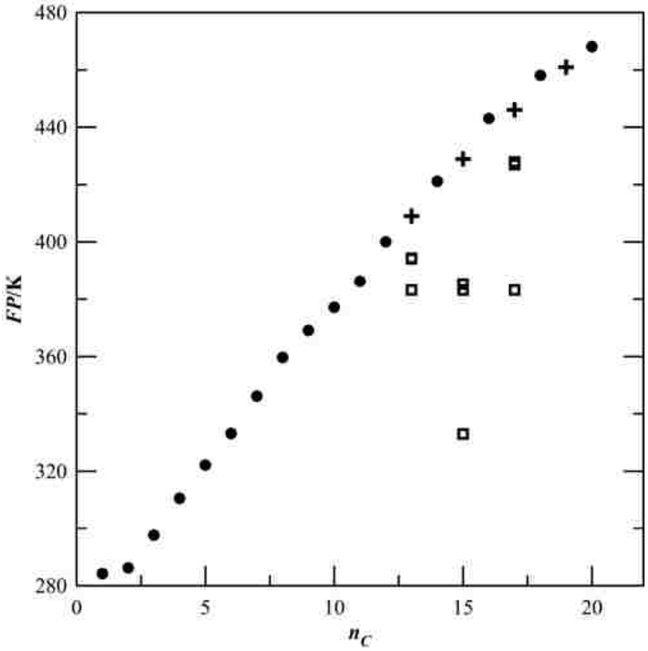

Figure 6.2. Trend of experimental flash point data (●) with carbon number for *n*-alcohols. Plots like this can be used to quickly spot erroneous data (□) and predict missing values (+)

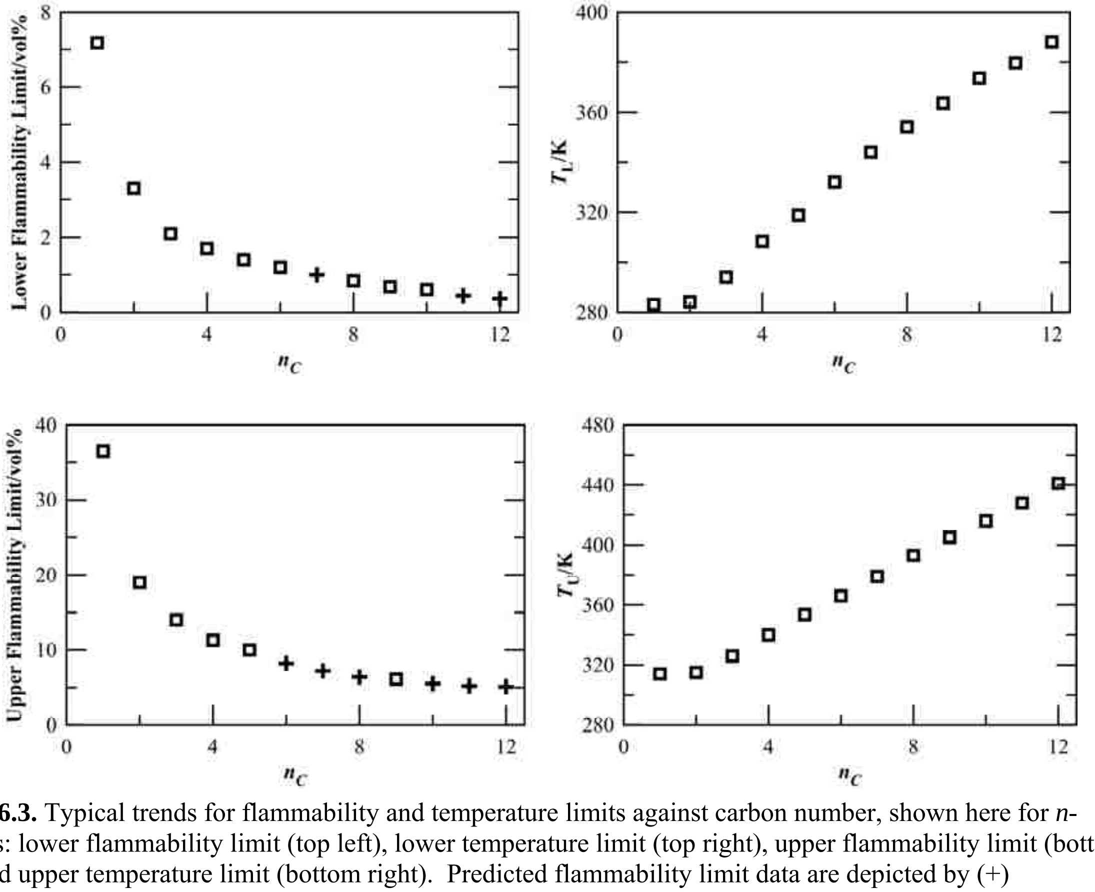

Figure 6.3. Typical trends for flammability and temperature limits against carbon number, shown here for *n*-alcohols: lower flammability limit (top left), lower temperature limit (top right), upper flammability limit (bottom left), and upper temperature limit (bottom right). Predicted flammability limit data are depicted by (+)

Flash point data of broader chemical classes (e.g., alkenes, aromatic hydrocarbons, alcohols) were evaluated for possible outliers by plotting the flash point against the normal boiling point, enthalpy of combustion, and enthalpy of vaporization at the flash point, and plotting the vapor pressure at the flash point against the enthalpy of combustion (Figure 6.4).

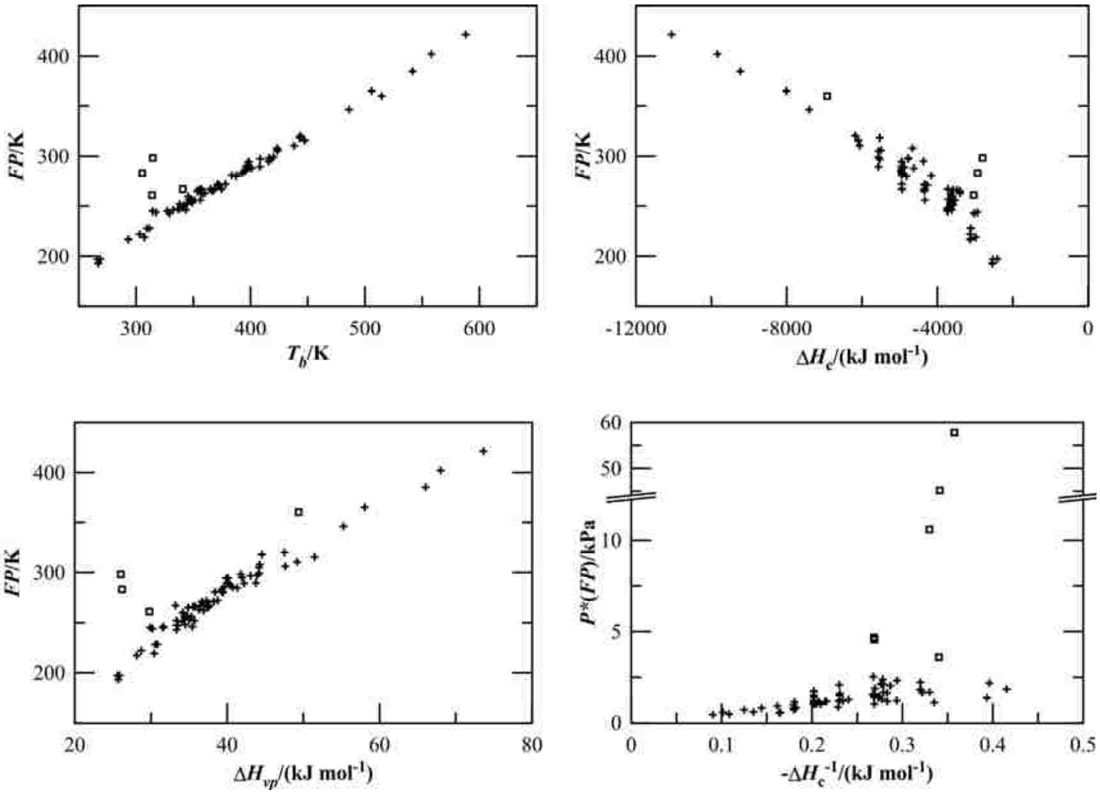

Figure 6.4. General flash point trends, shown here for alkenes and alkynes: *FP* vs. normal boiling point (T_b) (top left), *FP* vs. ΔH_c (top right), *FP* vs. ΔH_{vp} at the flash point (bottom left), and $P^*(FP)$ vs. ΔH_c^{-1} (bottom right). Possible outliers are depicted by (□)

Comparisons of two or more similar compounds were also used to obtain a rough estimate of a flash point, and more specific information for the flammability limit. For example, *sec*-butylbenzene, *iso*butylbenzene, and *n*-butylbenzene would be expected to have similar flash points. Experimental data in the DIPPR® 801 database report the flash point of these compounds as 325 K, 325 K, and 323 K, respectively. Because combustion properties are directly related to bond strength, differences in bond type and branching between otherwise similar compounds indicates the relative expected change in the flammability limits. For example, addition of a methyl branch decreases the lower flammability limit because the resulting compound is capable of forming more stable radicals. Thus the lower flammability limit for 2-methylpentane (1.2 vol%) is lower than the value for n-pentane (1.4 vol%), and the lower flammability limit of 2,4-dimethylpentane (1.1 vol%) is lower than that of 2-methylpentane. Flammability limits for geometric isomers were assumed to be identical.

Upper and lower flammability limit data from a single primary source were considered connected, and the analysis of both limits was performed simultaneously. If an upper flammability limit point constituted an irregularity in a family trend, it could eliminate the associated lower flammability point from being accepted. Accordingly, when a lower flammability limit point from a primary source was accepted, the corresponding upper flammability limit was deemed reliable as well.

6.3.4 Example Data Evaluations

Butanol

Flash point and flammability limit data for butanol are shown in Table 6.1.

Table 6.1. Reported flammability data for butanol

***FP*/K**	**Reference**	***LFL*/vol%**	**$T_{\mathrm{L,\,calc}}$/K**	**Reference**
302	[157]	1.4	304.6	[140]
302	[140]	1.7	307.5	[32]
302	[67]	1.7	307.5	[67]
310	[170]	1.4	304.6	[171]
302	[172]	1.7	307.5	[172]
310	[134]	1.63	307	[173]
308	[138]	1.4	304.6	[138]

The minimum calculated lower temperature limit exceeds the flash point reported by several compilations (302 K). The exact origin of the 302 K value is unknown; however, it was likely a calculated lower temperature limit from a lower flammability limit using poor vapor pressure data and has subsequently been mislabeled as a flash point. In any case, based on Equation 6.1, 302 K is not a valid flash point.

The best value of the flash point now depends on the value selected for the lower flammability limit. If 1.4 vol% is selected, 308 K is a valid flash point. Otherwise 310 K is the only remaining value consistent with the lower flammability limit. The 1.4 vol% lower flammability limit value was assumed to have been determined in an EN 1839-style apparatus, because it was found in the compilation of Nabert, Schön and Redeker [138]. The value reported by Kondo (1.63 vol%) was determined under reduced pressure. This leaves 1.7 vol% as the most likely value because data consistent with Bureau of Mines and ASHRAE flammability limits are preferred. This value could have been further verified through family plots, but to do so requires simultaneous evaluation of data for several compounds to create a family trend.

With 1.7 vol% as the accepted lower flammability limit, 310 K is the only option for the flash point. Predicting the flash point using the method of Leslie-Geniesse (Equation 3.2) returns 310.6 K, which agrees closely with the selected value. The flash point measured in this work was 310.5 ± 0.6 by PM, and 313.1 ± 0.7 by SS apparatus. The experimental lower temperature limit was 308.5 ± 0.5, and the lower flammability limit calculated at the lower temperature limit was 1.7 vol%.

Two important principles are demonstrated in this assessment: the most frequently reported value is not synonymous with the best value, nor is the lowest value necessarily the best value.

1,6-Hexanediol

1,6-Hexandiol represents a common problem encountered during the evaluation: no flammability limit data have been reported for this compound. The flash point data are given in Table 6.2.

Table 6.2. Flash point data for 1,6-hexanediol

FP/K	Reference	*FP*/K	Reference
420	[174]	394	[148]
372	[175]	375	[146]
374	[133]	373	[138]

To start the evaluation, several comparison compounds were selected: 1,3-propylene glycol, 1,4-butanediol, and 1,5-pentanediol, the structures of which are shown in Figure 6.5. The reported lower flammability limit of 1,3-propylene glycol is 2.6 vol% (T_L = 390 K), with no reported flash point data. Based on previous experience with how the flash point differs from the lower temperature limit limit, the flash point is expected to be between 392 K and 396 K. The method of Leslie and Geniesse predicts 393.4 K.

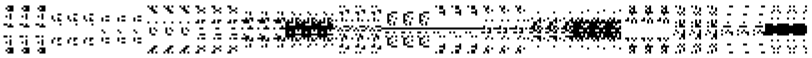

Figure 6.5. Structure of 1,6-hexanediol (top) and selected comparison compounds (left to right): 1,3-propylene glycol, 1,4-butanediol, and 1,5-pentanediol

There are two reported flash points for 1,4-butanediol, 407 K and 394 K (open-cup), and two reported lower flammability limits, 1.8 vol% (T_L = 401 K) and 1.95 vol% (T_L = 402.6 K). If either of the reported lower flammability limits is accurate, then by Equation 6.1 the flash point cannot be 394 K. Equation 3.2 predicts the flash point as 405.6 K.

There are no lower flammability limit data for 1,5-pentanediol, but several reported flash points. Three compilations report a flash point of 402 K, with one citing the value as open-cup. Another compilation reports 403 K (open-cup), and a material safety data sheet lists the flash point as 409 K. By Equation 3.2 the predicted flash point is 410.7 K. The flash point of 1,5-pentanediol should be greater than the flash point of 1,4-butanediol, since for a homologous series the flash point typically increases with increasing carbon number. Assuming 407 K is the best value for 1,4-butanediol (given that 394 K is inconsistent with the reported flammability limits), the flash point of 1,5-pentanediol is at least 409 K.

Of the reported flash points for 1,6-hexanediol, only 420 K is consistent with 409 K for 1,5-pentanediol, while the other values are significantly too low. 420 K is probably about 8 K too high, based on the trend of increasing flash point with increasing carbon number. In fact, the method of Leslie and Geniesse estimates the flash point as 412.8 K. The question then becomes, is it better to accept experimental data that is suspected of being too high, or to accept the predicted value? In this case, since there are no further comparison compounds to evaluate the accuracy of the prediction method for this type of chemical, and no well-developed family trends to examine for outliers, it’s possible that 420 K is the real flash point. The deviation between the predicted and reported value is about 1.7 %, which is within the estimated experimental error at this temperature anyway. Thus 420 K is the recommended flash point for 1,6-hexanediol.

The values for the flammability limits of these compounds will be predicted once an accurate method is established.

6.3.5 Special Considerations

For a number of compounds, the evaluation techniques discussed in this chapter will not work because the compounds either decompose or polymerize when heated. This is the case for many peroxides and heavy organic acids. When a compound decomposes upon heating, combustion typically occurs at the decomposition temperature if it is below the expected flash point. For example, tartaric acid is reported to decompose above 479 K. While the predicted flash point by Equation 3.2 is 586.5 K, there is an experimental point at 483 K, remarkably close to the reported decomposition temperature.

For compounds that polymerize upon heating, such as aspirin, the measured flash point may actually exceed the expected flash point. Equation 3.2 predicts a flash point of 439 K for aspirin. Nabert, Schön, and Redeker [138] report the flash point as 523 K.

6.4 Database Statistics

Statistics comparing the DIPPR® 801 database before and after the critical review indicate significant improvement in the database quality by the process. Figure 6.6 shows the number of reported experimental points added to the database for each property, for a total of 3665 data points. This is nearly a 60 % increase from the 6262 flammability data points previously in the database. The largest percent increase in the number of experimental data points was for the lower and upper flammability limits, which increased by 88 % and 86 %, respectively. The number of experimental flash point data points increased by 45 %, and the number of temperature limit points increased by 24 %.

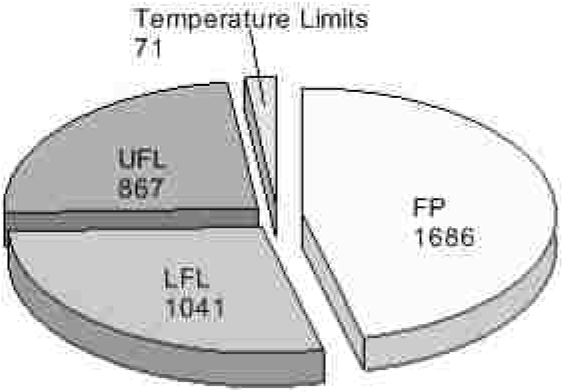

Figure 6.6. Increase in the number of experimental data points for each property added to the DIPPR database

The value added to the DIPPR® 801 database by the increased number of experimental points, however, depends on the amount of unique information obtained from the literature search. Figure 6.7 shows the change in the number of compounds in the database with at least one experimental point for each property. The number of compounds with at least one experimental flash point, lower flammability limit, upper flammability limit, and temperature limit data point increased by 10 %, 25 %, 27 %, and 14 %, respectively. This corresponds to an additional 5 % to 6 % of the 2061 compounds in the database with at least one experimental data point describing its flammability.

It is easy to establish how the review impacted the quantity of data in the database. It is more difficult, however, to discern how the review impacted the quality of the database. The total number of recommended points for each property increased only slightly because of the DIPPR policy to predict missing property data. The number of recommended values that are based on experimental data, on the other hand, changed by an average of 100 compounds for each of the reviewed properties, excluding temperature limits (Figure 6.8). Temperature limits were excluded from this analysis because the recommended values are almost entirely predicted.

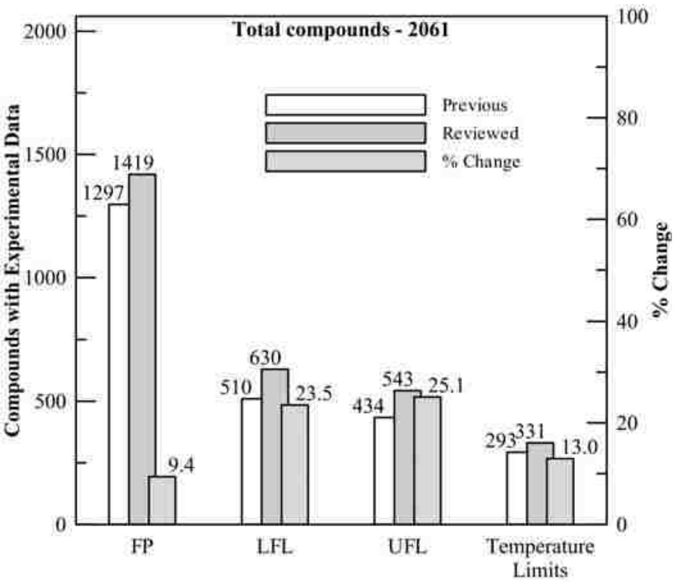

Figure 6.7. Number of compounds with at least one experimental data point in the previous DIPPR® 801 database and the reviewed database

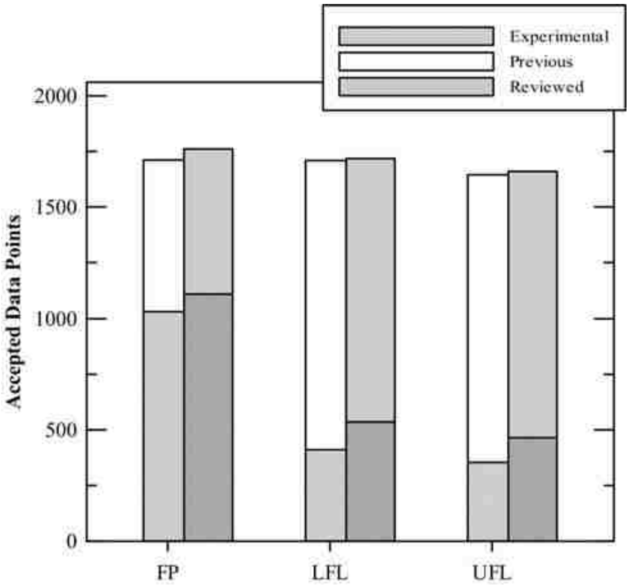

Figure 6.8. Number of accepted points in the previous DIPPR® 801 database compared with the reviewed DIPPR database; points are divided into experimental (hashed bars) and other

To further quantify the effect of the critical review on the database, statistics pertaining to the magnitude of the changes in recommended values were compiled, where

$$\% \text{ Change} = \frac{\text{New Value} - \text{Old Value}}{\text{Old Value}} \times 100 \ \% . \tag{6.7}$$

Only experimental data for which no change was made and experimental data which replaced a predicted or experimental recommended value will be included in the subsequent analysis; analysis of predicted points is covered in the next chapter.

Histograms of the changes show that 50 % of the recommended flash point, 55 % of the recommended lower flammability limit, and 57 % of the recommended upper flammability limit values received little or no change (Figures 6.9 and 6.10). The histograms also show a slight bias in shifting the flash point values higher between 1 % to 3 %. This is consistent with the idea of correcting data creep, as discussed in Section 6.1, but an interesting contrast to what appears to be a slight bias towards decreasing the lower flammability limit. The possibility of bias was further investigated by plotting the newly recommended values against the old, shown in Figures 6.11 and 6.12. The recommended flash points do appear to cluster immediately above the 45$^{\text{o}}$ line, especially when the former flash point was between 250 K to 290 K and 325 K to 400 K.

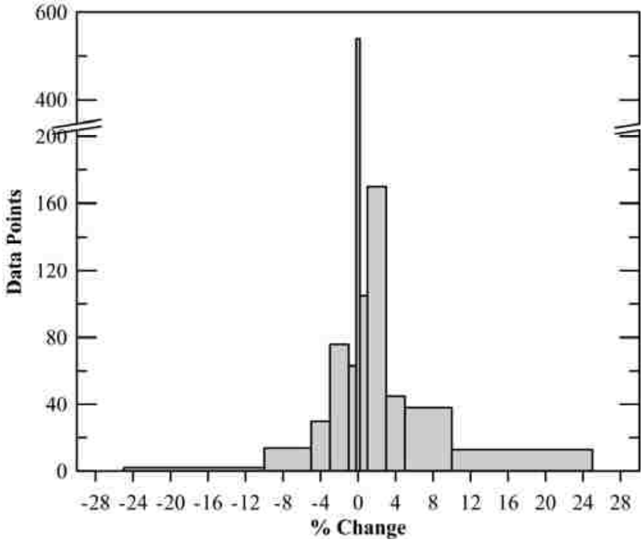

Figure 6.9. Histogram of changes in recommended values for flash point

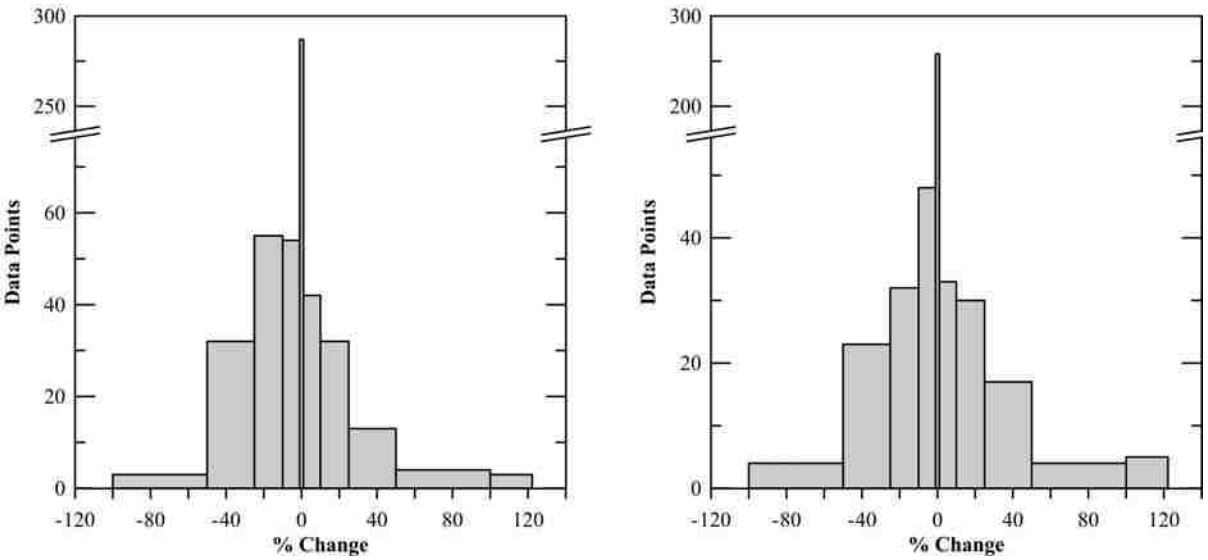

Figure 6.10. Histograms of changes in recommended values for lower flammability limit (left) and upper flammability limit

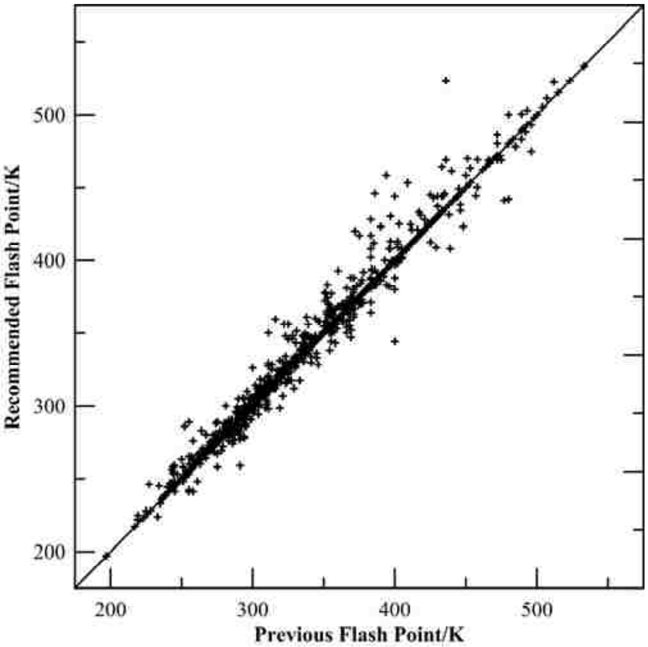

Figure 6.11. Previously recommended flash points vs. values recommended following the critical review

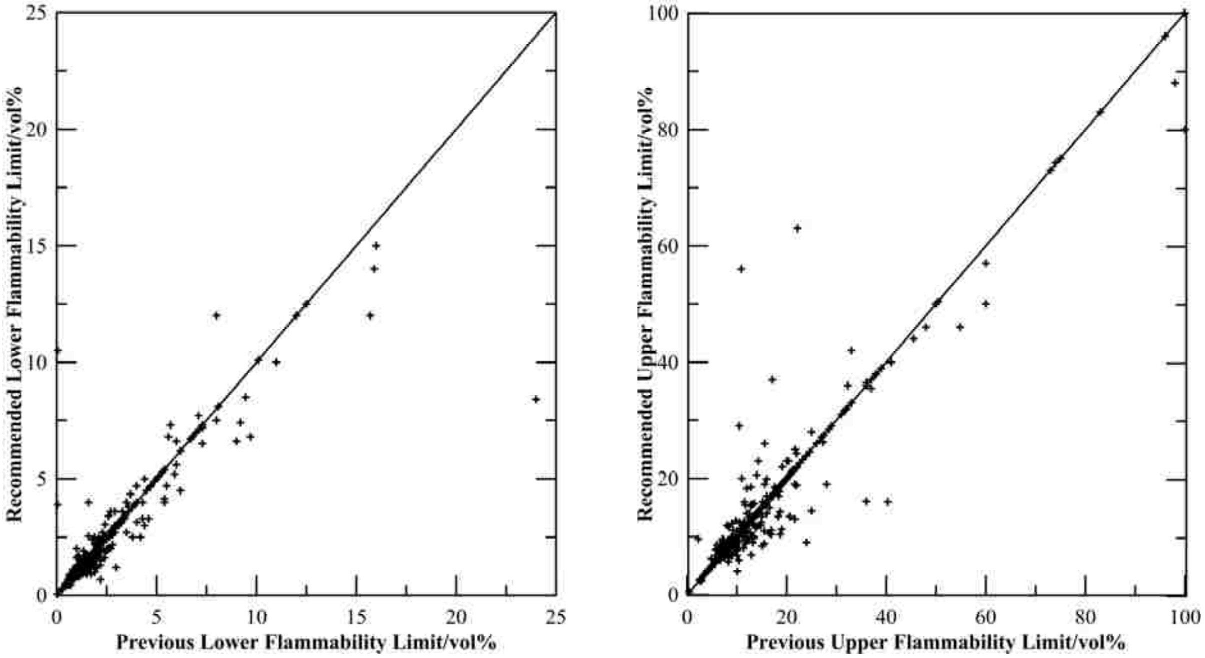

Figure 6.12. Previously recommended lower flammability limits (left) and upper flammability limits vs. values recommended following the critical review

Figure 6.12 shows some bias exists for the newly recommended lower flammability limit data towards lower values. It also shows several significant changes, or outliers of the "normal" changes made, in both lower and upper flammability limit data that were not apparent from the histograms. A summary of the absolute changes exceeding 100 % is given in Table 6.3. In most cases, when the difference between original and reviewed values was greater than 100 %, the original value was predicted and the reviewed value was experimental. There were only three exceptions:

Arsine

The lower flammability limit for arsine was reported in gm·m^{-3} in the original source, and the value in the database appears to be an erroneous attempt to convert it to vol%. Even with

Table 6.3. Absolute changes in the recommended value greater than 100 %

Property	**Compound**	**Previous Value/vol%**	**Previous Data Type**	**New Value/vol%**	**New Data Type**	**% Change**
LFL	Pentafluoroethyl Methyl Ether	0.054	Predicted	10.5	Experimental	19344
LFL	Arsine	0.051	Unknown	3.9	Experimental	7547
UFL	Diethylene Glycol	17.1	Predicted	37	Experimental	116
UFL	Nitromethane	22.2	Predicted	63	Experimental	184
UFL	1-Ethoxy-2-propanol	10.9	Predicted	56	Experimental	414
UFL	Trichloroethylene	10.5	Unknown	29	Experimental	176
UFL	Hexamethyleneimine	2.25	Experimental	9.6	Experimental	327

proper conversion, however, the original recommendation is far below the reported value of Nabert, Schön, and Redeker [138]. Furthermore, the upper flammability limit associated with the original value is approximately 2 vol% (with proper conversion), which is a narrow range of flammability for a reactive gas like arsine. It is possible that the original source mistakenly assigned gravimetric instead of volumetric units to the reported values. If so, then the values from the original source would correspond to a flammability range of 4.5 vol% to 68 vol%. This would bring the lower limit value into relatively good agreement with the lower limit reported by Nabert, Schön, and Redeker (3.9 vol%).

Trichloroethylene

The previously recommended upper flammability limit for trichloroethylene is cited in a a data compilation [135], and so the original source is uncertain. To be consistent with a well-established lower flammability limit of approximately 12 vol%, the previously recommended value must be greater than the 10.5 vol% reported. Much of the reported upper flammability limit data is in the range of 40 vol% to 50 vol%, but was obtained at about 373 K. Since the upper flammability limit increases significantly with increasing temperature, the experimental value determined by Kondo et al. [176] was accepted (29 vol%).

Hexamethyleneimine

The recommended upper flammability limit for hexamethyleneimine was increased from 2.25 vol% to 9.6 vol% because the recommended lower flammability limit was 1.58 vol%. As the compound is likely flammable over a wider range than 0.67 vol %, a measured value consistent with a wider flammability range was accepted.

The magnitude of these few "outlying" changes greatly influences the statistics of average changes made to the recommended values. Accordingly, Table 6.4 lists the average changes with and without these points. These statistics reaffirm the observation that newly recommended flash points tend to be higher, and newly recommended lower flammability limits tend to be lower than the previous values. They also show that the average change of the recommended value is greater if the previously recommended value was predicted rather than experimental.

Table 6.4. Average changes made to recommended values in the DIPPR® 801 database

				Excluding "Outlier" Changes	
	FP	**LFL**	**UFL**	**LFL**	**UFL**
Previously Experimental					
# of Recommended Values	944	399	344	398	343
Ave. Change/%	0.43	18.25	1.38	-0.67	0.43
Absolute Ave. Change/%	1.19	25.00	5.74	6.10	4.80
Ave. Change/(K or vol%)	1.44	-0.08	-0.22	-0.09	-0.24
Absolute Ave. Change/(K or vol%)	4.00	0.20	0.89	0.20	0.87
Previously Predicted					
# of Recommended Values	151	126	110	125	109
Ave. Change/%	1.20	148.56	3.36	-5.01	-0.40
Absolute Ave. Change/%	1.72	167.08	23.57	13.66	19.99
Ave. Change/(K or vol%)	3.87	-0.03	0.35	-0.11	-0.06
Absolute Ave. Change/(K or vol%)	6.01	0.35	3.04	0.27	2.65
Overall					
# of Recommended Values	1095	525	454	523	452
Ave. Change/%	0.54	49.53	1.86	-1.70	0.23
Absolute Ave. Change/%	1.26	59.10	10.06	7.91	8.47
Ave. Change/(K or vol%)	1.78	-0.07	-0.08	-0.10	-0.20
Absolute Ave. Change/(K or vol%)	4.28	0.24	1.41	0.21	1.30

CHAPTER 7. PROPERTY ESTIMATION

For many compounds, little or no experimental flash point and/or flammability limit data have been published. Many methods of estimating the flammability limits and flash point have been developed, as discussed in Sections 2.3 and 3.1.2. This chapter evaluates these methods for accuracy against the critically evaluated data discussed in the previous chapter. Additional methods are presented to more accurately predict the flammability limits and flash points of organic compounds.

7.1 Lower Flammability Limit

Prediction of the lower flammability limit is complicated by two main factors: flammability limits are dependent on initial measurement temperature and the flame propagation criterion used in determining a flammability limit significantly affects the value. Thus, prediction of the magnitude of the lower flammability limit, in other words the value at at a single temperature, is considered separately from estimation of the effect of temperature on the lower flammability limit. Compartmentalizing prediction in this manner allows the estimated effect of temperature to be applied to any predicted or experimental value, regardless of the flame propagation criterion used in determining the point.

7.1.1 Magnitude Estimation

Many prediction methods exist for estimating the lower flammability limit at a single temperature, as discussed in Section 2.3. These methods assume that the lower flammability limit was determined at 298 K, which is indeed the case for most gases. However, the flammability limits of liquids and solids are determined at an arbitrary and often unspecified temperature above saturation. For lack of a better option, flammability limit data of liquids and solids are assumed to be reported at the corresponding temperature limits when the temperature limits exceed 298 K. When the temperature dependence of the lower flammability limit (as discussed in Section 5.1) is considered, and if the difference between the lower temperature limit and the actual measurement temperature is between 50 K and 75 K, the average error introduced by assuming the measurement took place at the lower temperature limit ranges between 9 % and 13 %.

An equal, if not greater, source of error in the magnitude of the lower flammability limit is the differences in flame propagation criteria. A comparison of more than 100 values determined using both the Bureau of Mines and EN 1839 definitions of flame propagation showed an average deviation of 13 %, and deviations between values as large as 50 %, with the Bureau of Mines values typically exceeding the values from the EN 1839 method. These differences represent what may be called the lower flammability limit band: Bureau of Mines and ASHRAE data represent the concentration where full flame propagation just fails, EN 1839 measurements indicate the concentration at which no flame propagation will occur, and in between these values partial flame propagation is possible.

Thus, rather than treat these different measurements as experimental scatter, the magnitude of the lower flammability limit was estimated for datasets obtained using each of these three apparatuses, and a dataset composed of the values recommended during the critical review of the DIPPR® 801 database. Datasets are tabulated in Appendix E. Table 7.1 shows the accuracy of previously published methods of estimating the magnitude of the lower flammability limit, based on average absolute deviation (AAD) from the experimental values, defined by

$$\mathrm{AAD}(\%) = \frac{1}{p}\sum_{p}\left|\frac{\text{Predicted} - \text{Experimental}}{\text{Experimental}}\right| \times 100\,\%, \tag{7.1}$$

where p is the number of points compared. Several methods were not applicable to certain compounds because the methods lacked the structural groups necessary to describe these compounds. These "incomplete" methods are listed in Table 7.2 with the number of experimental points to which the method applied.

Table 7.1. Average absolute deviation (AAD) of published lower flammability methods for data from the Bureau of Mines apparatus (BoM), the European standardized method (EN), the ASHRAE apparatus, and recommended lower flammability limit values

	AAD/%			
Method	**BoM**	**EN**	**ASHRAE**	**Recommended LFL Values**
Chemical Equilibrium Methods				
Mashuga-Crowl [22]/Ervin et al. [23] (T_{ad} = 1200 K)	35.41	30.42	37.94	34.42
Melhelm [26] (T_{ad} = 1000 K)	51.90	47.91	54.32	50.80
Shebeko et al. [24]/Vidal et al. [25] (T_{ad} = 1600 K)	10.96	17.92	12.63	18.39
Calculated From FP and P^*				
$FP = T_L$	23.11	33.20	23.24	28.40
Shebeko ($FP - T_L = 1.9$) [96]	17.65	23.24	16.05	20.19
Pintar ($FP - T_L = 3$) [48]	17.56	19.37	15.18	18.43
Kueffer-Donaldson [110]	21.46	20.78	16.23	20.59
Evalnov [108]	23.32	25.94	24.45	21.88
Equation 5.12a	28.39	29.34	30.29	25.66
Empirical Correlations				
Affens - Approximation [35]	16.64	19.85	21.13	20.79
Affens [35]	11.73	20.07	20.05	17.06
Britton [33]	14.16	19.92	39.32	20.94
Britton-Approximation [33]	17.38	19.69	15.49	17.68
Dalmazzone [61]	13.71	16.07	22.81	15.79

Table 7.1. Continued

	AAD/%			
Method	**BoM**	**EN**	**ASHRAE**	**Recommended LFL Values**
Funk [54]	33.37	36.62	14.53	32.84
Goto [59]	11.37	18.52	17.13	16.07
Hanley [51]	12.58	22.18	21.02	18.66
Hshieh [63]	11.70	19.12	17.17	16.83
Jones [31-32]	12.92	21.17	14.46	21.93
Kondo [173, 177-178]	20.76	27.35	10.86	23.86
Miloshev [50]	37.07	38.98	38.88	40.31
Monakhov [39, 48]	17.77	23.88	16.25	29.42
Oehley [49]	14.93	26.33	29.90	27.38
Pintar [42]	13.89	14.86	14.90	14.21
Pintar-Approximate [42]	12.48	16.97	14.75	15.86
Shebeko [39]	12.22	19.85	15.67	20.37
Shimy [36]	19.32	23.77	22.59	24.54
Solovev-Baratov [37]	20.22	26.85	25.24	25.04
Spakowski [55]	11.65	17.17	19.46	15.28
Suzuki [62]	14.16	33.22	21.00	42.90
Suzuki-Ishida [56]	15.41	34.38	25.49	39.54
Thornton [46]	16.99	25.93	15.07	26.18

Table 7.2. Average absolute deviation (AAD) of published lower flammability limit methods that do not apply to general organic compounds

Dataset	**BoM**		**EN**	
	Compounds	194	**Compounds**	319
	Exp Points	200	**Exp Points**	319
Method	**AAD/%**	**Applicable Points**	**AAD/%**	**Applicable Points**
Albahri [43]	6.08	69	11.04	71
Hilado [45]	15.79	186	22.53	285
Möller [47]	13.27	165	17.28	240
Seaton [41]	14.33	137	17.95	188
Zatsepin [44]	9.29	164	16.58	230
Zatsepin from T_{ad} [30]	9.24	194	12.60	293
Dataset	**AHSRAE**		**Recommended LFL Values**	
	Compounds	119	**Compounds**	509
	Exp Points	124	**Exp Points**	509
Method	**AAD/%**	**Applicable Points**	**AAD/%**	**Applicable Points**
Albahri [43]	7.14	45	9.71	104
Hilado [45]	10.75	68	17.88	445
Möller [47]	11.86	74	20.55	383
Seaton [41]	15.65	61	19.53	287
Zatsepin [44]	11.03	80	16.66	352
Zatsepin from T_{ad} [30]	9.24	107	12.74	462

The methods listed in Table 7.1 are grouped into three classifactions: chemical equilibrium methods, described in Section 2.3.1; methods of estimating the lower flammability limit from the flash point; and other empirical correlations for predicting the lower flammability limit at a single temperature.

To allow for automated evaluation of the chemical equilibrium methods, two assumptions were applied: 1. combustion was complete with no disassociation of products, and 2. the heat capacities were independent of temperature, and equaled the reported values at 298 K. It has already been shown in Section 5.1.2 that little or no difference exists between flame temperatures at the lower flammability limit when they are calculated using Equation 5.1 compared to temperatures calculated using chemical equilibrium calculators. However, significant differences exist between calculated flame temperatures when the heat capacities are assumed to be independent of temperature. This assumption was made to simplify the calculation of the flame temperature, and decrease the computation time. Figure 7.1 shows that the flame temperatures calculated assuming constant heat capacities are related linearly for many compounds to the temperatures calculated by Equation 5.1. Therefore, the suggested flame temperature for each chemical equilibrium method was corrected to be consistent with the constant heat capacity assumption by

$$T_{\mathrm{ad,\,const}} = 1.2585 T_{\mathrm{ad}} - 227.66\,, \tag{7.2}$$

($R^2 > 0.999$) where $T_{\mathrm{ad,\ const}}$ is the flame temperature calculated assuming temperature-independent heat capacities.

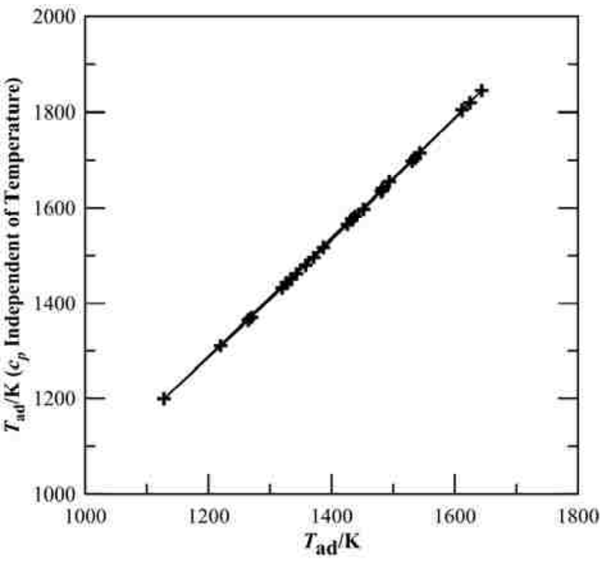

Figure 7.1. Adiabatic flame temperatures calculated assuming heat capacities independent of temperature are related linearly to flame temperatures calculated from Equation 5.1

In most cases the chemical equilibrium methods resulted in as large or larger AADs than the empirical correlations. The exception to this was when the lower flammability limit data from the Bureau of Mines were assumed to correspond to a constant adiabatic flame temperature of 1600 K, as proposed by Shebeko et al. [24] and Vidal et al [25].

The predictive power of the constant adiabatic flame temperature assumption was further analyzed by finding the T_{ad} that resulted in the lowest AAD for each data set. The AAD was minimized for both the ASHRAE and Bureau of Mines data sets when T_{ad} equaled 1580 K, at 12.54 % and 10.84 %, respectively. This not only agrees with the observation of Shebeko et al. and Vidal et al., but also shows how similar the data sets are. The AAD of the European measurement data set was minimized to 14.21 % when T_{ad} was 1486 K, and the set of recommended values achieved a minimum AAD of 16.59 % when T_{ad} was 1523 K.

A constant adiabatic flame temperature across chemical families appears to be a reasonable assumption, resulting in accuracy comparable to the most accurate empirical method currently published. Better accuracy, however, is obtained when the adiabatic flame temperature is estimated by the bond contributions proposed by Zatsepin.

Also shown in Table 7.1 is an evaluation of the usefulness of published relationships between the flash point and lower temperature limit, as well as the relationship between the lower flammability limit and flash proposed by Kueffer and Donaldson [110], in estimating the lower flammability limit. These methods actually calculate the lower flammability limit at the lower temperature limit (except for the method of Kueffer and Donaldson), but when the predicted value is corrected to 298 K for gases (assuming the temperature dependence follows the modified Burgess-Wheeler law) the AAD actually increases slightly for most methods. Two exceptions were the method of Evlanov, and use of Equation 5.12a, but the decreases in the AAD for these methods were not significant enough to make these methods useful.

It would appear that there is no advantage to estimating the lower flammability limit from the flash point over using other empirical methods that require little or no thermodynamic data. It is, however, interesting to note that the assumption of Pintar that the flash point is constantly 3 K higher than the lower temperature limit yielded the best results for every data set.

New Method

Development of a new method to accurately predict the lower flammability limit for each apparatus type began with Equation 5.1. Solving for the lower flammability limit and assuming the heat capacities are constant with respect to temperature yields

$$LFL = \frac{100 C_{p,\text{air}} (T_{\text{ad, const}} - T^{\circ})}{H_{\text{f}}(T^{\circ}) - \sum_{\text{products}} n_i H_i (T_{\text{ad, const}}) + \beta H_{\text{O}_2}(T_{\text{ad, const}}) + C_{p,\text{air}}(T_{\text{ad, const}} - T^{\circ})}, \tag{7.3}$$

where the enthalpy of each species relative to the idea gas enthalpy of formation at 298 K, H^{o}_{for}, is found using

$$H_j(T) = H^{\mathrm{o}}_{for,j} + C_{p,j}(T - 298\ \mathrm{K}), \tag{7.4}$$

and the subscripts f, O_2, air, and *i* represent the fuel, oxgen, air, and the *i*th combustion product, respectively. The combustion products are detailed in Equation 2.8. $T_{\mathrm{ad,\ const}}$ may be estimated from structural contributions,

$$T_{\mathrm{ad,\,const}} = \frac{\sum_j ng_j \cdot \Delta T_j}{\sum_k ng_k}, \tag{7.5}$$

where *ng* is the number of the j^{th} structural contribution, ΔT, given in Table 7.3, and the sum in the denominator of Equation 7.5 represents the total number of structural groups used to represent the compound.

Table 7.3. Structural contributions for Equation 7.5, regressed using lower flammability limit data from the Bureau of Mines apparatus (BoM), the European standardized method (EN), the ASHRAE method, and the recommended values

j	Group	ΔT (BoM)	ΔT (EN)	ΔT (ASHRAE)	ΔT (Recommended LFL Values)	Example
1	≡C-	793.03	1283.67	425.61	991.44	Vinylacetate
2	≡CH	1378.19	1289.76	1376.58	1237.85	Acetylene
3	=C<	1493.36	1567.28	2426.62	1834.42	Isobutene
4	=CH	1478.71	1711.28	1849.96	1751.82	*trans*-2-Butene
5	$=CH_2$	1818.77	1473.79	1333.41	1558.49	1-Hexene
6	$=CH\text{-}(C_a)$	1783.42	223.41	180.05	-76.72	Styrene
7	$=C\text{-}(C_a)$	1960.57	2098.98	1745.62	2091.10	α-Methylstyrene
8	>C<	2004.55	1477.56	2696.93	1957.78	Neopentane
9	-CH	1973.58	1716.78	1668.05	1558.73	Isopropanol
10	$-CH_2$	1883.60	1671.84	1814.53	1705.21	Propane
11	$-CH_3$	1796.71	1696.89	1645.18	1856.30	Butane
12	$CH_3\text{-}(C_a)$	2066.34	1685.99	2323.11	1862.04	Toluene

Table 7.3. Continued

j	**Group**	**ΔT (BoM)**	**ΔT (EN)**	**ΔT (ASHRAE)**	**ΔT (Recommended LFL Values)**	**Example**
13	C_a	2134.88	1326.49	1976.93	1719.69	Toluene
14	C_aH	1587.11	1755.10	1185.33	1731.92	Phenol
15	OH-(C)	1752.94	894.78	1148.85	786.14	1-Methylcyclohexanol
16	OH-(CH)	959.03	974.00	1497.97	1508.33	Isopropanol
17	OH-(CH2)	1141.20	1306.63	1424.50	1397.73	Butanol
18	OH-(C_a)	1076.30	569.03		1337.25	Phenol
19	OH-(CC≡C)	2450.45			2209.35	Propargyl Alcohol
20	O=C	1562.15	1561.56	1253.28	1532.45	3-Pentanone
21	O=C_R	1489.96	1220.78		954.03	Cyclohexanone
22	O=C-C=C	1667.50	1764.75		1761.66	Methacrolein
23	O=COC	945.68	1591.92	1152.74	1492.23	Hexyl Formate
24	(C)O(C)	1740.65	1294.44	1986.93	1325.57	Diethylene Glycol
25	COOH	1257.29	1108.82		1252.38	Formic Acid
26	O_R	2027.33	1258.47	1198.18	1402.11	Furan
27	O-O		-570.99		-728.23	Cumene
28	N	1609.73	1868.47	1520.93	1442.71	Triethylamine
29	N_a	2850.69	2170.58	1443.61	2622.13	Pyridine
30	N_R	1211.86	2114.09	1522.40	2124.88	Piperazine
31	NH	1939.13	1937.54	1869.06	1566.76	*n*-Pentylamine
32	N-(C_a)	1564.52	2527.05		2695.31	*n*-Ethylaniline
33	N≡C	1866.30	1356.08	1285.92	939.73	Benzonitrile
34	N=C=O	1690.67	1310.08	1526.56	1147.48	Methyl Isocyanate
35	NO_2	1651.00	1626.36		1777.58	Nitroethane
36	S	1690.08	513.17		1056.05	Thiophene
37	SH	2089.02	1810.42		1727.50	Ethyl Mercaptan
38	S=	-183.21	6.08		272.36	Carbon Disulfide
39	Si	1282.08	-13.98		-55.66	Trimethyl Silane
40	Si(O_3)		1712.12		2095.22	Tetraethoxysilane
41	(Si)-O-		-148.53		2347.17	Octamethyltrisiloxane
42	Si-(Cl)				1062.27	Monochlorosilane
43	Si-(Cl_2)	575.74	209.16		554.54	Dichlorosilane
44	Si-(Cl_3)				-34.35	Methyl Trichlorosilane
45	F_2-(C)	2359.34	2283.76	2544.35	2556.15	1,1-Difluoroethane
46	F_2-(C=C)	2092.42	2227.07	1907.51	2088.23	1,1-Difluoroethylene
47	F_3-(C)		2159.32	2152.32	2451.95	3,3,3-Trifluoropropene
48	F-(C)		2056.03	1706.91	1841.54	Methyl Fluoride
49	F-(C=C)		943.68	939.88	1477.04	Vinyl Fluoride
50	Cl_2-(C)	3237.87	3096.94	3097.27	2882.45	Dichloromethane
51	Cl_2(C=C)	2176.42		2928.55	2956.55	1,1-Dichloroethylene
52	Cl_3-(C)		3046.14	3106.43	3046.39	1,1,1-Trichloroethane
53	Cl-(C)	1906.24	2094.23	2705.66	1948.51	Isopropylchloride
54	Cl-(C=C)	1301.98	1929.16	2265.53	2294.79	Chloropropene
55	Cl-(C=C-Cl)	1818.80	2691.25	3773.88	3257.79	*o*-Dichlorobenzene
56	Br-	3368.52	3760.95	4117.76	3389.83	Methyl Bromide

Subscripts a and R indicate an aromatic atom and an atom in a nonaromatic ring, respectively.

As mentioned above, T^{o} would normally be assumed to be 298 K for gases and the lower temperature limit for solids and liquids. However, prediction with Equation 7.3 is greatly simplified if T^{o} is assumed to be 298 K for all compounds,

$$LFL = \frac{100}{1+\nu}, \tag{7.6}$$

where

$$\nu = \frac{H^{\mathrm{o}}_{for,\,\mathrm{f}} - \sum\limits_{\mathrm{products}} n_i H_i(T_{\mathrm{ad}}) + \beta H_{\mathrm{O_2}}(T_{\mathrm{ad}})}{C_{p,\mathrm{air}}(T_{\mathrm{ad}} - 298\ \mathrm{K})}. \tag{7.7}$$

The error this assumption introduces for liquids and gases is assumed to be minimized during the regression of the structural contributions for $T_{\mathrm{ad,\,const}}$. The values of the structural contributions were determined by minimizing the AAD of a training set of data selected from each apparatus data set (Appendix E). The predictive ability of Equation 7.6 was evaluated by considering the change in AAD between the training set and the test set. Results are given in Table 7.4.

Table 7.4. Average absolute deviations for values predicted using Equation 7.6

Data Set	**AAD/%**	**Data Points**	**Data Set**	**AAD/%**	**Data Points**
BoM Training Set	7.37	117	ASHRAE Training Set	8.18	70
BoM Test Set	7.10	83	ASHRAE Test Set	8.59	54
BoM Combined Sets	7.26	200	ASHRAE Combined Sets	8.36	124
EN Training Set	9.17	166	Recommended LFL Training Set	10.61	309
EN Test Set	9.42	153	Recommended LFL Test Set	10.76	200
EN Combined Sets	9.29	319	Recommended LFL Combined Sets	10.67	509

Equation 7.6 returns a lower AAD than every other published estimation method applicable to general organic compounds, predicting close to, if not within, experimental error. The difference between the AAD of the training and test sets is less than 0.5 %, indicating this method has high predictive potential. The errors are the most broadly distributed for the set of recommended data (Figure 7.2). This is not surprising, as this data set is a mixture of data from various sources: 10 % from the Bureau of Mines apparatus, 14 % from the ASHRAE apparatus, 18 % from the EN method, and the rest of the data from a broad range of sources. Prediction errors for the EN data set also have a large spread, most likely because the compilation [138] from which EN data were taken reports data from other apparatuses when no EN value is available.

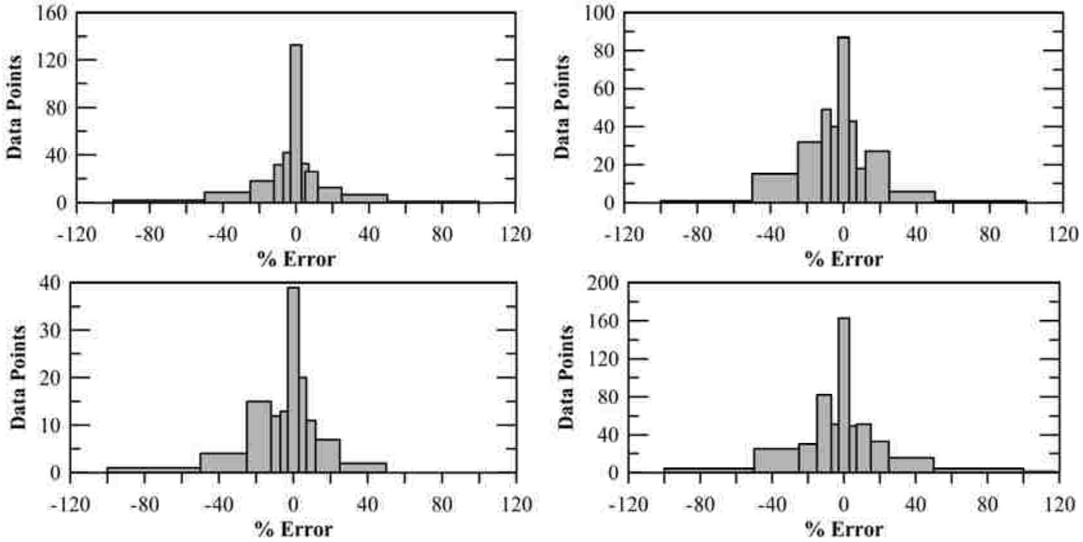

Figure 7.2. Distributions of errors from using Equation 7.6 to predict the lower flammability limit for data sets of (top left) Bureau of Mines, (top right) European, (bottom left) ASHRAE, and (bottom right) recommended values

Plots of the predicted values vs. experimental data indicate that the error increases with increasing flammability limit (Figure 7.3). This was expected, as lower flammability limits

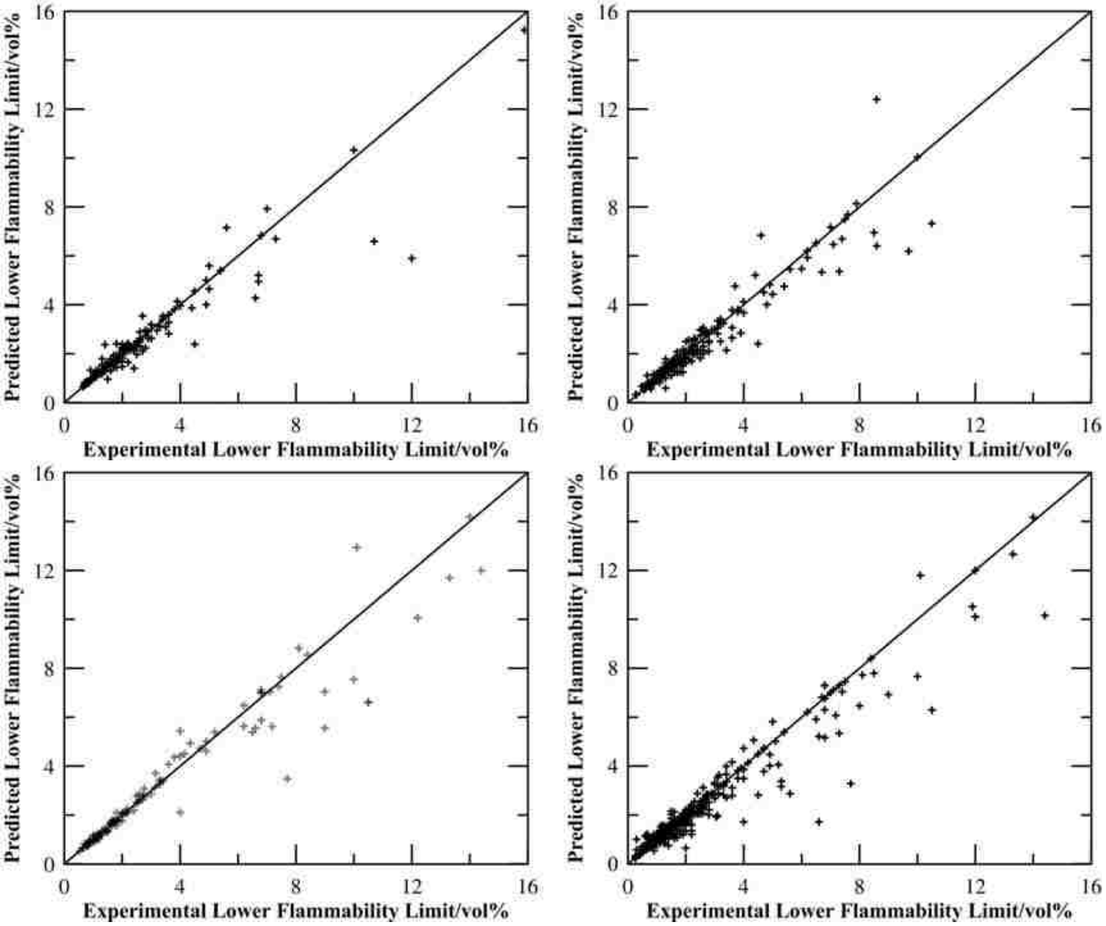

Figure 7.3. Predicted vs. experimental lower flammability limits from the (top left) Bureau of Mines, (top right) European, and (bottom left) ASHRAE apparatuses, and the (bottom right) recommended data set

above 7 vol% typically correspond to halogenated compounds, which have large errors associated with their measurements. These plots also show that most large errors are a result of Equation 7.6 under-predicting the lower flammability limit. Table 7.5 lists the points for which the absolute error from this method exceeds 30 %.

Most of the errors listed in Table 7.5 are for lower flammability limit data of questionable accuracy. For the set of recommended values, 24 of the 33 points with errors larger than 30 % had only one lower flammability limit value reported, and 23 of the compounds had flash point data that indicated the lower flammability limit should be shifted towards the predicted

Table 7.5. Errors exceeding 30 % when the lower flammability limit is predicted using Equation 7.6

Dataset	**Recommended Values**	
Compound	**LFL/vol%**	**Error/%**
Diacetone Alcohol	1.8	-30.44
N-Methylpiperidin	0.9	31.79
4-Formylmorpholine	1.2	32.31
Methacrylic Acid	1.6	32.62
Diethylenetriamine	2	-32.90
Dichlorodiethylsilane	1.13	34.73
N-Ethylaniline	1.6	-34.74
1,4-Dichlorobutane	1.5	35.05
Methyl Isocyanate	5.3	-36.30
Propionitrile	3.1	-36.42
Propylene Glycol 1-*tert*-Butyl	1.7	-36.86
Acrylonitrile	3.05	-36.88
3-(N,N-Dimethylamino) Propylamine	1.9	-37.27
2-Chloropropene	4.5	-37.52
Vinylacetylene	2.2	-38.21
Decamethyltetrasilaoxane	0.9	-39.16
Pentafluoroethyl Methyl Ether	10.5	-40.13
cis-1,3-Dichloropropene	5.3	-40.32
1,4-Dichloro-*trans*-2-butene	1.5	43.36
Hexamethylenediamine	0.7	44.88
Dopropylene Glycol	2.2	-45.00
1-Dodecene	0.4	45.21
α-Terpineol	0.5	45.38
Benzidine	1.4	-46.39
Hydrogen Cyanide	5.6	-48.70
Piperazine	4	-56.94
1,1,2,2,3-Pentafluoropropane	7.7	-57.42
Cylcohexylamine	0.66	66.06
Tris(2-Methoxyethoxy)vinylsilane	2	67.66
Cyanogen	6.6	-74.04
2-Propanol-1-methoxy-propanoate	0.6	89.62
m-Divinylbenzene	0.3	92.13
Methylglutaronitrile	0.3	234.74

Dataset	**BoM**	
Compound	**LFL/vol%**	**Error/%**
Ethylene	2.7	31.08
N,N-Dimethylformamide	1.8	33.86
Cyanogen	6.6	-35.20
Di-*n*-butyl Ether	1.5	-36.28
Isobutane	1.3	37.74
Methyl Chloride	10.7	-38.38
Isobutyl Acetate	2.4	-41.92
Triethylene Glycol	0.9	46.95
2-Chloropropene	4.5	-47.04
Trichloroethylene	12	-50.87
Maleic Anhydride	1.4	69.03

Dataset	**EN**	
Compound	**LFL/vol%**	**Error/%**
Tetrafluoroethylene	10.5	-30.27
3-(N,N-Dimethylamino) Propylamine	1.9	-34.66
trans-1,2-Dichloroethylene	9.7	-36.22
Methyl Acetoacetate	1.3	36.81
Dimethyldichlorosilane	3.4	-37.10
Hexamethyldisilazane	0.48	39.10
Methyl Bromide	8.6	44.18
2-Chloropropene	4.5	-46.59
Chlorotrifluoroethylene	4.6	48.67
Tetraethoxysilane	1.3	-54.89
o-Nitrotoluene	0.67	65.40

Dataset	**ASHRAE**	
Compound	**LFL/vol%**	**Error/%**
Acetaldehyde	4	35.73
Pentafluoroethyl Methyl Ether	10.5	-37.05
Vinyl Bromide	9	-38.32
Chloroprene	4	-47.32
1,1,2,2,3-Pentafluoropropane	7.7	-54.80

value. For example, the reported lower flammability limit of *m*-divinylbenzene corresponds to a T_L of 319 K. The recommended flash point for this compound is 340 K. The large difference between flash point and calculated lower temperature limit suggests the lower flammability limit may be too low. The predicted lower flammability limit (0.58 vol%) corresponds to a T_L of 331

K, which agrees reasonably well with the recommended flash point. However, not all errors are a result of poor lower flammability limit data. Legitimately large errors occur for highly halogenated compounds, and compounds at the beginning of a chemical series, e.g., hydrogen cyanide, cyanogen, and ethylene.

Although based on the same concept as the T_{ad} method of Zatsepin [30] discussed in Section 2.3.1, the proposed method has three distinct advantages. First, the method of Zatsepin requires the use of temperature-dependent heat capacity functions. The method proposed here assumes heat capacities are constant with temperature. This simplifying assumption makes no difference in the accuracy of the method, as the flame temperatures were also calculated for the regression using constant heat capacities. Second, the method of Zatsepin is only applicable to $C_xH_yO_zN_w$ chemicals. The proposed method may be used to predict the lower flammability limit for many $C_xH_yO_zN_wS_vX_uSi_t$ compounds, though as a consequence it requires more structural contributions. Third, this method uses structural groups instead of bond contributions, which results in more accurate prediction of the lower flammability limit.

7.1.2 Estimation of Temperature Dependence

It was shown in Section 5.1.2 that the widely-used modified Burgess-Wheeler law underestimates the effect of initial temperature on the lower flammability limit, because it assumes the calculated adiabatic flame temperature is constant with increasing initial temperature. A new expression for the dependence of the lower flammability limit on initial temperature is derived here.

The equation for the adiabatic flame temperature, Equation 2.6, may be rewritten as

$$LFL(T)\cdot(-\Delta H_{\mathrm{c}}^{\mathrm{o}}) + \overline{C}_{p,\text{fuel-air}}(T - 298\text{ K}) = \overline{C}_{p,\text{prod}}(T_{\mathrm{ad}} - 298\text{ K})\,, \tag{7.8}$$

where $\overline{C}_{p,\text{fuel-air}}$ and $\overline{C}_{p,\text{prod}}$ are the total heat capacities of the fuel-air and combustion product (including excess oxygen and nitrogen) mixtures, assumed independent of temperature, and $\Delta H_{\mathrm{c}}^{\mathrm{o}}$ is the heat of combustion for the gaseous reactant, which may be found from the standard state heat of combustion by:

$$\Delta H_{\mathrm{c}}^{\mathrm{o}} = \Delta H_{\mathrm{c}} + H_{for} - H_{for}^{\mathrm{o}}\,, \tag{7.9a}$$

or accordingly,

$$\Delta H_{\mathrm{c}}^{\mathrm{o}} = \Delta H_{\mathrm{c}} - \Delta H_{vp}^{\mathrm{o}}\,. \tag{7.9b}$$

In Equation 7.9, H_{for} is the standard state enthalpy of formation, H_{for}^{o} is the ideal gas enthalpy of formation, and $\Delta H_{vp}^{\mathrm{o}}$ is the heat of vaporization of the fuel at 298 K. It should also be noted that the enthalpy of combustion in Equation 7.7 is consistent with the DIPPR defintion, and is based on gaseous products, except for crystalline SiO_2.

By equating Equation 7.8 for two different temperatures and solving for the lower flammability limit at temperature T_2 one obtains

$$LFL(T_2) = LFL(T_1) + \frac{\overline{C}_{p,\text{fuel-air}}(T_1 - T_2) - \overline{C}_{p,\text{prod}}(T_{\mathrm{ad}}(T_1) - T_{\mathrm{ad}}(T_2))}{(-\Delta H_{\mathrm{c}}^{\mathrm{o}})}\,. \tag{7.10}$$

In Section 5.1.2 it was shown that the adiabatic flame temperature decreases linearly with initial test temperature. If a simple slope-intercept equation is substituted for the adiabatic flame temperatures, i.e.,

$$T_{\text{ad}}(T) = \gamma \cdot T + b , \tag{7.11}$$

then Equation 7.10 is greatly simplified to

$$LFL(T_2) = LFL(T_1) - \frac{\overline{C}_{p,\text{fuel-air}} - \gamma \cdot \overline{C}_{p,\text{prod}}}{(-\Delta H_{\text{c}}^{\text{o}})}(T_2 - T_1) , \tag{7.12}$$

where γ is the slope of the adiabatic flame temperature as a function of initial mixture temperature. This expression may be further simplified by assuming that the total heat capacity of the products is approximately equal to the mean heat capacity of the fuel-air mixture:

$$LFL(T_2) = LFL(T_1) - \frac{(1-\gamma)\overline{C}_{p,\text{fuel-air}}}{(-\Delta H_{\text{c}}^{\text{o}})}(T_2 - T_1) , \tag{7.13}$$

where the value of $\overline{C}_{p,\text{fuel-air}}$ is assumed to be the value at the reference temperature, T_1, calculated using Equation 2.3.

Equation 7.13 has the advantage that it may be easily modified to estimate the temperature dependence of the lower flammability limit obtained in different apparatuses by adjusting γ. For example, in small-diameter apparatuses, White [16] and Zabetakis, Lambiris, and Scott [17] found that the adiabatic flame temperature was constant with initial test temperature, or γ equals 0. In such a case, Equation 7.13 reduces to the modified Burgess-Wheeler law for gases.

For the data determined in this work, the adiabatic flame temperature slope, γ, appears to be a strong function of the number of carbon atoms in the fuel (Figure 7.4). Through linear regression, the slope of the adiabatic temperature as a function of carbon number was found to be

$$\gamma = -0.0125 \cdot n_C^{\ 2} - 0.779, \tag{7.14}$$

with a coefficient of determination (R^2) equal to 0.917. To be consistent with the assumptions of Equation 7.13, the adiabatic flame temperatures were calculated from the experimental lower flammability limit data assuming temperature-independent heat capacities, with heat capacity values taken at 298 K.

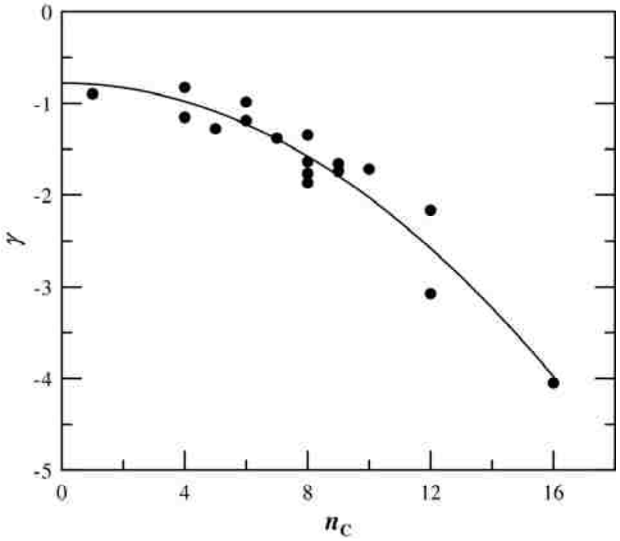

Figure 7.4. Slope of the adiabatic flame temperature, γ, as a function of carbon number, n_C. Equation 7.11 is shown by the solid line

A direct comparison of Equation 7.13, the method proposed by Britton and Frurip (Equation 2.14) and the modified Burgess-Wheeler law (Equation 2.4) is given in Figure 7.5. The lower flammability limit at the lower temperature limit was used as the reference point for all three methods to provide an unbiased analysis of the estimated temperature dependence from each method. The modified Burgess-Wheeler law and the method proposed by Britton and Frurip are nearly identical, because both methods are based on the assumption of a constant adiabatic flame temperature along the lower flammability limit curve. These methods clearly under-estimate the temperature dependence of the lower flammability limit when determined in large-diameter vessels. Equation 7.13 reproduces the temperature dependence of the lower flammability limit quite accurately, slightly overestimating the temperature dependence for just a few compounds. Direct comparison with the temperature dependence proposed by Catoire and Naudet is not possible because the temperature-dependence aspect of the method is not separable from Equation 2.16.

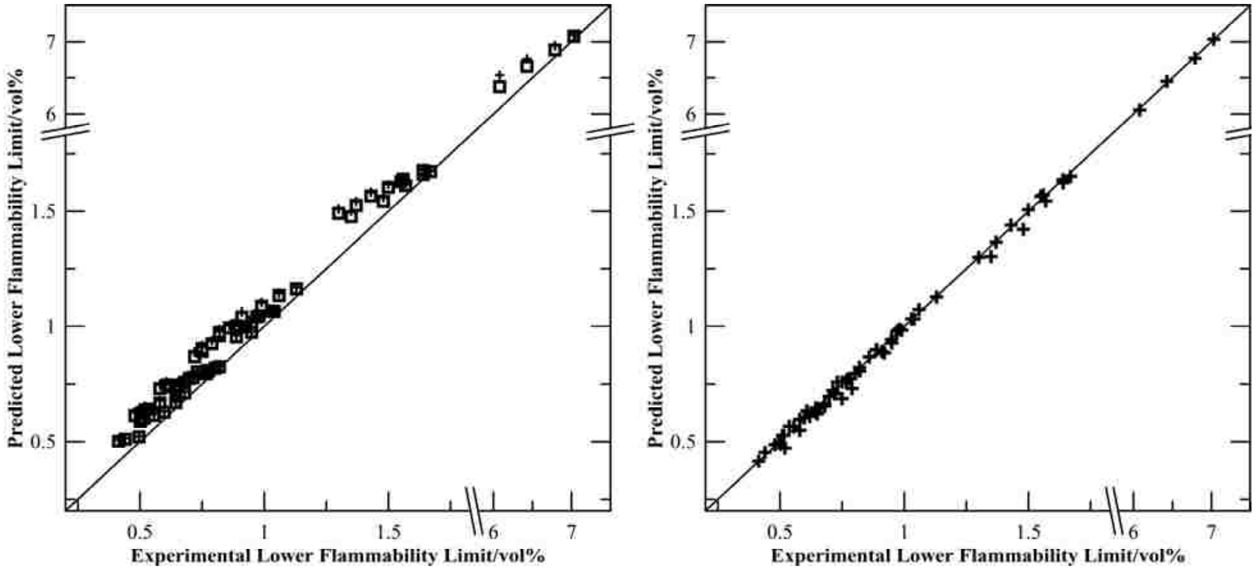

Figure 7.5. Evaluation of the temperature dependence of the lower flammability limit, as estimated by (left) Britton and Frurip (□), the modified Burgess-Wheeler law (+), and (right) Equation 7.13

7.1.3 Overall Estimation

Combined magnitude and temperature-dependence estimation of the lower flammability limit is performed by first predicting the lower flammability limit with Equation 7.6. The lower temperature limit is then calculated from the vapor pressure curve using Equation 3.5. If the calculated T_L is less than 298 K, then the reference temperature for Equation 7.13 is 298 K, otherwise the reference temperature is T_L. Figure 7.6 is a plot of the predicted values versus the experimental data given in Table 5.1. Group contribution values for the recommended dataset were used in Equation 7.5.

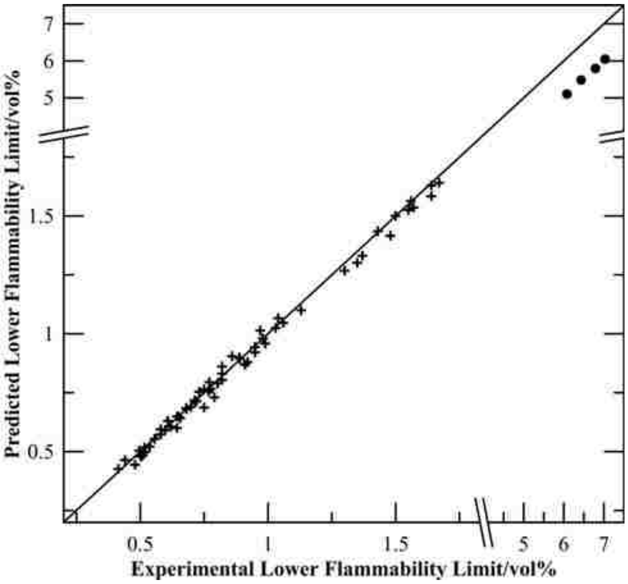

Figure 7.6. Predicted lower flammability limits using Equations 7.6 and 7.13 vs. experimental points in Table 5.1. Data for methanol are shown with solid circles

The main outliers in Figure 7.6 are a result of the magnitude estimation for methanol, shown with circles. The AAD for the 65 points was 3.29 %, and the maximum absolute deviation (MAD) was 16.07 % (methanol at 420 K). The predicted values using the proposed method are significantly more consistent with experimental data than the Bureau of Mines method (AAD = 22.96 %, MAD = 57.49 %), the method of Britton and Frurip (AAD = 13.18 %, MAD = 30.64 %), and the method developed by Catoire and Naudet (AAD = 12.93 %, MAD = 40.37 %), though the Bureau of Mines and Britton methods approximate the lower flammability limit of methanol far more accurately (Figure 7.7).

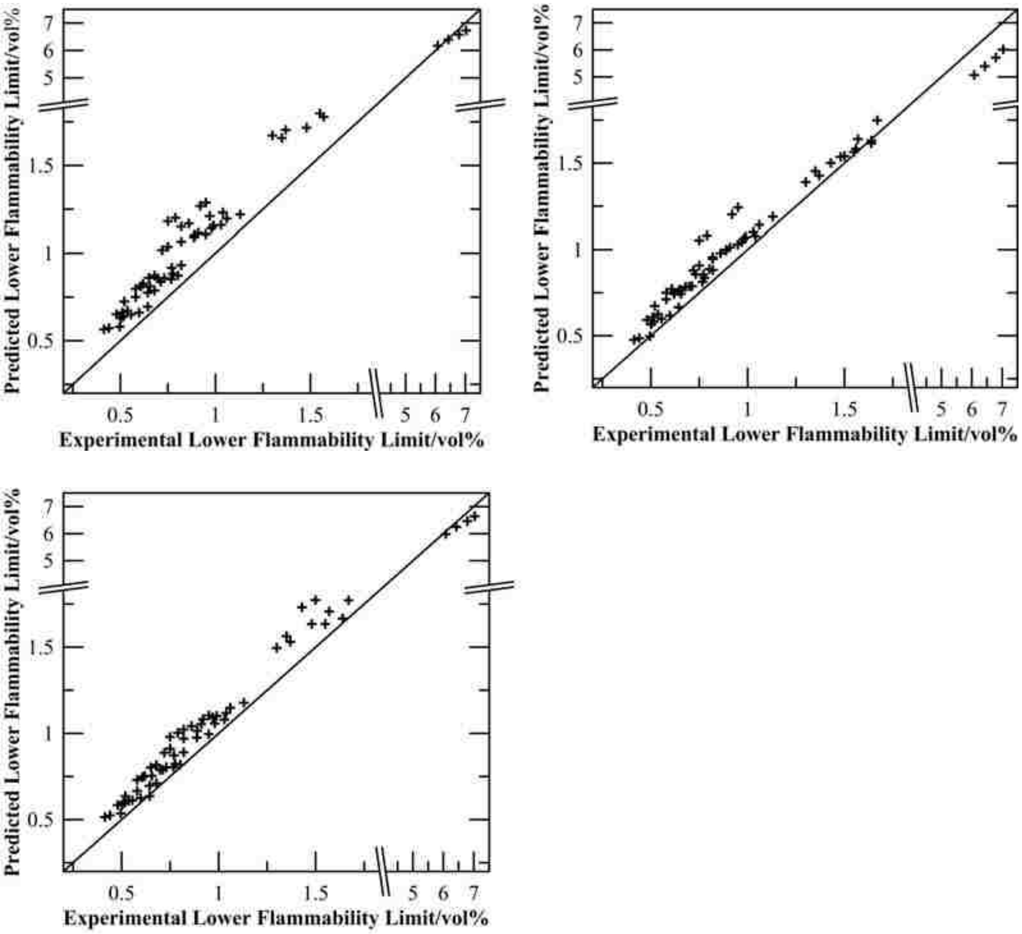

Figure 7.7. Predicted lower flammability limits using the methods of the Bureau of Mines (top left), Catoire and Naudet (top right), and Britton and Frurip (bottom) vs. experimental points from Table 5.1

7.2 Upper Flammability Limit

As with the lower flammability limit, prediction of the upper flammability limit is complicated by the temperature dependence of the upper flammability limit and the variance in data that exists because of differences in flame propagation criteria. The reported values of the upper flammability limit were assumed to have been determined at 298 K if the corresponding upper temperature limit was below 298 K, and T_U otherwise. To reduce prediction error from differences in flame propagation criteria, data were divided into test sets based on measurement apparatus (Appendix E).

Table 7.6 lists the AAD of the published estimation methods for the upper flammability limit, with methods that did not apply to all compounds in the test sets listed in Table 7.7. It is clear from these tables that a more accurate method to estimate the upper flammability limit of general organic chemicals is needed, as the minimum error was 25.62 % for the set of recommended upper flammability limit points.

Table 7.6. Average absolute deviation (AAD) of published upper flammability methods for data from the Bureau of Mines apparatus (BoM), the European standardized method (EN), the ASHRAE apparatus, and recommended upper flammability limit data

	AAD/%			
Method	**BoM**	**EN**	**ASHRAE**	**Recommended UFL Values**
Affens [35]	20.82	24.64	18.57	25.62
Affens from LFL [35]	20.59	23.30	18.16	24.86
Hanley [51]	20.42	27.85	71.93	36.94
Jones [31-32]	21.80	26.03	52.75	35.83
Kondo [173, 177-178]	22.35	28.87	18.16	32.40
Miloshev [50]	31.07	37.87	27.88	38.10
Monakhov [48]	16.98	21.74	34.51	28.59
Nuzhda [40]	19.25	23.54	29.07	28.10
Pintar-Approximation [42]	27.07	29.70	63.38	41.19
Pintar [42]	169.76	137.89	23.43	117.31
Shimy [36]	22.42	27.31	25.71	29.89
Spakowski from LFL [55]	21.03	23.05	24.17	25.47
Suzuki [53]	18.97	32.07	19.71	43.33
Thornton [46]	43.86	43.27	31.94	45.01

Table 7.7. Average absolute deviation (AAD) of published upper flammability limit methods that do not apply to general organic compounds

Dataset	**BoM**		**EN**	
	Compounds	105	**Compounds**	287
	Exp Points	105	**Exp Points**	291
Method	**AAD/%**	**Applicable Points**	**AAD/%**	**Applicable Points**
Albahri [43]	13.12	42	15.15	72
Hilado [45]	19.16	101	26.07	256
High-Danner [38]	48.98	98	51.00	248
Seaton [41]	25.04	97	51.27	267
Dataset	**AHSRAE**		**Recommended UFL Values**	
	Compounds	80	**Compounds**	393
	Exp Points	82	**Exp Points**	393
Method	**AAD/%**	**Applicable Points**	**AAD/%**	**Applicable Points**
Albahri [43]	17.96	43	13.34	79
Hilado [45]	36.31	53	28.49	337
High-Danner [38]	90.54	62	47.95	328
Seaton [41]	25.00	73	48.17	356

Better accuracy was achieved with a correlation between the upper flammability limit and the concentration required for stoichiometric combustion (Equation 2.11):

$$UFL = aC_{st}^{b} + \frac{\sum_{j} ng_{j} \cdot ufl_{j}}{\sum_{k} ng_{k}} . \qquad (7.15)$$

The structural groups, *ufl*, are the same as the groups developed for estimation of the lower flammability limit. Regression of the parameter values was performed by minimizing the AAD for the training sets. Contributions for these groups, as well as values for *a* and *b* for each dataset, are listed in Table 7.8. Values for many of the groups for the ASHRAE and Bureau of Mines data sets could not be determined because of limited data. Consequently, the scope of Equation 7.15 is severaly limited for these datasets. The real value of Equation 7.15 is in predicting upper flammability values consistent with the values in the recommended dataset.

Table 7.8. Structural contributions for the prediction of the upper flammability limit using Equation 7.15

j	**Group/Parameter**	***ufl*** **(BoM)**	***ufl*** **(EN)**	***ufl*** **(ASHRAE)**	***ufl*** **(Recommended UFL Values)**
	a	1.00	3.71	-89.24	4.30
	b	2.60	0.78	-10.52	0.72
1	≡C-		-59.02		-8.65
2	≡CH	97.96	70.71	100.02	61.25
3	=C<	9.00	-0.12	2.78	-7.15
4	=CH	10.49	-0.26	8.10	0.30
5	=CH2	8.71	3.27	15.42	3.06
6	=CH-(Ca)		-12.07		-11.24
7	=C-(C$_a$)		-1.83		-5.13
8	>C<	8.18	0.81	-4.76	-0.23
9	-CH	5.84	2.44	1.46	0.62
10	-CH2	5.93	0.56	6.39	-0.30
11	-CH3	5.42	-0.21	10.10	-1.12
12	CH$_3$-(C$_a$)	9.27	-1.12		-4.49
13	C$_a$	1.26	3.06		5.50
14	C$_a$H	6.20	0.51		-1.25
15	OH-(C)	7.42	11.91		4.90
16	OH-(CH)	14.33	3.11		0.12
17	OH-(CH2)	24.20	7.25	29.67	5.32
18	OH-(C$_a$)		1.22		9.15
19	OH-(CC≡C)	12.69			15.57
20	O=C	13.18	1.83		2.50
21	O=C$_R$		6.69		-11.84
22	O=C-C=C	9.71	9.24		6.00
23	O=COC	10.15	2.09	27.97	0.47
24	(C)O(C)	19.09	9.75	-11.55	13.38
25	COOH		-6.52		-5.12
26	O$_R$	49.16	15.41	69.64	26.05
27	O-O				0.76
28	N	16.02	9.86		8.85
29	N$_a$	30.36	5.33		4.46
30	N$_R$	119.09	14.22		13.32
31	NH	18.51	5.98		-0.78
32	N-(C$_a$)	15.41	2.47		-7.25
33	N≡C	14.52	15.15		-9.72
34	N=C=O		4.72		4.95
35	NO$_2$		34.31		-11.46
36	S	41.88	4.81		23.55
37	SH	34.57	11.75		12.67
38	S=	66.56	66.06		53.67
39	Si		143.16		78.90
40	Si(O$_3$)		112.26		120.24
41	(Si)-O-		-80.34		-67.75
42	Si-(Cl)				-13.93
43	Si-(Cl$_2$)		137.62		62.48
44	Si-(Cl$_3$)				-18.52
45	F$_2$-(C)		-10.17	46.33	-4.95
46	F$_2$-(C=C)		7.89	46.33	3.43
47	F$_3$-(C)		-0.34	45.66	-12.81
48	F-(C)		3.40	26.69	0.80

Table 7.8. Continued

j	Group/Parameter	*ufl* (BoM)	*ufl* (EN)	*ufl* (ASHRAE)	*ufl* (Recommended UFL Values)
49	F-(C=C)		-2.98	42.06	15.38
50	Cl_2-(C)		-18.99	37.52	-22.73
51	Cl_2(C=C)			15.59	-15.5
52	Cl_3-(C)		-18.44	32.16	-26.31
53	Cl-(C)	14.22	-4.62	21.15	-5.20
54	Cl-(C=C)	61.26	11.72	9.28	0.16
55	Cl-(C=C-Cl)	32.02	-10.64	22.91	-13.14
56	Br-	-65.50	-12.19	16.97	-24.38

The AAD of the training, test, and combined datasets are given in Table 7.9. Figure 7.8 shows the performance of Equation 7.15 in estimating the upper flammability limit for the EN and recommended-value datasets. There exists a lot of scatter below the 45^o line, indicating that when the method fails, it under-predicts the upper flammability limit. Inspection of the data of such compounds gives insight as to why the upper flammability limit is so difficult to predict. Not only have relatively few experimental upper flammability limit data points been reported, but experimental data often differ significantly. A good example of variance in reported upper flammability limits is the upper flammability limit data of acetaldehyde. Values have been reported at 10.4 vol%, 13.0 vol%, 57.0 vol%, and 60.0 vol%. This large variance in data is a result of the sensitivity of the upper flammability limit to measurement conditions. The upper flammability limit of diethyl ether has been reported as 9.4 vol%, 25.9 vol%, 36.0 vol%, 36.5 vol%, 46 vol%, and 48 vol%, in vessels varying between a 5-cm diameter tube to a 12-L spherical flask. In addition to vessel diameter, studies have shown the upper flammability limit may be significantly affected by residence time [179-180], and the possible presence of cool flames makes interpretation of test results difficult.

Table 7.9. Average absolute deviations for prediction of the upper flammability limit using Equation 7.15

Data Set	AAD/%	Data Points	Data Set	AAD/%	Data Points
BoM Training Set	10.69	62	ASHRAE Training Set	11.65	47
BoM Test Set	15.47	43	ASHRAE Test Set	13.29	35
BoM Combined Sets	12.65	105	ASHRAE Combined Sets	12.35	82
EN Training Set	13.41	178	Recommended UFL Training Set	15.69	257
EN Test Set	15.31	113	Recommended UFL Test Set	17.76	136
EN Combined Sets	14.15	291	Recommended UFL Combined Sets	16.40	393

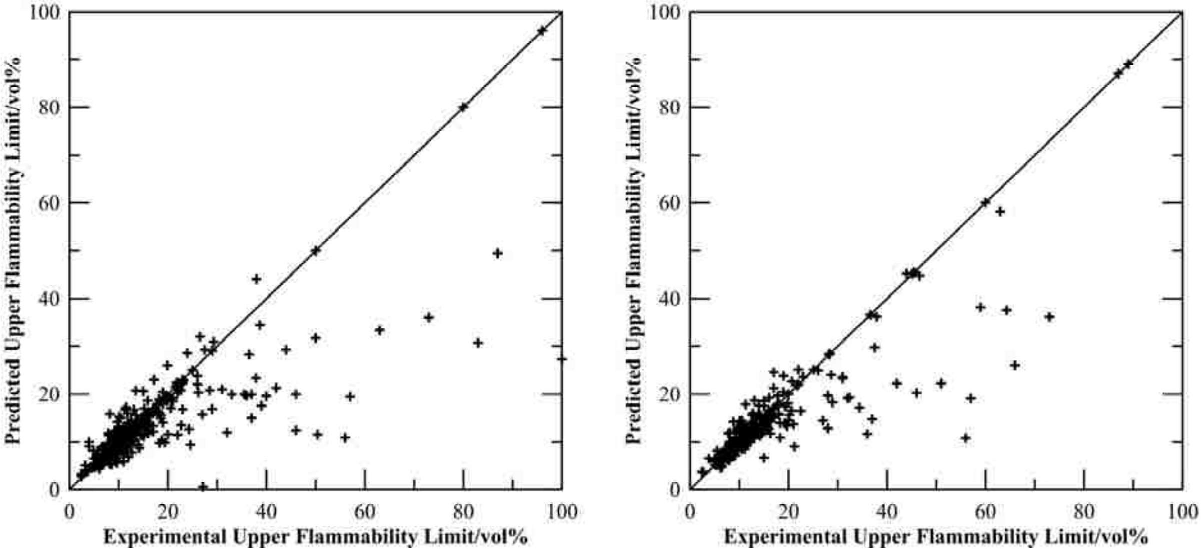

Figure 7.8. Predicted upper flammability limits from Equation 7.15 vs. the recommended data values (left) and data determined using the European standardized method

However, not all the error associated with predicting the upper flammability limit using Equation 7.15 can be explained by experimental scatter. For example, the method fails to estimate the lack of an upper limit for ethylene oxide, estimates an upper flammability limit well below the lower flammability limit of dimethyldimethoxysilane, and otherwise underestimates the recommended upper flammability limit by at least 50 % for 14 compounds. Table 7.10 lists the compounds for which this method resulted in an error exceeding 50 %.

Table 7.10. Errors exceeding 50 % when Equation 7.15 is used to estimate the upper flammability limit

Dataset	**Recommended Values**		**Dataset**	**BoM**	
Compound	**UFL/vol%**	**Error/%**	**Compound**	**UFL/vol%**	**Error/%**
Diethylene Glycol	37	-59.54	Ethylene	36	-65.68
Acetaldehyde	57	-65.89	Methane	15	90.26
Formaldehyde	73	-50.66	Acetaldehyde	60	-78.83
Methyl Vinyl Ether	39	-54.97	Acrolein	31	-59.28
Methyl Ethyl Ether	10.1	51.54	Diethyl Ether	36	-74.95
Diethyl Ether	46	-72.98	Divinyl Ether	27	-52.30
Ethylene Oxide	100	-72.77	Methyl Vinyl Ether	39	-67.71
Vinyltrichlorosilane	50.41	-77.09	Ethylene Oxide	100	-77.62
Dimethyldimethoxysilane	27.12	-98.00	**Dataset**	**EN**	
Trichlorosilane	83	-63.02	**Compound**	**UFL/vol%**	**Error/%**
Ethyleneimine	46	-56.60	Ethylene Glycol	51	-56.48
Cyanogen	32	-62.49	Diethylene Glycol	37	-60.09
Methylglutaronitrile	3.25	54.40	Glycerol	11.3	57.89
Hydrogen Cyanide	40	-51.10	Formaldehyde	73	-50.49
1-Ethoxy-2-Propanol	56	-80.57	Acetaldehyde	57	-66.49
2-(2-Butoxyethoxy)Ethanol	24.6	-61.92	Isophorone	3.8	70.77
4-Formylmorpholine	8.2	93.18	*n*-Propyl Formate	7.8	51.26
4-(2-Aminoethyl) Morpholine	7.9	50.08	Diethyl Ether	36	-67.59
Pentafluoroethyl Methyl Ether	13.5	53.54	Diisopropyl Ether	21.2	-57.48
Benzoyl Chloride	4.9	65.98	Ethyl Vinyl Ether	28	-54.11
1,1,2,2,3-Pentafluoropropane	11.5	50.01	Diphenyl Ether	15	-55.77
1,4-Dichloro-*trans*-2-butene	4	149.43	Dioctyl Phthalate	2.4	51.33
1,4-Dichlorobutane	4	125.70	Ethyleneimine	46	-56.03
Dataset	**ASHRAE**		*trans*-Crotonitrile	8.8	61.34
Compound	**UFL/vol%**	**Error/%**	*cis*-Crotonitrile	8.8	61.34
Ethylene	36	-57.18	1-Ethoxy-2-propanol	56	-80.70
Ethylcyclohexane	6.6	-52.02	α-Epichlorohydrin	34.4	-50.04
Tetrafluoroethylene	50	-50.89	Methyl Iodide	66	-60.62
Vinyl Chlordie	33	-66.86			

Despite these many errors, Equation 7.15 estimates the upper flammability limit of general organic compounds with an AAD lower than any of the previously published methods for all the datasets studied. When considering the set of recommended upper flammability limit values, the next most accurate method results in an AAD of nearly 25 %, significantly higher than the 16.4 % AAD obtained using this method.

7.3 Flash Point

7.3.1 Property Correlations

During the course of the critical review, it was observed that for many compounds the ratio of the flash point and the temperature at which a stoichiometric concentration of vapors is formed, T_{st}, is approximately constant:

$$\frac{T_{\mathrm{st}}}{FP} = k\,. \tag{7.16}$$

Only a vapor pressure correlation and the chemical formula are needed to calculate T_{st}:

$$\frac{P^*(T_{\mathrm{st}})}{1\ \mathrm{atm}} = \frac{1}{1 + 4.773\beta}\,. \tag{7.17}$$

A training set of approximately 500 compounds (Training Set 1 of Table E.17) was randomly selected from the critically reviewed flash point data discussed in Chapter 6. Using least-squares minimization, the parameter k was determined to be 1.03, with a standard error of 0.036. This value resulted in an AAD of 1.20 %/4.31 K for the training set.

Increased accuracy is obtained if the assumption of a constant ratio is relaxed. The ratio appears to be a function of the stability of the dominant radical formed during combustion, or in other words, the bond that affects the combustion reaction the most. This dependence on bond-type is easily described using group contributions. Table 7.11 lists the groups fitted using data for the compounds in the training set. Because the ratio is a function of only the *dominant* bond,

Table 7.11. Structural groups that determine the parameter *k* for Equation 7.16

Group	***k***	**Excludes compounds that contain**	**Examples**
SiO_3	1.052		Tetraethoxysilane
C_a-Si-Cl	$1.03-0.0075n_{Cl}$		Phenyltrichlorosilane
Si-Cl	1.04		Vinyltrichlorosilane
C_a-C(=O)-Cl	0.935		Isophthaloyl Chloride
Si-O-Si	1.02		Hexamethyldisiloxane
C-O-C(=O)-O-C	1.018		Propylene Carbonate
C=C-C≡N	1.02	O; C_a	Acrylonitrile
F	1.01	NO_2	p-Chlorobenzotrifluoride
Cl	1.015	NO_2; CHOH	Benzyl Dichloride o-Chloroaniline
Br	1.02	NO_2	m-Dibromobenzene
I	1.025	NO_2	*n*-Butyl Iodide
C_{R3}	1.055	C=C; non-hydrocarbons	Adamantane
C≡N x 2	1.08	O	Succinonitrile
O=C=N x 2	1.01		Isophorone Diisocyanate
COOH x 2	1.04	C_a	Azelaic Acid
NO_2	1.048	Amines	2-Nitropropane Nitrobenzene
C≡N (O)	1.02		Methyl Cyanoacetate
O-OH	1.053		Peracetic Acid Ethyl Hydroperoxide
$C_{a2}C_R$	1.049	Non-hydrocarbons	Indane
$C_{a2}C_{a2}C_aC_{a2}$	1.012	Non-hydrocarbons	Anthracene
COOH x2 (aromatic)	1.125		Phthalic Acid
Nitroamines	1.01		o-Nitroaniline
C≡N	1.039		Acetonitrile
CH=O	1.039	C_R; OH; N; C=C	2-Ethylhexanal 3-(Methylmercapto)propanal
COOH (*n*-Aliphatic)	$1.074-0.012n_C+ 6\text{x}10^{-4}n_C^2$		*n*-Nonanoic Acid Thioglycolic Acid
CH=O	1.039	C_R; OH; N; C=C	2-Ethylhexanal 3-(Methylmercapto)propanal
COOH (*n*-Aliphatic)	$1.074-0.012n_C+ 6\text{x}10^{-4}n_C^2$		*n*-Nonanoic Acid Thioglycolic Acid
Naphthalenes	1.035	Non-hydrocarbons	2-Ethylnaphthalene
COOH (aromatic)	1.045		Benzoic Acid Niacin
Polyols	1.03	C=O; N	Ethylene Glycol p-Hydroquinone
Other aliphatic acids	$1.074- 9.94\text{x}10^{-3}n_C +4.84\text{x}10^{-4}n_C^2$		Isobutyric Acid cis-Crotonic Acid
Terpenes	1.033	Non-hydrocarbons	1-Methylcyclopentene Terpinolene
OH (aliphatic)	1.02	C(C)C; C_a; COC; C=O; N	1-Octanol 1-Ethylthioethanol
OH (other)	1.027	C=O; N	Tetrahydrofurfuryl Alcohol 2,3-Xylenol 1,3-Dichloro-2-propanol
N	$1.013+ 2.319\text{x}10^{-3}\, n_C$	C=N; N_R	Dimethylamine p-Toluidine Urea

Table 7.11. Continued

Group	k	Excludes compounds that contain	Examples
Dialkenes (terminal)	1.049	C_a; C_R; non-hydrocarbons	1,5-Hexadiene
Dialkenes (ring)	1.019	C_a; non-hydrocarbons	1,3-Cyclohexadiene
Other dialkenes	1.006	C_a; C_R; non-hydrocarbons	1,4-Hexadiene
C=C(C)C	1.02	C_a; C_R; non-hydrocarbons	Isobutene 2,2,4-Trimethyl-1-pentene
CC(C)C...C=C	1.0	C_a; C_R; non-hydrocarbons	3-Methyl-1-hexane
CC=CC	1.02	C_a; C_R; non-hydrocarbons	Trans-2-Pentene
CH_2=CH	1.029	C_a; C_R; non-hydrocarbons	1-Heptene
C=C (ring)	1.037	C_a; non-hydrocarbons	Cycloheptene Vinylnorbornene
C≡C	1.036	C_a; non-hydrocarbons	2-Hexyne
Alkylbenzenes	$1.023+1.997\text{x}10^{-3}(n_C\text{-}6)$	Non-hydrocarbons	Toluene 1,3,5-Triisopropylbenzene
Alkylcyclopentanes/ Alkylcyclohexanes	1.025	Non-hydrocarbons	Ethylcyclopentane 1,1-Dimethylcyclohexane
n-Alkanes	$1.041\text{-}1.723\text{x}10^{-3}\, n_C$		*n*-Hexane *n*-Tridecane
Cycloalkanes	1.038		cis-Decahydronaphthalene Cyclooctane
NC > 2	$0.887+0.044\, n_N$		Tetraethylenepentamine
All other compounds	1.03		

C_a represents an aromatic carbon, C_{Rn} represents a non-aromatic carbon belonging to n rings, and C_{an} represents an aromatic carbon belonging to n rings.

only one group contribution is used for a given compound. The tabulated groups are ordered by priority, with the highest priority groups listed first. Example calculations are shown in Table 7.12.

The AAD of Equation 7.16 for a test set of 550 compounds was 1.07 %/3.76 K, and 0.98 %/3.36 K when groups are used to find k. The AADs for the combined training and test sets of data are compared with results for other published flash point estimation methods in Table 7.13. According to ASTM [29], the reproducibility of one common flash point measurement method is 3.5 K for $FP < 377$ K and 8.5 K if $FP \geq 377$ K. If these values are assumed to approximate the

Table 7.12. Sample calculations for Equation 7.16 using groups from Table 7.11

Compound	β	T_{st}	**Group**	k	FP_{calc}	FP_{exp}
Hydroacrylonitrile	3.75	407.59	C#N (O)	1.02	399.59	402.15
Terephthaloyl Chloride	7.5	423.19	CaC(=O)Cl	0.935	452.61	453.15
Dimethyl Carbonate	3.0	296.0	COC(=O)OC	1.018	290.77	289.85
1,2-Dimethyladamantane	17.0	342.31	C_{R3}	1.055	324.46	325.15
Bicyclo[2.2.2]octane	11.5	325.38	Cycloalkanes	1.038	313.47	313.15
1,4-Hexadiene	8.5	254.15	Other dialkenes	1.006	252.64	252.15
Suberic Acid	9.5	504.31	COOH x 2	1.04	484.92	483.15
Triethylenetetramine	10.5	431.75	NC > 2	0.887+0.044(4)	406.16	408.15
Cyclopropylamine	4.75	254.27	N	$1.013+2.319\text{x}10^{-3}(3)$	249.29	248.15
Trimethylolpropane	8.0	461.06	Polyols	1.03	447.63	449.15
Isobutyl Isobutyrate	11.0	317.79	Other compounds	1.03	308.53	311.15
2,3-Dimethylhexane	12.5	286.82	Other compounds	1.03	278.46	280.15

Table 7.13. Average absolute deviation by estimation method for 1062 organic compounds in DIPPR® 801 database

Method	**AAD/%**	**AAD/K**
Equation 7.16 with groups	0.99	3.43
Equation 7.16	1.12	4.00
Leslie-Geniesse [81]	1.17	4.10
Modified Thornton [82]	1.48	5.06
Catoire-Naudet [80]	1.82	6.26
Ishiuchi [95]	2.03	7.24
Prugh [97]	2.11	7.68
Metcalfe [98]	2.37	8.50
Blinov [96]	2.54	8.89
Shebeko [96]	2.67	9.27
Korol'chenko [96]	3.17	11.01
Modified Satyanarayana-Kakati [99]	3.21	11.62
Patil [93]	3.24	10.92
Wang-Sun [87]	3.32	11.29
Hshieh [85]	3.34	11.72
Oehley [49]	3.86	13.29
Möller [47]	4.60	16.36
Satyanarayana-Rao/ Satyanarayana-Krishna [86, 94]	4.64	15.38
Li-Moore [84]	4.66	14.84
Fujii-Hermann [83]	5.63	22.55
Suzuki [102]	10.15	35.69
Akhmetzhanov [181]	10.68	39.39

experimental errors of the test set, this corresponds to an average experimental uncertainty of 1.34 %/4.62 K. Though this is only an approximate analysis of the experimental error in the data and does not account for differences in experimental methods, it appears that the ratio method is already within the limit of experimental accuracy without including groups. This analysis also indicates that the method of Leslie and Geniesse is within the accuracy of the experimental data, and any difference in accuracy between the Leslie-Geniesse and ratio methods would therefore have little or no significance. Comparison of the histograms of the prediction error (Figure 7.9), as well as plots of the predicted values against the experimental data (Figure 7.10) show very little difference between the Leslie-Geniesse method and Equation 7.16.

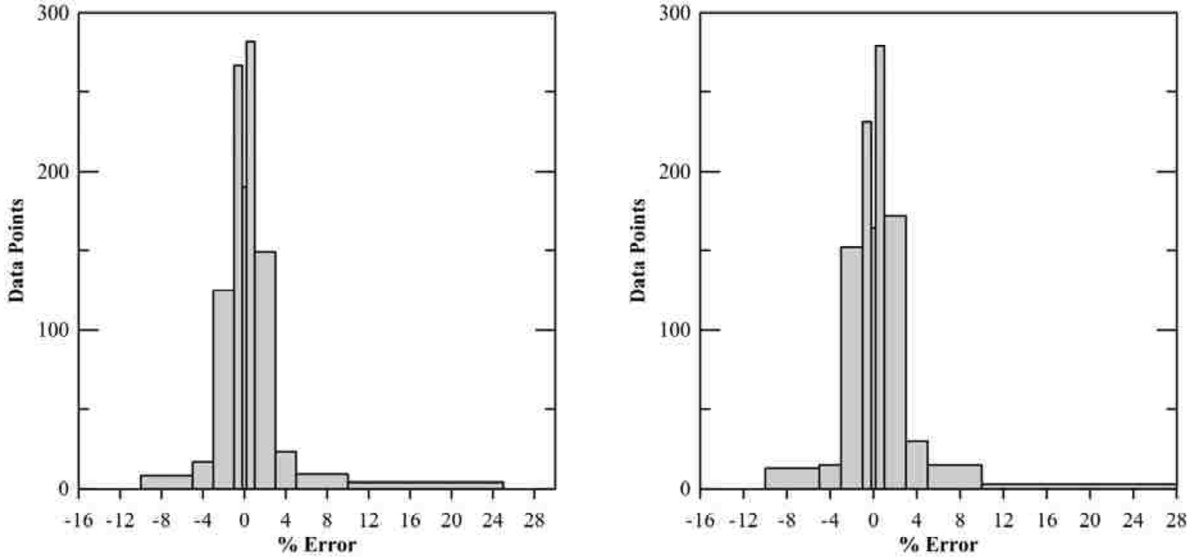

Figure 7.9. Histogram of errors between experimental flash points and values predicted using Equation 7.16 (left) with groups to determine *k*, and the method of Leslie and Geniesse

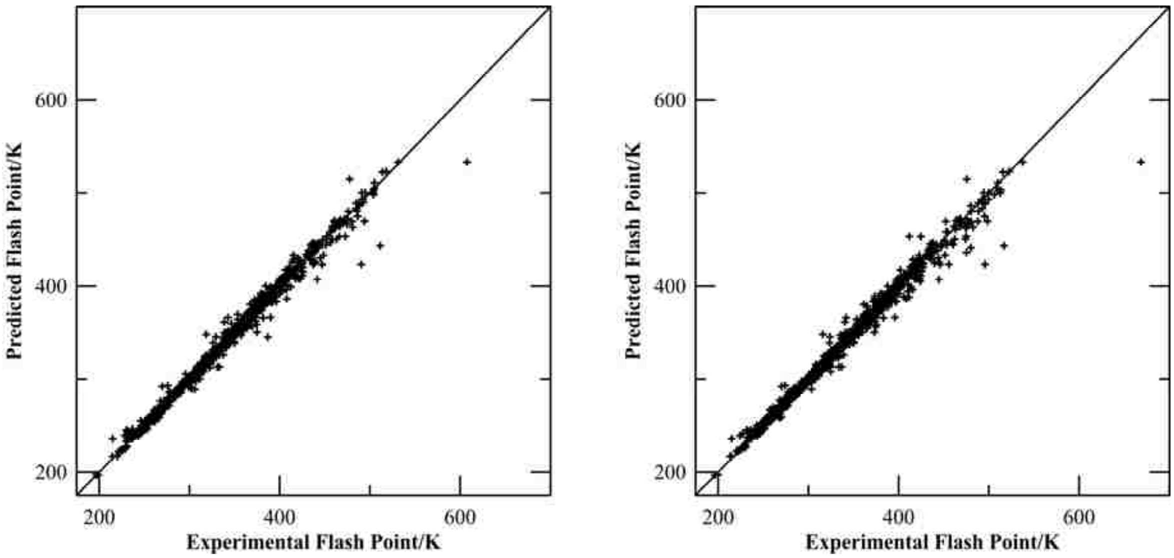

Figure 7.10. Experimental flash points vs. values predicted using Equation 7.16 (left) with groups to determine *k*, and the method of Leslie and Geniesse

The ratio method shares the same weakness as the other two most accurate published methods listed in Table 7.13: an accurate vapor pressure correlation is necessary. Therefore, another flash point estimation method was generated that does not rely on the vapor pressure:

$$\begin{aligned} FP(\mathrm{K}) = 0.2554\frac{T_b}{(\beta+1)^{0.2164}}\left(\frac{\Delta H_{vp}}{\mathrm{R}}\right)^{0.1606} &+ 6.31(\beta+1)^{0.7} \\ -5.6\times10^{-5}\,\frac{\Delta H^{\mathrm{o}}_{vp}T_b}{\mathrm{R}(\beta+1)} + 0.0208\left(\frac{\Delta H^{\mathrm{o}}_{vp}}{\mathrm{R}}\right)^{0.8767} &, \end{aligned} \tag{7.18}$$

where ΔH_{vp} and $\Delta H^{\mathrm{o}}_{vp}$ are the enthalpies of vaporization at the normal boiling point and 298 K, respectively.

The training set mentioned above was used to determine the coefficients for Equation 7.18, returning an AAD of 1.26 %/4.49 K. The AAD for the test set was 1.18 %/4.18 K, and for the combined data set the AAD was 1.22 %/4.30 K. The average error is again within the expected accuracy of the data, and compares well to the AAD of 1.82 %/6.26 K obtained for the test set using the method of Catoire and Naudet, the most accurate of the published methods that do not rely on knowledge of the vapor pressure.

When information pertaining to ΔH_{vp}^{o} is not readily available, as is often the case without an accurate vapor pressure correlation, it may be calculated from ΔH_{vp} and the critical temperature, T_c, using the Watson correlation [182]:

$$\Delta H_{vp}^{o} = \Delta H_{vp} \left(\frac{1 - \frac{298.15\,\mathrm{K}}{T_c}}{1 - \frac{T_b}{T_c}} \right). \tag{7.19}$$

This substitution results in only a small change in the accuracy of the method (1.26 %/4.47 K AAD for combined data set).

Figure 7.11 shows a histogram of the errors for Equation 7.18, and a plot of the predicted vs. experimental flash point for the combined training and test sets of data. The vast majority of the deviations from experimental data are under 3 %.

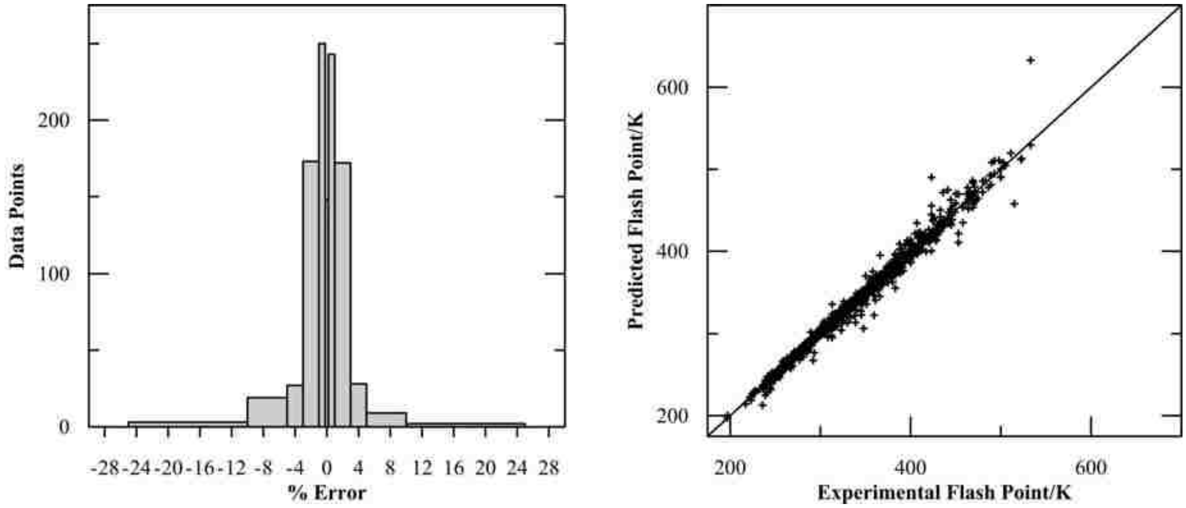

Figure 7.11. Histogram of errors and plot of predicted vs. experimental flash points for Equation 7.18 using the combined training and test sets

Several strong outliers are common for both methods presented in this section, as detailed in Table 7.14. The majority of these outliers occur for compounds with only one reported flash point and no reported lower flammability limit. The accuracy of such data is difficult to verify, and it is therefore uncertain if the data or the methods are in error. The reported lower flammability limit for methyl ethyl ether, however, corresponds to a lower temperature limit that agrees within 2% of the predicted flash point values of all three methods.

Table 7.14. Reported flash points that differ significantly from the values predicted by the presented methods

			Prediction Error/%	
Compound	**Recommended FP/K**	**Equation 7.16**	**Equation 7.16 with groups**	**Equation 7.18**
Oxazole	292	-7.54	-7.54	-8.41
Hexachlorobenzene	515	-8.61	-7.25	-11.98
Methyl Ethyl Ether	236	-8.87	-8.87	-9.88
Terephthaloyl Chloride	453	-9.33	-0.12	-9.43
Trichloroacetaldehyde	348	-9.77	-8.44	-11.98
Acetoacetanilide	423	16.56	15.86	15.76
Terephthalic Acid	533	24.45	13.97	18.74

7.3.2 Structural Contribution Method

A severe drawback of the methods described in the previous section is that they require knowledge of thermodynamic properties to estimate the flash point. For many compounds, such information is not known, and a purely predictive method, a method that predicts the flash point based entirely on the structure, is needed. Methods proposed by Tetteh [103], and Zhokhova [104] are limited in their usefulness because they are based on neural networks, and require specialized software to implement. As discussed in Section 3.1.2 Suzuki [183] proposed a method based on group contributions and the Kier-Hall first-order connectivity index. As seen in Table 7.13, this method predicts the flash point relatively poorly.

Derivation of a new method based solely on structural contributions began with the well-known Clausius-Clapeyron equation,

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{vp}}{\mathrm{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{7.20}$$

If T_1 is the normal boiling point, T_b, and T_2 the flash point, then P_1 is 101.3 kPa, and P_2 may be approximated by Equation 3.2. The Clausius-Clapeyron equation then becomes

$$\ln(8\beta) = \frac{\Delta H_{vp}}{\mathrm{R}}\left(\frac{1}{FP} - \frac{1}{T_b}\right), \tag{7.21}$$

which is easily solved for the flash point:

$$FP = \frac{T_b}{\frac{T_b}{\Delta H_{vp}}\mathrm{R}\ \ln(8\beta) + 1}. \tag{7.22}$$

The ratio $\frac{T_b}{\Delta H_{vp}}$ is equivalent to the inverse of the entropy of vaporization, which Trouton [184] showed is approximately a constant for many chemicals (λ). Furthermore, if T_b is estimated from structural contributions (fp_i), then Equation 7.22 reduces to

$$FP = \frac{\sum_i \left(ng_i \cdot fp_i\right) + \delta}{\lambda\ \ln(8\beta) + 1} + \varepsilon\ , \tag{7.23}$$

where ε is an error term, and δ is a constant. Assuming ε is constant, the parameters for Equation 7.23 were determined by minimizing the percent AAD of a reduced training set of only 375 compounds (Training set 2, Table E.17), and are given in Table 7.15. Because the entropy of vaporization appears to differ for alcohols, two sets of parameters were regressed, one for alcohols (when group 39 or 40 in Table 7.15 is found in the chemical), and one for all other organics. The AAD of values calculated using Equation 7.23 from the experimental flash point was 2.42 %/8.52 K for the training set. The AAD for the test set (compounds not included in training set 2 of Table E.17) was 3.08 %/10.57 K.

Table 7.15. Parameters and structural contributions for Equation 7.23

Parameter	**Alcohols (group 39 or 40 > 0)**	**Other Organics**
λ	2.4	2.13
δ	-208.3	-510.49
ε	196.68	235.21

i	**Group**	***fp***	**Example**
1	$\equiv C-$ (HC)	256.43	2-Pentyne
2	$\equiv CH$ (HC)	-61.94	1-Hexyne
3	$=C<$ (HC)	483.40	2-Methyl-1-octene
4	$=C_R<$ (HC)	378.53	d-Limonene
5	$=CH-$ (HC)	219.78	1-Pentene
6	$=C_RH-$ (HC)	124.16	Cyclohexene
7	$=CH_2$ (HC)	-99.53	1-Pentene
8	$>C<$ (HC)	561.32	Neopentane
9	$>C_R<$ (HC)	98.67	1,1-Diethylcyclohexane
10	$>CH-$ (HC)	418.55	4-Methylheptane
11	$>C_RH-$ (HC)	313.87	Methylcyclohexane
12	$>CH_2$ (HC)	191.61	Pentane
13	$-C_RH_2-$ (HC)	122.22	Cyclopentane
14	$-CH_3$ (HC)	-59.62	Propane
15	$>CH-$	119.79	Isobutyl Formate
16	$>C_RH-$	201.98	Cyclohexanol
17	$>CH_2$	162.43	Butanol
18	$-C_RH_2-$	149.72	Cyclohexanol
19	$-CH_3$	77.80	Ethanol
20	$=C<$	194.11	Chloroprene
21	$=C_R<$	236.45	Phenol
22	$=C=$	-239.01	Carbon Disulfide
23	$=CH-$	148.59	Acrolein
24	$=C_RH-$	163.28	Maleic Anhydride

Table 7.15. Continued

i	Group	*fp*	Example
25	$=CH_2$	37.56	Methacrolein
26	$C_R-C_R=$ (fused ring)	-59.24	α-Pinene
27	>C<	108.68	Acetone Cyanohydrin
28	$>C_R<$	130.20	Isophorone Diisocyanate
29	>C=O	494.20	2-Pentanone
30	$>C_R=O$	551.77	Cyclopentanone
31	O=CH- (aldehyde)	437.19	Propanal
32	$O=C_RO_R-$	1192.63	Diketene
33	-COO- (ester, nonring)	529.37	Ethyl Acrylate
34	-COOH (acid)	1034.70	Thioglycolic Acid
35	$O=C_RO_RC_R=O$ (aliphatic ring)	1750.35	Succinic Anhydride
36	=O	623.68	Di-n-propyl Sulfone
37	-O-	176.69	Methyl Ethyl Ether
38	$-O_R-$	128.89	Tetrahydrofuran
39	-OH (alcohol)	803.82	Propanol
40	-OH (phenol)	806.21	Nonylphenol
41	>N-	153.69	Tripropylamine
42	>NH	354.79	Diisopropylamine
43	$>N_RH$	325.82	Ethyleneimine
44	$-NH_2$	362.58	Urea
45	-N=	196.10	Acetaldoxime
46	$-N_R=$	243.93	Oxazole
47	$>N_R-$	369.80	4-(2-Aminoethyl) Morpholine
48	$-N-C_a$	797.35	Diphenylamine
49	-CN	640.67	Ethyl Cyanoacetate
50	-NC=O	1193.67	*n*-Methylacetamide
51	$O=C=N-C_a$	697.80	Phenyl Isocyanate
52	NO_2-C- (aliphatic)	898.17	Nitroethane
53	$-NO_2$	525.91	*m*-Nitrotoluene
54	-S-	405.65	Diethyl Sulfide
55	$-S_R-$	221.89	Thiophene
56	-SH	469.16	Propyl Mercaptan
57	-Br	386.51	Bromoethane
58	-Cl	251.85	1-Chloropentane
59	-F	-55.41	Benzotrifluoride
60	-I	622.38	Hexyl Iodide
61	-Si-	89.55	Dimethyldichlorosilane
62	-O-(Si)	96.01	Hexamethyldisiloxane

HC indicates the group only applies to hydrocarbons, subscript R is an atom belonging to any ring, and C_a is explicitly an aromatic carbon.

Figure 7.12 compares the results of the test and training set. Many of the outliers seen in the test set are for silanes, siloxanes and polyfunctional chemicals. These chemicals were examined for similar structural groups, but not enough of a single group was found to warrant addition to the contributions in Table 7.15.

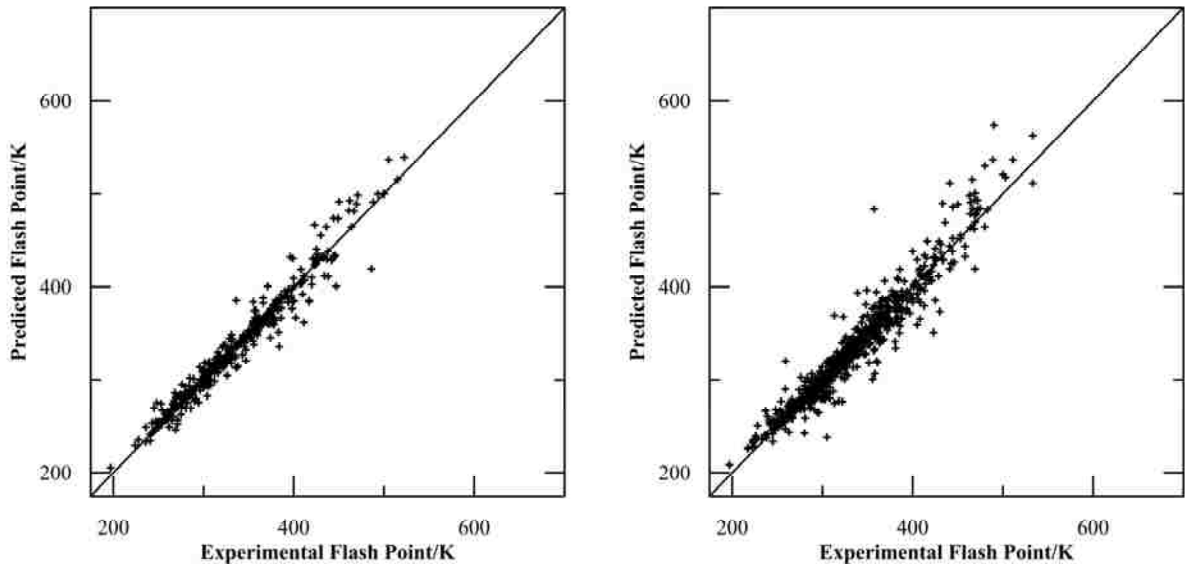

Figure 7.12 Experimental flash points vs. values predicted using Equation 7.23, shown here for the training set (left) and the test set

The combined AAD for both the test and training data sets was 2.84 %/9.84 K. On the other hand, if the most accurate boiling point methods are used to estimate the flash point by substituting an estimated normal boiling point (calculated using the DIPPR recommended methods), the minimum AAD was 4.35 %.

When the vapor pressure of a chemical is known, clearly Equation 7.16 or the method of Leslie and Geniesse should be used. If the vapor pressure is not known, but the boiling point and enthalpy of vaporization at the boiling point are well-known, Equation 7.18 may be used to predict the flash point within experimental error (on average). If, however, no information is known concerning the compound, the structural contribution-based method of Equation 7.23 may be used to estimate the flash point with reasonable accuracy for many compounds.

CHAPTER 8. SUMMARY AND RECOMMENDATIONS

8.1 Summary

Analysis of lower flammability limit measurements in a large spherical vessel showed that many of the previously reported data were determined in vessels too narrow to overcome wall effects. The adiabatic flame temperature, which was previously assumed to be independent of initial mixture temperature, was shown to decrease linearly with increasing initial temperature. Consequently, the well-established modified Burgess-Wheeler law underestimates the effect of initial temperature on the lower flammability limit. Analysis of lower flammability limit data, combined with measurements of CO and CO_2 concentrations, also verified that radical production coupled with CO oxidation determine whether a flame will propagate or not.

Flash point and lower temperature limit measurements showed that the flash point is a poor approximation of the lower temperature limit, the difference between the two temperatures increasing with increasing lower temperature limit. Above about 350 K, values determined in a Pensky-Martens apparatus are a worse approximation of the lower temperature limit, than values measured using a small-scale apparatus. Pensky-Martens values also appear to be more sensitive to impurities.

Flammability data in the DIPPR® 801 database and over 3600 additional data points were evaluated for accuracy based on experimental methods, relationships between chemical properties, and trends of chemical series. The most probable value was then recorded in the DIPPR® 801 database. On average the recommended flash point increased slightly, and the recommended flammability limits decreased.

This critically reviewed set of data was then used to develop predictive correlations for the flammability limits and flash point, so that values may be accurately predicted for chemicals with no experimental data.

Based on a combination of chemical equilibrium and structural contribution methods, the estimation method developed for the lower flammability limit predicts both the magnitude and temperature dependence of the lower flammability limit, on average reproducing the experimental data of this work within 4 %. Parameters were also determined to predict values consistent with data determined using the Bureau of Mines, EN 1839, and ASHRAE apparatuses.

Estimation of the upper flammability limit proved more difficult, a result of the scatter in reported data. The correlation developed in this work is far more consistent with experimental data than previously published methods, but still results in errors exceeding 50 % for nearly 6 % of the 393 data points studied. Again, parameters were also fit to predict values consistent with data determined using the Bureau of Mines, EN 1839, and ASHRAE apparatuses.

Three new flash point estimation methods were developed. A method based on the vapor pressure predicts within 1 % on average for more than 1000 compounds. A second method was developed to estimate the flash point when an accurate vapor pressure correlation in not known. Based on the enthalpy of vaporization and normal boiling point, this method typically predicted within the expected experimental error. Finally, a method based entirely on structural contributions was developed to estimate the flash point for compounds with little or no thermodynamic data. Although less accurate than the first two methods, this method still predicts the flash point with an average error less than 3 %.

8.2 Recommendations

Additional lower flammability limit measurements should be directed towards accomplishing three goals: 1. The set of chemicals for which the temperature dependence has been explored should be expanded. Lower flammability limit measurements at different temperatures for nitrogen, silicon, and sulfur containing compounds would verify and further generalize the temperature dependence described in Equation 7.13. 2. The possibility of parallel lower flammability limit curves from different apparatuses, in particular the ASHRAE and EN 1839 apparatuses, should be explored. If, in general, the lower flammability limit curves obtained in different apparatuses are indeed parallel, this could be a large step towards showing the existence of a fundamental flammability limit. 3. The ASHRAE dataset available in the DIPPR® 801 database should be expanded and the predictive ability of the proposed lower flammability limit prediction method should then be enhanced based on the expanded dataset.

Further flash point measurements are recommended for compounds in the DIPPR® 801 database that are noted to polymerize or decompose near or below their expected flash points.

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APPENDIX A. VARIABLES AFFECTING FLAMMABILITY LIMITS

Pressure

Decreasing below atmospheric pressure causes the flammability range to narrow, the upper flammability limit to decrease significantly and the lower flammability limit to increase slightly, until the flammability limits meet at the critical flammability pressure where flame propagation is impossible. This was first shown by White [185] for ether/air mixtures and later by Laffitte and Delbourgo [186] for C_1 through C_5 of the *n*-alkanes in air. Both studies also demonstrated that at sub-atmospheric pressures two independent ranges of flammability may exist, one for normal flame and one for cool flame propagation, even though at atmospheric pressure only the normal flame range may exist.

Increasing the initial pressure widens the flammability limits, or in other words decreases the lower flammability limit and increases the upper flammability limit, though again the lower limit is less significantly affected than the upper limit [20, 120, 187-188]. Zabetakis [32] suggested an equation for the pressure dependence based on natural gas data:

$$FL(P) = FL(P_0) + C\left(\frac{P}{P_0}\right), \tag{A.1}$$

where $FL(P)$ is the upper or lower flammability limit at the elevated pressure P, $FL(P_0)$ is the known flammability limit at some given pressure P_0, and C is a constant equal to -0.71 for the lower flammability limit and 20.4 for the upper flammability limit. For the upper flammability limit of saturated hydrocarbons in air, Bodurtha claimed that the using $C = 20.6$ gives a better fit [90].

Vanderstraeten et al. [189] found that the UFL for methane was better fit using a second order equation:

$$UFL(P) = UFL(P_0)\left[1 + a\left(\frac{P}{P_0} - 1\right) + b\left(\frac{P}{P_0} - 1\right)^2\right]. \tag{A.2}$$

The parameters a and b depend on the fuel-air mixture, and are 0.0466 and -0.000269, respectively, for methane-air mixtures. According to Van den Schoor [190], the pressure dependence of the upper flammability limit is best described using a bilinear form, as there is a sudden strong decrease in slope at elevated pressures.

Studies by Mason and Wheeler [123] on methane/air mixtures up to 6 atm and Gibbon et al. [19] on ethanol/air and 1-propanol/air mixtures up to 7 atm found that the lower flammability limit actually increased with increasing pressure. This phenomenon has also been observed for hydrogen/air mixtures and carbon monoxide/air mixtures [191]. Payman and Wheeler [192] observed that for mixtures of C_2 through C_5 with air, the lower flammability limit initially decreased for several atmospheres before increasing.

Vessel Volume

As a general rule, increasing vessel volume decreases the quenching effects of the walls and therefore widens the flammability range. The propagation criteria used in the flammability test, however, should be taken into account when determining the size of the vessel. For example, for methods such as EN 1839 where only the presence of a flame is required, a considerably smaller vessel may be used. For all propagation criteria, however, the diameter of the vessel should be sufficiently large to eliminate wall quenching effects. White [193] found that that after 5 cm, the effect of increasing the diameter played little role in determining the flammability limits in long tubes. Studying the effect of vessel height and diameter in 8 different sized cylinders, Takahashi et al. [194] determined that, for the infinite propagation criterion, the ideal cylinder size is 30 cm in diameter and 60 cm tall. Using the ASHRAE propagation criterion, they found that the 12-L flask results correspond closely to full propagation in a jumbo cylinder, 45 cm x 100 cm, confirming the similar findings of Richard [195].

Kul et al. [196-197] used percolation theory to describe the effect of spherical vessel volume on flammability limits. Spherical flask methods typically use the propagation criterion that the flame must subtend a cone of a specified angle. Accordingly, when the vessel volume is increased, the conical volume that the flame front must fill also increases, thus requiring the presence of a stronger flame for a mixture to be considered flammable. Therefore, once quenching from wall effects has been eliminated, increasing vessel volume would result in an increased lower flammability limit until some infinite limit is reached. Kul et al. found that the lower flammability limit ($mol \cdot m^{-3}$) varied nearly linearly with diameter, D, by $D^{-1/0.9}$.

Direction of Propagation

Experimental work by White [198] showed conclusively that flames propagate more easily upward than downward, with the midpoint corresponding approximately to horizontal propagation. Research by Ronney and Wachman [199] verified that the lower limit using downward propagation in microgravity resembled the limit using horizontal propagation in 1 g. From this, Ronney and Wachman concluded that the downward limits occur when the flame front is no longer able to propagate downward against the buoyant product gases, and the upward limits occur when the burning velocities become too slow for propagation. Similar conclusions were reached by Levy [13], who studied buoyancy effects on the flammability limits using high speed and Schlieren photography.

Ignition Source

Common sources of ignition for flammability limit testing include fusing wire, spark, and match head ignition. It is ideal to find a source of ignition powerful enough that further increasing the ignition energy does not affect the flammability limits. Richard and Shankland [128] studied the effect of ignition source on several refrigerants and found that for chemicals that are difficult to ignite, the match head source gave the widest range of flammability. For materials that ignite more easily, the three ignition sources produced very similar results.

Takahashi et al. [200] studied ignition using fusing wires and found that the ignitibility depends on the metal, thickness, length, and electric source used. The authors recommended use of a molybdenum wire, 0.33 mm thick and 2 cm long, fused with DC 36-48 volts.

Kondo et al. [201] studied the effect of spark gap and duration using AC spark ignition. They recommended tungsten electrodes sharpened to a point with a spark gap of 6-8 mm and spark duration of 0.1-0.2 seconds. This is similar to the tungsten wire ignition setup used in the ASHRAE method (6.4 mm spark gap, 0.2 – 0.4 second spark duration).

Oxygen Concentration

Changes in the oxygen concentration have little effect on the lower flammability limit, as the mixture is fuel lean. However, the upper flammability limit increases significantly by an increase in oxygen concentration as oxygen is the limiting species [164, 202].

Humidity

Humidity affects the flammability limits only when the fuel contains fewer hydrogen atoms than halogen atoms, particularly fluorine [203]. Smith, as cited by Wilson and Richard [204], showed that certain refrigerant/air mixtures were not flammable without the presence of humidity, but when moist air was used, the same mixtures would readily propagate a flame. The current standard is to use 50% relative humidity at 296 K.

Residence Time

Several investigators have shown that while an increase in residence time prior to ignition has little effect on the lower flammability limit, the upper flammability limit may be reduced significantly by the resulting occurrence of partial oxidation [179-180, 205].

Turbulence

Coward and Jones [4] originally reported that the lower flammability limit of methane/air mixtures decreased when stirred with a fan. Abdel-Gayed and Bradely [206], however, found that the flammability range of methane/air mixtures narrowed linearly, and thus the lower flammability limit increased, with increasing fan revolutions. Kagan and Sivashinsky [207] determined numerically that with increasing flow the limits first widen at moderate speeds, and then narrow. This same result was found experimentally by Palmer and Tonkin [208], and Crescitelli et al. [209].

If a liquid is present, turbulence may result in mists, which generally have broader flammability ranges than vapors [48]. Increasing turbulence when mists are present widens the flammability range.

Temperature

Section 2.2 describes the effect of initial temperature on the lower flammability limit, as described in the literature. Cato et al. [210] found that the upper flammability limit increased by 19 vol% to 28 vol% per 100 K increase until a critical temperature was reached, at which point cool flame propagation was supported. Further increase in temperature past this point raises the upper flammability limit by at least 200 vol% per 100 K. At sub-ambient temperature and in a Bureau of Mines apapratus, Wierzba et al. [211] found that the change in the upper flammability limit of light alkanes and alkenes ranged from 2.2 % to 13.9 % per 100 K. Van den Schoor and Verplaetsen [190], and Vanderstraeten et al. [189] found that the temperature dependence of both the flammability limits increases with increasing pressure, but remains linear.

APPENDIX B. SUMMARY OF PUBLISHED ESTIMATION METHODS

Flammability Limit Estimation Methods

The methods discussed in this section estimate the flammability limits at a single temperature point, assumed to be 298 K for gases and the temperature limit for liquids and solids, unless otherwise noted.

Affens

For alkanes, Affens [35] observed that the flammability limits at 298 K are directly related to the number of carbon atoms in the compound:

$$\frac{1}{LFL} = 0.1347 n_{\mathrm{C}} + 0.04353\,, \tag{B.1a}$$

$$\frac{1}{UFL} = 0.01337 n_{\mathrm{C}} + 0.05151\,. \tag{B.1b}$$

For general hydrocarbons, the lower flammability limit may be calculated using the heat of combustion ($\mathrm{kcal \cdot mol^{-1}}$),

$$LFL = \frac{1091}{\Delta H_{\mathrm{c}}}. \tag{B.2}$$

Affens also showed that the upper flammability limit is related to the lower flammability limit:

$$\frac{1}{UFL} = 0.0993 \frac{1}{LFL} + 0.0472. \tag{B.3}$$

Albahri

Albahri [43] proposed that the flammability limits could be estimated for hydrocarbons from

$$\Phi = a + b\left(\sum_i \Phi_i\right) + c\left(\sum_i \Phi_i\right)^2 + d\left(\sum_i \Phi_i\right)^3 + e\left(\sum_i \Phi_i\right)^4, \tag{B.4}$$

where Φ is either the lower or upper flammability limit, depending on which values of the structural contributions, Φ_i, and the coefficients *a*, *b*, *c*, *d*, and *e*, are used. Parameter values are given in Table B.1.

Britton

Britton [33-34] provided a simple method to approximate the lower flammability limit based on the oxygen coefficient for stoichiometric combustion:

Table B.1. Parameters for lower and upper flammability limit prediction using Equation B.4

i	Group/Parameter	LFL$_i$	UFL$_i$	*i*	Group/Paramete	LFL$_i$	UFL$_i$
	a	4.174	18.14	8	=C=	-0.4473	0.0675
	b	0.8093	3.4135	9	≡CH	-1.2849	3.8518
	c	0.0689	0.3587	10	≡C-	-0.4396	1.3924
	d	0.00265	0.01747	11	$>C_RH_2$	-1.0035	-0.8386
	e	3.76E-05	3.40E-04	12	$>C_RH-$	-0.4955	-0.9648
1	$-CH_3$	-1.4407	-0.8394	13	$>C_R<$	0.1058	-2.2754
2	$>CH_2$	-0.8736	-1.1219	14	$=C_RH-$	-0.87	-0.0821
3	>-CH-	-0.2925	-1.2598	15	$>C_R=$	-0.5283	-0.1252
4	>C<	0.2747	-2.1941	16	$=C_aH-$	-0.8891	-1.2966
5	$=CH_2$	-1.3126	0.2479	17	$>C_aH_2$	-1.0884	-1.6166
6	=CH-	-0.7679	-0.3016	18	$>C_a=$ (fused)	-0.3694	-1.4722
7	>C=	-0.2016	-0.6524	19	$>C_a=$	-0.2847	0.6649

The subscripts a and R represent an aromatic and non-aromatic ring, respectively.

$$LFL = \frac{10}{\beta}\,. \tag{B.5}$$

A more accurate method was also given to estimate the lower flammability limit, discussed in detail in Section 2.3.2.

Dalmazonne

Based on thermal hazard criteria used in CHETAH, Dalmazzone, Laforest, and Petit [61] proposed that the lower flammability limit of hydrocarbons could be estimated using

$$\frac{10\left(\frac{LFL}{100}\Delta H_{\mathrm{c}}\right)^2}{\left[\frac{LFL}{100}MW + 28384\left(1-\frac{LFL}{100}\right)\right]\left[\frac{LFL}{100}n_{\mathrm{C+H}} + 2\left(1-\frac{LFL}{100}\right)\right]} = 15.1\,, \tag{B.6}$$

where *MW* is the molecular weight of the fuel, $n_{\mathrm{C+H}}$ is the number of carbon and hydrogen atoms, and the heat of combustion is given in (kcal·mol^{-1}).

Funk

According to Funk [54], the lower flammability limit may be calculated from

$$\log(LFL) = a - b\log(\beta)\,, \tag{B.7}$$

where the coefficients *a* and *b* depend on the chemical class, and are listed in Table B.2.

Table B.2. Coefficients for lower flammability limit prediction using Equation B.7

Chemical Type	***a***	***b***
Alkenes	0.77815	0.73492
Alkynes and Dienes	0.68574	0.7756
Dichloro	1.17609	1.0299
Monochloro	1.07555	1.008
Nitrogen-containing	1.20412	1.1296
Others	0.90037	0.87024

Gharagheizi

Gharagheizi used a quantitative structure-property relationship (QSPR) study to develop models for the lower [65] and upper [57] flammability limits:

$$LFL = 0.76022 - 3.57754PW_5 - 1.47971AAC + 8.57528SIC_0 - 0.01981MLOGP\,, \tag{B.8a}$$

$$\begin{aligned} UFL = {} & 10.35415 - 1.35486Jhetv - 42.28779PW_5 + 18.59571SIC_0 \\ & - 0.98203MATS4m + 0.68363MLOGP \end{aligned}, \tag{B.8b}$$

where PW_5 is the path/walk Randic shape index, *AAC* is the mean information index on atomic composition, SIC_0 is the structural information content with zero-order neighborhood symmetry, *MLOGP* is the Moriguchi octanol-water partition coefficient (log *P*), *Jhetv* is the Balaban-type index from van der Waals weighted distance matrix, and *MATS*4*m* is the Moran autocorrelation-lag 4 weighted by atomic masses. These correlations are of little use, as information on these molecular descriptors is not commonly available.

Goto

Goto and Hirai [59] showed that a linear relationship existed between the heat of combustion kcal·mol^{-1} and the inverse of the lower flammability limit:

$$LFL = \frac{100}{0.09\left|\Delta H_{\mathrm{c}}\right| + 1.56}. \tag{B.9}$$

Hanley

Hanley [51] also observed that the heat of combustion and flammability limits (*FL*) were related linearly by

$$FL = a\left(-\Delta H_{\mathrm{c}}\right)^{-1}, \tag{B.10}$$

where *a* is 11.2 for the lower flammability limit, and 54.2 for the upper flammability limit, and the heat of combustion is given in kcal·mol^{-1}.

High-Danner

High and Danner [38] developed a structural contribution method for the upper flammability limit:

$$\ln(UFL) = 3.817 - 0.2627 n_{\mathrm{C}} + 0.0102 n_{\mathrm{C}}^2 + \frac{\sum_i ng_i \cdot UFL_i}{\sum_j ng_j}. \tag{B.11}$$

The sum in the denominator is the total number of groups used to represent the compound, and contributions for UFL_i are given in Table B.3.

Table B.3. Structural contributions for upper flammability limit prediction using Equation B.11

i	***Group***	***UFL_i***	***i***	***Group***	***UFL_i***
1	CH3	-0.9307	13	Cl	-0.8153
2	CH2	-0.5225	14	2Cl	1.311
3	CH	0	15	3Cl	-2.011
4	C	0	16	F	0
5	H	-0.5625	17	2F	0
6	OH	0	18	3F	0
7	O	1.4528	19	*n*Br	0
8	C=O	0	20	NH2	0
9	COOH	0	21	C=N	0
10	C=C	1.118	22	N	0
11	C≡C	4.275	23	NO2	0
12	C(O)=O	0	24	C_6 Ring	0

Hilado

Hilado [45] expanded the method of Jones (see Section 2.3.2) to estimate the upper and lower flammability limits based on the concentration needed for stoichiometric combustion:

$$FL = a\,C_{\mathrm{st}}. \tag{B.12}$$

The coefficient depends on the chemical class for both the upper and lower flammability limits. Values are given in Table B.4.

Table B.4. Coefficients for lower and upper flammability limit prediction using Equation B.12

LFL		***UFL***	
Chemical Class	***a***	**Chemical Class**	***a***
CHO	0.537	CHO	$2.0 + 0.20n_C$
Amines	0.692	Aromatic Hydrocarbons	3.16
Chlorides	0.609	Aldehydes	4.8
Dichlorides	0.716	Ethers	7.03
Bromides	1.147	Oxides	10.19
Contains Sulfur	0.577	Amines	3.58
		Alkyl Chlorides	$1.4+0.58n_C$
		Chlorides/Dichlorides	2.61
		Bromides	1.5
		Contains Sulfur	3.95

Hshieh

Hshieh [52, 63] related the flammability limits of organic and organosilicon compounds to the heat of combustion ($\text{kJ}\cdot\text{mol}^{-1}$):

$$FL = a(-\Delta H_c)^b + c. \tag{B.13}$$

The parameters *a*, *b*, and *c* are 1145.2246, -0.7972 and -0.3822, respectively, for the lower flammability limit, and 13514, -0.81, and 6.71 for the upper flammability limit.

Jones

The method of Jones [31-32], commonly called the Bureau of Mines method, claims that the flammability limit is proportional to the concentration needed for stoichiometric combustion, i.e.,

$$FL = aC_{st}, \tag{B.14}$$

where a is 0.55 for the lower flammability limit, and 3.5 for the upper flammability limit.

Kondo

Kondo [173, 177-178] developed a method based on much of his own experimental flammability data from an ASHRAE-style apparatus. The flammability limits may be estimated from

$$LFL = G(1-F)\times 100\,, \tag{B.15a}$$

$$UFL = \frac{G}{1-F}\times 100\,, \tag{B.15b}$$

where

$$G = C_{\mathrm{st}}\left(1+0.00312(MW-32)+\frac{G_1}{n_{\mathrm{H}}+n_{\mathrm{F}}+n_{\mathrm{Cl}}+n_{\mathrm{Br}}}+\frac{G_2}{n_{\mathrm{C}}-1}\right), \tag{B.15c}$$

$$F = 0.556\left(1-0.22\,C_1+\frac{F_1+F_4}{n_{\mathrm{H}}+n_{\mathrm{F}}+n_{\mathrm{Cl}}+n_{\mathrm{Br}}}+\frac{F_2}{n_{\mathrm{C}}-1}+\frac{F_3}{n_{\mathrm{C}}}\right), \tag{B.15d}$$

C_1 is 1 when the compound only has one carbon atom, and equals 0 otherwise, and G_i and F_i are group sums with contribution values found in Table B.5. When the sum of fluorine and chlorine atoms exceeds the number of hydrogen atoms, the chlorine atoms are assumed to form chlorine molecules, and C_{st} is then calculated by

$$C_{\mathrm{st}} = \frac{1}{1+4.773(n_{\mathrm{C}}+(n_{\mathrm{H}}-n_{\mathrm{F}}+2n_{\mathrm{O}})/4}\,. \tag{B.15d}$$

Table B.5. Structural contributions for the method of Kondo (Equation B.15)

Group	***i***	**G_i**	**F_i**
Br	1	-1.23	-2.77
Cl	1	-0.31	-0.75
F	1	0	-0.16
Br on Unsaturated Carbon	1	-0.79	-0.19
Cl on Unsaturated Carbon	1	-0.79	-0.19
F on Unsaturated Carbon	1	-0.65	-0.21
OH	1	0	-0.54
Ether	2	-0.09	0.39
Epoxy	2	0.29	0.61
Ester	2	0.13	0.09
Aliphatic Ring	2	0.31	-0.01
=	2	0.42	0.26
≡	2	0.84	0.52
Carbon with two Halogens	3		-0.07
Carbon with three Halogens	3		-0.1
O-F	4		-1.06

Miloshev

Miloshev [50] correlated the lower and upper flammability limits of hydrocarbons with the normal boiling point (^{o}C) and obtained

$$FL = a\frac{813.1 - T_b}{b + T_b} . \tag{B.16}$$

Values for parameters *a* and *b* are given in Table B.6.

Table B.6. Parameters for flammability limit prediction using Equation B.16

	LFL		***UFL***	
Chemical Class	***a***	***b***	***a***	***b***
Aromatics	0.4	123.9	6.21	479.5
Cyclohexanes	0.43	185.9	6.92	611
Cyclopentanes	0.42	182.6	6.82	601.9
Saturated Hydrocarbons	0.4	189.2	6.87	618.5

Möller

The method developed by Möller [47] estimates the lower flammability limit of organic compounds from a linear relation with C_{st}:

$$LFL = aC_{\mathrm{st}} + b\,. \tag{B.17}$$

Values for the parameters *a* and *b* vary by chemical class, and are given in Table B.7.

Table B.7. Parameters for flammability limit prediction using Equation B.17

Chemical Class	***a***	***b***	**Chemical Class**	***a***	***b***
Aliphatic hydrocarbons	0.45	0.12	Aliphatic monoketones	0.53	0.14
Alkenes, alkynes and dienes (halogen free)	0.25	0.66	Aliphatic aldehydes	0.53	0.23
Aliphatic mononitriles	0.33	0.74	Aliphatic esters from valeric up	0.45	0.12
Alkenes, alkynes and dienes (halogen free)	0.25	0.66	Aliphatic formates	0.49	0.24
Monobromoalkanes	0.69	0.66	Aliphatic acetates	0.56	0.05
Aliphatic monoamines	0.71	0.48	Epoxyalkanes	0.24	0.79
Alkoxyalcohols	0.57	0.3	Cycloalkanes	0.56	0.06
Aliphatic monoalcohols (halogen free)	0.5	0.08	Benzoles	0.48	0.03
Dialkanols	0.45	0.01	Naphthyls	0.69	0.29
Aliphatic diethers (acetals/ketals)	0.47	0.1	Monochloroalkanes	0.65	0.3
Aliphatic monoethers	0.36	0.37	Dichloroalkanes	0.8	0.49
Aliphatic monocarboxylic acids (halogen free)	0.32	0.63			

Monakhov

Monakhov [39, 48] proposed a simple relationship between the flammability limits and oxygen coefficient for stoichiometric combustion:

$$FL = \frac{100}{a\beta + b}\,. \tag{B.18}$$

When estimating the lower flammability limit, the parameters *a* and *b* are 8.684 and 4.679, respectively. When estimating the upper flammability limit, the values of *a* and *b* depend on the value of β: if β is less than or equal to 7.5, *a* and *b* equal 1.55 and 0.56, respectively; otherwise, *a* is 0.768 and *b* is 6.554.

Nuzhda

Nuzhda [40] used structural contributions (Table B.8) to estimate the upper flammability limit of organic compounds with the correlation

$$UFL = \left(15.4 + \sum_i ng_i \cdot A_i\right)\exp\left(-0.15(n_\mathrm{C} - 1)^{0.5}\right). \tag{B.19}$$

Table B.8. Structural contributions for prediction of upper flammability limit using Equation B.19

i	Group	A_i	*i*	Group	A_i
1	-OH	2.9	11	F	5.8
2	-O-	2.4	12	2F	12.2
3	C=O	2.2	13	3F	19.2
4	-COOH	0	14	Cl	4
5	OCO	6.2	15	2Cl	7
6	-C=C-	1.2	16	3Cl	0
7	-SH	9.9	17	Br	-0.3
8	$-NH_3$	1.9	18	Cyclohexane	0.4
9	=NH	2.5	19	Fused Benzene	3.8
10	Cyclopropane	1.5	20	Benzene	0.6

Oehley

The method of Oehley [49] estimates the lower flammability limit of organic compounds with just β, using

$$LFL = \frac{44}{\beta}. \tag{B.20}$$

Pan

Pan et al. [58] developed a method for estimating the upper flammability limit of organic compounds from QSPR in the form

$$UFL = 51.028 - 17.452 BELm_1 - 2.610 BEHp_3 + 6.824 qpos - 8.430 E_1 p\,, \tag{B.21}$$

where $BELm_1$ is the lowest eigenvalue of the Burden matrix when weighted by atomic masses, $BEHp_3$ is the highest eigenvalue of the Burden matrix when weighted by atomic polarizabilities, $qpos$ is the maximum positive charge in the molecule, and E_1p is the first component accessibility directional WHIM index, weighted by atomic polarizabilities. Again, methods based on QSPR are rarely implemented because they typically involve molecular descriptors that are not readily available, but may be calculated using quantum mechanical packages.

Pintar

Pintar [42] modified the coefficients of the method proposed by Jones because he claimed it gave a better approximation of the flammability limits. For the lower flammability limit, Pintar recommended the coefficient equal 0.512 for hydrocarbons and esters, and 0.5 for all other chemicals. For the upper flammability limit, he recommended the coefficient equal 3.8.

Pintar also created a method based entirely on structural contributions:

$$FL = \frac{100}{\sum_i ng_i \cdot FL_i}\,, \tag{B.22}$$

where structural contributions for the lower and upper flammability limits are given in Table B.9.

Table B.9. Structural contributions for the Pintar method of predicting upper and lower flammability limits (Equation B.22)

i	Group	LFL_i	UFL_i
1	*cis* Correction	-6.835	1.804
2	*trans* Correction	0.5821	0.9183
3	≡	17.547	0.7842
4	=	4.2821	2.0269
5	=C=N-	2.5963	-1.1463
6	>C<	5.5291	-0.8422
7	>C=O	4.6752	0.6009
8	>CH-	10	0.2183
9	>NH	3.2709	-1.9112
10	>N-NH_2	-3.5071	-0.29897
11	-2Br	-16.0809	8.0036
12	-2Cl	-5.9764	3.1943
13	-2F	-2.1224	0.6847
14	-2I	-44	22.86
15	-3Br	-21.9	12.0054
16	-3Cl	-8.0892	4.2024
17	-3F	-5.13	1.1952
18	-3I	-60	34.29
19	Additional Ring	14.2712	3.1127
20	Benzene Ring	45.0633	-5.9925
21	-Br	-8.0405	4.0018
22	-C(=O)OC(=O)-	4.674	2.4751
23	-C_6H_5	73.8338	9.6661
24	-CH_2-	13.7022	1.4959
25	-CH_3	17.275	3.8461
26	-CHO	10.3801	-1.2148
27	-Cl	-2.9697	1.4008
28	-CN	8.099	3.6918
29	-CO_3-	2.4103	-3.4894
30	-COO-	1.2955	-1.184
31	-COOH	4.889	1.6121
32	-F	-1.2615	0.3984
33	-H	2.725	2.8206
34	-I	-22	11.43
35	*m*-C_6H_4	57.4447	7.245
36	-N=	-7.2149	-2.3309
37	-NH_2	3.7078	1.8802
38	-NO_2	-3.1507	0.8011
39	Non-aromatic Ring	2.9082	3.776
40	-O-	-3.0156	-2.2427
41	*o*-C_6H_4	57.4447	7.9291
42	-OH	2.1797	0.5856
43	-O-O-	-6.0312	-4.4854
44	*p*-C_6H_4	57.4447	7.6126
45	-S-	11.0079	-1.9832
46	-SH	7.9424	0.5344
47	Si-C	-2.2855	-3.0576
48	Si-Cl	4.101	9.7131
49	SiH	8.313	-24.416
50	Si-N	15.896	1.6577
51	Si-O	2.5034	1.4282
52	-SO-	3.9115	-4.1834
53	-PO_4<	-11.5096	-6.026
54	-SO_2-	5.54	
55	-SO_3-	2.86	
56	-SO_4-	0.18	
57	-OPO_2-	7.1419	
58	-P<	47.6909	
59	-PO-	7.1515	
60	B	47.3806	
61	SiH_2	16.626	
62	SiH_3	24.939	
63	-$CONH_2$		2.4811

Seaton

The method of Seaton [41] also estimates the flammability limits based on the structural contributions shown in Table B.10:

$$FL = \frac{\sum_i ng_i f_i}{\sum_i ng_i f_i / h_i} . \tag{B.23}$$

Table B.10. Structural contributions for the Seaton method of predicting upper and lower flammability limits (Equation B.23)

LFL			**UFL**		
Group	f_i	h_i	**Group**	f_i	h_i
C-(C)(C$_B$)(H)$_2$	0.18308	0.01344	C-(C)(C$_B$)(H)$_2$	3.28264	0.37109
C-(C)(CO)(H)$_2$	0.02613	0.0098	C-(C)(C$_d$)(H)$_2$	0	100
C-(C)(H)$_2$(Cl)	11.55786	6.21312	C-(C)(CO)(H)$_2$	0.09181	0.14551
C-(C)(H)$_2$(O)	0.00242	0.00322	C-(C)(H)$_2$(Cl)	65.79851	15.89991
C-(C)(H)$_3$	12.50732	3.1242	C-(C)(H)$_2$(N)	8.11656	20.66602
C-(C)$_2$(C$_B$)(H)	0.0944	0.00323	C-(C)(H)$_2$(O)	32.23775	11.16797
C-(C)$_2$(CO)(H)	0.49969	0.02893	C-(C)(H)$_3$	65.69279	12.23829
C-(C)$_2$(H)(O)	0.02488	0.00298	C-(C)$_2$(CO)(H)	0	100
C-(C)$_2$(H)2	0.15461	0.04492	C-(C)$_2$(H)(O)	2.54507	0.39893
C-(C)$_3$(H)	0.01656	0.00103	C-(C)$_2$(H)$_2$	3.66985	1.55859
C-(C)$_4$	0.33819	0.01178	C-(C)$_3$(H)	1.08653	39737.61
C-(C$_B$)(H)$_3$	18.80642	1.33971	C-(C)$_4$	99.99675	2.95898
C-(C$_d$)(H)$_2$(Cl)	1.0165	5.14586	C-(C$_d$)(H)$_2$(Cl)	1.4489	12.48047
C-(C$_d$)(H)$_3$	0.15532	1.32511	C-(C$_d$)(H)$_3$	2.61722	11.9668
C-(CO)H$_3$	11.57657	3.81915	C-(CO)H$_3$	0.08697	492.8667
C-(H)$_3$(O)	13.10617	9.23645	C-(H)$_3$(O)	3.01463	43.39455
C$_B$-(C)	0.18524	0.0375	C$_B$-(C)	12.19265	15392.84
C$_B$-(C$_B$)	0.07821	0.0027	C$_B$-(H)	22.40435	7.14
C$_B$-(H)	6.01743	1.28777	C$_d$-(C)(CO)	0.00725	0.0874
C$_B$-(N)	26.25975	1.2771	C$_d$-(C)(H)	0	100
C$_B$-(O)	74.99764	25.99844	C$_d$-(C)$_2$	0.25125	1.26758
C$_d$-(C)(H)	0.05835	142.799	C$_d$-(CO)(H)	0.00015	883.9084
C$_d$-(CO)(H)	6.88905	1.88402	C$_d$-(H)(Cl)	0.00002	12.8
C$_d$-(H)(Cl)	2.3175	5.42088	C$_d$-(H)$_2$	0.00007	28.6
C$_d$-(H)$_2$	1.31449	2.61055	CO-(C)(C$_d$)	0.03769	4.81641
CO-(C)(H)	12.05977	4.68871	CO-(C)(H)	43.57364	54.90223
CO-(C)(O)	0.001	51.59168	CO-(C)(O)	0.01264	2.6178
CO-(C)$_2$	0.31889	0.10826	CO-(C)$_2$	90.85265	8.71534
CO-(C$_d$)(O)	0.00215	0.02738	CO-(C$_d$)(O)	0.00059	5.99268
N-(C$_B$)(H)$_2$	6.9131	3.89132	CO-(H)(O)	0.87166	57.00002
O-(C)(CO)	0.03929	0.01247	N-(C)(H)$_2$	31.57786	13.35889
O-(C)(H)	10.62441	5.12929	O-(C)(CO)	0.27914	2.82715
O-(C)$_2$	0.2185	0.04338	O-(C)(H)	63.42825	35.71059
O-(C$_B$)(H)	74.99712	0.61106	O-(C)$_2$	24.26403	15.71485
O-(CO)$_2$	0.01228	0.00441	O-(CO)(H)	0	100
Cyclohexane Ring	17.33727	-3.48684	O-(CO)$_2$	0.00127	0.13476
Cyclopentane Ring	28.97878	6.47494	Cyclohexane Ring	99.9977	8.58692
Gauche interaction	-5.04752	0.92017	Gauche interaction	-0.7102	-0.18164

The subscript B indicates an aromatic carbon, and d is a carbon with a double bond.

Shebeko

Shebeko [39] showed the lower flammability limit could be estimated using almost exclusively atomic contributions. The single exception is a group he added to account for triple bonds. The lower flammability limit is calculated directly from the sum of the contributions,

$$LFL = \frac{100}{\sum_i ng_i \cdot lfl_i}, \tag{B.24}$$

using the contributions listed in Table B.11.

Table B.11. Structural contributions for estimating the lower flammability limit using Equation B.24

i	**Group**	lfl_i	i	**Group**	lfl_i
1	Cl	-4.38	7	H	2.17
2	Si	1.3	8	I	17.5
3	C	9.1	9	N	1.38
4	C≡C	14.07	10	O	-2.68
5	F ($n_\mathrm{H} \geq n_\mathrm{F}$)	-4.18	11	P	9.6
6	F ($n_\mathrm{H} < n_\mathrm{F}$)	-2.55	12	S	10.9

Shimy

The lower flammability limit is estimated by the method of Shimy [36] using

$$LFL = \frac{a}{n_\mathrm{C}} + b, \tag{B.25a}$$

where a equals 6 for paraffins, olefins and their isomers, and 8 for aromatic hydrocarbons and alcohols. The parameter b is 0.2, 0.1, 0, and -0.7 for paraffins/olefins, their isomers, aromatic hydrocarbons, and alcohols, respectively.

To estimate the upper flammability limit, Shimy developed distinct equations for each of these chemical classes:

$$UFL = \frac{60}{n_\mathrm{H}} + \frac{n_\mathrm{C}}{20} + 2.2 \text{ for paraffins and olefins}, \tag{B.25b}$$

$$UFL = \frac{60}{n_{\mathrm{H}}} + \frac{n_{\mathrm{C}}}{20} + 2.3 \text{ for paraffinic and olefinic isomers,} \tag{B.25c}$$

$$UFL = \frac{86}{2n_{\mathrm{H}}} \text{ for aromatic hydrocarbons, and} \tag{B.25d}$$

$$UFL = \frac{80 - 2n_{\mathrm{H}}}{2n_{\mathrm{C}}} + 3 \text{ for alcohols.} \tag{B.25e}$$

Solovev-Baratov

Solovev and Baratov [37] estimated the lower flammability limit by

$$LFL = \frac{1}{a(n_{\mathrm{C}} - 1) + b}\,. \tag{B.26}$$

For alkanes, a equals 0.108 and b equals 0.164; for alcohols, a is 0.154 and b is 0.164; for acetates, a is 0.164 and b is 0.23; and a is 0.116 and b is 0.18 for formates.

Spakowsi

Spakowski [55] showed that the product of the lower flammability limit and heat of combustion is essentially a constant. Thus,

$$LFL = \frac{4354}{-\Delta H_{\mathrm{c}}}\,, \tag{B.27a}$$

when the heat of combustion is given in $\mathrm{kJ \cdot mol^{-1}}$.

Spakowski also correlated the upper flammability limit to the lower flammability limit:

$$UFL = 7.1\,LFL^{0.56}\,. \tag{B.27b}$$

Suzuki

Suzuki [53, 62] estimated the flammability limits using empirical correlations based on the gross heat of combustion ($\Delta H_{\mathrm{c,\,g}}$) in 10^3 kJ·mol:

$$LFL = \frac{-3.42}{\Delta H_{\mathrm{c,\,g}}} + 0.569\Delta H_{\mathrm{c,\,g}} + 0.0538\Delta H_{\mathrm{c,\,g}}^{2} + 1.80\,, \tag{B.28a}$$

$$UFL = 6.30\Delta H_{\mathrm{c,\,g}} + 0.567\Delta H_{\mathrm{c,\,g}}^{2} + 23.5\,. \tag{B.28b}$$

Suzuki [56] later developed a correlation for the lower flammability limit that included the critical temperature, T_c,and pressure,P_c (bar):

$$LFL = \frac{-4.57}{\Delta H_{\mathrm{c,\,g}}} + 0.0124MW - 0.00237T_c + 0.0205P_c - 0.46\,. \tag{B.28c}$$

Thornton

According to Thornton [46], the flammability limits may be estimated from the oxygen coefficient for stoichiometric combustion using

$$LFL = \frac{100}{1 + 4.85(2\beta - 1)}, \tag{B.29a}$$

$$UFL = \frac{200}{2 + 4.85\beta}. \tag{B.29b}$$

Zatsepin

In addition to the method based on the adiabatic flame temperature discussed in Section 2.3.1, Zatsepin [44] developed a method that uses structural contributions to estimate the coefficient in the method proposed by Jones. Contributions are listed in Table B.12.

Table B.12. Structural contributions for coefficient *a* in Equation B.14

i	Group	a_i	i	Group	a_i
1	-CH3	0.533	14	-OH (acids)	0.699
2	-CH2-	0.578	15	-O- (strained rings)	0.238
3	-CH<	0.647	16	-NH2	0.531
4	>C<	0.685	17	>NH	0.464
5	CH2=	0.487	18	N≡C-	0.635
6	-CH=	0.573	19	>N-	0.449
7	=C<	0.671	20	-NO2	0.0738
8	CH≡	0.319	21	N in aromatic ring	0.518
9	-C≡	0.213	22	-Cl	0.533
10	>C=O	0.57	23	-Br	1.909
11	-OH	0.502	24	Benzene	0.521
12	-O-	0.486	25	Cyclohexane	0.573
13	HC=O	0.527			

Flash Point Estimation Methods

Affens

Affens [35] proposed several methods of estimating the flash point of hydrocarbons. He first related the flash point of alkanes to the number of carbon atoms,

$$FP(^{\circ}\mathrm{C}) = \sqrt{10410\,n_{\mathrm{C}}} - 277.3\,. \qquad \text{(B.30a)}$$

For hydrocarbons, the flash point may be calculated from the normal boiling point ($^{\circ}$C),

$$FP(^{\circ}\mathrm{C}) = 0.6946T_b + 199.45\,, \qquad \text{(B.30b)}$$

or alternatively if an accurate vapor pressure correlation is available, the flash point ($^{\circ}$C) may be estimated by

$$\frac{P^*(FP)}{101.3\ \mathrm{kPa}} = \frac{1}{MW - 2.016}\,. \qquad \text{(B.30b)}$$

Akhmetzhanov

Akhmetzhanov [181] developed a linear correlation between the flash point and normal boiling point ($^{\circ}$C):

$$FP(^{\circ}\mathrm{C}) = a\,T_b + b\,. \qquad \text{(B.31)}$$

The parameters *a* and *b* take on the values 0.62 and -37, respectively, for alcohols, 0.75 and -50 for carboxylic acids, and 0.65 and -64 for paraffinic hydrocarbons.

Albahri

With the equation he developed for the flammability limits (Equation B.4), Albahri [43] estimated the flash point of hydrocarbons using the structural contributions in Table B.13.

Table B.13. Parameters for flash point prediction using Equation B.4

i	Group/Parameter	FP_i	*i*	Group	FP_i
	a	84.65	16	=C=	0.8659
	b	64.18	17	#CH	0.4475
	c	-5.6345	18	#C-	0.8387
	d	0.36	19	>C_RH_2	0.608
	e	-0.0101	20	>C_RH-	0.4217
1	-CH3	0.4832	21	α->C_RH- (*cis*)	0.7148
2	>CH2	0.5603	22	α->C_RH- (*trans*)	0.6986
3	α->CH-	0.5275	23	β->C_RH- (*cis*)	0.6518
4	β->CH-	0.5499	24	β->C_RH- (*trans*)	0.4601
5	γ->CH-	0.4778	25	γ->C_RH- (*cis*)	0.7167
6	δ->CH-	0.4543	26	γ->C_RH- (*trans*)	0.5899
7	α->C<	0.4008	27	>C_R<	0.1847
8	β->C<	0.5281	28	=C_RH-	0.5287
9	-C_2H_5 (branch)	1.037	29	=C_aH-	0.6205
10	=CH_2	0.4078	30	>C_aH2	1.5159
11	=CH-	0.6037	31	>C_a= (fused)	0.8898
12	=CH- (*cis*)	0.5913	32	>C_a=	0.615
13	=CH- (*trans*)	0.6216	33	>C_a= (ortho)	0.7535
14	α->C=	0.7135	34	>C_a= (meta)	0.7384
15	β->C=	0.655	35	>C_a= (para)	0.7675

The subscripts R and a indicate a carbon atom in a non-aromatic ring, and in an aromatic ring, respectively. In noncyclic compounds, α-, β-, γ-, and δ- refer to the second,, third, fourth, and fifth positions along the hydrocarbon chain, respectively. In cyclic compounds, α-, β-,and γ- refer to the second, third, and fourth position along the cyclic ring with respect to group 20, respectively.

Blinov

Blinov [48, 96] developed a method similar to the method of Leslie and Geniesse (see Section 3.2.2), but Blinov's method involves the diffusion coefficient, D_o ($cm^2 \cdot s^{-1}$):

$$FP = \frac{4}{\beta P^*(FP)\, D_o}, \tag{B.32a}$$

where the vapor pressure at the flash point is given in atm. D_o may be estimated from

$$D_o = \frac{1}{\sqrt{n g_i k_i}}, \tag{B.32b}$$

where k_i are the atomic contributions given in Table B.14.

Table B.14. Atomic contributions for the diffusion coefficient in Equation B.32

i	**Element**	***k_i***	***i***	**Element**	***k_i***
1	H	1	6	Br	79
2	O	17	7	C_a	25
3	N	16	8	C_R, $n_C \leq 8$	$25 + 2n_C$
4	S	48	9	C_R, $n_C > 8$	42
5	Cl	37	10	C, $n_C \leq 8$	$25 + 3n_C$
			11	C, $n_C > 8$	50

Bodhurtha

According to Bodhurtha [90], the flash point is a linear function of the normal boiling point (^{o}C) given by

$$FP(^\circ\mathrm{C}) = 0.683 T_b + 201.45. \tag{B.33}$$

Butler

Butler et al. [89] found that the flash point (^{o}F) of pure hydrocarbons occurred approximately at the temperature where

$$MW \cdot P^*(FP) = 15.19 \text{ psi}, \tag{B.34a}$$

where MW is in gm·mol^{-1}. For hydrocarbon flash points measured in a Pensky-Martens apparatus, Butler et al. proposed a linear relationship with the boiling point ($^{\text{o}}$F):

$$FP(^{\circ}\text{F}) = 0.683T_b - 119. \tag{B.34b}$$

Catoire-Naudet

Catoire and Naudet [80] achieved accurate prediction of the flash point of organic compounds using the normal boiling point (K), and standard enthalpy of vaporization at 298.15 K (kJ·mol^{-1}):

$$FP = 1.477\,T_b^{\;0.79686} \times \Delta H_{vp}^{\text{o}\;0.16845} \times n_{\text{C}}^{\;-0.05948}. \tag{B.35}$$

Fujii-Hermann

Fujii and Hermann [83] found a strong relationship between the inverse of the flash point of organic compounds and the log of the vapor pressure (mm Hg) at 298 K:

$$\frac{1}{FP} = 2.996 + 0.324\log[P^*(298\text{ K})] + 0.074\log[P^*(298\text{ K})]^2. \tag{B.36}$$

Hshieh

Hshieh [85] correlated the closed-cup flash point of organic and silicon-containing compounds with the normal boiling point ($^{\circ}$C) and obtained

$$FP(^{\circ}\mathrm{C}) = a + bT_b + cT_b^{\,2}, \qquad \text{(B.37)}$$

where *a*, *b*, and *c* are -51.2385, 0.4994, and 0.00047, respectively, for silicon-containing compounds, and -54.5377, 0.5883, and 0.00022 for general organic compounds.

Ishiuchi

Ishiuchi [95] found that a stronger relationship with the normal boiling point existed when different parameters were used for associating compounds as opposed to non-associating compounds in the equation

$$FP = \left[T_b^{\,a} + b\left(\frac{\beta}{760}\right)^{-a} + c \right]^{1/a}, \qquad \text{(B.38)}$$

where *a*, *b*, and *c* are 0.105, 0.0570, and 0.142 for associating chemicals, and 0.119, 0.0656, and 0.185 for all other compounds.

Katritzky

Katritzky et al. [100-101] developed a three-parameter QSPR model:

$$FP = 0.72T_b + 76.99RNCG + 2.05HDCA - 8.40, \qquad \text{(B.39)}$$

where *RNCG* is the ratio of the absolute maximum atomic partial negative surface charge and the sum of similar negative charges in the molecule, and *HDCA* is the hydrogen donor charged solvent accessible surface area.

Korol'chenko

Korol'chenko [212] proposed another linear relationship between the flash point and boiling point, but with the addition of the bond contributions, *fp*, listed in Table B.15:

$$FP = 20 + 0.659T_b + \sum_i ng_i \cdot fp_i \; . \tag{B.40}$$

Table B.15. Bond contributions for flash point prediction using Equation B.40

i	Group	*fp_i*	*i*	Group	*fp_i*
1	C=C	1.72	11	C-Cl	15.11
2	C=O	11.06	12	C-Br	19.4
3	C=S	-11.91	13	N-H	5.83
4	C-C	-2.03	14	O-H	23.9
5	C-C (aromatic)	-0.28	15	P=O	9.64
6	C-H	1.105	16	P-O	3.27
7	C-N	14.15	17	S-H	5.64
8	C-O	2.47	18	Si-C	-4.84
9	C-S	2.09	19	Si-Cl	10.07
10	C-F	3.33	20	Si-H	11

Leslie-Geniesse

For a detailed discussion on the Leslie-Geniesse method, see Section 3.2.2.

Li-Moore

Li and Moore [84] suggested yet another linear relationship between the flash point of organic compounds and the normal boiling point:

$$FP = 57.6 + 0.64T_b\,. \tag{B.41}$$

The authors reported an average error of about 5 % for values predicted using this correlation.

Metcalfe

Metcalfe and Metcalfe [98] added the specific gravity (*sp. gr.*) of a compound to the classic linear relationship between the flash point (^{o}C) and normal boiling point (^{o}C):

$$FP = a + bT_b + c(sp.\ gr.)\,. \tag{B.42}$$

When the alcohol functional group R-OH is present, *a*, *b*, and *c* are -81.018, 0.5544, and 52.658, respectively; for all other compounds, *a*, *b* and *c* are -87.769, 0.6223, and 38.285, respectively.

Modified Thornton

Mack [82] modified the Thornton method of estimating the lower flammability limit to estimate the flash point:

$$\frac{P^*(FP)}{101.3\ \text{kPa}} = \frac{1}{1 + 4.76(2\beta - 1)}\,. \tag{B.43}$$

Möller

Möller [47] fit coefficients for the linear relationship between the normal boiling point (^{o}C) and the flash point for 42 different chemical classes:

$$FP(^{\circ}\mathrm{C}) = aT_b - b\,. \tag{B.44}$$

Coefficient values for this method are found in Table B.16.

Table B.16. Coefficients for flash point prediction using Equation B.44

Chemical Class	***a***	***b***	**Chemical Class**	***a***	***b***
Aliphatic acetates	0.6	49.4	Aromatic monoamines, primary	0.84	80
Aliphatic alcohols (halogen free)	0.6	37.8	Aromatic monoamines, tertiary	0.82	93
Aliphatic aldehydes	0.66	61.8	Aromatic monoesters	0.44	1.2
Aliphatic butyrates	0.62	50.8	Benzoles	0.68	68
Aliphatic carboxylic acid chlorides	0.6	43	Cyclohexanes	0.67	74.6
Aliphatic diamines	0.67	54.1	Di- and trichlorobenzenes	1.24	154
Aliphatic diethers (acetals/ketals)	0.78	70.9	Dialkanols	0.78	55
Aliphatic esters from valeric up	0.62	48.6	Dialkyl disulfides	0.66	59.2
Aliphatic formates	0.58	46	Dialkyl sulfides	0.71	72.9
Aliphatic hydrocarbons	0.68	73.3	Dichloroalkanes	0.61	44.6
Aliphatic monoamines	0.58	55.4	Epoxyalkanes	0.67	57
Aliphatic monocarboxylic acids (halogen free)	0.55	14.7	Isocyanates	0.96	111
Aliphatic monoethers	0.64	64	Monobromoalkanes	1.81	189.2
Aliphatic monoketones	0.62	55	Monochloroalkanes	0.69	68.6
Aliphatic mononitriles	0.83	72.4	Monochlorobenzoles	0.7	65.3
Alkenes, alkynes and dienes (halogen free)	0.71	74.3	Monofluorobenzoles	0.78	81.4
Alkoxyalcohols	0.73	55.6	Mononitro alkanes	0.74	48
Alkyl mercaptans	0.69	68.9	Mononitro aromatics	0.7	47
Amides	0.66	49.9	Naphthyls	0.69	72
Aminoalcohols	0.58	21	Phenols	0.64	36
Aminoethers	0.79	73	Phthalate esters	0.54	17

Oehley

Oehley [49] took a different approach to the relationship between the boiling point and flash point and obtained

$$FP = T_b - 18\sqrt{4(n_{\mathrm{C}} + n_{\mathrm{S}}) + n_{\mathrm{H}} + n_{\mathrm{N}} - 2(n_{\mathrm{O}} + n_{\mathrm{Cl}}) - 3n_{\mathrm{F}} - 5n_{\mathrm{Br}}}\,. \tag{B.45}$$

Pan

Pan [105] developed a method based on structural contributions, *x*, to estimate the flash point of alkanes,

$$FP = 175.234 + \sum_i ng_i x_i \ . \tag{B.46}$$

Table B.17 lists the structural groups for this method.

Table B.17. Structural contributions for flash point prediction using Equation B.46

i	Group	x_i	*i*	Group	x_i	*i*	Group	x_i
1	CH_3-CH_2-	9.180	4	-CH_2-CH_2-	17.194	7	>CH-CH<	20.660
2	CH_3-CH<	11.232	5	-CH_2-CH<	18.802	8	>CH-C<	24.413
3	CH_3-C<	9.796	6	-CH_2-C<	20.685	9	>C-C<	29.851

Patil

Patil [93] claimed that the flash point of all organic compounds could be accurately predicted using the correlation

$$FP = a + b + c \times 10^{-3} T_b^{\ 2} \ . \tag{B.47}$$

For acids, *a*, *b*, and *c* equal 314.0, -0.429, and 1.14, respectively; for alcohols, the coefficients are 241.7, -0.210, and 0.957, respectively; and for all other compounds *a*, *b*, and *c* are 4.656, 0.844, and -0.234.

Prugh

Prugh [97] developed a correlation of the form

$$FP = \frac{T_b}{a - b\ln(C_{\mathrm{st}})}, \tag{B.48}$$

where a and b are 1.3611 and 0.0697 for alcohols, and 1.442 and 0.08512 for other organic compounds.

Riazi-Daubert

Riazi and Daubert [91] found the flash point of pure hydrocarbons are correlated with the normal boiling point ($^{\mathrm{o}}$R) by

$$\frac{1}{FP(^{\circ}\mathrm{R})} = -0.014568 + \frac{2.84947}{T_b} + 1.903 \times 10^{-3}\ln(T_b). \tag{B.49}$$

Satyanarayana-Kakati

Satyanarayana and Kakati [88] originally used a linear relationship to estimate the flash point of hydrocarbons from the normal boiling point ($^{\mathrm{o}}$F),

$$FP(^{\circ}\mathrm{F}) = -124.81 + 0.69T_b. \tag{B.50a}$$

Later, they expanded this correlation [99] to apply to organic compounds by adding the specific gravity:

$$FP(^{\circ}\mathrm{C}) = -83.3362 + 0.5811T_b + \frac{0.1118\times10^{-3}}{T_b^{\;2}} + 38.734(sp.\,gr.)\,, \tag{B.50b}$$

when the normal boiling point is given in °C. Finally, a nonlinear correlation with the normal boiling point was developed [86, 94] with coefficients dependent on chemical class (Table B.18):

$$FP = a + \frac{b\left(\frac{c}{T_b}\right)^2 \exp\left(-\frac{c}{T_b}\right)}{\left(1-\exp\left(-\frac{c}{T_b}\right)\right)^2}\,, \tag{B.50c}$$

where temperatures are given in K.

Table B.18. Coefficients for flash point prediction using Equation B.50

Chemical Class	***a***	***b***	***c***
Hydrocarbons	225.1	537.6	2217
Alcohols	230.8	390.5	1780
Amines	222.4	416.6	1900
Acids	323.2	600.1	2970
Ethers	275.9	700	2879
Ketones	260.5	296	1908
Sulfur	238	577.9	2297
Esters	260.8	449.2	2217
Halogens	262.1	414	2154
Aldehydes	264.5	293	1970
Phosphorus	201.7	416.1	1666
Nitrogens	185.7	432	1645
Halogens	262.1	414	2154
Amines	222.4	416.6	1900
Silanes	218.767	668.2057	2281.015

Shebeko

Shebeko et al. [96] used the heat of combustion (kJ·mol^{-1}) to estimate the flash point:

$$FP(^{\circ}\mathrm{C}) = aT_b - b|\Delta H_{\mathrm{c}}|, \tag{B.51}$$

where the normal boiling is in °C, *a* is 0.79 for compounds with bromine atoms, 0.855 for compounds with chlorine atoms, and 0.833 for all other compounds. The coefficient *b* is likewise dependent on the presence of bromine (0.0147) and chorine (0.0114), and is 0.0082 for all other compounds.

Suzuki

Suzuki [102] developed the only known method for estimating the flash point of organic compounds based entirely on chemical structure. This method is discussed in detail in Section 3.2.2. Structural contributions are listed in Table B.19.

Table B.19. Structural contributions for Equation 3.3

Group	***h***	**Group**	***h***
C (aromatic)	3.1	-NH2	32.5
-O-	2.8	-NO2	41.3
-OH (phenols)	31.4	-SH	27.3
-OH (alcohols)	55.8	-S-	30.8
-COO-	13.3	-SO2-	102.3
>COOH	85.7	-NCS	57.9
-CHO	21.4	-CONH-	112.7
>C=O	25.3	-NCO	21.1
-CON<	41.3	F	-7.4
-CN	52.8	Cl	21.7
>N-(aliphatic)	6	Br	46.4
N (aromatic)	15.9	I	63
-NH	20.4		

Tetteh

Tetteh et al. [103] used neural networks to predict the flash point of organic compounds. Although they claimed excellent results, general implementation of neural network-based methods is not possible because it requires specialized software.

Wang-Sun

Wang and Sun [87] reported slightly different coefficients for estimating the flash point from the normal boiling point:

$$FP = 0.67465T_b + 33.176\,. \tag{B.52}$$

Zhokhova

Zhokhova [104] also used neural networks to predict the flash point of organic compounds. Again, implementation of such methods requires specialized software.

APPENDIX C. APPARATUS SPECIFICATIONS

ASHRAE Flammability Apparatus

Oven

An insulated chamber was constructed from 16-gage stainless steel sheet metal. Inside chamber dimensions were 51 cm × 57 cm × 51 cm high. To insulate the box, mineral wool 7.6 cm thick was set between the inner chamber and an outside steel covering. For safety purposes, a 31 cm × 23 cm panel of sheet metal was removed from the back of the oven, and reattached by tacking with a thin wire. An unexpected pressure rise would thus be vented out the back of the box, away from the operator.

The chamber door was insulated in the same manner as the steel box, with two panes of fire glass, 33 cm × 33 cm, set 7.6 cm from the top of the door for viewing flame propagation. A 90^o angle was painted on the glass with glow-in-the-dark paint, and during ignition the vertex of the angle was aligned with the ignition source to provide an unbiased interpretation of the extent of flame propagation. A 7.6 cm wide fiberglass gasket was fastened at the contact point of the chamber frame and the door to minimize heat loss. When shut, the door was secured by two latch clamps mounted on the side of the box.

The oven was heated using two 750 W, 9.5-mm diameter heating elements. Air inside the chamber was circulated by a 13 cm-diameter blower wheel, mounted through the back of the chamber (8 mm diameter shaft), and driven by an external motor (1550 RPM). The temperature was controlled using an Omega® CN7500 controller coupled with a K-type thermocouple positioned near the flask, about half the height of the chamber.

A 9.5 mm diameter hole was bored through the bottom of the box to accommodate a 11-mm diameter shaft attached to a circular magnet. The magnet was driven using an external motor mounted below the oven, the speed controlled by a variable autotransformer.

Another hole (7.6 cm diameter) was centered in the top of the box for the stopper assembly. On two sides of this opening were bolts, mounted with springs and wing nuts to hold the stopper assembly in place until ignition. An annular aluminum disk with notched wings transferred the pressure from the springs to the stopper.

Cover Assembly

A silicon-rubber stopper was used for the flask cover, with 6-mm ID glass tubing driven through it for the sample and air inlet, covered with a rubber septum. Additional glass tubing was driven through the stopper, 32 mm apart, to house 4-mm diameter welding electrodes, and the tubing was sealed on both ends with high-temperature silicon cement. The electrodes were threaded, and 1-mm diameter tungsten electrode wire, 2 cm long, was mounted to each electrode using No. 6 ring tongue terminals. The electrodes extended approximately 29 cm into the flask.

A 2-mm ID diameter stainless steel pipe was also driven through the rubber stopper, and connected to an Ashcroft digital pressure gage to determine the pressure inside the flask during evacuation. During tests, this line was isolated by closing a valve 10 cm from the stopper.

Two more holes, 3-mm diameter, were bored into the rubber stopper for the resistance temperature detectors to pass through.

Ignition Source

The ignition source consisted of a 15 kV (30 mA) neon transformer attached to the top-ends of the welding electrodes by solderless terminals. A custom interval timer was constructed (Figure C.1) using a 555 timer and a 5 A solid state relay to limit the duration of the load on the transformer to an adjustable time between 0.05 s and 0.55 s. For the lower flammability tests, the duration was set to 0.4 s, as calculated by

$$t = 1.1 R \cdot C \,, \tag{C.1}$$

where R is the resistance of R_1 in Figure C.1, adjusted by a 5 MΩ potentiometer, and C is the capacitance of C_1, 0.1 μF.

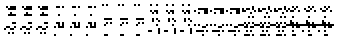

Figure C.1. Circuit diagram for ignition source interval timer

Vacuum Pump

Evacuation of the vessel was done using a Precision® vacuum pump, capable of displacing 25 ($L \cdot min^{-1}$), with a reported maximum vacuum capability of less than 0.01 Pa.

Flask

The vessel was a 12-L borosilicate round-bottom boiling flask, with a short ringed neck. The volume of the flask, 12.59 ± 0.01 L, was calibrated by weighing the flask and cover assembly empty and then full of water, repeated twice.

The flask was equipped with a magnetic stirrer, constructed by attaching a 6.35 cm bar magnet to a shaft that also held a thin 13 cm rectangle of aluminum with the edges twisted into fan blades. The magnetic stirrer was supported just above the flask bottom by an aluminum bar between the magnet and fan blades that extended to the flask walls (~14.6 cm). This stirrer assembly was driven by the round magnet through the bottom of the box.

An aluminum sleeve was used to lift the flask so that the neck of the flask extended through the hole in the top of the insulated chamber, and the lip of the flask was flush with the top of the oven. Electrical heating tape with the current through it controlled by a variable autotransformer was wrapped around the neck in the insulated region of the box to keep the fuel-air mixture in the neck the same temperature as the mixture in the body of the flask.

Resistance Temperature Detectors

Two platinum resistance temperature detectors (RTD) were used to determine the temperature inside the vessel, one positioned in the vessel neck, and the other at the vessel's midpoint. Electrical resistance (ohms) was output by a Keithley® 199 system scanner. The temperature was then calculated from the resistance, R_T, using

$$T(^{\circ}\mathrm{C}) = 0.0012\,R_T^{\;2} + 2.3172 R_T - 243.64\,, \tag{C.2}$$

which was regressed from the calibration curves provided by the manufacturer ($R^2 = 1.0$). The RTDs were further checked for calibration using a NIST-traceable thermometer, and were also compared with the reading from the K-type thermocouple (Figure C.2). Temperature measurements from the RTDs and the K-type thermocouple averaged between (0.6 and 0.7) °C above the NIST-traceable thermometer, but were remarkably consistent with one another.

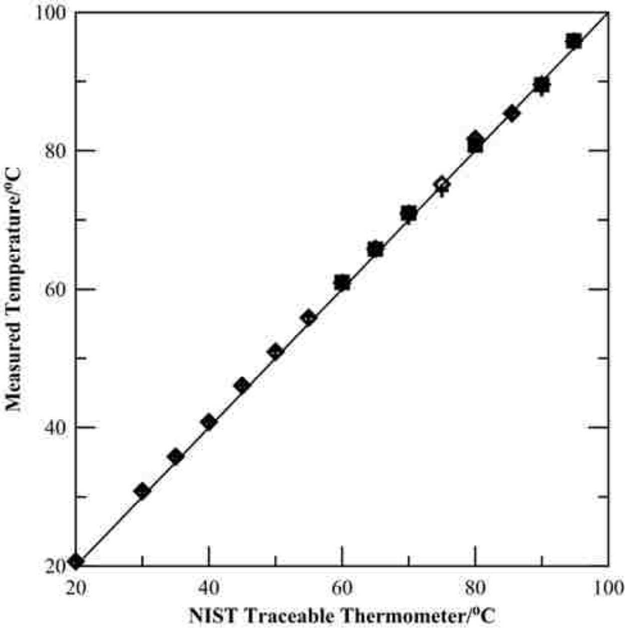

Figure C.2. Calibration curves for the RTDs (👓, +) and K-type thermocouple (■) against a NIST-traceable thermometer

Barometer

The barometric pressure of the lab was measured using a NIST-traceable PRINCO Instruments Fortin type mercurial barometer. The reading was corrected for temperature and gravity using tabulated correction factors supplied by the manufacturer. The reported accuracy of the barometer was ± 0.2 mm Hg (± 26.66 Pa).

Injection Syringe

To inject liquid samples into the flask, a glass 1.0 mL syringe mounted with a 26 gage, 2.54 cm needle was used. Because injections were into a vacuum, the syringe volume was calibrated to account for the extra sample drawn from the needle (Figure C.3). Calibration was performed by filling the syringe to a specified volume, then expunging the contents into a glass flask on a laboratory bench-top scale. The plunger was pumped vigorously several times to ensure all droplets were expelled from the needle. The weight of the sample was then calculated from the molecular weight and reported molar density at the lab temperature (using the molar density correlation from the DIPPR® 801 database), and the difference between the expected and actual volume was recorded. The average sample volume added by the needle was 0.032 mL.

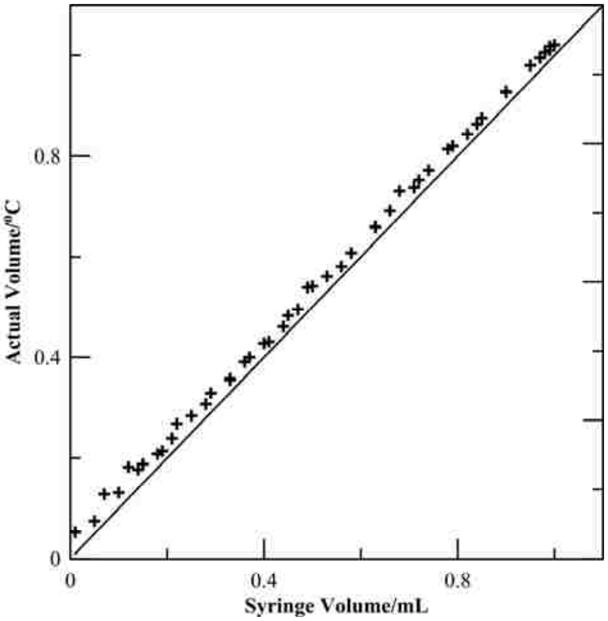

Figure C.3. Calibration curve for the syringe used to inject liquid sample into the flask

Pressure Correction

The lower temperature limit and flash point are both defined at 101.3 kPa. Because the measurements took place at high altitude, the observed values were corrected to 101.3 kPa using the vapor pressure equation found in DIPPR:

$$P^*(T) = \exp\left(a + \frac{b}{T} + c\ln(T) + d\,T^{e}\right)\text{Pa}\,, \tag{C.3}$$

where the coefficients depend on the chemical. When Equation C.3 is evaluated at the observed flash point, $FP_{\text{obs,}}$ and then at the corrected flash point, FP_{corr}, and 101.3 kPa and the two the resultant expressions are substracted, the expression

$$\ln\left(\frac{101.3\text{ kPa}}{P_{\text{lab}}}\right) = \left(b\left(\frac{1}{FP_{\text{corr}}} - \frac{1}{FP_{\text{obs}}}\right) + c\ln\left(\frac{FP_{\text{corr}}}{FP_{\text{obs}}}\right) + d\left(FP_{\text{corr}}^{\text{e}} - FP_{\text{obs}}^{6}\right)\right)\text{Pa} \tag{C.4}$$

is obtained, where P_{lab} is the barometric pressure at the time of measurement. Equation C.4 may be solved iteratively to find the flash point corrected to 101.3 kPa.

Flash Point Apparatuses

Cup Dimensions

Dimensions of the Penksy-Martens and small-scale test cups are given in Table C.1.

Table C.1. Dimensions of Flash Point Apparatuses

Dimension	**Pensky-Martens**	**Small-scale**
Diameter/cm	5.32	4.94
Height/cm	5.56	0.95
Volume/mL	123.36	18.26
Approximate Distance between Sample and Flame/cm	2.18	0.85/0.74

Thermometer Calibration

The manufacturers of the flash point apparatuses provided NIST-traceable thermometers. Consistency of the thermometers was confirmed by comparing the measured temperature of a liquid during heating (Figure C.4). Measurements from another NIST-traceable thermometer (mentioned in the section discussing calibration of the RTDs) were also compared.

The deviations seen in the small-scale measurements when compared with the 9C Pensky-Martens thermometer arise from the difference in precision. To obtain better precision, the temperatures of the small-scale flash points were recorded from the digital display on the apparatus, in ^{o}F, and not the NIST-traceable thermometer. Figure C.5 shows that the digital and mercurial temperature values were essentially the same.

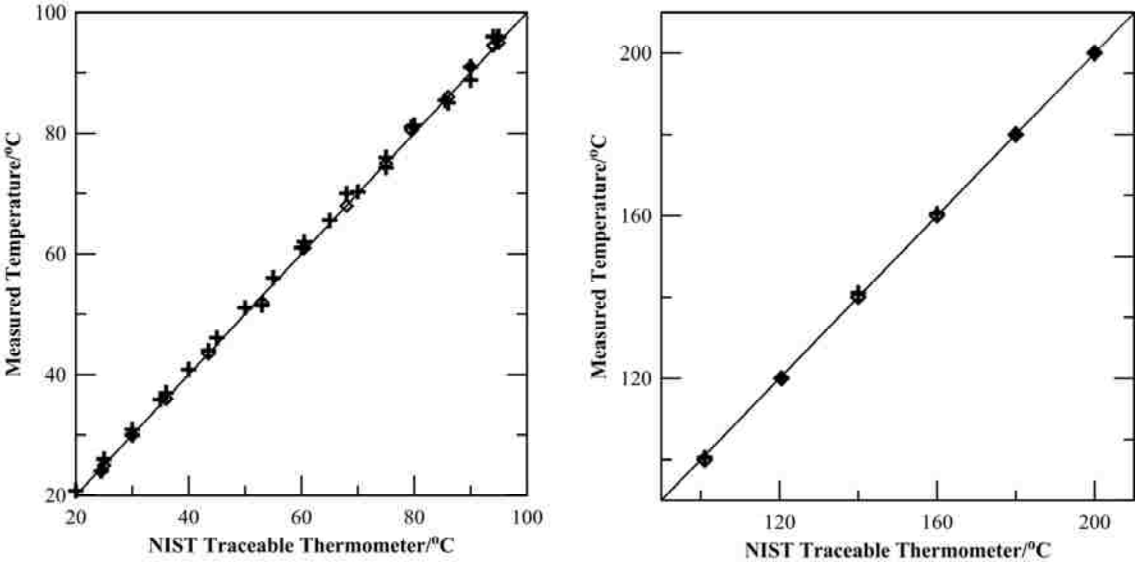

Figure C.4. Calibration curves for the 9C (left) and 10C (right) thermometers used with the Penksy-Martens apparatus (👓), and the thermometer used with the small-scale apparatus (+) against another NIST-traceable thermometer

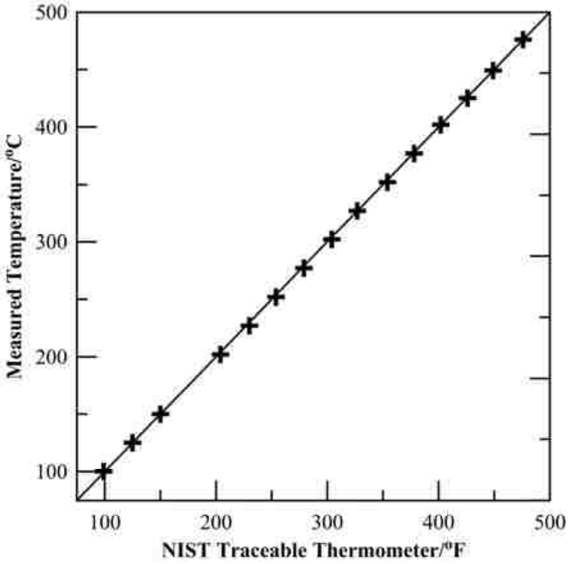

Figure C.5. Calibration curve for digital temperature reading of the small-scale apparatus against the NIST traceable thermometer provided by the manufacturer

APPENDIX D. EXPERIMENTAL RESULTS

Raw Data

Lower Flammability Limit

Table D.1. Raw lower flammability limit data

Corrected* V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T^o/K	T_{ave}/K	LFL /vol%
1-Hexyne									
0.422	No	653.7	8.67E-03	125.73	127.73	126.73	342.44	341.8	0.950
0.427	Go	653.2	8.67E-03	125.75	127.46	126.61	342.12	341.8	0.960
0.427	Go	653.2	8.67E-03	125.74	127.31	126.52	341.90	341.8	0.960
0.422	No	653.2	8.67E-03	125.69	127.09	126.39	341.55	341.8	0.948
0.427	Go	652.9	8.67E-03	125.73	127.01	126.37	341.50	341.8	0.959
0.422	No	652.9	8.67E-03	125.76	126.99	126.38	341.51	341.8	0.948
0.382	Go	651.8	8.67E-03	135.07	135.64	135.35	365.13	364.9	0.919
0.377	No	651.5	8.67E-03	135.08	135.82	135.45	365.39	364.9	0.908
0.382	Go	651.5	8.67E-03	134.98	135.35	135.17	364.64	364.9	0.919
0.377	No	651.1	8.67E-03	135.01	135.48	135.25	364.85	364.9	0.907
0.382	No	650.8	8.67E-03	134.98	135.33	135.15	364.61	364.9	0.919
0.387	Go	650.2	8.67E-03	135.00	135.47	135.24	364.82	364.9	0.932
0.267	Go	647.7	8.66E-03	166.03	166.50	166.26	447.94	448.0	0.792
0.262	No	647.4	8.66E-03	165.99	166.52	166.26	447.93	448.0	0.778
0.267	Go	647.3	8.66E-03	165.98	166.43	166.20	447.79	448.0	0.793
0.262	No	647.2	8.66E-03	165.97	166.32	166.14	447.62	448.0	0.778
0.267	Go	646.9	8.66E-03	165.98	166.79	166.39	448.28	448.0	0.794
0.262	No	646.6	8.66E-03	165.98	166.91	166.45	448.44	448.0	0.780
0.242	Go	646.5	8.67E-03	175.01	175.60	175.31	472.61	472.3	0.759
0.237	No	644.1	8.67E-03	174.94	175.43	175.19	472.28	472.3	0.746
0.242	Go	644.0	8.67E-03	174.93	175.43	175.18	472.26	472.3	0.762
0.237	No	643.5	8.66E-03	174.92	175.41	175.17	472.22	472.3	0.746
0.242	Go	643.5	8.66E-03	174.98	175.32	175.15	472.18	472.3	0.762
0.237	No	643.5	8.66E-03	174.94	175.46	175.20	472.31	472.3	0.746

*Includes the additional 0.032 mL added to correct for sample in syringe needle

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T°/K	T_{ave}/K	LFL /vol%
Phenetole									
0.432	No	632.2	7.86E-03	131.35	131.59	131.47	354.88	354.5	0.944
0.437	Go	632.1	7.86E-03	131.23	131.14	131.18	354.14	354.5	0.953
0.437	Go	632.1	7.86E-03	131.27	131.61	131.44	354.80	354.5	0.955
0.432	No	631.7	7.86E-03	131.20	131.20	131.20	354.18	354.5	0.943
0.437	Go	631.5	7.86E-03	131.18	131.32	131.25	354.31	354.5	0.955
0.432	No	631.3	7.86E-03	131.33	131.47	131.40	354.55	354.5	0.945
0.382	No	638.6	7.86E-03	140.87	141.63	141.25	380.76	379.0	0.887
0.387	Go	638.6	7.86E-03	140.63	140.10	140.36	378.40	379.0	0.893
0.382	No	639.0	7.86E-03	140.74	140.10	140.42	378.56	379.0	0.881
0.387	Go	639.0	7.86E-03	140.71	140.51	140.61	379.05	379.0	0.894
0.382	No	639.0	7.86E-03	140.68	140.29	140.48	378.72	379.0	0.882
0.387	Go	639.3	7.86E-03	140.68	140.32	140.50	378.77	379.0	0.893
0.277	Go	642.6	7.86E-03	168.35	168.18	168.26	453.38	453.3	0.761
0.272	No	642.6	7.86E-03	168.14	167.31	167.73	451.93	453.3	0.745
0.272	No	642.1	7.86E-03	168.39	168.28	168.33	453.57	453.3	0.748
0.277	Go	642.1	7.86E-03	168.44	168.59	168.51	454.07	453.3	0.763
0.272	No	642.1	7.86E-03	168.49	168.58	168.54	454.13	453.3	0.749
0.277	Go	642.1	7.86E-03	168.29	167.78	168.03	452.75	453.3	0.760
0.247	Go	639.1	7.86E-03	178.10	178.67	178.38	481.04	481.2	0.724
0.242	No	639.0	7.86E-03	178.31	178.18	178.24	480.66	481.2	0.709
0.247	Go	638.8	7.86E-03	178.02	178.12	178.07	480.18	481.2	0.723
0.242	No	638.6	7.86E-03	178.35	178.00	178.18	480.47	481.2	0.709
0.247	Go	638.6	7.86E-03	178.65	178.59	178.62	481.69	481.2	0.725
0.242	No	638.6	7.86E-03	178.59	179.88	179.24	483.39	481.2	0.713
4-Methyl-2-Pentanol									
0.552	Go	651.5	7.87E-03	127.54	127.54	127.54	344.57	344.6	1.138
0.547	No	651.5	7.87E-03	127.57	127.57	127.57	344.63	344.6	1.128
0.547	No	650.6	7.87E-03	127.52	127.52	127.52	344.51	344.6	1.129
0.552	Go	650.6	7.87E-03	127.53	127.53	127.53	344.55	344.6	1.140
0.547	No	650.6	7.87E-03	127.56	127.56	127.56	344.62	344.6	1.129
0.552	Go	650.3	7.87E-03	127.52	127.52	127.52	344.51	344.6	1.140
0.472	No	651.8	7.87E-03	138.67	138.67	138.67	373.91	373.9	1.055
0.477	Go	651.8	7.87E-03	138.67	138.67	138.67	373.90	373.9	1.067
0.472	No	651.8	7.87E-03	138.63	138.63	138.63	373.79	373.9	1.055
0.477	Go	651.8	7.87E-03	138.67	138.67	138.67	373.90	373.9	1.067
0.477	No	651.7	7.87E-03	138.67	138.67	138.67	373.92	373.9	1.067
0.482	Go	651.8	7.87E-03	138.59	138.59	138.59	373.71	373.9	1.077
0.392	No	648.2	7.86E-03	156.58	156.58	156.58	421.74	421.7	0.993
0.397	Go	648.2	7.86E-03	156.54	156.54	156.54	421.66	421.7	1.005
0.392	Go	647.8	7.87E-03	156.57	156.57	156.57	421.74	421.7	0.995
0.387	No	647.8	7.87E-03	156.62	156.62	156.62	421.85	421.7	0.982
0.392	Go	647.1	7.87E-03	156.55	156.55	156.55	421.68	421.7	0.996
0.387	No	647.1	7.87E-03	156.54	156.54	156.54	421.66	421.7	0.983
0.322	Go	646.5	7.87E-03	174.49	174.49	174.49	470.39	470.6	0.913
0.317	No	646.5	7.87E-03	174.57	174.57	174.57	470.60	470.6	0.899
0.322	Go	646.4	7.87E-03	174.58	174.58	174.58	470.61	470.6	0.914
0.317	No	646.1	7.87E-03	174.66	174.66	174.66	470.83	470.6	0.900
0.322	Go	646.0	7.87E-03	174.59	174.59	174.59	470.65	470.6	0.914
0.317	No	645.8	7.87E-03	174.57	174.57	174.57	470.59	470.6	0.900

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T°/K	T_{ave}/K	LFL /vol%
2-Methyl-1,3-Propanediol									
0.452	Go	646.0	1.12E-02	156.78	157.00	156.89	422.59	422.1	1.639
0.447	No	645.6	1.12E-02	156.69	156.65	156.67	422.00	422.1	1.619
0.452	No	645.6	1.12E-02	156.67	156.65	156.66	421.97	422.1	1.637
0.457	Go	645.3	1.12E-02	156.69	156.68	156.68	422.04	422.1	1.657
0.452	No	645.3	1.12E-02	156.68	156.75	156.71	422.12	422.1	1.639
0.457	Go	645.0	1.12E-02	156.69	156.71	156.70	422.08	422.1	1.658
0.402	No	639.7	1.12E-02	165.74	165.66	165.70	446.41	446.6	1.555
0.407	Go	639.7	1.12E-02	165.72	165.79	165.76	446.57	446.6	1.575
0.402	Go	639.2	1.12E-02	165.74	165.92	165.83	446.78	446.6	1.556
0.397	No	639.2	1.12E-02	165.74	165.83	165.78	446.64	446.6	1.536
0.372	No	647.1	1.12E-02	174.68	174.59	174.63	470.77	470.9	1.500
0.372	Go	647.0	1.12E-02	174.70	174.63	174.66	470.85	470.9	1.500
0.372	Go	647.1	1.12E-02	174.70	174.67	174.68	470.91	470.9	1.499
0.372	No	646.8	1.12E-02	174.74	174.72	174.73	471.02	470.9	1.500
0.372	No	646.6	1.12E-02	174.70	174.69	174.69	470.93	470.9	1.500
0.377	Go	646.6	1.12E-02	174.67	174.64	174.66	470.83	470.9	1.520
0.337	Go	645.7	1.12E-02	183.63	183.65	183.64	495.50	495.5	1.432
0.332	No	645.7	1.12E-02	183.63	183.59	183.61	495.42	495.5	1.411
0.342	Go	645.5	1.12E-02	183.64	183.60	183.62	495.45	495.5	1.454
0.337	No	645.5	1.12E-02	183.67	183.65	183.66	495.57	495.5	1.433
0.337	Go	645.5	1.12E-02	183.66	183.63	183.65	495.52	495.5	1.433
0.337	No	645.7	1.12E-02	183.67	183.64	183.65	495.54	495.5	1.432
Dibutylamine									
0.522	Go	645.5	5.87E-03	125.83	127.43	126.63	342.18	341.1	0.804
0.517	No	645.4	5.87E-03	125.77	127.05	126.41	341.60	341.1	0.795
0.522	No	645.4	5.87E-03	125.74	126.55	126.15	340.91	341.1	0.801
0.527	Go	645.4	5.87E-03	125.76	126.42	126.09	340.76	341.1	0.809
0.527	Go	645.4	5.87E-03	125.75	126.38	126.06	340.69	341.1	0.808
0.522	No	645.4	5.87E-03	125.77	126.21	125.99	340.49	341.1	0.800
0.442	Go	639.2	5.86E-03	135.13	136.37	135.75	366.18	365.1	0.735
0.437	No	639.3	5.86E-03	135.02	135.56	135.29	364.97	365.1	0.724
0.442	Go	639.2	5.86E-03	135.05	135.62	135.33	365.09	365.1	0.733
0.437	No	639.3	5.86E-03	135.02	135.47	135.24	364.84	365.1	0.724
0.442	No	639.3	5.86E-03	135.02	135.35	135.18	364.69	365.1	0.732
0.447	Go	639.6	5.86E-03	135.00	135.31	135.16	364.61	365.1	0.740
0.307	Go	650.0	5.86E-03	165.98	166.82	166.40	448.32	447.6	0.614
0.302	No	650.1	5.86E-03	165.88	166.20	166.04	447.35	447.6	0.603
0.307	Go	650.1	5.86E-03	165.85	166.01	165.93	447.03	447.6	0.613
0.302	No	650.1	5.86E-03	165.88	166.27	166.08	447.44	447.6	0.603
0.307	Go	650.0	5.86E-03	165.88	166.39	166.13	447.59	447.6	0.613
0.302	No	650.0	5.86E-03	165.90	166.44	166.17	447.69	447.6	0.604
0.272	No	648.5	5.86E-03	174.95	175.51	175.23	472.40	472.2	0.575
0.277	Go	648.5	5.86E-03	174.90	175.34	175.12	472.10	472.2	0.585
0.272	No	648.5	5.86E-03	174.92	175.42	175.17	472.24	472.2	0.575
0.277	Go	648.5	5.86E-03	174.87	175.30	175.08	472.00	472.2	0.585
0.277	Go	648.2	5.86E-03	174.93	175.48	175.21	472.34	472.2	0.586
0.272	No	648.2	5.86E-03	174.95	175.46	175.20	472.33	472.2	0.575

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T^o/K	T_{ave}/K	LFL /vol%
α-Pinene									
0.402	Go	645.1	6.30E-03	129.61	131.09	130.35	351.95	351.4	0.684
0.397	No	645.4	6.30E-03	129.51	130.37	129.94	350.86	351.4	0.673
0.407	Go	650.7	6.30E-03	129.56	130.52	130.04	351.13	351.4	0.685
0.402	No	650.2	6.30E-03	129.51	130.44	129.97	350.96	351.4	0.677
0.407	Go	650.3	6.30E-03	129.56	130.65	130.11	351.31	351.4	0.686
0.402	No	650.7	6.29E-03	129.64	131.10	130.37	352.00	351.4	0.678
0.362	Go	650.5	6.29E-03	139.55	138.81	139.18	375.26	373.9	0.651
0.357	No	650.5	6.30E-03	138.68	138.44	138.56	373.62	373.9	0.640
0.362	Go	650.6	6.29E-03	138.61	138.14	138.38	373.14	373.9	0.647
0.357	No	650.1	6.29E-03	138.71	138.60	138.65	373.87	373.9	0.640
0.362	Go	650.1	6.29E-03	138.69	138.71	138.70	373.99	373.9	0.649
0.357	No	650.1	6.29E-03	138.63	138.45	138.54	373.56	373.9	0.639
0.282	Go	639.6	6.29E-03	156.49	153.67	155.08	417.71	422.6	0.574
0.277	No	639.5	6.29E-03	156.91	158.64	157.77	424.98	422.6	0.574
0.282	Go	639.7	6.29E-03	156.78	157.34	157.06	423.04	422.6	0.581
0.277	No	639.7	6.29E-03	156.82	157.24	157.03	422.97	422.6	0.571
0.282	No	639.7	6.29E-03	156.88	158.28	157.58	424.45	422.6	0.583
0.287	Go	639.7	6.29E-03	156.78	156.88	156.83	422.43	422.6	0.591
0.222	No	639.7	6.29E-03	174.71	174.85	174.78	471.17	471.5	0.510
0.227	Go	639.8	6.29E-03	174.77	175.28	175.03	471.84	471.5	0.522
0.227	Go	640.5	6.29E-03	174.70	174.89	174.80	471.21	471.5	0.520
0.222	No	640.6	6.29E-03	174.75	175.23	174.99	471.74	471.5	0.509
2-Nonanone									
0.462	No	649.5	5.75E-03	139.00	140.79	139.90	377.17	375.7	0.764
0.467	Go	649.4	5.75E-03	138.90	139.98	139.44	375.95	375.7	0.770
0.462	No	651.0	5.75E-03	138.90	139.83	139.37	375.76	375.7	0.759
0.467	Go	651.0	5.75E-03	138.76	139.22	138.99	374.76	375.7	0.766
0.467	No	651.0	5.75E-03	138.81	139.49	139.15	375.18	375.7	0.766
0.472	Go	651.0	5.75E-03	138.79	139.68	139.24	375.42	375.7	0.775
0.412	Go	654.3	5.75E-03	148.02	149.05	148.54	400.18	399.9	0.718
0.407	No	654.2	5.75E-03	148.00	148.87	148.44	399.91	399.9	0.708
0.407	No	654.2	5.75E-03	147.96	148.80	148.38	399.75	399.9	0.708
0.412	Go	654.1	5.75E-03	147.97	148.77	148.37	399.72	399.9	0.717
0.412	Go	653.9	5.75E-03	148.02	148.81	148.41	399.84	399.9	0.717
0.407	No	653.9	5.75E-03	148.03	148.83	148.43	399.89	399.9	0.709
0.337	Go	651.9	5.75E-03	166.22	167.16	166.69	449.11	448.2	0.662
0.332	No	651.6	5.75E-03	166.19	166.24	166.21	447.81	448.2	0.650
0.337	Go	651.4	5.75E-03	166.15	166.28	166.21	447.81	448.2	0.660
0.332	No	651.4	5.75E-03	166.18	166.59	166.38	448.28	448.2	0.651
0.332	No	650.8	5.75E-03	166.20	166.55	166.37	448.24	448.2	0.651
0.337	Go	650.6	5.75E-03	166.18	166.51	166.34	448.17	448.2	0.661
0.327	Go	650.8	5.75E-03	175.33	175.10	175.21	472.36	472.6	0.676
0.322	No	650.8	5.75E-03	175.34	175.49	175.41	472.89	472.6	0.666
0.332	Go	650.8	5.75E-03	175.26	175.38	175.32	472.64	472.6	0.687
0.327	No	650.7	5.75E-03	175.29	175.36	175.33	472.67	472.6	0.676
0.332	Go	650.6	5.75E-03	175.30	175.30	175.30	472.59	472.6	0.687
0.327	No	650.6	5.75E-03	175.27	175.31	175.29	472.56	472.6	0.676
0.322	Go	640.8	5.75E-03	178.58	177.73	178.16	480.42	482.8	0.688
0.317	No	640.5	5.75E-03	178.74	180.96	179.85	485.07	482.8	0.684
0.312	Go	639.4	5.76E-03	182.18	183.74	182.96	493.64	492.8	0.687
0.307	No	638.8	5.76E-03	182.19	182.54	182.36	491.99	492.8	0.674

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T°/K	T_{ave}/K	LFL /vol%
Methyl Benzoate									
0.447	Go	636.7	7.97E-03	138.72	138.53	138.63	373.79	373.8	1.035
0.442	No	636.7	7.96E-03	138.67	138.22	138.44	373.31	373.8	1.022
0.447	No	636.6	7.96E-03	138.69	138.34	138.51	373.50	373.8	1.034
0.452	Go	636.3	7.96E-03	138.70	138.76	138.73	374.07	373.8	1.048
0.452	Go	636.0	7.96E-03	138.68	138.66	138.67	373.91	373.8	1.048
0.447	No	636.0	7.96E-03	138.68	139.04	138.86	374.42	373.8	1.038
0.392	Go	635.6	7.96E-03	147.49	147.97	147.73	398.02	398.6	0.968
0.387	No	635.5	7.96E-03	147.86	147.57	147.72	397.99	398.6	0.956
0.392	No	635.5	7.96E-03	147.95	148.03	147.99	398.71	398.6	0.970
0.397	Go	635.4	7.96E-03	147.94	148.50	148.22	399.33	398.6	0.984
0.392	Go	636.0	7.96E-03	147.94	148.31	148.12	399.07	398.6	0.970
0.387	No	636.0	7.96E-03	147.91	147.76	147.83	398.29	398.6	0.956
0.317	Go	642.6	7.96E-03	165.32	165.28	165.30	445.33	450.5	0.866
0.312	No	642.6	7.96E-03	165.99	164.92	165.45	445.75	450.5	0.853
0.317	Go	642.3	7.95E-03	165.92	166.83	166.38	448.26	450.5	0.871
0.312	No	642.5	7.95E-03	165.90	166.33	166.11	447.53	450.5	0.856
0.317	Go	642.5	7.95E-03	165.86	166.14	166.00	447.23	450.5	0.869
0.312	No	642.3	7.95E-03	165.86	166.22	166.04	447.33	450.5	0.856
0.282	Go	638.6	7.96E-03	174.95	175.27	175.11	472.07	472.1	0.822
0.277	No	638.6	7.96E-03	174.96	175.48	175.22	472.36	472.1	0.808
0.282	No	638.4	7.96E-03	174.99	175.87	175.43	472.95	472.1	0.824
0.287	Go	638.4	7.96E-03	174.89	174.88	174.88	471.45	472.1	0.836
0.282	Go	638.4	7.96E-03	174.89	174.90	174.90	471.48	472.1	0.821
0.277	No	638.4	7.96E-03	174.92	175.28	175.10	472.05	472.1	0.808
Decyl Acetate									
0.457	Go	651.5	4.31E-03	148.03	148.32	148.17	399.20	399.6	0.597
0.452	No	651.5	4.31E-03	148.03	148.34	148.18	399.23	399.6	0.591
0.457	Go	651.3	4.31E-03	148.08	148.38	148.23	399.36	399.6	0.598
0.452	No	651.3	4.31E-03	147.09	148.00	147.55	397.53	399.6	0.589
0.452	No	642.6	4.30E-03	148.18	149.23	148.70	400.62	399.6	0.601
0.457	Go	642.6	4.30E-03	148.10	149.02	148.56	400.25	399.6	0.607
0.452	Go	642.5	4.30E-03	148.08	148.97	148.52	400.13	399.6	0.600
0.447	No	642.5	4.30E-03	148.03	149.09	148.56	400.24	399.6	0.593
0.452	No	643.0	4.30E-03	148.04	149.00	148.52	400.14	399.6	0.599
0.457	Go	643.0	4.30E-03	147.99	148.72	148.36	399.69	399.6	0.605
0.397	Go	636.8	4.31E-03	157.19	158.09	157.64	424.62	423.6	0.565
0.392	No	636.7	4.31E-03	157.09	157.22	157.15	423.30	423.6	0.556
0.397	No	636.7	4.31E-03	157.17	157.96	157.56	424.41	423.6	0.564
0.402	Go	637.1	4.31E-03	156.99	157.70	157.35	423.82	423.6	0.570
0.397	Go	637.7	4.31E-03	156.98	157.77	157.37	423.89	423.6	0.563
0.392	No	637.7	4.31E-03	156.95	157.57	157.26	423.59	423.6	0.555
0.392	Go	645.5	4.30E-03	156.96	157.01	156.98	422.84	423.6	0.547
0.387	No	645.5	4.30E-03	157.03	157.62	157.32	423.76	423.6	0.541
0.392	No	645.1	4.30E-03	156.95	157.00	156.97	422.82	423.6	0.547
0.397	Go	645.0	4.30E-03	156.94	157.05	157.00	422.88	423.6	0.555
0.352	Go	649.7	4.31E-03	165.95	166.27	166.11	447.54	447.3	0.517
0.347	No	650.1	4.31E-03	165.85	165.66	165.76	446.57	447.3	0.508
0.352	Go	650.6	4.31E-03	165.83	165.80	165.81	446.73	447.3	0.515
0.347	No	650.6	4.31E-03	165.81	165.73	165.77	446.61	447.3	0.508

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T°/K	T_{ave}/K	LFL /vol%
Decyl Acetate (continued)									
0.352	Go	650.2	4.31E-03	165.83	165.85	165.84	446.79	447.3	0.516
0.347	No	650.0	4.31E-03	165.85	166.19	166.02	447.29	447.3	0.509
0.352	Go	644.9	4.30E-03	166.18	167.34	166.76	449.30	447.3	0.523
0.347	No	644.9	4.30E-03	166.12	166.37	166.25	447.91	447.3	0.514
0.352	No	644.9	4.30E-03	166.01	165.58	165.79	446.66	447.3	0.519
0.357	Go	644.9	4.30E-03	166.03	166.06	166.04	447.35	447.3	0.528
0.322	No	650.5	4.31E-03	174.88	175.13	175.01	471.79	471.6	0.498
0.327	Go	650.5	4.31E-03	174.82	174.99	174.91	471.52	471.6	0.505
0.322	No	652.8	4.31E-03	174.83	174.97	174.90	471.49	471.6	0.496
0.327	Go	652.6	4.31E-03	174.82	174.92	174.87	471.41	471.6	0.504
0.322	No	643.8	4.30E-03	175.08	174.96	175.02	471.83	471.6	0.503
0.327	Go	643.3	4.30E-03	175.05	174.83	174.94	471.61	471.6	0.511
0.322	No	637.1	4.31E-03	182.00	182.18	182.09	491.24	491.2	0.529
0.327	Go	637.0	4.31E-03	181.95	182.12	182.03	491.08	491.2	0.538
5-*o*-Tolyl-2-Pentene									
0.377	Go	638.0	5.93E-03	138.87	139.79	139.33	375.66	374.7	0.652
0.372	No	637.3	5.93E-03	138.78	139.35	139.07	374.97	374.7	0.643
0.372	No	637.3	5.93E-03	138.71	138.94	138.82	374.32	374.7	0.642
0.377	Go	637.3	5.93E-03	138.69	138.88	138.79	374.22	374.7	0.650
0.372	Go	636.6	5.93E-03	138.78	139.06	138.92	374.57	374.7	0.643
0.367	No	636.3	5.93E-03	138.71	138.88	138.80	374.24	374.7	0.634
0.272	No	637.7	5.93E-03	156.82	156.69	156.75	422.23	422.6	0.529
0.277	Go	637.7	5.93E-03	156.49	156.77	156.63	421.89	422.6	0.538
0.277	Go	637.5	5.93E-03	156.94	157.42	157.18	423.36	422.6	0.540
0.272	No	637.4	5.93E-03	156.92	157.27	157.09	423.14	422.6	0.530
0.277	No	637.0	5.93E-03	156.76	156.89	156.83	422.42	422.6	0.539
0.282	Go	637.2	5.93E-03	156.72	156.89	156.80	422.36	422.6	0.549
0.242	No	638.3	5.92E-03	165.76	165.78	165.77	446.61	446.8	0.497
0.247	Go	638.3	5.92E-03	165.81	165.84	165.82	446.76	446.8	0.507
0.242	No	638.4	5.92E-03	165.77	165.79	165.78	446.64	446.8	0.497
0.247	Go	638.4	5.92E-03	165.76	165.77	165.77	446.60	446.8	0.507
0.252	Go	638.3	5.92E-03	165.86	166.06	165.96	447.13	446.8	0.518
0.247	No	638.4	5.92E-03	165.82	166.03	165.92	447.02	446.8	0.507
0.222	No	643.0	5.93E-03	174.66	174.74	174.70	470.94	470.9	0.477
0.227	Go	643.0	5.93E-03	174.73	174.60	174.66	470.85	470.9	0.488
Isopropyl Myristate									
0.342	No	643.8	3.14E-03	166.32	167.62	166.97	449.88	449.7	0.372
0.347	Go	643.6	3.14E-03	166.13	168.37	167.25	450.62	449.7	0.378
0.347	No	643.3	3.14E-03	165.98	167.65	166.82	449.45	449.7	0.377
0.352	Go	642.9	3.14E-03	165.94	167.28	166.61	448.89	449.7	0.382
0.357	No	640.8	3.14E-03	165.62	166.23	165.92	447.02	446.0	0.388
0.362	Go	640.8	3.14E-03	165.62	165.75	165.69	446.38	446.0	0.392
0.362	Go	640.8	3.14E-03	165.69	164.75	165.22	445.12	446.0	0.391
0.357	No	640.8	3.14E-03	165.70	165.10	165.40	445.61	446.0	0.386
0.372	No	650.0	3.14E-03	174.67	174.67	174.67	470.88	470.9	0.419
0.377	Go	647.5	3.14E-03	174.70	174.70	174.70	470.95	470.9	0.426
0.377	No	646.8	3.14E-03	174.72	174.72	174.72	471.00	470.9	0.427
0.382	Go	646.3	3.14E-03	174.72	174.72	174.72	471.00	470.9	0.433
0.377	Go	646.1	3.14E-03	174.72	174.72	174.72	471.00	470.9	0.427
0.372	No	645.9	3.14E-03	174.62	174.62	174.62	470.74	470.9	0.421
0.372	No	640.8	3.14E-03	174.66	174.26	174.46	470.30	470.8	0.425

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T°/K	T_{ave}/K	LFL /vol%
Isopropyl Myristate (continued)									
0.377	Go	640.8	3.14E-03	174.71	174.89	174.80	471.21	470.8	0.432
0.322	Go	640.0	3.14E-03	183.76	183.56	183.66	495.57	495.7	0.388
0.317	No	639.7	3.14E-03	183.84	183.53	183.68	495.63	495.7	0.382
0.322	Go	639.1	3.14E-03	183.83	184.42	184.13	496.85	495.7	0.390
0.317	No	638.8	3.14E-03	183.78	183.13	183.46	495.00	495.7	0.382
0.317	Go	639.6	3.14E-03	183.83	183.90	183.86	496.13	495.7	0.383
0.312	No	639.1	3.14E-03	183.78	183.24	183.51	495.15	495.7	0.376
Methanol									
1.234	Go	641.5	2.47E-02	110.61	110.61	110.61	300.50	301.1	7.072
1.229	No	641.5	2.47E-02	110.10	110.10	110.10	299.17	301.1	7.012
1.229	Go	641.0	2.47E-02	111.15	111.15	111.15	301.88	301.1	7.081
1.224	No	641.0	2.47E-02	111.30	111.30	111.30	302.28	301.1	7.062
1.214	Go	639.3	2.47E-02	111.55	111.55	111.55	302.93	301.1	7.038
1.209	No	639.3	2.47E-02	110.34	110.34	110.34	299.81	301.1	6.937
1.064	No	641.1	2.47E-02	123.15	123.15	123.15	333.07	333.4	6.763
1.069	Go	641.1	2.47E-02	123.29	123.29	123.29	333.45	333.4	6.802
1.064	No	640.3	2.47E-02	123.29	123.29	123.29	333.43	333.4	6.779
1.069	Go	640.3	2.47E-02	123.28	123.28	123.28	333.42	333.4	6.810
1.064	No	640.2	2.47E-02	123.31	123.31	123.31	333.49	333.4	6.781
1.069	Go	640.2	2.47E-02	123.29	123.29	123.29	333.44	333.4	6.812
0.907	Go	640.2	2.47E-02	137.95	137.95	137.95	372.01	372.1	6.448
0.902	No	640.2	2.47E-02	138.05	138.05	138.05	372.27	372.1	6.417
0.912	Go	644.2	2.47E-02	138.05	138.05	138.05	372.27	372.1	6.448
0.907	No	644.6	2.47E-02	138.01	138.01	138.01	372.15	372.1	6.406
0.917	No	644.4	2.47E-02	138.03	138.03	138.03	372.21	372.1	6.480
0.912	Go	644.4	2.47E-02	138.03	138.03	138.03	372.23	372.1	6.445
0.907	Go	643.4	2.47E-02	137.94	137.94	137.94	371.97	372.1	6.415
0.902	No	643.4	2.47E-02	137.94	137.94	137.94	371.97	372.1	6.380
0.767	Go	643.4	2.47E-02	155.95	155.95	155.95	420.05	420.1	6.126
0.762	No	643.4	2.47E-02	155.99	155.99	155.99	420.18	420.1	6.088
0.762	Go	643.3	2.47E-02	155.94	155.94	155.94	420.04	420.1	6.087
0.757	No	643.3	2.47E-02	155.96	155.96	155.96	420.09	420.1	6.048
Butanol									
0.607	Go	645.8	1.09E-02	120.54	122.48	121.51	328.79	328.4	1.668
0.602	No	645.6	1.09E-02	120.53	122.70	121.62	329.07	328.4	1.657
0.607	Go	645.5	1.09E-02	120.41	122.41	121.41	328.52	328.4	1.668
0.602	No	645.0	1.09E-02	120.41	122.31	121.36	328.41	328.4	1.655
0.607	No	644.8	1.09E-02	120.36	121.76	121.06	327.61	328.4	1.665
0.612	Go	644.6	1.09E-02	120.43	121.87	121.15	327.85	328.4	1.681
0.507	Go	644.5	1.09E-02	137.53	137.56	137.55	370.93	371.5	1.575
0.502	No	644.5	1.09E-02	137.55	137.60	137.58	371.01	371.5	1.560
0.507	Go	644.5	1.09E-02	137.56	137.68	137.62	371.13	371.5	1.576
0.502	No	644.5	1.09E-02	137.49	137.58	137.54	370.91	371.5	1.560
0.502	Go	644.5	1.09E-02	137.61	137.62	137.62	371.12	371.5	1.561
0.497	No	644.5	1.09E-02	137.58	137.56	137.57	371.00	371.5	1.545
0.502	No	644.6	1.09E-02	138.13	138.60	138.37	373.10	371.5	1.569
0.507	Go	644.9	1.09E-02	137.99	138.57	138.28	372.88	371.5	1.583
0.422	Go	645.2	1.09E-02	156.43	156.51	156.47	421.46	421.5	1.488
0.417	No	645.2	1.09E-02	156.48	156.54	156.51	421.57	421.5	1.471
0.422	Go	644.7	1.09E-02	156.47	156.58	156.53	421.61	421.5	1.490

Table D.1. Continued

Corrected V_{inj}/mL	**Result**	**P_{lab} /(mm Hg)**	**ρ /(mol·mL^{-1})**	**RTD_1 /Ω**	**RTD_2 /Ω**	**RTD_{ave} /Ω**	**T^o/K**	**T_{ave}/K**	**LFL /vol%**
Butanol (continued)									
0.417	No	644.62	1.09E-02	156.50	156.55	156.53	421.61	421.5	1.472
0.422	Go	645.0	1.09E-02	156.44	156.53	156.49	421.50	421.5	1.489
0.417	No	644.7	1.09E-02	156.47	156.52	156.50	421.53	421.5	1.472
0.342	No	644.1	1.09E-02	174.19	174.57	174.38	470.07	470.2	1.348
0.347	Go	643.7	1.09E-02	174.33	174.48	174.41	470.14	470.2	1.368
0.342	Go	643.3	1.09E-02	174.42	174.48	174.45	470.26	470.2	1.350
0.337	No	642.7	1.09E-02	174.40	174.52	174.46	470.29	470.2	1.331
0.342	No	642.6	1.09E-02	174.41	174.53	174.47	470.32	470.2	1.351
0.347	Go	642.6	1.09E-02	174.40	174.53	174.47	470.31	470.2	1.371
1-Octanol									
0.442	No	640.4	6.36E-03	138.96	139.18	139.07	374.96	374.8	0.815
0.447	Go	639.9	6.36E-03	138.83	138.79	138.81	374.29	374.8	0.824
0.447	No	639.6	6.36E-03	138.83	139.11	138.97	374.71	374.8	0.825
0.452	Go	639.2	6.36E-03	138.88	139.53	139.20	375.33	374.8	0.836
0.447	Go	639.0	6.36E-03	138.91	139.73	139.32	375.64	374.8	0.828
0.442	No	638.8	6.36E-03	138.73	138.73	138.73	374.07	374.8	0.815
0.392	No	643.3	6.36E-03	148.09	146.82	147.45	397.28	398.2	0.763
0.397	Go	643.0	6.36E-03	148.18	147.64	147.91	398.50	398.2	0.775
0.392	No	642.8	6.36E-03	148.18	147.91	148.05	398.86	398.2	0.766
0.397	Go	642.6	6.36E-03	148.17	147.76	147.97	398.65	398.2	0.776
0.392	Go	642.6	6.36E-03	148.15	147.39	147.77	398.12	398.2	0.765
0.387	No	642.6	6.36E-03	148.11	147.09	147.60	397.66	398.2	0.754
0.292	No	640.2	6.36E-03	174.54	174.54	174.54	470.52	470.1	0.676
0.297	Go	639.7	6.36E-03	174.49	174.49	174.49	470.37	470.1	0.688
0.292	No	642.4	6.36E-03	174.10	174.10	174.10	469.30	470.1	0.672
0.297	Go	642.3	6.36E-03	174.23	174.23	174.23	469.65	470.1	0.684
0.292	No	643.3	6.36E-03	174.38	174.38	174.38	470.07	470.1	0.672
0.297	Go	643.6	6.36E-03	174.63	174.63	174.63	470.74	470.1	0.684
0.267	No	642.6	6.36E-03	181.78	181.78	181.78	490.38	489.9	0.642
0.272	Go	642.1	6.36E-03	181.38	181.38	181.38	489.28	489.9	0.653
0.277	Go	639.1	6.36E-03	181.63	181.63	181.63	489.98	489.9	0.669
0.272	No	641.9	6.36E-03	181.61	181.61	181.61	489.92	489.9	0.654
***n*-Hexyl Formate**									
0.567	No	647.5	6.72E-03	129.60	130.73	130.16	351.45	352.3	1.025
0.572	Go	647.5	6.72E-03	129.82	132.65	131.23	354.27	352.3	1.042
0.567	No	647.5	6.72E-03	129.67	130.98	130.32	351.87	352.3	1.026
0.572	Go	646.7	6.72E-03	129.53	130.47	130.00	351.02	352.3	1.034
0.572	Go	646.7	6.72E-03	129.66	131.73	130.70	352.86	352.3	1.039
0.567	No	646.6	6.72E-03	129.66	131.19	130.43	352.15	352.3	1.028
0.512	Go	646.4	6.72E-03	138.99	141.38	140.19	377.93	375.5	0.997
0.507	No	646.4	6.72E-03	138.77	138.70	138.73	374.08	375.5	0.977
0.507	Go	646.5	6.72E-03	138.82	139.10	138.96	374.68	375.5	0.978
0.502	No	646.5	6.72E-03	138.80	139.08	138.94	374.62	375.5	0.968
0.502	Go	643.6	6.72E-03	139.04	141.16	140.10	377.71	375.5	0.981
0.497	No	643.4	6.72E-03	138.78	138.88	138.83	374.33	375.5	0.963
0.497	No	643.4	6.72E-03	138.74	138.43	138.59	373.69	375.5	0.961
0.502	Go	643.4	6.72E-03	138.90	140.49	139.69	376.63	375.5	0.978
0.412	Go	651.3	6.73E-03	157.00	156.90	156.95	422.76	423.4	0.891
0.407	No	651.3	6.73E-03	157.21	160.41	158.81	427.76	423.4	0.890
0.407	No	651.3	6.72E-03	156.92	156.82	156.87	422.54	423.4	0.879

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T°/K	T_{ave}/K	LFL /vol%
***n*-Hexyl Formate (continued)**									
0.412	Go	651.3	6.72E-03	156.98	157.10	157.04	422.99	423.4	0.891
0.407	No	651.5	6.72E-03	156.93	156.77	156.85	422.48	423.4	0.879
0.412	Go	651.5	6.72E-03	156.96	156.48	156.72	422.13	423.4	0.889
0.342	Go	653.0	6.72E-03	175.04	174.91	174.98	471.70	472.4	0.822
0.337	No	652.8	6.72E-03	175.12	174.96	175.04	471.88	472.4	0.811
0.342	Go	652.6	6.72E-03	175.14	175.73	175.43	472.96	472.4	0.825
0.337	No	652.5	6.72E-03	175.10	175.75	175.43	472.93	472.4	0.813
***n*-Octyl Formate**									
0.492	Go	649.5	5.50E-03	138.86	139.91	139.39	375.81	376.4	0.776
0.487	No	649.4	5.50E-03	138.91	140.57	139.74	376.74	376.4	0.770
0.492	Go	648.2	5.50E-03	138.96	141.16	140.06	377.59	376.4	0.781
0.487	No	648.0	5.50E-03	138.81	140.21	139.51	376.14	376.4	0.770
0.492	No	647.6	5.50E-03	138.86	140.23	139.55	376.24	376.4	0.779
0.497	Go	647.6	5.50E-03	138.87	139.79	139.33	375.66	376.4	0.785
0.392	No	646.5	5.50E-03	157.00	156.04	156.52	421.59	423.2	0.696
0.397	Go	646.4	5.50E-03	157.02	157.73	157.37	423.90	423.2	0.709
0.392	Go	646.4	5.50E-03	157.04	157.60	157.32	423.76	423.2	0.700
0.387	No	646.1	5.50E-03	157.02	157.84	157.43	424.05	423.2	0.692
0.392	Go	646.3	5.50E-03	156.98	157.07	157.02	422.95	423.2	0.699
0.387	No	646.3	5.50E-03	157.02	157.18	157.10	423.15	423.2	0.690
0.312	No	648.2	5.50E-03	175.32	177.26	176.29	475.30	473.5	0.623
0.317	Go	648.2	5.50E-03	175.14	175.75	175.44	472.99	473.5	0.630
0.312	Go	648.0	5.50E-03	175.26	175.89	175.58	473.36	473.5	0.621
0.307	No	647.8	5.50E-03	175.14	176.36	175.75	473.83	473.5	0.612
0.312	Go	648.0	5.50E-03	175.18	175.67	175.42	472.93	473.5	0.620
0.307	No	647.6	5.50E-03	175.00	175.58	175.35	472.72	473.5	0.610
Diisobutyl Phthalate									
0.382	Go	644.9	3.73E-03	168.22	167.04	167.63	451.66	452.2	0.494
0.377	No	644.9	3.73E-03	167.79	168.14	167.96	452.57	452.2	0.489
0.382	No	644.7	3.73E-03	168.31	168.40	168.36	453.63	452.2	0.497
0.387	Go	644.6	3.73E-03	168.20	169.02	168.61	454.33	452.2	0.504
0.382	No	644.5	3.73E-03	168.05	165.25	166.65	448.99	452.2	0.492
0.387	Go	644.4	3.73E-03	168.06	167.24	167.65	451.71	452.2	0.501
0.327	Go	644.1	3.73E-03	175.26	172.72	173.99	469.01	472.5	0.440
0.322	No	644.0	3.73E-03	175.34	173.92	174.63	470.75	472.5	0.435
0.327	Go	643.8	3.73E-03	175.46	175.84	175.65	473.55	472.5	0.444
0.322	No	643.4	3.73E-03	175.31	176.76	176.04	474.61	472.5	0.439
0.327	Go	643.4	3.73E-03	175.28	176.43	175.85	474.11	472.5	0.445
0.322	No	643.3	3.73E-03	175.26	175.49	175.38	472.80	472.5	0.437
0.287	No	645.0	3.73E-03	182.41	182.95	182.68	492.86	493.1	0.405
0.292	Go	645.0	3.73E-03	182.40	183.06	182.73	493.01	493.1	0.412
0.292	No	645.2	3.73E-03	182.42	183.21	182.81	493.22	493.1	0.413
0.297	Go	645.3	3.73E-03	182.46	183.14	182.80	493.19	493.1	0.419
0.297	Go	645.1	3.73E-03	182.32	182.94	182.63	492.71	493.1	0.419
0.292	No	645.1	3.73E-03	182.32	183.42	182.87	493.39	493.1	0.413

Table D.1. Continued

Corrected V_{inj}/mL	Result	P_{lab} /(mm Hg)	ρ /(mol·mL^{-1})	RTD_1 /Ω	RTD_2 /Ω	RTD_{ave} /Ω	T^o/K	T_{ave}/K	LFL /vol%
Ethyl Lactate									
0.697	Go	643.9	8.68E-03	129.42	131.91	130.67	352.77	352.0	1.643
0.692	No	643.9	8.68E-03	129.41	131.71	130.56	352.50	352.0	1.629
0.697	Go	643.9	8.68E-03	129.34	129.72	129.53	349.79	352.0	1.629
0.692	No	643.7	8.68E-03	129.37	131.26	130.31	351.85	352.0	1.627
0.697	No	643.7	8.68E-03	129.38	131.72	130.55	352.47	352.0	1.642
0.702	Go	643.7	8.68E-03	129.41	131.90	130.65	352.74	352.0	1.655
0.622	Go	643.3	8.69E-03	138.68	139.07	138.87	374.44	374.2	1.559
0.617	No	643.3	8.69E-03	138.67	138.87	138.77	374.16	374.2	1.545
0.622	Go	643.3	8.69E-03	138.64	138.82	138.73	374.07	374.2	1.557
0.617	No	643.1	8.69E-03	138.67	139.13	138.90	374.51	374.2	1.547
0.622	Go	643.3	8.69E-03	138.64	138.89	138.76	374.16	374.2	1.558
0.617	No	642.7	8.69E-03	138.64	138.73	138.68	373.95	374.2	1.546
0.452	No	638.1	8.68E-03	165.97	166.98	166.47	448.52	446.6	1.367
0.457	Go	638.1	8.68E-03	165.85	165.04	165.44	445.72	446.6	1.373
0.452	No	637.9	8.68E-03	165.84	165.09	165.47	445.78	446.6	1.359
0.457	Go	637.7	8.68E-03	165.84	165.21	165.52	445.93	446.6	1.375
0.457	Go	637.4	8.68E-03	165.89	165.84	165.87	446.87	446.6	1.378
0.452	No	637.2	8.68E-03	165.87	165.87	165.87	446.87	446.6	1.363
0.412	Go	640.3	8.68E-03	174.93	174.91	174.92	471.55	471.4	1.305
0.407	No	640.1	8.68E-03	174.91	174.98	174.94	471.61	471.4	1.290
0.412	No	639.8	8.68E-03	174.87	174.73	174.80	471.22	471.4	1.305
0.417	Go	639.4	8.68E-03	174.88	174.68	174.78	471.17	471.4	1.321
0.412	Go	639.3	8.68E-03	174.87	174.82	174.85	471.35	471.4	1.306
0.407	No	639.1	8.68E-03	174.88	174.71	174.80	471.21	471.4	1.290

Lower Temperature Limit

Table D.2. Raw lower temperature limit data

RTD_1/Ω	RTD_2/Ω	P_{lab}/(mm Hg)	Result	Corrected T/K*
1-Octanol				
129.60	130.03	644.9	No	353.23
130.75	130.92	644.9	Go	353.81
129.82	129.98	644.9	No	352.63
130.42	130.68	644.9	Go	353.44
129.61	129.73	644.9	No	353.14
130.25	130.45	644.9	Go	353.42
129.95	130.11	644.6	No	352.49
130.25	130.44	644.3	Go	355.24
129.89	130.03	638.3	Go	354.46
129.17	129.31	638.1	No	352.73
129.75	129.76	650.8	No	352.10
130.17	130.19	650.6	Go	353.92
130.22	130.23	650.1	No	353.92
130.54	130.56	649.5	Go	353.07

*Reflects correction for pressure and RTD calibration

Table D.2. Continued

RTD_1/Ω	RTD_2/Ω	P_{lab}/(mm Hg)	Result	Corrected T/K*
2-Methyl-1,3-Propanediol				
142.67	142.73	650.4	No	386.98
142.96	142.97	650.4	Go	387.70
142.63	142.71	649.9	No	386.92
142.96	142.99	649.9	Go	387.74
142.57	142.29	640.7	No	386.81
142.49	143.23	640.5	Go	387.90
2-Nonanone				
124.60	124.12	652.5	Go	338.40
124.31	124.12	652.3	No	338.01
124.27	124.05	652.3	No	337.87
124.82	125.33	652.1	Go	340.33
124.71	124.65	651.9	Go	338.35
124.30	124.26	651.6	No	338.41
4-*iso*Propyl-*m*-cresol				
143.72	141.73	646.8	No	390.11
145.83	143.81	646.7	Go	395.85
145.20	142.96	646.5	No	394.13
145.56	144.82	646.2	Go	395.12
145.46	143.81	645.9	No	394.86
145.89	144.28	645.8	Go	396.04
144.27	143.91	644.9	Go	391.66
143.88	143.21	644.5	No	390.62
5-*o*-Tolyl-2-Pentene				
130.29	130.32	640.6	Go	354.72
130.14	130.19	640.6	No	350.74
130.36	130.41	640.6	No	354.93
130.75	130.80	640.6	Go	356.03
129.89	129.91	655.5	No	353.16
130.29	130.30	655.5	Go	354.21
Adamantane				
130.87	125.75	645.1	Go	355.63
130.69	128.13	644.9	No	355.16
130.97	129.38	644.5	No	355.92
131.27	130.60	644.3	Go	356.73
130.94	130.86	644.1	No	355.87
131.20	130.19	643.9	Go	356.56
131.23	130.01	643.7	Go	356.64
130.60	130.08	643.6	No	354.96
Butanol				
112.69	112.67	639.7	Go	307.78
112.64	112.60	639.5	No	307.62
112.69	112.57	639.3	Go	307.65
112.59	112.51	639.3	No	307.48
112.67	112.66	639.3	No	307.75
113.14	112.78	639.3	Go	308.52
112.90	112.66	639.3	Go	308.05
112.68	112.49	639.3	No	307.53
112.12	112.02	639.3	Go	306.44
112.00	112.01	639.3	No	306.17

Table D.2. Continued

RTD$_1$/Ω	RTD$_2$/Ω	P$_{lab}$/(mm Hg)	Result	Corrected T/K*
Diisobutyl Phthalate				
159.44	159.70	637.6	No	432.51
159.80	160.02	637.6	Go	433.47
159.47	159.70	637.3	No	432.57
159.74	160.03	637.3	Go	433.48
159.49	159.72	637.3	No	432.62
159.81	160.05	637.3	Go	433.43
Dodecanoic Acid				
158.27	157.63	640.5	No	428.84
159.03	157.37	640.8	Go	430.92
158.59	157.56	641.0	Go	429.71
158.40	157.23	641.5	No	429.17
158.78	157.45	641.6	Go	430.20
158.39	157.53	641.5	No	429.13
158.37	157.53	641.6	No	429.09
158.62	155.05	641.7	Go	429.76
Ethyl Lactate				
119.14	119.00	641.5	Go	324.84
118.77	118.73	641.5	No	323.98
119.18	119.13	641.1	Go	325.08
118.88	118.87	641.0	No	324.33
119.22	119.18	640.6	Go	325.21
118.93	118.90	640.4	No	324.45
Hexadecanol				
155.28	154.33	645.2	No	420.43
155.69	155.86	645.2	Go	421.54
155.25	154.33	644.8	Go	420.35
154.92	154.68	644.5	No	419.48
154.93	154.85	644.2	No	419.49
155.34	154.98	643.8	Go	420.61
155.27	155.06	643.6	No	420.44
155.62	155.39	643.6	Go	421.39
Methyl Benzoate				
152.19	152.19	640.6	No	412.38
152.53	152.46	640.1	Go	413.35
152.24	152.26	640.1	Go	412.57
151.93	151.94	639.7	No	411.71
151.88	151.88	638.8	Go	411.59
151.53	151.54	638.4	No	410.67
Decyl Acetate				
138.50	138.59	650.5	No	375.69
138.95	139.04	649.8	Go	376.93
138.58	138.70	649.5	No	375.96
139.00	139.09	649.3	Go	377.07
138.67	138.75	648.8	No	376.17
138.85	138.94	648.6	Go	376.68
Octyl Formate				
125.82	125.63	647.1	Go	342.33
215.53	125.40	646.9	No	341.64
125.89	125.98	646.3	Go	342.91
125.61	125.98	646.0	No	342.56
125.88	125.89	645.7	Go	342.81
125.56	125.67	645.5	No	342.10

Table D.2. Continued

RTD_1/Ω	RTD_2/Ω	P_{lab}/(mm Hg)	Result	Corrected T/K*
***p*-Cumylphenol**				
161.75	157.48	641.3	No	438.57
162.31	160.12	641.1	Go	440.14
161.95	159.69	641.1	No	439.13
162.38	160.19	641.0	Go	440.33
162.39	160.45	640.5	No	440.37
162.55	160.83	640.2	Go	440.83
162.39	160.88	640.0	Go	440.38
162.30	161.67	640.0	No	440.15
Phenetole				
118.45	118.45	638.9	No	323.19
118.50	118.50	638.9	Go	323.35
118.87	119.23	638.4	Go	324.36
118.46	119.18	638.4	No	323.23
118.83	118.02	638.4	Go	324.23
118.54	117.80	638.1	No	323.46
Hexadecanol				
154.44	153.08	645.8	Go	419.30
154.12	152.30	645.8	No	418.47
154.42	153.43	645.6	Go	419.63
154.13	153.48	645.5	No	418.45
154.55	155.34	645.2	Go	418.74
154.12	153.85	645.1	No	418.52
154.23	151.82	645.1	Go	419.30
154.15	154.52	645.1	No	418.41

Flash Point

Table D.3. Raw flash point data from the Pensky-Martens apparatus

P_{lab}/(mm Hg)	FP/°C	Corrected FP/K	P_{lab}/(mm Hg)	FP/°C	Corrected FP/K
1-Octanol			**4-Methyl-2-Pentanol**		
648.8	86	361.9	648.6	40	315.9
648.8	85	361.9	647.7	41	317.0
652	86	361.9	645.6	41	317.0
642.1	86	362.1	646.5	40	316.0
640.5	85	361.1	648.1	40	314.9
2-Methyl-1,3-Propanediol			**α-Pinene**		
646.5	120	396.6	651.0	30	305.9
645.6	121	397.6	650.7	29	304.9
647.5	122	398.6	649.8	27	302.9
647.2	122	398.6	647.2	30	306.0
648.5	119	395.5	645.2	29	305.0
648.5	118	394.5			
2-Nonanone			**Adamantane**		
651.6	69	345.2	653.2	70	345.8
650.5	70	346.3	653.4	69	344.8

Table D.3. Continued

P_{lab}/(mm Hg)	FP/°C	Corrected FP/K	P_{lab}/(mm Hg)	FP/°C	Corrected FP/K
Anthraquinone			**Butanol**		
643.4	210	487.2	644.3	35	310.7
642.4	206	483.1	645.1	34	309.7
642.4	214	491.3	644.7	35	310.7
646.6	212	489.1	644.5	35	310.7
642.2	208	484.3	648.3	35	310.7
Dibutylamine			**Diisobutyl Phthalate**		
650.3	39	314.9	656.1	169	445.5
650.7	38	313.9	642.2	172	448.8
650.8	40	315.9	645.7	171	447.7
641.9	38	314.1	648.7	173	449.7
644.2	40	316.1	648.8	170	446.6
Dodecanoic Acid			**Ethyl Lactate**		
653.3	166	442.3	646.6	57	333.7
645.8	166	442.5	644.8	55	331.7
640.2	164	440.7	652.6	57	333.5
638.0	165	441.8	652.0	54	330.5
648.5	161	437.4	648.8	56	332.2
Hexadecanol			**Hexyl Formate**		
650.0	172	448.5	644.5	44	320.1
649.2	166	442.4	644.6	43	319.1
645.2	170	446.6	645.8	44	320.1
644.8	171	447.6	645.1	43	319.1
647.7	172	448.5	648.6	44	320.0
Isopropyl Myristate			**Methyl Benzoate**		
654.1	158	434.4	656.1	77	353.2
655.0	158	434.3	651.9	77.5	353.8
653.5	154	430.3	651.7	77.5	353.7
651.0	154	430.4	633.6	77.5	354.3
Decyl Acetate			**Niacin**		
653.3	116	392.3	645.8	180	457.8
654.2	114	390.2	644.9	179	456.8
653.6	113	389.2	642.3	180	458.0
648.4	114	390.4	644.3	178	455.8
646.1	110	386.3	642.1	174	449.5
Octyl Formate			***p*-Cumylphenol**		
643.5	77	353.8	644.3	164	440.7
644.0	72	348.6	645.1	172	448.8
643.3	76	352.8	644.4	173	449.9
643.3	73	349.7	647.9	172	448.7
647.8	75	351.6	647.2	178	454.9
643.5	77	353.8	644.3	164	440.7
Succinic Anhydride			**Trimellitic Anhydride**		
647.0	148	424.4	640.8	302	581.2
646.7	144	420.3	643.2	302	581.0
646.5	156	432.6	641.8	294	572.9
645.5	156	433.6	645.4	294	572.8
645.5	156	433.6	643.5	300	575.9

Table D.3. Continued

P_{lab}/(mm Hg)	FP/°C	Corrected FP/K	P_{lab}/(mm Hg)	FP/°C	Corrected FP/K
Phenetole			**5-*o*-Tolyl-2-Pentene**		
645.2	52	328.2	651.2	87	364.3
646.7	52	328.2	651.0	88	365.3
646.2	51	327.1	651.0	86	363.4
645.3	52	328.2	**Urea**		
			649.1	120	395.4
			649.0	120	395.4

Table D.4. Raw flash point data from the small-scale apparatus

P_{lab}/(mm Hg)	Go/°F	No Go/°F	Corrected FP/K	P_{lab}/(mm Hg)	Go/°F	No Go/°F	Corrected FP/K
1-Octanol				**4-Methyl-2-Pentanol**			
646.5	184	183	360.1	648.6	106	105	316.8
643.9	186	185	360.7	645.6	106	105	316.8
633.4	183	182	359.9	647.5	107	106	317.4
635.7	182	181	359.3	647.5	108	107	317.9
648.6	181	180	358.4	648.5	107	106	317.3
2-Nonanone				**4-*iso*Propyl-*m*-cresol**			
652.8	158	157	345.9	645.2	239	238	391.5
651.4	157	156	345.4	646.7	243	242	393.7
646.6	157	156	345.5	646.2	242	241	393.1
646.6	156	155	345.0	646.0	236	235	389.7
Adamantane				**α-Pinene**			
648.9	185	184	360.7	648.6	91	90	308.5
648.9	185	184	360.7	648.6	90	89	307.9
643.3	183	182	360.0	648.6	90	89	307.9
642.4	184	183	360.6	648.6	90	89	307.9
640.6	184	183	360.6	646.1	90	89	308.0
Butanol				**Dibutylamine**			
644.3	99	98	312.7	642.4	106	105	317.0
645.4	99	98	312.7	642.3	106	105	317.0
645.1	99	98	312.7	642.3	107	106	317.6
645.0	101	100	313.8	641.9	106	105	317.0
644.9	100	99	313.3	642.7	105	104	316.4
Diisobutyl Phthalate				**Dodecanoic Acid**			
647.6	336	335	445.2	649.4	322	321	437.1
636.2	334	333	444.4	654.1	322	321	437.0
643.6	333	332	443.6	653.5	322	321	437.0
644.5	334	333	444.1	650.0	322	321	437.1
648.8	337	336	445.7	648.5	322	321	437.2
Ethyl Lactate				**Hexadecanol**			
651.6	130	129	330.3	645.2	333	332	443.5
651.5	132	131	331.4	646.4	332	331	442.9
651.4	132	131	331.4	646.5	332	331	442.9
651.4	133	132	332.0	646.1	331	330	442.3
648.8	129	128	329.8	648.2	333	332	443.3

Table D.4. Continued

P_{lab}/(mm Hg)	Go/^{o}F	No Go/^{o}F	Corrected FP/K	P_{lab}/(mm Hg)	Go/^{o}F	No Go/^{o}F	Corrected FP/K
Hexyl Formate				**Decyl Acetate**			
644.6	112	111	320.3	646.1	231	230	386.6
644.7	112	111	320.3	646.4	230	229	386.0
644.7	112	111	320.3	644.7	229	228	385.5
644.3	112	111	320.3	641.0	233	232	387.7
648.6	112	111	320.2	646.1	229	228	385.5
Isopropyl Myristate				**Methyl Benzoate**			
646.9	300	299	425.1	643.2	171	170	353.5
646.5	299	298	424.3	641.8	169	168	352.4
646.0	299	298	424.5	645.2	169	168	352.3
646.6	298	297	423.9	643.7	169	168	352.3
Niacin				**Octyl Formate**			
648.8	346	345	449.5	642.6	162	161	348.6
648.2	345	344	449.0	644.0	164	163	349.7
651.4	343	342	447.8	644.0	165	164	350.3
641.9	344	343	448.6	643.6	164	163	349.7
642.1	340	339	446.3	647.8	163	162	349.0
***p*-Cumylphenol**				**Phenetole**			
644.3	337	336	446.0	643.7	129	128	329.9
645.6	335	334	444.8	646.2	129	128	329.8
645.7	338	337	446.5	645.1	131	130	331.0
647.2	337	336	445.9	643.9	129	128	329.9
648.5	323	322	437.9	648.1	128	127	329.2
5-o-Tolyl-2-Pentene				**Anthraquinone**			
651.0	182	180	360.0	640.1	385	384	469.1
651.0	183	182	360.8	644.1	384	383	470.3
651.0	184	183	361.5	642.5	382	381	469.2
Succinic Anhydride				**Trimellitic Anhydride**			
648.0	298	297	424.7	645.2	472	471	523.3
647.7	298	297	424.8	653.2	473	472	522.8
646.0	297	296	424.2	651.7	474	473	522.1
647.3	298	297	424.8	652.5	475	474	521.9
2-Methyl-1,3-Propanediol				**Methanol**			
648.1	248	247	396.3	646.6	55	54	288.6
653.5	245	244	394.4	644.5	55	54	288.6
652.7	245	244	394.4	644.1	55	54	288.6
651.4	246	245	395.0	**Trioctylamine**			
648.5	239	238	391.1	653.3	336	335	444.5
648.5	240	239	392.0	648.4	337	336	445.2
				647.9	336	335	444.7
				647.1	333	332	443.0

Confidence Regions from Lower Flammability Limit Regression

Linear regressions of the lower flammability limits vs. temperature curves were performed in [R], a freeware statistical package. Multidimensional confidence regions for the regressed parameters are shown in Figures D.1-D.17 for each chemical.

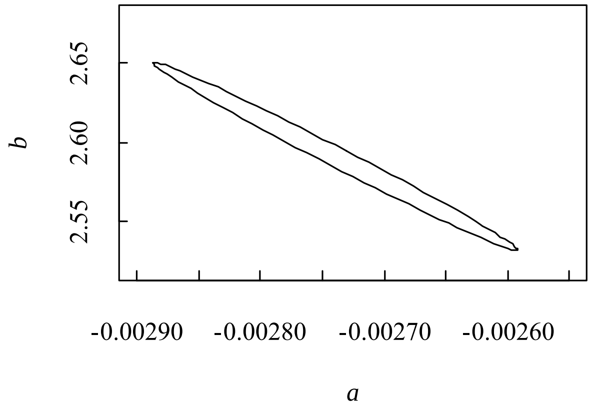

Figure D.1. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for ethyl lactate

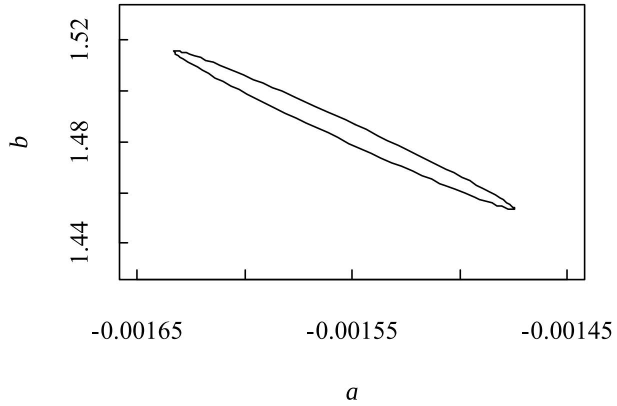

Figure D.2. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for 1-hexyne

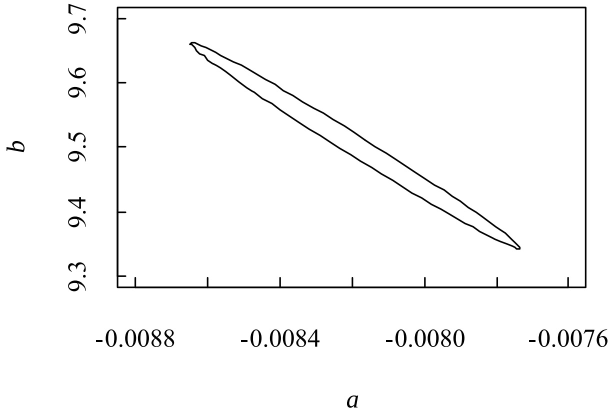

Figure D.3. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for methanol

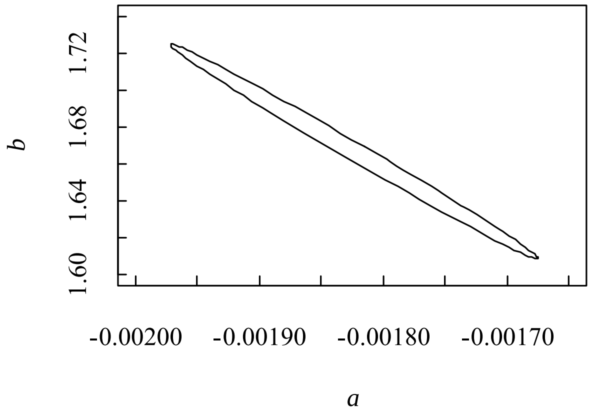

Figure D.4. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for hexyl formate

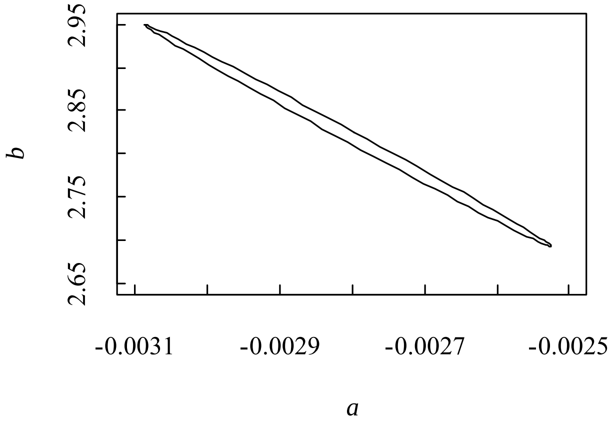

Figure D.5. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for 2-methyl-1,3-propanediol

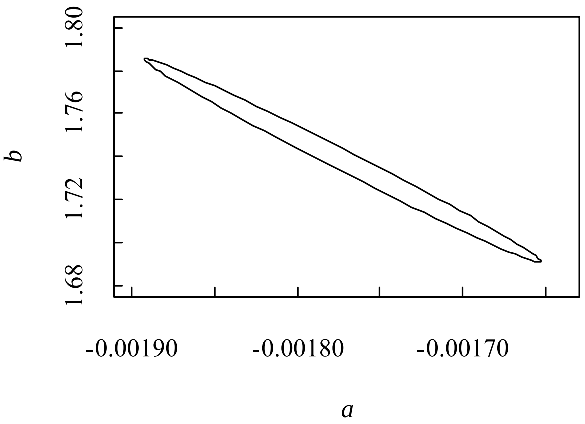

Figure D.6. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for 4-methyl-2-pentanol

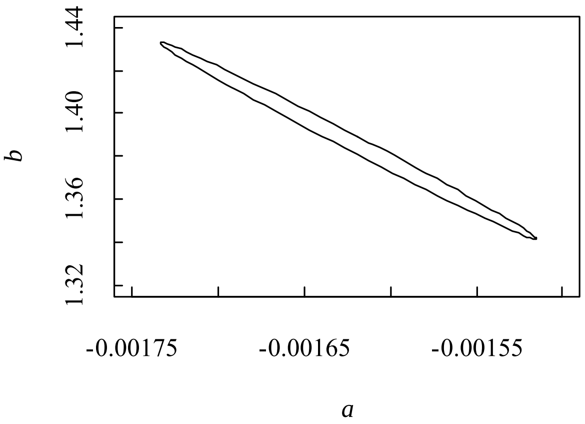

Figure D.7. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for octyl formate

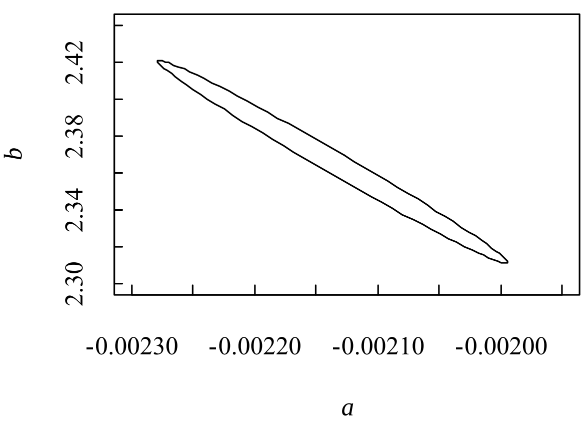

Figure D.8. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for methanol

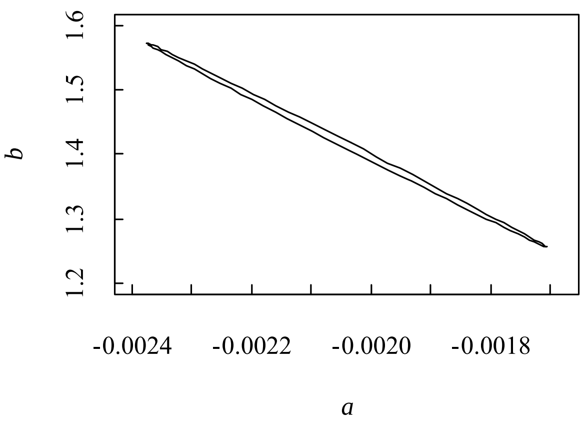

Figure D.9. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for diisobutyl phthalate

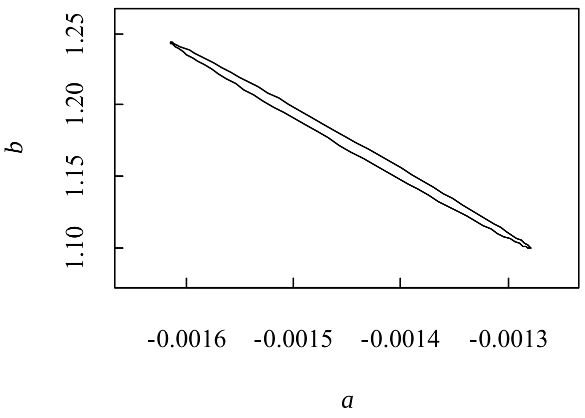

Figure D.10. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for decyl acetate

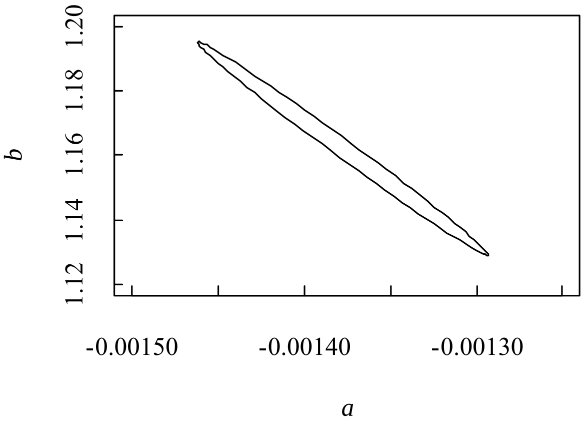

Figure D.11. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for α-pinene

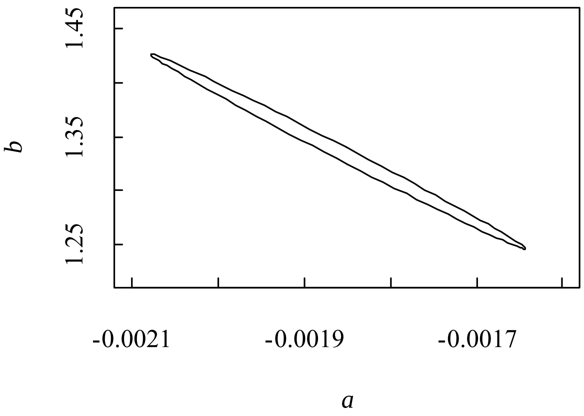

Figure D.12. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for 5-*o*-tolyl-2-pentene

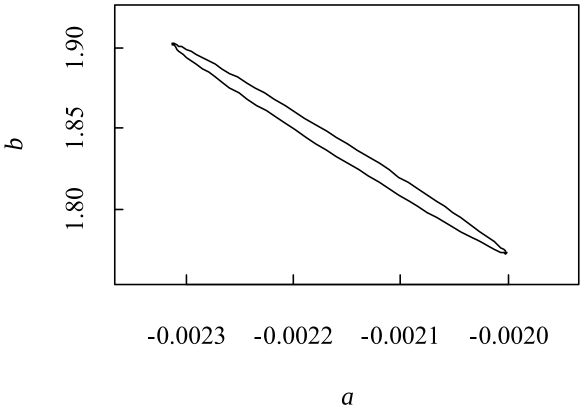

Figure D.13. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for methyl benzoate

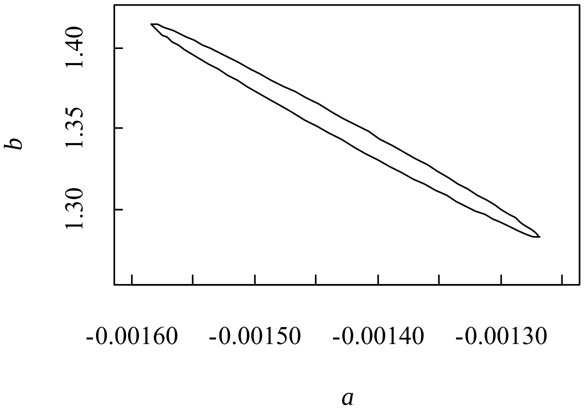

Figure D.14. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for 1-octanol

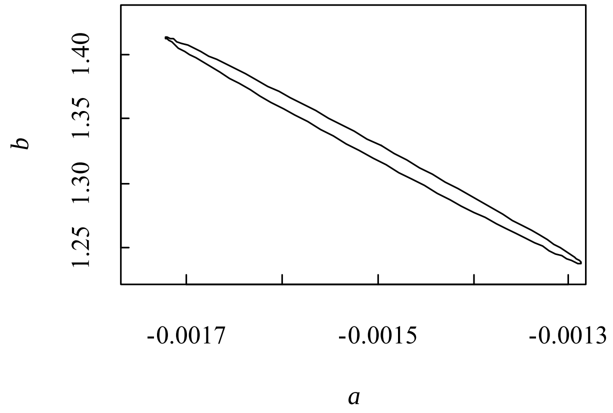

Figure D.15. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for 2-nonanone

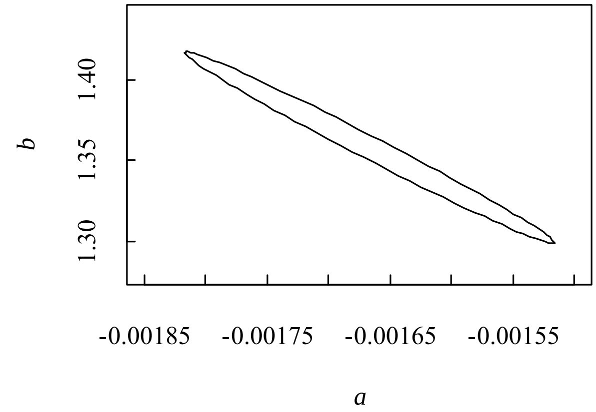

Figure D.16. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for dibutylamine

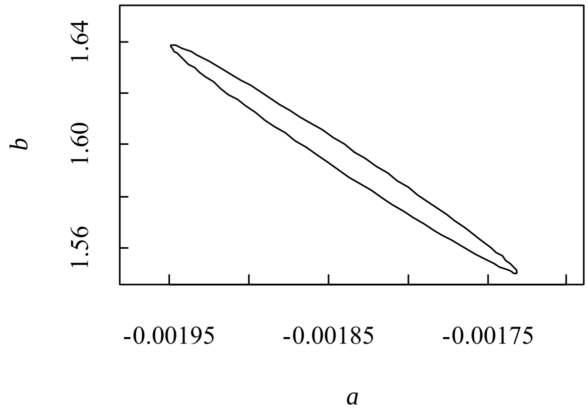

Figure D.17. Confidence region of slope (*a*) vs. intercept (*b*) of lower flammability limit data for phenetole

APPENDIX E. REGRESSION DATASETS

Table E.1. Training set of recommended lower flammability limit data

Name	Formula	LFL/vol%	Name	Formula	LFL/vol%
Methylacetylene	C_3H4	1.7	Methyl para-Toluate	$C_9H_{10}O_2$	1.0
Dimethylacetylene	C_4H_6	1.37	Dioctyl Phthalate	$C_{24}H_{38}O_4$	0.3
1-Dodecene	$C_{12}H_{24}$	0.4	Diisooctyl Phthalate	$C_{24}H_{38}O_4$	0.26
1-Heptene	C_7H_{14}	1.0	Diisobutyl Phthalate	$C_{16}H_{22}O_4$	0.53
Ethylene	C_2H_4	2.7	Methyl Benzoate	$C_8H_8O_2$	1.09
cis-2-Butene	C_4H_8	1.7	Ethyl Benzoate	$C_9H_{10}O_2$	1.0
trans-2-Butene	C_4H_8	1.7	Methyl Lactate	$C_4H_8O_3$	2.2
2-Methyl-1-Butene	C_5H_{10}	1.4	Diethylene Glycol Monobutyl Ether Acetate	$C_{10}H_{20}O_4$	0.76
4-Methyl-1-Pentene	C_6H_{12}	1.2	Propylene Glycol Monomethyl Ether Acetate	$C_6H_{12}O_3$	1.3
3-Methyl-1-Butene	C_5H_{10}	1.5	Ethyl Lactate	$C_5H_{10}O_3$	1.7
2-Methyl-2-Butene	C_5H_{10}	1.4	Ethyl Acetoacetate	$C_6H_{10}O_3$	1.4
Vinylcyclohexene	C_8H_{12}	0.98	Methyl Acetoacetate	$C_5H_8O_3$	1.8
d-Limonene	$C_{10}H_{16}$	0.75	2-Ethoxyethyl Acetate	$C_6H_{12}O_3$	1.2
1,3-Butadiene	C_4H_6	1.69	Ethyl-3-Ethoxypropionate	$C_7H_{14}O_3$	1.05
Methylcyclopentadiene	C_6H_8	1.3	Formic Acid	CH_2O_2	12.0
1,4-Hexadiene	C_6H_{10}	1.18	*n*-Hexanoic Acid	$C_6H_{12}O_2$	1.3
Propadiene	C_3H_4	2.2	*n*-Butyric Acid	$C_4H_8O_2$	2.0
n-Octane	C_8H_{18}	0.96	Methacrylic Acid	$C_4H_6O_2$	1.6
Propane	C_3H_8	2.1	*trans*-Crotonic Acid	$C_4H_6O_2$	2.2
n-Heptane	C_7H_{16}	1.05	Isovaleric Acid	$C_5H_{10}O_2$	1.4
n-Hexane	C_6H_{14}	1.2	Isobutyric Acid	$C_4H_8O_2$	2.0
n-Tetradecane	$C_{14}H_{30}$	0.5	2-Ethyl Hexanoic Acid	$C_8H_{16}O_2$	0.9
3-Methylpentane	C_6H_{14}	1.2	Acrylic Acid	$C_3H_4O_2$	2.4
Isopentane	C_5H_{12}	1.4	Cumene Hydroperoxide	$C_9H_{12}O_2$	0.9
Neopentane	C_5H_{12}	1.4	Carbon Disulfide	CS_2	1.3
2,2-Dimethylbutane	C_6H_{14}	1.2	Dimethyl Sulfide	C_2H_6S	2.2
2,3-Dimethylpentane	C_7H_{16}	1.1	Thiophene	C_4H_4S	1.5
2,2,3-Trimethylbutane	C_7H_{16}	1.0	Methyl Mercaptan	CH_4S	3.9
2,2,4-Trimethylpentane	C_8H_{18}	0.95	Ethyl Mercaptan	C_2H_6S	2.8
Cycloheptane	C_7H_{14}	1.1	*n*-Nonylamine	$C_9H_{21}N$	0.6
Cyclohexane	C_6H_{12}	1.3	*n*-Pentylamine	$C_5H_{13}N$	1.32
Cyclopentane	C_5H_{10}	1.5	Ethylamine	C_2H_7N	2.7
1,1-Diethylcyclohexane	$C_{10}H_{20}$	0.75	Methylamine	CH_5N	4.9
sec-Butylcyclohexane	$C_{10}H_{20}$	0.74	*n*-Octylamine	$C_8H_{19}N$	0.69
Bicyclohexyl	$C_{12}H_{22}$	0.65	Trimethylamine	C_3H_9N	2.0
trans-Decahydronaphthalene	$C_{10}H_{18}$	0.71	Tripropylamine	$C_9H_{21}N$	0.7

Table E.1. Continued

Name	Formula	LFL/vol%
Benzene	C_6H_6	1.2
Toluene	C_7H_8	1.1
Ethylbenzene	C_8H_{10}	1.0
1,2,4-Trimethylbenzene	C_9H_{12}	0.9
m-Xylene	C_8H_{10}	1.1
Cumene	C_9H_{12}	0.88
o-Xylene	C_8H_{10}	1.1
p-Cymene	$C_{10}H_{14}$	0.7
p-Diethylbenzene	$C_{10}H_{14}$	0.8
1,2,3-Trimethylbenzene	C_9H_{12}	0.8
5-*o*-Tolyl-2-Pentene	$C_{12}H_{16}$	0.68
m-Methylstyrene	C_9H_{10}	0.7
Styrene	C_8H_8	1.1
p-Methylstyrene	C_9H_{10}	0.8
Naphthalene	$C_{10}H_8$	0.88
1-Methylnaphthalene	$C_{11}H_{10}$	0.68
Anthracene	$C_{14}H_{10}$	0.6
Vinylnorbornene	C_9H_{12}	0.8
Butanol	$C_4H_{10}O$	1.7
1-Pentanol	$C_5H_{12}O$	1.4
Ethanol	C_2H_6O	3.3
1-Propanol	C_3H_8O	2.1
1-Nonanol	$C_9H_{20}O$	0.68
Isopropanol	C_3H_8O	2.2
2-Methyl-2-Propanol	$C_4H_{10}O$	1.84
2-Butanol	$C_4H_{10}O$	1.7
2-Methyl-1-Pentanol	$C_6H_{14}O$	1.1
3-Methyl-1-Butanol	$C_5H_{12}O$	1.2
3-Methyl-2-Butanol	$C_5H_{12}O$	1.2
4-Methyl-2-Pentanol	$C_6H_{14}O$	1.2
2-Octanol	$C_8H_{18}O$	0.8
2-Methyl-1-Propanol	$C_4H_{10}O$	1.7
2-Ethyl-1-Hexanol	$C_8H_{18}O$	0.88
2-Methyl-1-Butanol	$C_5H_{12}O$	1.4
2-Ethyl-1-Butanol	$C_6H_{14}O$	1.2
Cyclohexanol	$C_6H_{12}O$	1.2
2,6-Xylenol	$C_8H_{10}O$	1.4
Phenol	C_6H_6O	1.7
o-Cresol	C_7H_8O	1.3
Neopentyl Glycol	$C_5H_{12}O_2$	1.34
2-Butyne-1,4-Diol	$C_4H_6O_2$	1.88
Ethylene Glycol	$C_2H_6O_2$	3.1
Dipropylene Glycol	$C_6H_{14}O_3$	2.2
1,2-Propylene Glycol	$C_3H_8O_2$	2.6
1,3-Butanediol	$C_4H_{10}O_2$	1.8
Hexylene Glycol	$C_6H_{14}O_2$	1.0
1,4-Butanediol	$C_4H_{10}O_2$	1.8
Trimethylolpropane	$C_6H_{14}O_3$	1.3
tert-Butylamine	$C_4H_{11}N$	1.7
Dimethylamine	C_2H_7N	2.8
Isopropylamine	C_3H_9N	2.0
Di-*n*-Propylamine	$C_6H_{15}N$	0.87
N-Ethylaniline	$C_8H_{11}N$	1.6
Benzidine	$C_{12}H_{12}N_2$	1.4
Aniline	C_6H_7N	1.3
o-Phenylenediamine	$C_6H_8N_2$	1.5
o-Toluidine	C_7H_9N	1.5
3-Methylpyridine	C_6H_7N	1.3
Pyridine	C_5H_5N	1.8
p-Phenylenediamine	$C_6H_8N_2$	1.5
Cyclohexylamine	$C_6H_{13}N$	0.66
N-Methylpiperidine	$C_6H_{13}N$	0.9
3-(N,N-Dimethylamino) Propylamine	$C_5H_{14}N_2$	1.9
Hexamethylenediamine	$C_6H_{16}N_2$	0.7
Piperazine	$C_4H_{10}N_2$	4.0
Pyrrolidine	C_4H_9N	1.6
Allylamine	C_3H_7N	2.03
Ethylenediamine	$C_2H_8N_2$	2.5
1-Amino-2-Propanol	C_3H_9NO	1.9
N,N-Dimethylformamide	C_3H_7NO	2.3
2-Aminoethoxyethanol	$C_4H_{11}NO_2$	2.0
Dimethylethanolamine	$C_4H_{11}NO$	1.4
N,N-Dimethylacetamide	C_4H_9NO	1.8
Methyl Isocyanate	C_2H_3NO	5.3
n-Butyl Isocyanate	C_5H_9NO	1.3
1,6-Hexamethylene Diisocyanate	$C_8H_{12}N_2O_2$	0.9
n-Butyronitrile	C_4H_7N	1.57
Adiponitrile	$C_6H_8N_2$	1.0
Methylglutaronitrile	$C_6H_8N_2$	0.3
Propionitrile	C_3H_5N	3.1
cis-Crotonitrile	C_4H_5N	1.7
Benzonitrile	C_7H_5N	0.9
Cyanogen	C_2N_2	6.6
1-Nitropropane	$C_3H_7NO_2$	2.2
Nitroethane	$C_2H_5NO_2$	3.4
p-Nitrotoluene	$C_7H_7NO_2$	1.6
Nitromethane	CH_3NO_2	7.3
Dipropylene Glycol Monomethyl Ether	$C_7H_{16}O_3$	1.1
2-(2-Ethoxyethoxy)Ethanol	$C_6H_{14}O_3$	1.2
2-Butoxyethanol	$C_6H_{14}O_2$	1.1
1-Ethoxy-2-Propanol	$C_5H_{12}O_2$	1.3
Furfuryl Alcohol	$C_5H_6O_2$	1.8
Diacetone Alcohol	$C_6H_{12}O_2$	1.8
2-Ethoxyethanol	$C_4H_{10}O_2$	1.7
Dipropylene Glycol *n*-Propyl Ether	$C_9H_{20}O_3$	0.9
Propylene Glycol *n*-Butyl Ether	$C_7H_{16}O_2$	1.1

Table E.1. Continued

Name	Formula	LFL/vol%	Name	Formula	LFL/vol%
Triethylene Glycol	$C_6H_{14}O_4$	0.9	Tetrahydrofurfuryl Alcohol	$C_5H_{10}O_2$	1.5
2-Ethylhexanal	$C_8H_{16}O$	0.85	Diethylene Glycol Monopropyl Ether	$C_7H_{16}O_3$	0.85
Acrolein	C_3H_4O	2.8	Ethylene Glycol Monopropyl Ether	$C_5H_{12}O_2$	1.26
trans-Crotonaldehyde	C_4H_6O	2.1	N-Methyl-2-Pyrrolidone	C_5H_9NO	1.3
Butanal	C_4H_8O	1.9	4-(2-Aminoethyl) Morpholine	$C_6H_{14}N_2O$	1.3
Benzaldehyde	C_7H_6O	1.4	Acetone Cyanohydrin	C_4H_7NO	2.2
Acetaldehyde	C_2H_4O	4.0	2-Butoxime	C_4H_9NO	1.9
Pentanal	$C_5H_{10}O$	1.4	N-Ethyl-Morpholine	$C_6H_{13}NO$	1.0
Acetophenone	C_8H_8O	1.1	4-Formylmorpholine	$C_5H_9NO_2$	1.2
Acetylacetone	$C_5H_8O_2$	1.7	Cyclohexanone Oxime	$C_6H_{11}NO$	1.3
Methyl Ethyl Ketone	C_4H_8O	1.8	Dimethyl Sulfoxide	C_2H_6OS	2.6
Camphor	$C_{10}H_{16}O$	0.6	Benzoyl Chloride	C_7H_5ClO	1.2
2-Heptanone	$C_7H_{14}O$	1.1	Methyl Chloroacetate	$C_3H_5ClO_2$	4.0
Methyl Isopropenyl Ketone	C_5H_8O	1.8	Dichloroacetyl Chloride	C_2HCl_3O	11.9
Diketene	$C_4H_4O_2$	2.0	Di(2-chloroethyl)Ether	$C_4H_8Cl_2O$	2.0
2-Pentanone	$C_5H_{10}O$	1.55	Acetyl Chloride	C_2H_3ClO	7.3
5-Methyl-2-Hexanone	$C_7H_{14}O$	1.05	Methyl Chloroformate	$C_2H_3ClO_2$	6.7
Diisobutyl Ketone	$C_9H_{18}O$	0.8	*p*-Chloroaniline	C_6H_6ClN	2.2
2-Nonanone	$C_9H_{18}O$	0.82	1-Chloro-2,4-Dinitrobenzene	$C_6H_3ClN_2O_4$	2.0
n-Octyl Formate	$C_9H_{18}O_2$	0.83	*p*-Bromotoluene	C_7H_7Br	1.35
Isobutyl Formate	$C_5H_{10}O_2$	1.7	1-Bromobutane	C_4H_9Br	2.6
n-Butyl Formate	$C_5H_{10}O_2$	1.7	2-Bromopropane	C_3H_7Br	3.2
n-Propyl Formate	$C_4H_8O_2$	2.3	Bromoethane	C_2H_5Br	6.8
Ethyl Formate	$C_3H_6O_2$	2.76	Methyl Bromide	CH_3Br	10.1
1-Methylvinyl Acetate	$C_5H_8O_2$	1.6	Methyl Fluoride	CH_3F	7.1
n-Hexyl Acetate	$C_8H_{16}O_2$	0.9	1,1,2,2,3-Pentafluoropropane	$C_3H_3F_5$	7.7
Ethylene Glycol Diacetate	$C_6H_{10}O_4$	1.6	1,1,2-Trifluoroethane	$C_2H_3F_3$	6.2
Isopropyl Acetate	$C_5H_{10}O_2$	1.76	Ethyl Fluoride	C_2H_5F	3.15
Glyceryl Triacetate	$C_9H_{14}O_6$	1.1	1,1-Difluoroethane	$C_2H_4F_2$	4.35
n-Propyl Acetate	$C_5H_{10}O_2$	1.8	3,3,3-Trifluoropropene	$C_3H_3F_3$	4.7
Cyclohexyl Acetate	$C_8H_{14}O_2$	1.0	Methyl Iodide	CH_3I	8.5
Isopentyl Acetate	$C_7H_{14}O_2$	1.1	1-Chloro-1,1-Difluoroethane	$C_2H_3ClF_2$	6.8
Allyl Acetate	$C_5H_8O_2$	1.7	1,1-Dichloro-1-Fluoroethane	$C_2H_3Cl_2F$	9.0
2-Ethylhexyl Acetate	$C_{10}H_{20}O_2$	0.76	Chlorotrifluoroethylene	C_2ClF_3	8.4
Methyl Acetate	$C_3H_6O_2$	3.13	Isopropyl Chloride	C_3H_7Cl	2.8
Vinyl Acetate	$C_4H_6O_2$	2.6	2,3-Dichloropropene	$C_3H_4Cl_2$	2.6
Isobutyl Isobutyrate	$C_8H_{16}O_2$	0.96	3,4-Dichloro-1-Butene	$C_4H_6Cl_2$	2.5
Acetic Anhydride	$C_4H_6O_3$	2.7	2-Chloropropene	C_3H_5Cl	4.5
Phthalic Anhydride	$C_8H_4O_3$	1.2	*n*-Butyl Chloride	C_4H_9Cl	1.8
Butyric Anhydride	$C_8H_{14}O_3$	1.09	*n*-Propyl Chloride	C_3H_7Cl	2.6
Methyl Vinyl Ether	C_3H_6O	2.6	Chloroprene	C_4H_5Cl	2.5
Ethyl Vinyl Ether	C_4H_8O	1.67	1,1-Dichloropropane	$C_3H_6Cl_2$	3.1
Diisobutyl Ether	$C_8H_{18}O$	0.9	1,2-Dichloropropane	$C_3H_6Cl_2$	3.3
Ethyl Propyl Ether	$C_5H_{12}O$	1.7	*cis*-1,3-Dichloropropene	$C_3H_4Cl_2$	5.3
Di-*n*-Butyl Ether	$C_8H_{18}O$	0.9	1,4-Dichloro-*trans*-2-Butene	$C_4H_6Cl_2$	1.5
Methyl *tert*-Butyl ether	$C_5H_{12}O$	1.6	Isobutyl Chloride	C_4H_9Cl	2.0
Diethyl Ether	$C_4H_{10}O$	1.7	Benzyl Chloride	C_7H_7Cl	1.1
Paraldehyde	$C_6H_{12}O_3$	1.3	1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	2.5
Methylal	$C_3H_8O_2$	2.54	*o*-Chlorotoluene	C_7H_7Cl	1.3

Table E.1. Continued

Name	Formula	LFL/vol%	Name	Formula	LFL/vol%
1,2-Dimethoxyethane	$C_4H_{10}O_2$	1.6	*o*-Dichlorobenzene	$C_6H_4Cl_2$	2.2
Acetal	$C_6H_{14}O_2$	1.6	*trans*-1,2-Dichloroethylene	$C_2H_2Cl_2$	6.8
1,2-Epoxy-2-Methylpropane	C_4H_8O	1.5	1,1,2-Trichloroethane	$C_2H_3Cl_3$	6.8
1,2-Epoxybutane	C_4H_8O	1.7	Trichloroethylene	C_2HCl_3	12
1,3-Propylene Oxide	C_3H_6O	2.8	Dichloromethane	CH_2Cl_2	14
1,2-Propylene Oxide	C_3H_6O	2.2	Vinyl Chloride	C_2H_3Cl	3.6
Ethylene Oxide	C_2H_4O	3.0	1,1,1-Trichloroethane	$C_2H_3Cl_3$	7.5
1,4-Dioxane	$C_4H_8O_2$	2.0	1,2-Dichloroethane	$C_2H_4Cl_2$	4.5
Trioxane	$C_3H_6O_3$	3.6	Ethyl Chloride	C_2H_5Cl	3.8
Isobutyl Acrylate	$C_7H_{12}O_2$	1.2	1,1-Dichloroethane	$C_2H_4Cl_2$	5.4
Ethyl Acrylate	$C_5H_8O_2$	1.6	Hexamethyldisiloxane	$C_6H_{18}OSi_2$	0.8
n-Butyl Acrylate	$C_7H_{12}O_2$	1.2	Dichlorosilane	Cl_2H_2Si	4.7
Ethyl Methacrylate	$C_6H_{10}O_2$	1.8	Hexamethyldisilazane	$C_6H_{19}NSi_2$	0.8
2-Ethylhexyl Acrylate	$C_{11}H_{20}O_2$	0.7	Trichlorosilane	Cl_3HSi	7.0
Methyl Methacrylate	$C_5H_8O_2$	2.1	Dimethyldimethoxysilane	$C_4H_{12}O_2Si$	1.5
β-Propiolactone	$C_3H_4O_2$	2.9	Dichlorodiethylsilane	$C_4H_{10}Cl_2Si$	1.13
γ-Butyrolactone	$C_4H_6O_2$	2.1	Monochlorosilane	ClH_3Si	4.7
Di(2-ethylhexyl)adipate	$C_{22}H_{42}O_4$	0.4	Tris(2-Methoxyethoxy)Vinylsilane	$C_{11}H_{24}O_6Si$	2.0
Dimethyl Phthalate	$C_{10}H_{10}O_4$	0.9	Vinyltrichlorosilane	$C_2H_3Cl_3Si$	3.0
Diisodecyl Phthalate	$C_{28}H_{46}O_4$	0.27	Methyl Trichlorosilane	CH_3Cl_3Si	5.1
Di-*n*-Butyl Phthalate	$C_{16}H_{22}O_4$	0.5	Methyl Dichlorosilane	CH_4Cl_2Si	3.4
Benzyl Benzoate	$C_{14}H_{12}O_2$	0.69			

Table E.2. Test set of recommended lower flammability limit data

Name	Formula	LFL/vol%	Name	Formula	LFL/vol%
Vinylacetylene	C_4H_4	2.2	Diisopropyl Ether	$C_6H_{14}O$	1.0
Acetylene	C_2H_2	2.5	Methyl ethyl Ether	C_3H_8O	2.0
1-Hexyne	C_6H_{10}	1.1	Phenetole	$C_8H_{10}O$	1.0
1-Hexene	C_6H_{12}	1.2	Diphenyl Ether	$C_{12}H_{10}O$	0.8
1-Decene	$C_{10}H_{20}$	0.55	Anisole	C_7H_8O	1.2
1-Octene	C_8H_{16}	0.8	Tetrahydrofuran	C_4H_8O	2.0
1-Pentene	C_5H_{10}	1.4	Furan	C_4H_4O	2.0
1-Butene	C_4H_8	1.6	Methyl Acrylate	$C_4H_6O_2$	2.18
Propylene	C_3H_6	2.15	Dibutyl Sebacate	$C_{18}H_{34}O_4$	0.44
trans-2-Octene	C_8H_{16}	0.9	Dimethyl-1,4-Cyclohexanedicarboxylate	$C_{10}H_{16}O_4$	0.77
trans-2-Heptene	C_7H_{14}	1.0	Diethyl Phthalate	$C_{12}H_{14}O_4$	0.75
Isobutene	C_4H_8	1.8	Trioctyl Trimellitate	$C_{33}H_{54}O_6$	0.26
2-Methyl-1-Pentene	C_6H_{12}	1.2	Dimethyl Terephthalate	$C_{10}H_{10}O_4$	0.8
Cyclohexene	C_6H_{10}	1.2	2-Propanol-1-Methoxy-Propanoate	$C_7H_{14}O_3$	0.6
α-Pinene	$C_{10}H_{16}$	0.74	Ethylene Glycol Monobutyl Ether Acetate	$C_8H_{16}O_3$	0.88
1,2-Butadiene	C_4H_6	1.6	2-Hydroxyethyl Acrylate	$C_5H_8O_3$	1.8
Dicyclopentadiene	$C_{10}H_{12}$	0.8	Diethylene Glycol Ethyl Ether Acetate	$C_8H_{16}O_4$	0.98
Isoprene	C_5H_8	1.5	*n*-Pentanoic Acid	$C_5H_{10}O_2$	1.6

Table E.2. Continued

Name	Formula	LFL/vol%	Name	Formula	LFL/vol%
n-Dodecane	$C_{12}H_{26}$	0.6	Propionic Acid	$C_3H_6O_2$	2.9
Ethane	C_2H_6	3.0	Acetic Acid	$C_2H_4O_2$	4.0
n-Nonane	C_9H_{20}	0.85	Salicylic Acid	$C_7H_6O_3$	1.1
n-Decane	$C_{10}H_{22}$	0.75	Adipic Acid	$C_6H_{10}O_4$	1.6
n-Tridecane	$C_{13}H_{28}$	0.55	Di-*t*-Butyl Peroxide	$C_8H_{18}O_2$	0.74
n-Pentane	C_5H_{12}	1.4	Tetrahydrothiophene	C_4H_8S	1.1
n-Butane	C_4H_{10}	1.6	*n*-Butylamine	$C_4H_{11}N$	1.7
Methane	CH_4	5.0	*n*-Propylamine	C_3H_9N	2.0
2-Methylpentane	C_6H_{14}	1.2	Diisopropylamine	$C_6H_{15}N$	1.1
2-Methylhexane	C_7H_{16}	1.0	Di-*n*-Butylamine	$C_8H_{19}N$	0.84
Isobutane	C_4H_{10}	1.8	Triethylamine	$C_6H_{15}N$	1.2
2,3-Dimethylbutane	C_6H_{14}	1.2	Tri-*n*-Butylamine	$C_{12}H_{27}N$	0.44
3,3-Diethylpentane	C_9H_{20}	0.7	Diethylamine	$C_4H_{11}N$	1.7
2,2,3,3-Tetramethylpentane	C_9H_{20}	0.8	2-Methylpyridine	C_6H_7N	1.4
Cyclopropane	C_3H_6	2.4	N,N-Dimethylaniline	$C_8H_{11}N$	1.2
Cyclobutane	C_4H_8	1.8	Quinoline	C_9H_7N	1.2
Methylcyclohexane	C_7H_{14}	1.15	4-Methylpyridine	C_6H_7N	1.3
Ethylcyclohexane	C_8H_{16}	0.95	*p*-Toluidine	C_7H_9N	1.1
Ethylcyclopentane	C_7H_{14}	1.1	Hexamethyleneimine	$C_6H_{13}N$	1.58
n-Propylcyclopentane	C_8H_{16}	0.95	Diethylenetriamine	$C_4H_{13}N_3$	2.0
cis-Decahydronaphthalene	$C_{10}H_{18}$	0.71	Tetramethylethylenediamine	$C_6H_{16}N_2$	1.0
n-Butylbenzene	$C_{10}H_{14}$	0.8	Pyrrole	C_4H_5N	2.0
n-Propylbenzene	C_9H_{12}	0.88	Ethyleneimine	C_2H_5N	3.6
Mesitylene	C_9H_{12}	0.88	Diallylamine	$C_6H_{11}N$	0.93
p-Xylene	C_8H_{10}	1.1	Monoethanolamine	C_2H_7NO	3.0
sec-Butylbenzene	$C_{10}H_{14}$	0.8	Diethanolamine	$C_4H_{11}NO_2$	1.7
Isobutylbenzene	$C_{10}H_{14}$	0.8	N-Methylformamide	C_2H_5NO	3.8
tert-Butylbenzene	$C_{10}H_{14}$	0.8	Diethylethanolamine	$C_6H_{15}NO$	1.4
α-Methylstyrene	C_9H_{10}	0.9	2,4-Toluene Diisocyanate	$C_9H_6N_2O_2$	0.9
m-Divinylbenzene	$C_{10}H_{10}$	0.3	Acrylonitrile	C_3H_3N	3.05
1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	0.84	Methacrylonitrile	C_4H_5N	1.89
Biphenyl	$C_{12}H_{10}$	0.7	*trans*-Crotonitrile	C_4H_5N	1.7
1-Decanol	$C_{10}H_{22}O$	0.6	Isobutyronitrile	C_4H_7N	1.57
1-Hexanol	$C_6H_{14}O$	1.2	Hydrogen Cyanide	CHN	5.6
Methanol	CH_4O	7.18	Acetonitrile	C_2H_3N	3
1-Octanol	$C_8H_{18}O$	0.84	Hydracrylonitrile	C_3H_5NO	2.3
2-Pentanol	$C_5H_{12}O$	1.2	3-Methoxypropionitrile	C_4H_7NO	1.9
2-Methyl-2-Butanol	$C_5H_{12}O$	1.3	*o*-Nitrotoluene	$C_7H_7NO_2$	2.2
2,6-Dimethyl-4-Heptanol	$C_9H_{20}O$	0.7	2-Nitropropane	$C_3H_7NO_2$	2.5
α-Terpineol	$C_{10}H_{18}O$	0.5	Propylene Glycol Monomethyl Ether	$C_4H_{10}O_2$	1.9
3-Pentanol	$C_5H_{12}O$	1.2	2-(2-Methoxyethoxy)Ethanol	$C_5H_{12}O_3$	1.38
Allyl Alcohol	C_3H_6O	2.5	Propylene Glycol 1-*tert*-Butyl Ether	$C_7H_{16}O_2$	1.7
Propargyl Alcohol	C_3H_4O	2.4	2-Methoxyethanol	$C_3H_8O_2$	2.4
2,2-Dimethyl-1-Propanol	$C_5H_{12}O$	1.2	Furfural	$C_5H_4O_2$	2.1
1-Methylcyclohexanol	$C_7H_{14}O$	1.0	2-(2-Butoxyethoxy)Ethanol	$C_8H_{18}O_3$	0.85

Table E.2. Continued

Name	Formula	LFL/vol%	Name	Formula	LFL/vol%
p-Cresol	C_7H_8O	1.1	Dipropylene Glycol *n*-Butyl Ether	$C_{10}H_{22}O_3$	0.6
m-Cresol	C_7H_8O	1.1	ε-Caprolactam	$C_6H_{11}NO$	1.4
2-Methyl-1,3-Propanediol	$C_4H_{10}O_2$	1.73	Morpholine	C_4H_9NO	1.67
1,3-Propylene Glycol	$C_3H_8O_2$	2.6	2-Mercaptoethanol	C_2H_6OS	2.3
Diethylene Glycol	$C_4H_{10}O_3$	1.7	Chloroacetic Acid	$C_2H_3ClO_2$	8.0
Glycerol	$C_3H_8O_3$	2.6	2-Chloroethanol	C_2H_5ClO	4.9
cis-2-Butene-1,4-Diol	$C_4H_8O_2$	1.7	Pentafluoroethyl Methyl Ether	$C_3H_3F_5O$	10.5
trans-2-Butene-1,4-Diol	$C_4H_8O_2$	1.7	α-Epichlorohydrin	C_3H_5ClO	2.5
1,3-Benzenediol	$C_6H_6O_2$	1.4	3,4-Dichloroaniline	$C_6H_5Cl_2N$	2.8
Octanal	$C_8H_{16}O$	1.0	Vinyl Bromide	C_2H_3Br	6.6
cis-Crotonaldehyde	C_4H_6O	2.1	1-Bromopropane	C_3H_7Br	3.3
Methacrolein	C_4H_6O	2.48	Vinyl Fluoride	C_2H_3F	3.41
Propanal	C_3H_6O	2.6	1,2-Difluoroethane	$C_2H_4F_2$	4.15
Formaldehyde	CH_2O	7.0	Difluoromethane	CH_2F_2	13.3
2-Methylpropanal	C_4H_8O	1.6	1,1,1-Trifluoroethane	$C_2H_3F_3$	7.4
Acetone	C_3H_6O	2.6	1,1-Difluoroethylene	$C_2H_2F_2$	4.7
Methyl Isobutyl Ketone	$C_6H_{12}O$	1.2	Tetrafluoroethylene	C_2F_4	10.0
Cyclohexanone	$C_6H_{10}O$	1.3	Chlorofluoromethane	CH_2ClF	14.4
2-Hexanone	$C_6H_{12}O$	1.22	1-Chloropentane	$C_5H_{11}Cl$	1.4
3-Pentanone	$C_5H_{10}O$	1.6	3-Chloropropene	C_3H_5Cl	2.71
Isophorone	$C_9H_{14}O$	0.84	1,2,3-Trichloropropane	$C_3H_5Cl_3$	3.2
Mesityl Oxide	$C_6H_{10}O$	1.3	1,4-Dichlorobutane	$C_4H_8Cl_2$	1.5
Methyl Isopropyl Ketone	$C_5H_{10}O$	1.4	*p*-Chlorotoluene	C_7H_7Cl	1.3
n-Hexyl Formate	$C_7H_{14}O_2$	1.1	Monochlorobenzene	C_6H_5Cl	1.3
Methyl Formate	$C_2H_4O_2$	5.2	Methyl Chloride	CH_3Cl	8.1
n-Pentyl Acetate	$C_7H_{14}O_2$	1.1	*cis*-1,2-Dichloroethylene	$C_2H_2Cl_2$	6.8
Ethyl Acetate	$C_4H_8O_2$	2.18	1,1-Dichloroethylene	$C_2H_2Cl_2$	6.5
n-Decyl Acetate	$C_{12}H_{24}O_2$	0.64	Tetramethylsilane	$C_4H_{12}Si$	1.0
n-Butyl Acetate	$C_6H_{12}O_2$	1.4	Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	0.75
Isobutyl Acetate	$C_6H_{12}O_2$	1.42	Trimethylchlorosilane	C_3H_9ClSi	1.8
Methyl Propionate	$C_4H_8O_2$	2.4	Decamethyltetrasiloxane	$C_{10}H_{30}O_3Si_4$	0.9
Ethyl Propionate	$C_5H_{10}O_2$	1.8	Trimethyl Silanol	$C_3H_{10}OSi$	1.45
Isobutyric Anhydride	$C_8H_{14}O_3$	1.09	Vinyltrimethoxysilane	$C_5H_{12}O_3Si$	1.4
Propionic Anhydride	$C_6H_{10}O_3$	1.48	Dimethyldichlorosilane	$C_2H_6Cl_2Si$	3.4
Dimethyl Ether	C_2H_6O	3.3	Trimethyl Silane	$C_3H_{10}Si$	1.3
tert-Butyl Ethyl Ether	$C_6H_{14}O$	1.03	Octamethyltrisiloxane	$C_8H_{24}O_2Si_3$	0.9
Divinyl Ether	C_4H_6O	1.7	Tetraethoxysilane	$C_8H_{20}O_4Si$	1.3

Table E.3. Training set of lower flammability limit data from the Bureau of Mines

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
Acetylene	C_2H_2	2.5	Methyl Formate	$C_2H_4O_2$	5.0
Ethylene	C_2H_4	2.7	Ethyl Formate	$C_3H_6O_2$	2.8
1-Butene	C_4H_8	1.6	Vinyl Acetate	$C_4H_6O_2$	2.6
1-Pentene	C_5H_{10}	1.4	*n*-Butyl Acetate	$C_6H_{12}O_2$	1.4
cis-2-Butene	C_4H_8	1.7	Isopentyl Acetate	$C_7H_{14}O_2$	1.1
2-Methyl-2-Butene	C_5H_{10}	1.4	Maleic Anhydride	$C_4H_2O_3$	1.4
Cyclohexene	C_6H_{10}	1.2	Acetic Anhydride	$C_4H_6O_3$	2.7
α-Pinene	$C_{10}H_{16}$	0.7	Phthalic Anhydride	$C_8H_4O_3$	1.2
Isoprene	C_5H_8	2.0	Diethyl Ether	$C_4H_{10}O$	1.9
Methylcyclopentadiene	C_6H_8	1.3	Divinyl Ether	C_4H_6O	1.7
n-Butane	C_4H_{10}	1.8	Diisopropyl Ether	$C_6H_{14}O$	1.4
n-Pentane	C_5H_{12}	1.4	Paraldehyde	$C_6H_{12}O_3$	1.3
n-Heptane	C_7H_{16}	1.1	Furan	C_4H_4O	2.3
n-Heptane	C_7H_{16}	1.05	1,4-Dioxane	$C_4H_8O_2$	2.0
n-Nonane	C_9H_{20}	0.85	Methyl Acrylate	$C_4H_6O_2$	2.8
Methane	CH_4	5.0	β-Propiolactone	$C_3H_4O_2$	2.9
Isobutane	C_4H_{10}	1.8	Ethyl Lactate	$C_5H_{10}O_3$	1.5
Isobutane	C_4H_{10}	1.3	Acetic Acid	$C_2H_4O_2$	5.4
2-Methylpentane	C_6H_{14}	1.2	*n*-Butyric Acid	$C_4H_8O_2$	2.0
Neopentane	C_5H_{12}	1.4	Dimethyldichlorosilane	$C_2H_6Cl_2Si$	3.4
2,3-Dimethylpentane	C_7H_{16}	1.1	Dimethyl Sulfide	C_2H_6S	2.2
3,3-Diethylpentane	C_9H_{20}	0.7	Carbon Disulfide	CS_2	1.3
2,2,3,3-Tetramethylpentane	C_9H_{20}	0.8	Methyl Mercaptan	CH_4S	3.9
Cyclobutane	C_4H_8	1.8	Ethylamine	C_2H_7N	3.5
Cyclohexane	C_6H_{12}	1.3	Methylamine	CH_5N	4.9
1,1-Diethylcyclohexane	$C_{10}H_{20}$	0.75	Trimethylamine	C_3H_9N	2.0
Methylcyclohexane	C_7H_{14}	1.1	Triethylamine	$C_6H_{15}N$	1.2
Ethylcyclohexane	C_8H_{16}	0.95	Pyridine	C_5H_5N	1.8
n-Butylbenzene	$C_{10}H_{14}$	0.82	Ethyleneimine	C_2H_5N	3.6
Toluene	C_7H_8	1.2	Allylamine	C_3H_7N	2.2
Isobutylbenzene	$C_{10}H_{14}$	0.82	N,N-Dimethylformamide	C_3H_7NO	1.8
p-Cymene	$C_{10}H_{14}$	0.85	Acetonitrile	C_2H_3N	4.4
p-Diethylbenzene	$C_{10}H_{14}$	0.8	Cyanogen	C_2N_2	6.6
m-Xylene	C_8H_{10}	1.1	Hydrogen Cyanide	CHN	5.6
Styrene	C_8H_8	1.1	1-Nitropropane	$C_3H_7NO_2$	2.2
1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	0.84	2-Nitropropane	$C_3H_7NO_2$	2.5
Naphthalene	$C_{10}H_8$	0.88	Nitrobenzene	$C_6H_5NO_2$	1.8
Biphenyl	$C_{12}H_{10}$	0.7	2-Methoxyethanol	$C_3H_8O_2$	2.5
Ethanol	C_2H_6O	3.3	2-Ethoxyethanol	$C_4H_{10}O_2$	1.8
1-Propanol	C_3H_8O	2.2	2-Butoxyethanol	$C_6H_{14}O_2$	1.1
1-Butanol	$C_4H_{10}O$	1.7	Acetone Cyanohydrin	C_4H_7NO	2.2
1-Pentanol	$C_5H_{12}O$	1.4	Dimethyl Sulfoxide	C_2H_6OS	2.6
Methanol	CH_4O	6.7	2-Chloroethanol	C_2H_5ClO	4.9
Propargyl Alcohol	C_3H_4O	2.4	Bromoethane	C_2H_5Br	6.7
Propargyl Alcohol	C_3H_4O	2.2	1-Bromobutane	C_4H_9Br	2.5
2-Methyl-1-Propanol	$C_4H_{10}O$	1.7	2-Chloropropene	C_3H_5Cl	4.5
2-Butanol	$C_4H_{10}O$	1.7	*n*-Butyl Chloride	C_4H_9Cl	1.8
1-Methylcyclohexanol	$C_7H_{14}O$	1.0	1-Chloropentane	$C_5H_{11}Cl$	1.6
1,3-Propylene Glycol	$C_3H_8O_2$	2.6	1-Chloropentane	$C_5H_{11}Cl$	1.4
Triethylene Glycol	$C_6H_{14}O_4$	0.9	1-Chloropentane	$C_5H_{11}Cl$	1.6
Acetaldehyde	C_2H_4O	4.0	*o*-Dichlorobenzene	$C_6H_4Cl_2$	2.2
cis-Crotonaldehyde	C_4H_6O	2.1	Monochlorobenzene	C_6H_5Cl	1.4

Table E.3. Continued

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
trans-Crotonaldehyde	C_4H_6O	2.1	Vinyl Chloride	C_2H_3Cl	3.6
Formaldehyde	CH_2O	7.0	1,1,2-Trichloroethane	$C_2H_3Cl_3$	6.8
Acetone	C_3H_6O	2.6	1,2-Dichloroethane	$C_2H_4Cl_2$	4.5
2-Pentanone	$C_5H_{10}O$	1.6	Trichloroethylene	C_2HCl_3	12.0
Methyl Isopropenyl Ketone	C_5H_8O	1.8	Dichloromethane	CH_2Cl_2	15.9
Methyl Isobutyl Ketone	$C_6H_{12}O$	1.4	Methyl Chloride	CH_3Cl	10.7
Isophorone	$C_9H_{14}O$	0.84			

Table E.4. Test set of lower flammability limit data from the Bureau of Mines

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
Methylacetylene	C_3H_4	1.7	3-Pentanone	$C_5H_{10}O$	1.6
Propylene	C_3H_6	2.4	Cyclohexanone	$C_6H_{10}O$	1.1
trans-2-Butene	C_4H_8	1.7	2-Hexanone	$C_6H_{12}O$	1.2
Isobutene	C_4H_8	1.8	Diisobutyl Ketone	$C_9H_{18}O$	0.79
3-Methyl-1-Butene	C_5H_{10}	1.5	*n*-Butyl Formate	$C_5H_{10}O_2$	1.7
d-Limonene	$C_{10}H_{16}$	0.75	Isobutyl Formate	$C_5H_{10}O_2$	2.0
Propadiene	C_3H_4	2.16	Methyl Acetate	$C_3H_6O_2$	3.2
Propadiene	C_3H_4	2.2	Ethyl Acetate	$C_4H_8O_2$	2.2
1,3-Butadiene	C_4H_6	2.0	*n*-Propyl Acetate	$C_5H_{10}O_2$	1.8
n-Decane	$C_{10}H_{22}$	0.75	Isobutyl Acetate	$C_6H_{12}O_2$	2.4
Ethane	C_2H_6	3.0	*n*-Pentyl Acetate	$C_7H_{14}O_2$	1.0
Propane	C_3H_8	2.1	Methyl Propionate	$C_4H_8O_2$	2.4
n-Hexane	C_6H_{14}	1.2	Ethyl Propionate	$C_5H_{10}O_2$	1.8
n-Octane	C_8H_{18}	0.95	Dimethyl Ether	C_2H_6O	3.4
Isopentane	C_5H_{12}	1.4	Methyl Vinyl Ether	C_3H_6O	2.6
2,2-Dimethylbutane	C_6H_{14}	1.2	Methyl Ethyl Ether	C_3H_8O	2.0
2,3-Dimethylbutane	C_6H_{14}	1.2	Ethyl Propyl Ether	$C_5H_{12}O$	1.7
2,2,3-Trimethylbutane	C_7H_{16}	1.0	Di-*n*-Butyl Ether	$C_8H_{18}O$	1.5
2,2,4-Trimethylpentane	C_8H_{18}	0.95	Acetal	$C_6H_{14}O_2$	1.6
Cyclopropane	C_3H_6	2.4	Ethylene Oxide	C_2H_4O	3.6
Cyclopentane	C_5H_{10}	1.5	Trioxane	$C_3H_6O_3$	3.6
Cycloheptane	C_7H_{14}	1.1	Tetrahydrofuran	C_4H_8O	2.0
Ethylcyclopentane	C_7H_{14}	1.1	γ-Butyrolactone	$C_4H_6O_2$	2.0
Bicyclohexyl	$C_{12}H_{22}$	0.65	Methyl Lactate	$C_4H_8O_3$	2.2
Benzene	C_6H_6	1.3	Ethyl Mercaptan	C_2H_6S	2.8
Ethylbenzene	C_8H_{10}	1.0	*n*-Propylamine	C_3H_9N	2.0
sec-Butylbenzene	$C_{10}H_{14}$	0.77	*n*-Butylamine	$C_4H_{11}N$	1.7
tert-Butylbenzene	$C_{10}H_{14}$	0.77	Dimethylamine	C_2H_7N	2.8
o-Xylene	C_8H_{10}	1.1	Diethylamine	$C_4H_{11}N$	1.8
p-Xylene	C_8H_{10}	1.1	*tert*-Butylamine	$C_4H_{11}N$	1.7
Cumene	C_9H_{12}	0.88	Aniline	C_6H_7N	1.2
1-Hexanol	$C_6H_{14}O$	1.2	Acrylonitrile	C_3H_3N	3.0
Allyl Alcohol	C_3H_6O	2.5	Nitroethane	$C_2H_5NO_2$	3.4
Isopropanol	C_3H_8O	2.2	Nitromethane	CH_3NO_2	7.3
2-Methyl-2-Propanol	$C_4H_{10}O$	1.9	Furfuryl Alcohol	$C_5H_6O_2$	1.8
3-Methyl-1-Butanol	$C_5H_{12}O$	1.4	Methyl Bromide	CH_3Br	10.0
Cyclohexanol	$C_6H_{12}O$	1.2	3-Chloropropene	C_3H_5Cl	2.9

Table E.4. Continued

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
m-Cresol	C_7H_8O	1.1	*n*-Propyl Chloride	C_3H_7Cl	2.6
Acrolein	C_3H_4O	2.8	Isobutyl Chloride	C_4H_9Cl	2
Propanal	C_3H_6O	2.9	Benzyl Chloride	C_7H_7Cl	1.1
Butanal	C_4H_8O	2.5	Ethyl Chloride	C_2H_5Cl	3.8
Methyl Ethyl Ketone	C_4H_8O	1.9			

Table E.5. Training set of lower flammability limit data from the European method

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
Acetylene	C_2H_2	2.3	1,2-Epoxybutane	C_4H_8O	1.5
Methylacetylene	C_3H_4	1.8	Tetrahydrofuran	C_4H_8O	1.5
Propylene	C_3H_6	2	1,4-Dioxane	$C_4H_8O_2$	1.9
1-Pentene	C_5H_{10}	1.4	2-Ethylhexyl Acrylate	$C_{11}H_{20}O_2$	0.78
1-Hexene	C_6H_{12}	1.2	Ethyl Methacrylate	$C_6H_{10}O_2$	1.8
1-Heptene	C_7H_{14}	1	Isobutyl Acrylate	$C_7H_{12}O_2$	1.2
trans-2-Butene	C_4H_8	1.6	β-Propiolactone	$C_3H_4O_2$	2.9
3-Methyl-1-Butene	C_5H_{10}	1.5	Dioctyl Phthalate	$C_{24}H_{38}O_4$	0.3
Cyclohexene	C_6H_{10}	1.2	Diethylene Glycol Monobutyl Ether Acetate	$C_{10}H_{20}O_4$	0.65
Vinylcyclohexene	C_8H_{12}	0.98	Methyl Acetoacetate	$C_5H_8O_3$	1.3
Dicyclopentadiene	$C_{10}H_{12}$	0.8	*n*-Butyric Acid	$C_4H_8O_2$	2
Propadiene	C_3H_4	1.7	*n*-Pentanoic Acid	$C_5H_{10}O_2$	1.6
1,2-Butadiene	C_4H_6	1.6	Formic Acid	CH_2O_2	10
1,3-Butadiene	C_4H_6	1.4	Isovaleric Acid	$C_5H_{10}O_2$	1.4
n-Decane	$C_{10}H_{22}$	0.7	Di-*t*-Butyl Peroxide	$C_8H_{18}O_2$	0.74
n-Dodecane	$C_{12}H_{26}$	0.6	Dimethyl Sulfide	C_2H_6S	2.2
Propane	C_3H_8	1.7	Thiophene	C_4H_4S	1.5
Methane	CH_4	4.4	Tetrahydrothiophene	C_4H_8S	1.1
3-Methylpentane	C_6H_{14}	1.1	Carbon Disulfide	CS_2	0.6
2-Methylhexane	C_7H_{16}	1	Methyl Mercaptan	CH_4S	3.8
Cyclopropane	C_3H_6	2.4	Ethylamine	C_2H_7N	2.7
Cyclobutane	C_4H_8	1.8	*n*-Propylamine	C_3H_9N	2
Methylcyclohexane	C_7H_{14}	1.1	*n*-Butylamine	$C_4H_{11}N$	1.7
Ethylcyclohexane	C_8H_{16}	0.9	Methylamine	CH_5N	4.9
cis-Decahydronaphthalene	$C_{10}H_{18}$	0.7	Dimethylamine	C_2H_7N	2.8
Bicyclohexyl	$C_{12}H_{22}$	0.6	Trimethylamine	C_3H_9N	2
Benzene	C_6H_6	1.2	Diethylamine	$C_4H_{11}N$	1.7
n-Propylbenzene	C_9H_{12}	0.8	Tripropylamine	$C_9H_{21}N$	0.7
tert-Butylbenzene	$C_{10}H_{14}$	0.8	Pyridine	C_5H_5N	1.7
Styrene	C_8H_8	1.1	Aniline	C_6H_7N	1.2
α-Methylstyrene	C_9H_{10}	0.9	2-Methylpyridine	C_6H_7N	1.4
Biphenyl	$C_{12}H_{10}$	0.6	3-Methylpyridine	C_6H_7N	1.3
Vinylnorbornene	C_9H_{12}	0.8	4-Methylpyridine	C_6H_7N	1.3
1-Butanol	$C_4H_{10}O$	1.4	Pyrrolidine	C_4H_9N	1.6
1-Pentanol	$C_5H_{12}O$	1.3	Tetramethylethylenediamine	$C_6H_{16}N_2$	1
1-Octanol	$C_8H_{18}O$	0.8	N-Methylformamide	C_2H_5NO	3.8
1-Nonanol	$C_9H_{20}O$	0.68	N,N-dimethylformamide	C_3H_7NO	2.3
Methanol	CH_4O	6	1-Amino-2-Propanol	C_3H_9NO	1.9
Isopropanol	C_3H_8O	2	2-Aminoethoxyethanol	$C_4H_{11}NO_2$	2

Table E.5. Continued

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
2-Methyl-1-Propanol	$C_4H_{10}O$	1.7	N,N-Dimethylacetamide	C_4H_9NO	1.8
2-Pentanol	$C_5H_{12}O$	1.2	2,4-Toluene Diisocyanate	$C_9H_6N_2O_2$	0.9
2-Methyl-1-Butanol	$C_5H_{12}O$	1.2	Acetonitrile	C_2H_3N	3
p-Cresol	C_7H_8O	1	Acrylonitrile	C_3H_3N	2.8
1,2-Propylene Glycol	$C_3H_8O_2$	2.6	*cis*-Crotonitrile	C_4H_5N	1.7
Glycerol	$C_3H_8O_3$	2.6	2-Nitropropane	$C_3H_7NO_2$	2.2
1,3-Butanediol	$C_4H_{10}O_2$	1.8	*o*-Nitrotoluene	$C_7H_7NO_2$	0.67
Diethylene Glycol	$C_4H_{10}O_3$	1.7	Tetrahydrofurfuryl Alcohol	$C_5H_{10}O_2$	1.5
Hexylene Glycol	$C_6H_{14}O_2$	1	2-Butoxyethanol	$C_6H_{14}O_2$	1.1
Acetaldehyde	C_2H_4O	4	Morpholine	C_4H_9NO	1.8
Acrolein	C_3H_4O	2.8	N-Methyl-2-Pyrrolidone	C_5H_9NO	1.3
Propanal	C_3H_6O	2.3	Cyclohexanone Oxime	$C_6H_{11}NO$	1.3
trans-Crotonaldehyde	C_4H_6O	2.1	Dimethyl Sulfoxide	C_2H_6OS	1.8
Pentanal	$C_5H_{10}O$	1.4	2-Mercaptoethanol	C_2H_6OS	2.3
Benzaldehyde	C_7H_6O	1.4	Acetyl Chloride	C_2H_3ClO	7.3
2-Ethylhexanal	$C_8H_{16}O$	1	Methyl Chloroformate	$C_2H_3ClO_2$	7.5
Methyl Ethyl Ketone	C_4H_8O	1.8	α-Epichlorohydrin	C_3H_5ClO	2.3
Methyl Isopropyl Ketone	$C_5H_{10}O$	1.4	1-Chloro-2,4-Dinitrobenzene	$C_6H_3ClN_2O_4$	1.9
Acetylacetone	$C_5H_8O_2$	1.7	Bromoethane	C_2H_5Br	6.7
Methyl Isobutyl Ketone	$C_6H_{12}O$	1.2	2-Bromopropane	C_3H_7Br	3.2
3-Heptanone	$C_7H_{14}O$	1	*p*-Bromotoluene	C_7H_7Br	1.35
2-Heptanone	$C_7H_{14}O$	1	1,1-Difluoroethane	$C_2H_4F_2$	3.7
Isophorone	$C_9H_{14}O$	0.8	3,3,3-Trifluoropropene	$C_3H_3F_3$	3.2
Diisobutyl Ketone	$C_9H_{18}O$	0.8	Methyl Iodide	CH_3I	8.5
Ethyl Formate	$C_3H_6O_2$	2.7	Chlorotrifluoroethylene	C_2ClF_3	4.6
n-Propyl Formate	$C_4H_8O_2$	2.3	1,1-Dichloro-1-Fluoroethane	$C_2H_3Cl_2F$	7.4
n-Butyl Formate	$C_5H_{10}O_2$	1.7	1-Chloro-1,1-Difluoroethane	$C_2H_3ClF_2$	6.2
1-Methylvinyl Acetate	$C_5H_8O_2$	1.6	2,3-Dichloropropene	$C_3H_4Cl_2$	2.6
n-Butyl Acetate	$C_6H_{12}O_2$	1.2	2-Chloropropene	C_3H_5Cl	4.5
n-Pentyl Acetate	$C_7H_{14}O_2$	1.1	Isopropyl Chloride	C_3H_7Cl	2.8
Cyclohexyl Acetate	$C_8H_{14}O_2$	0.9	*n*-Propyl Chloride	C_3H_7Cl	2.6
Glyceryl Triacetate	$C_9H_{14}O_6$	1.1	3,4-Dichloro-1-Butene	$C_4H_6Cl_2$	2.5
Ethyl Propionate	$C_5H_{10}O_2$	1.8	1-Chloropentane	$C_5H_{11}Cl$	1.4
Acetic Anhydride	$C_4H_6O_3$	2	*p*-Chlorotoluene	C_7H_7Cl	1.3
Butyric Anhydride	$C_8H_{14}O_3$	1.09	*cis*-1,2-Dichloroethylene	C2H2Cl2	6.2
Dimethyl Ether	C_2H_6O	2.7	*trans*-1,2-Dichloroethylene	C2H2Cl2	9.7
Diethyl Ether	$C_4H_{10}O$	1.7	1,1,1-Trichloroethane	C2H3Cl3	6.5
Ethyl Vinyl Ether	C_4H_8O	1.7	Ethyl Chloride	C2H5Cl	3.6
Methyl *tert*-Butyl Ether	$C_5H_{12}O$	1.6	Dimethyldichlorosilane	C2H6Cl2Si	3.4
Di-*n*-Butyl Ether	$C_8H_{18}O$	0.9	Trimethyl Silane	C3H10Si	1.3
Diisobutyl Ether	$C_8H_{18}O$	0.9	Vinyltrimethoxysilane	C5H12O3Si	0.7
Diphenyl Ether	$C_{12}H_{10}O$	0.8	Hexamethyldisilazane	C6H19NSi2	0.48
1,2-Dimethoxyethane	$C_4H_{10}O_2$	1.6	Tetraethoxysilane	C8H20O4Si	1.3
Anisole	C_7H_8O	1.2	Methyl Dichlorosilane	CH4Cl2Si	2.8

Table E.6. Test set of lower flammability limit data from the European method

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
Dimethylacetylene	C_4H_6	1.37	Isopentyl Acetate	$C_7H_{14}O_2$	1.0
Ethylene	C_2H_4	2.3	*n*-Hexyl Acetate	$C_8H_{16}O_2$	0.9
1-Butene	C_4H_8	1.6	Methyl Propionate	$C_4H_8O_2$	2.4
cis-2-Butene	C_4H_8	1.6	Isobutyric Anhydride	$C_8H_{14}O_3$	1.0
Isobutene	C_4H_8	1.6	Phthalic Anhydride	$C_8H_4O_3$	1.7
d-Limonene	$C_{10}H_{16}$	0.7	Methyl Ethyl Ether	C_3H_8O	2.0
Isoprene	C_5H_8	1.4	Divinyl Ether	C_4H_6O	1.7
Methylcyclopentadiene	C_6H_8	1.3	Diisopropyl Ether	$C_6H_{14}O$	1.0
n-Undecane	$C_{11}H_{24}$	0.6	Methylal	$C_3H_8O_2$	2.6
n-Tridecane	$C_{13}H_{28}$	0.55	Paraldehyde	$C_6H_{12}O_3$	1.3
Ethane	C_2H_6	2.5	Ethylene Oxide	C_2H_4O	2.6
n-Butane	C_4H_{10}	1.4	1,2-Propylene Oxide	C_3H_6O	1.9
n-Hexane	C_6H_{14}	0.92	Trioxane	$C_3H_6O_3$	3.6
n-Octane	C_8H_{18}	0.8	Furan	C_4H_4O	2.26
n-Nonane	C_9H_{20}	0.7	1,2-Epoxy-2-Methylpropane	C_4H_8O	1.5
Isobutane	C_4H_{10}	1.3	Ethyl Acrylate	$C_5H_8O_2$	1.7
2-Methylpentane	C_6H_{14}	1.1	Methyl Methacrylate	$C_5H_8O_2$	1.7
2,2-Dimethylbutane	C_6H_{14}	1.1	*n*-Butyl Acrylate	$C_7H_{12}O_2$	1.2
3,3-Diethylpentane	C_9H_{20}	0.7	Diisooctyl Phthalate	$C_{24}H_{38}O_4$	0.26
Cyclohexane	C_6H_{12}	1.1	Ethyl Benzoate	$C_9H_{10}O_2$	1.0
Cycloheptane	C_7H_{14}	1.0	Ethyl Lactate	$C_5H_{10}O_3$	1.5
Ethylcyclopentane	C_7H_{14}	1.1	Acetic Acid	$C_2H_4O_2$	4.0
trans-Decahydronaphthalene	$C_{10}H_{18}$	0.7	Propionic Acid	$C_3H_6O_2$	2.1
n-Butylbenzene	$C_{10}H_{14}$	0.8	2-Ethyl Hexanoic acid	$C_8H_{16}O_2$	0.9
Toluene	C_7H_8	1.1	Ethyl Mercaptan	C_2H_6S	2.8
Ethylbenzene	C_8H_{10}	1.0	*tert*-Butylamine	$C_4H_{11}N$	1.5
Isobutylbenzene	$C_{10}H_{14}$	0.8	Ethyleneimine	C_2H_5N	3.6
sec-Butylbenzene	$C_{10}H_{14}$	0.8	Ethylenediamine	$C_2H_8N_2$	2.5
o-Xylene	C_8H_{10}	1.0	Allylamine	C_3H_7N	2.2
m-Xylene	C_8H_{10}	1.0	3-(N,N-Dimethylamino) Propylamine	$C_5H_{14}N_2$	1.9
p-Xylene	C_8H_{10}	1.0	Monoethanolamine	C_2H_7NO	2.5
Cumene	C_9H_{12}	0.8	Diethanolamine	$C_4H_{11}NO_2$	1.7
1,2,4-Trimethylbenzene	C_9H_{12}	0.8	*n*-Butyl Isocyanate	C_5H_9NO	1.3
Mesitylene	C_9H_{12}	0.8	1,6-Hexamethylene Diisocyanate	$C_8H_{12}N_2O_2$	0.9
1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	0.8	Cyanogen	C_2N_2	3.9
Naphthalene	$C_{10}H_8$	0.9	Methacrylonitrile	C_4H_5N	1.7
1-Methylnaphthalene	$C_{11}H_{10}$	0.68	*trans*-Crotonitrile	C_4H_5N	1.7
Anthracene	$C_{14}H_{10}$	0.6	*n*-Butyronitrile	C_4H_7N	1.57
1-Decanol	$C_{10}H_{22}O$	0.6	Isobutyronitrile	C_4H_7N	1.57
Ethanol	C_2H_6O	3.1	Benzonitrile	C_7H_5N	0.9
1-Propanol	C_3H_8O	2.1	Hydrogen Cyanide	CHN	5.4
1-Hexanol	$C_6H_{14}O$	1.1	3-Methoxypropionitrile	C_4H_7NO	1.9
1-Heptanol	$C_7H_{16}O$	0.89	1-Nitropropane	$C_3H_7NO_2$	2.2
Allyl Alcohol	C_3H_6O	2.5	Nitromethane	CH_3NO_2	7.1
2-Methyl-2-Butanol	$C_5H_{12}O$	1.3	2-Methoxyethanol	$C_3H_8O_2$	2.4
2,2-Dimethyl-1-Propanol	$C_5H_{12}O$	1.2	2-Ethoxyethanol	$C_4H_{10}O_2$	1.8

Table E.6. Continued

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
3-Methyl-1-Butanol	$C_5H_{12}O$	1.2	Propylene Glycol Monomethyl Ether	$C_4H_{10}O_2$	1.5
3-Methyl-2-Butanol	$C_5H_{12}O$	1.2	1-Ethoxy-2-Propanol	$C_5H_{12}O_2$	1.3
4-Methyl-2-Pentanol	$C_6H_{14}O$	1.0	2-(2-Methoxyethoxy)Ethanol	$C_5H_{12}O_3$	1.5
2,6-Dimethyl-4-Heptanol	$C_9H_{20}O$	0.7	Furfural	$C_5H_4O_2$	2.1
Cyclohexanol	$C_6H_{12}O$	1.5	Furfuryl Alcohol	$C_5H_6O_2$	1.8
Phenol	C_6H_6O	1.3	Propylene Glycol *n*-Butyl Ether	$C_7H_{16}O_2$	1.1
o-Cresol	C_7H_8O	1.3	Chloroacetic Acid	$C_2H_3ClO_2$	8.6
m-Cresol	C_7H_8O	1.0	2-Chloroethanol	C_2H_5ClO	4.8
Ethylene Glycol	$C_2H_6O_2$	3.1	Di(2-Chloroethyl)Ether	$C_4H_8Cl_2O$	2.0
1,4-Butanediol	$C_4H_{10}O_2$	1.8	Vinyl Bromide	C_2H_3Br	5.6
Neopentyl Glycol	$C_5H_{12}O_2$	1.1	1-Bromopropane	C_3H_7Br	3.3
Triethylene Glycol	$C_6H_{14}O_4$	0.9	1-Bromobutane	C_4H_9Br	2.6
2-Methylpropanal	C_4H_8O	1.6	Methyl Bromide	CH_3Br	8.6
Octanal	$C_8H_{16}O$	1.0	Tetrafluoroethylene	C_2F_4	10.5
Formaldehyde	CH_2O	7.0	1,1-Difluoroethylene	$C_2H_2F_2$	4.7
Diketene	$C_4H_4O_2$	2.0	Fluorobenzene	C_6H_5F	1.3
2-Pentanone	$C_5H_{10}O$	1.5	3-Chloropropene	C_3H_5Cl	3.2
Cyclohexanone	$C_6H_{10}O$	1.3	1,2,3-Trichloropropane	$C_3H_5Cl_3$	3.2
3-Hexanone	$C_6H_{12}O$	1.0	Chloroprene	C_4H_5Cl	2.5
2-Hexanone	$C_6H_{12}O$	1.2	Isobutyl Chloride	C_4H_9Cl	1.95
5-Methyl-2-Hexanone	$C_7H_{14}O$	1.05	*n*-Butyl Chloride	C_4H_9Cl	1.8
Acetophenone	C_8H_8O	1.1	Monochlorobenzene	C_6H_5Cl	1.3
Methyl Formate	$C_2H_4O_2$	5.0	Benzyl Chloride	C_7H_7Cl	1.1
Isobutyl Formate	$C_5H_{10}O_2$	1.7	*o*-Chlorotoluene	C_7H_7Cl	1.3
Methyl Acetate	$C_3H_6O_2$	3.1	Vinyl Chloride	C_2H_3Cl	3.8
Vinyl Acetate	$C_4H_6O_2$	2.6	Trichloroethylene	C_2HCl_3	7.9
Ethyl Acetate	$C_4H_8O_2$	2.0	Methyl Chloride	CH_3Cl	7.6
n-Propyl Acetate	$C_5H_{10}O_2$	1.7	Trimethyl Silanol	$C_3H_{10}OSi$	1.4
Isopropyl Acetate	$C_5H_{10}O_2$	1.8	Tetramethylsilane	$C_4H_{12}Si$	1.0
Allyl Acetate	$C_5H_8O_2$	1.7	Hexamethyldisiloxane	$C_6H_{18}OSi_2$	0.8
Isobutyl Acetate	$C_6H_{12}O_2$	1.6			

Table E.7. Training set of lower flammability limit data from the ASHRAE apparatus

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
Acetylene	C_2H_2	2.5	Diisobutyl Phthalate	$C_{16}H_{22}O_4$	0.53
1-Hexyne	C_6H_{10}	1.0	Ethyl Lactate	$C_5H_{10}O_3$	1.7
Propylene	C_3H_6	2.0	*n*-Pentylamine	$C_5H_{13}N$	1.32
1-Butene	C_4H_8	1.6	Dibutylamine	$C_8H_{19}N$	0.84
1-Pentene	C_5H_{10}	1.5	Allylamine	C_3H_7N	2.03
cis-2-Butene	C_4H_8	1.7	Methacrylonitrile	C_4H_5N	1.89
trans-2-Butene	C_4H_8	1.8	2-Chloroethanol	C_2H_5ClO	4.9
Isobutene	C_4H_8	1.8	Pentafluoroethyl Methyl Ether	$C_3H_3F_5O$	10.5

Table E.7. Continued

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
α-Pinene	$C_{10}H_{16}$	0.74	α-Epichlorohydrin	C_3H_5ClO	2.5
n-Decane	$C_{10}H_{22}$	0.8	Vinyl Bromide	C_2H_3Br	9.0
Propane	C_3H_8	2.1	Vinyl Bromide	C_2H_3Br	6.6
n-Butane	C_4H_{10}	1.6	1-Bromobutane	C_4H_9Br	2.6
n-Octane	C_8H_{18}	1.0	Tetrafluoroethylene	C_2F_4	10.0
n-Nonane	C_9H_{20}	0.8	1,1-Difluoroethylene	$C_2H_2F_2$	4.7
Methane	CH_4	4.9	Vinyl Fluoride	C_2H_3F	3.41
Isopentane	C_5H_{12}	1.4	1,1,1-Trifluoroethane	$C_2H_3F_3$	7.4
2-Methylpentane	C_6H_{14}	1.0	1,1,2-Trifluoroethane	$C_2H_3F_3$	6.2
2-Methylhexane	C_7H_{16}	1.0	1,2-Difluoroethane	$C_2H_4F_2$	4.15
2,3-Dimethylpentane	C_7H_{16}	1.1	1,1,2,2,3-Dentafluoropropane	$C_3H_3F_5$	7.7
3,3-Diethylpentane	C_9H_{20}	0.7	Difluoromethane	CH_2F_2	13.3
1,1-Diethylcyclohexane	$C_{10}H_{20}$	0.8	Chlorotrifluoroethylene	C_2ClF_3	8.4
Methylcyclohexane	C_7H_{14}	1.2	1,1-Dichloro-1-Dluoroethane	$C_2H_3Cl_2F$	9.0
Ethylcyclohexane	C_8H_{16}	0.9	1-Chloro-1,1-Difluoroethane	$C_2H_3ClF_2$	6.8
Methylcyclopentane	C_6H_{12}	1.0	Chlorofluoromethane	CH_2ClF	14.4
1-Butanol	$C_4H_{10}O$	1.63	3-Chloropropene	C_3H_5Cl	2.71
Butanol	$C_4H_{10}O$	1.7	1,2-Dichloropropane	$C_3H_6Cl_2$	3.3
2-Methyl-2-Propanol	$C_4H_{10}O$	1.84	Isopropyl Chloride	C_3H_7Cl	2.8
2-Methyl-1-3-Propanediol	$C_4H_{10}O_2$	1.73	*n*-Propyl Chloride	C_3H_7Cl	2.6
2-Nonanone	$C_9H_{18}O$	0.82	Chloroprene	C_4H_5Cl	4.0
Hexyl Formate	$C_7H_{14}O_2$	1.1	*n*-Butyl Chloride	C_4H_9Cl	1.8
Methyl Acetate	$C_3H_6O_2$	3.13	*cis*-1,2-Dichloroethylene	$C_2H_2Cl_2$	6.8
Isobutyl Acetate	$C_6H_{12}O_2$	1.42	1,1,1-Trichloroethane	$C_2H_3Cl_3$	7.5
Diethyl Ether	$C_4H_{10}O$	1.7	1,2-Dichloroethane	$C_2H_4Cl_2$	6.2
Methylal	$C_3H_8O_2$	2.54	Trichloroethylene	C_2HCl_3	12.2
Phenetole	$C_8H_{10}O$	1.0	Dichloromethane	CH_2Cl_2	14

Table E.8. Test set of lower flammability limit data from ASHRAE apparatus

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
Ethylene	C_2H_4	2.7	Ethyl Formate	$C_3H_6O_2$	2.76
Propylene	C_3H_6	2.15	Octyl Formate	$C_9H_{18}O_2$	0.83
3-Methyl-1-Butene	C_5H_{10}	1.5	*n*-Decyl Acetate	$C_{12}H_{24}O_2$	0.64
1,3-Butadiene	C_4H_6	1.69	Dimethyl Ether	C_2H_6O	3.3
Isoprene	C_5H_8	1.5	Ethyl Vinyl Ether	C_4H_8O	1.67
1,4-Hexadiene	C_6H_{10}	1.18	1,2-Propylene Oxide	C_3H_6O	2.2
1,4-Hexadiene	C_6H_{10}	1.18	Furan	C_4H_4O	2.0
Methylcyclopentadiene	C_6H_8	1.3	Methyl Acrylate	$C_4H_6O_2$	2.18
Ethane	C_2H_6	3.0	Ethyl Acrylate	$C_5H_8O_2$	1.6
n-Pentane	C_5H_{12}	1.5	Methyl Benzoate	$C_8H_8O_2$	1.09
n-Hexane	C_6H_{14}	1.1	Morpholine	C_4H_9NO	1.67

Table E.8. Continued

Compound	Formula	LFL/vol%	Compound	Formula	LFL/vol%
n-Heptane	C_7H_{16}	1.1	Pentafluoroethyl Methyl Ether	$C_3H_3F_5O$	10.5
Isobutane	C_4H_{10}	1.8	Methyl Chloroacetate	$C_3H_5ClO_2$	4.0
3-Methylpentane	C_6H_{14}	1.2	Bromoethane	C_2H_5Br	6.8
Neopentane	C_5H_{12}	1.4	2,4,4-Trimethyl-1-Pentene	C_8H_{16}	0.88
2,2-Dimethylbutane	C_6H_{14}	1.2	Methyl Bromide	CH_3Br	10.1
2,3-Dimethylbutane	C_6H_{14}	1.2	1,1-Difluoroethane	$C_2H_4F_2$	4.35
Cyclopropane	C_3H_6	2.4	Ethyl Fluoride	C_2H_5F	3.15
Cyclohexane	C_6H_{12}	1.3	Methyl Fluoride	CH_3F	7.1
Cycloheptane	C_7H_{14}	1.1	2,3-Dichloropropene	$C_3H_4Cl_2$	3.31
Ethylcyclopentane	C_7H_{14}	1.1	Isobutyl Chloride	C_4H_9Cl	2.0
5-*o*-Tolyl-2-Pentene	$C_{12}H_{16}$	0.68	1-Chloropentane	$C_5H_{11}Cl$	1.6
Octanol	$C_8H_{18}O$	0.84	*trans*-1,2-Dichloroethylene	$C_2H_2Cl_2$	6.8
Methanol	CH_4O	7.18	1,1-Dichloroethylene	$C_2H_2Cl_2$	6.5
4-Methyl-2-Pentanol	$C_6H_{14}O$	1.2	Vinyl Chloride	C_2H_3Cl	3.6
Acetaldehyde	C_2H_4O	4.0	Ethyl Chloride	C_2H_5Cl	3.8
Methyl Formate	$C_2H_4O_2$	5.2	Methyl Chloride	CH_3Cl	8.1

Table E.9. Training set of recommended upper flammability limit data

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Acetylene	C_2H_2	80.0	Methyl Methacrylate	$C_5H_8O_2$	12.5
1-Dodecene	$C_{12}H_{24}$	4.7	*n*-Butyl Acrylate	$C_7H_{12}O_2$	8.0
Propylene	C_3H_6	11.2	Dimethyl-1,4-Cyclohexanedicarboxylate	$C_{10}H_{16}O_4$	5.6
1-Butene	C_4H_8	10.0	γ-Butyrolactone	$C_4H_6O_2$	13.4
1-Pentene	C_5H_{10}	8.7	Dimethyl Terephthalate	$C_{10}H_{10}O_4$	11.8
trans-2-Butene	C_4H_8	9.7	Dioctyl Phthalate	$C_{24}H_{38}O_4$	2.4
3-Methyl-1-Butene	C_5H_{10}	9.1	Diisooctyl Phthalate	$C_{24}H_{38}O_4$	2.7
2-Methyl-2-Butene	C_5H_{10}	8.7	Methyl *para*-Toluate	$C_9H_{10}O_2$	9.5
2,4,4-Trimethyl-1-Pentene	C_8H_{16}	6.0	Diethylene Glycol Monobutyl Ether Acetate	$C_{10}H_{20}O_4$	10.7
Dicyclopentadiene	$C_{10}H_{12}$	6.3	Methyl Acetoacetate	$C_5H_8O_3$	8.0
1,2-Butadiene	C_4H_6	18.3	Ethyl Acetoacetate	$C_6H_{10}O_3$	9.5
1,3-Butadiene	C_4H_6	16.0	2-Ethoxyethyl Acetate	$C_6H_{12}O_3$	10.7
Isoprene	C_5H_8	8.9	*n*-Butyric Acid	$C_4H_8O_2$	10.0
Ethane	C_2H_6	12.4	*Trans*-Crotonic Acid	$C_4H_6O_2$	15.1
Propane	C_3H_8	9.5	Methacrylic Acid	$C_4H_6O_2$	8.7
n-Pentane	C_5H_{12}	7.8	Cumene Hydroperoxide	$C_9H_{12}O_2$	6.5
Methane	CH_4	15.0	Tris(2-Methoxyethoxy)Vinylsilane	$C_{11}H_{24}O_6Si$	21.0
Isopentane	C_5H_{12}	7.6	Vinyltrichlorosilane	$C_2H_3Cl_3Si$	50.41
2-Methylpentane	C_6H_{14}	7.0	Trimethyl Silanol	$C_3H_{10}OSi$	27.5
3-Methylpentane	C_6H_{14}	7.0	Trimethylchlorosilane	C_3H_9ClSi	6.0
Neopentane	C_5H_{12}	7.5	Dimethyldimethoxysilane	$C_4H_{12}O_2Si$	27.12
2,2,4-Trimethylpentane	C_8H_{18}	6.0	Tetramethylsilane	$C_4H_{12}Si$	37.9
3,3-diethylpentane	C_9H_{20}	5.7	Vinyltrimethoxysilane	$C_5H_{12}O_3Si$	23.94
Cyclopropane	C_3H_6	10.4	Hexamethyldisiloxane	$C_6H_{18}OSi_2$	18.6

Table E.9. Continued

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Cyclobutane	C_4H_8	10.0	Tetraethoxysilane	$C_8H_{20}O_4Si$	23.0
1,1-Diethylcyclohexane	$C_{10}H_{20}$	6.0	Octamethyltrisiloxane	$C_8H_{24}O_2Si_3$	13.75
Ethylcyclohexane	C_8H_{16}	6.6	Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	7.4
cis-Decahydronaphthalene	$C_{10}H_{18}$	4.9	Methyl Trichlorosilane	CH3Cl3Si	11.9
Bicyclohexyl	$C_{12}H_{22}$	5.1	Methyl Dichlorosilane	CH4Cl2Si	87.0
n-Butylbenzene	$C_{10}H_{14}$	5.8	Dichlorosilane	Cl2H2Si	96.0
Benzene	C_6H_6	8.0	Trichlorosilane	Cl3HSi	83.0
Toluene	C_7H_8	7.1	Dimethyl Sulfide	C2H6S	19.7
Ethylbenzene	C_8H_{10}	6.7	Carbon Disulfide	CS2	50.0
p-Cymene	$C_{10}H_{14}$	5.6	Ethyl Mercaptan	C2H6S	18.0
o-Xylene	C_8H_{10}	6.4	Methyl Mercaptan	CH4S	21.8
p-Xylene	C_8H_{10}	6.6	Ethylamine	C2H7N	14.0
Cumene	C_9H_{12}	6.5	*n*-Octylamine	C8H19N	9.64
Mesitylene	C_9H_{12}	7.29	*n*-Nonylamine	C9H21N	8.6
Styrene	C_8H_8	6.1	Dimethylamine	C2H7N	14.4
p-Methylstyrene	C_9H_{10}	11.0	Isopropylamine	C3H9N	10.4
α-Methylstyrene	C_9H_{10}	6.1	Triethylamine	C6H15N	8.0
1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	5.0	Tripropylamine	C9H21N	5.6
Naphthalene	$C_{10}H_8$	5.9	Aniline	C6H7N	11.0
1-Methylnaphthalene	$C_{11}H_{10}$	6.5	2-Methylpyridine	C6H7N	8.6
Biphenyl	$C_{12}H_{10}$	5.8	4-Methylpyridine	C6H7N	8.7
1-Propanol	C_3H_8O	14.0	*p*-Toluidine	C7H9N	6.6
1-Butanol	$C_4H_{10}O$	11.3	Ethylenediamine	C2H8N2	12.0
Methanol	CH_4O	36.5	Allylamine	C3H7N	24.3
Allyl Alcohol	C_3H_6O	18.0	Piperazine	C4H10N2	14.0
Isopropanol	C_3H_8O	12.7	Pyrrole	C4H5N	12.0
2-Methyl-1-Propanol	$C_4H_{10}O$	11.0	3-(N,N-Dimethylamino) Propylamine	C5H14N2	10.7
2-Butanol	$C_4H_{10}O$	9.8	Cyclohexylamine	C6H13N	9.4
2-Methyl-2-Propanol	$C_4H_{10}O$	9.0	N-Methylpiperidine	C6H13N	11.5
2-Methyl-2-Butanol	$C_5H_{12}O$	9.0	N-Methylformamide	C2H5NO	17.8
2,2-Dimethyl-1-Propanol	$C_5H_{12}O$	9.1	N,N-Dimethylformamide	C3H7NO	16.0
3-Pentanol	$C_5H_{12}O$	9.0	1-Amino-2-Propanol	C3H9NO	10.4
2-Methyl-1-Pentanol	$C_6H_{14}O$	9.65	Diethanolamine	C4H11NO2	9.8
4-Methyl-2-Pentanol	$C_6H_{14}O$	5.5	2-Aminoethoxyethanol	C4H11NO2	15.5
2-Ethyl-1-Butanol	$C_6H_{14}O$	8.8	N,N-Dimethylacetamide	C4H9NO	11.5
2-Ethyl-1-Hexanol	$C_8H_{18}O$	9.7	*n*-Butyl Isocyanate	C5H9NO	10.0
2-Octanol	$C_8H_{18}O$	7.4	2,4-Toluene Diisocyanate	C9H6N2O2	9.5
Cyclohexanol	$C_6H_{12}O$	11.1	Cyanogen	C2N2	32.0
Phenol	C_6H_6O	8.6	Acrylonitrile	C3H3N	17.0
Ethylene Glycol	$C_2H_6O_2$	42.0	Propionitrile	C3H5N	14.0
Glycerol	$C_3H_8O_3$	11.3	*trans*-Crotonitrile	C4H5N	8.8
2-Butyne-1,4-Diol	$C_4H_6O_2$	14.8	Isobutyronitrile	C4H7N	12.7
cis-2-butene-1,4-Diol	$C_4H_8O_2$	13.3	Adiponitrile	C6H8N2	5.0
Hexylene Glycol	$C_6H_{14}O_2$	9.9	Methylglutaronitrile	C6H8N2	3.25
Trimethylolpropane	$C_6H_{14}O_3$	9.7	Hydrogen Cyanide	CHN	40.0
Triethylene Glycol	$C_6H_{14}O_4$	9.2	Hydracrylonitrile	C3H5NO	12.1
1,3-Benzenediol	$C_6H_6O_2$	12.8	2-Nitropropane	C3H7NO2	11.0
Acetaldehyde	C_2H_4O	57.0	Nitromethane	CH3NO2	63.0
Acrolein	C_3H_4O	31.0	Tetrahydrofurfuryl Alcohol	C5H10O2	9.7

Table E.9. Continued

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Propanal	C_3H_6O	16.1	1-Ethoxy-2-Propanol	C5H12O2	56.0
cis-Crotonaldehyde	C_4H_6O	15.5	2-(2-Methoxyethoxy)Ethanol	C5H12O3	22.7
2-Methylpropanal	C_4H_8O	11.0	Furfural	C5H4O2	19.3
Benzaldehyde	C_7H_6O	8.5	Furfuryl Alcohol	C5H6O2	16.3
Formaldehyde	CH_2O	73.0	2-Butoxyethanol	C6H14O2	12.7
Methyl Ethyl Ketone	C_4H_8O	11.0	2-(2-Ethoxyethoxy)Ethanol	C6H14O3	16.0
3-Pentanone	$C_5H_{10}O$	8.0	Propylene Glycol *n*-Butyl Ether	C7H16O2	8.4
2-Pentanone	$C_5H_{10}O$	8.2	2-(2-Butoxyethoxy)Ethanol	C8H18O3	24.6
Methyl Isopropyl Ketone	$C_5H_{10}O$	9.02	Acetone Cyanohydrin	C4H7NO	12.0
Mesityl Oxide	$C_6H_{10}O$	8.8	Morpholine	C4H9NO	15.2
Cyclohexanone	$C_6H_{10}O$	9.4	N-Methyl-2-Pyrrolidone	C5H9NO	9.5
Methyl Isobutyl Ketone	$C_6H_{12}O$	8.0	ε-Caprolactam	C6H11NO	8.0
2-Hexanone	$C_6H_{12}O$	8.0	4-(2-Aminoethyl) Morpholine	C6H14N2O	7.9
5-Methyl-2-Hexanone	$C_7H_{14}O$	8.2	Dimethyl Sulfoxide	C2H6OS	28.5
Acetophenone	C_8H_8O	6.7	2-Mercaptoethanol	C2H6OS	18.0
Isophorone	$C_9H_{14}O$	3.8	Acetyl Chloride	C2H3ClO	19.0
Diisobutyl Ketone	$C_9H_{18}O$	6.2	Methyl Chloroformate	C2H3ClO2	26.0
Methyl Formate	$C_2H_4O_2$	23.0	2-Chloroethanol	C2H5ClO	15.9
n-Butyl Formate	$C_5H_{10}O_2$	8.0	α-Epichlorohydrin	C3H5ClO	21.0
Isobutyl Formate	$C_5H_{10}O_2$	8.0	1-Chloro-2,4-Dinitrobenzene	C6H3ClN2O4	22.0
Vinyl Acetate	$C_4H_6O_2$	13.4	3,4-Dichloroaniline	C6H5Cl2N	7.2
n-Propyl Acetate	$C_5H_{10}O_2$	8.0	Bromoethane	C2H5Br	8.0
Allyl Acetate	$C_5H_8O_2$	9.3	1-Bromobutane	C4H9Br	6.6
1-Methylvinyl Acetate	$C_5H_8O_2$	10.0	Tetrafluoroethylene	C2F4	50
Ethylene Glycol Diacetate	$C_6H_{10}O_4$	8.4	1,1-Difluoroethylene	C2H2F2	21.5
n-Butyl Acetate	$C_6H_{12}O_2$	7.6	Vinyl Fluoride	C2H3F	25.0
Isobutyl Acetate	$C_6H_{12}O_2$	8.0	1,1,1-Trifluoroethane	C2H3F3	17.0
sec-Butyl Acetate	$C_6H_{12}O_2$	7.6	1,1,2-Trifluoroethane	C2H3F3	22.6
Glyceryl Triacetate	$C_9H_{14}O_6$	7.7	1,1-Difluoroethane	C2H4F2	17.5
Methyl Propionate	$C_4H_8O_2$	13.0	1,2-Difluoroethane	C2H4F2	19.0
Ethyl Propionate	$C_5H_{10}O_2$	11.0	Ethyl Fluoride	C2H5F	17.5
Propionic Anhydride	$C_6H_{10}O_3$	11.9	3,3,3-Trifluoropropene	C3H3F3	13.5
Butyric Anhydride	$C_8H_{14}O_3$	7.6	Difluoromethane	CH2F2	29.3
Isobutyric Anhydride	$C_8H_{14}O_3$	7.7	Chlorotrifluoroethylene	C2ClF3	38.7
Dimethyl Ether	C_2H_6O	26.2	1,1-Dichloro-1-Fluoroethane	C2H3Cl2F	15.4
Methyl Vinyl Ether	C_3H_6O	39.0	1-Chloro-1,1-Difluoroethane	C2H3ClF2	18.2
Methyl Ethyl Ether	C_3H_8O	10.1	2,3-Dichloropropene	C3H4Cl2	11.0
Diethyl Ether	$C_4H_{10}O$	46.0	1,2,3-Trichloropropane	C3H5Cl3	12.6
Divinyl Ether	C_4H_6O	27.0	1,2-Dichloropropane	C3H6Cl2	14.5
Ethyl Vinyl Ether	C_4H_8O	19.0	Isopropyl Chloride	C3H7Cl	10.7
Methyl *tert*-Butyl Ether	$C_5H_{12}O$	8.4	*n*-Propyl Chloride	C3H7Cl	11.1
Ethyl Propyl Ether	$C_5H_{12}O$	9.0	Chloroprene	C4H5Cl	20.0
Diisopropyl Ether	$C_6H_{14}O$	7.9	1,4-Dichlorobutane	C4H8Cl2	4.0
Diphenyl Ether	$C_{12}H_{10}O$	6.0	*n*-Butyl Chloride	C4H9Cl	10.1
Methylal	$C_3H_8O_2$	18.5	1-Chloropentane	C5H11Cl	8.6
1,2-Dimethoxyethane	$C_4H_{10}O_2$	10.4	*o*-Chlorotoluene	C7H7Cl	8.3
1,2-Propylene Oxide	C_3H_6O	35.5	*trans*-1,2-Dichloroethylene	C2H2Cl2	15.3
Trioxane	$C_3H_6O_3$	29.0	1,1-Dichloroethylene	C2H2Cl2	15.5
Furan	C_4H_4O	23.0	Vinyl Chloride	C2H3Cl	33.0

Table E.9. Continued

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
1,2-Epoxy-2-Methylpropane	C_4H_8O	13.5	1,1,1-Trichloroethane	C2H3Cl3	12.5
1,2-Epoxybutane	C_4H_8O	18.3	1,1-Dichloroethane	C2H4Cl2	11.4
Tetrahydrofuran	C_4H_8O	11.8	1,2-Dichloroethane	C2H4Cl2	16.0
1,4-Dioxane	$C_4H_8O_2$	22.0	Ethyl Chloride	C2H5Cl	15.4
2-Ethylhexyl Acrylate	$C_{11}H_{20}O_2$	8.2	Dichloromethane	CH2Cl2	22.0
Methyl Acrylate	$C_4H_6O_2$	14.4	Methyl Chloride	CH3Cl	17.2
Ethyl Acrylate	$C_5H_8O_2$	11.0			

Table E.10. Test set of recommended upper flammability limit data

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
1-Decene	$C_{10}H_{20}$	5.7	Trioctyl Trimellitate	$C_{33}H_{54}O_6$	2.5
Ethylene	C_2H_4	36.0	Propylene Glycol monomethyl Ether Acetate	$C_6H_{12}O_3$	13.1
1-Octene	C_8H_{16}	6.8	Diethylene Glycol Ethyl Ether Acetate	$C_8H_{16}O_4$	19.4
cis-2-Butene	C_4H_8	9.7	Acetic Acid	$C_2H_4O_2$	19.9
Isobutene	C_4H_8	9.6	Propionic Acid	$C_3H_6O_2$	12.0
Cyclohexene	C_6H_{10}	7.7	*n*-Pentanoic Acid	$C_5H_{10}O_2$	7.6
d-Limonene	$C_{10}H_{16}$	6.1	Formic Acid	CH_2O_2	38.0
Propadiene	C_3H_4	17.0	Acrylic Acid	$C_3H_4O_2$	17.0
1,4-Hexadiene	C_6H_{10}	7.9	Isobutyric Acid	$C_4H_8O_2$	9.2
Methylcyclopentadiene	C_6H_8	7.6	2-Ethyl Hexanoic acid	$C_8H_{16}O_2$	8.64
n-Decane	$C_{10}H_{22}$	5.4	Trimethyl Silane	$C_3H_{10}Si$	44.0
n-Butane	C_4H_{10}	8.4	Hexamethyldisilazane	$C_6H_{19}NSi_2$	23.2
n-Heptane	C_7H_{16}	6.7	Thiophene	C_4H_4S	12.5
n-Octane	C_8H_{18}	6.5	Tetrahydrothiophene	C_4H_8S	12.3
n-Nonane	C_9H_{20}	5.6	*n*-Propylamine	C_3H_9N	10.4
Isobutane	C_4H_{10}	8.4	*n*-Butylamine	$C_4H_{11}N$	9.8
2-Methylhexane	C_7H_{16}	6.0	Methylamine	CH_5N	20.7
2,2-Dimethylbutane	C_6H_{14}	7.0	Tri-*n*-Butylamine	$C_{12}H_{27}N$	6.18
2,3-Dimethylbutane	C_6H_{14}	7.0	Trimethylamine	C_3H_9N	11.6
2,3-Dimethylpentane	C_7H_{16}	6.7	Diethylamine	$C_4H_{11}N$	10.1
2,2,3,3-Tetramethylpentane	C_9H_{20}	4.9	*tert*-Butylamine	$C_4H_{11}N$	8.9
Cyclohexane	C_6H_{12}	7.8	Diisopropylamine	$C_6H_{15}N$	8.5
Cycloheptane	C_7H_{14}	6.7	Di-*n*-Butylamine	$C_8H_{19}N$	9.62
sec-Butylcyclohexane	$C_{10}H_{20}$	5.47	Pyridine	C_5H_5N	12.0
Methylcyclohexane	C_7H_{14}	6.7	3-Methylpyridine	C_6H_7N	8.7
Methylcyclopentane	C_6H_{12}	8.4	N,N-Dimethylaniline	$C_8H_{11}N$	7.0
Ethylcyclopentane	C_7H_{14}	6.7	Ethyleneimine	C_2H_5N	46.0
trans-Decahydronaphthalene	$C_{10}H_{18}$	4.9	Diethylenetriamine	$C_4H_{13}N_3$	6.7
Isobutylbenzene	$C_{10}H_{14}$	6.0	Diallylamine	$C_6H_{11}N$	14.2
sec-Butylbenzene	$C_{10}H_{14}$	6.9	Hexamethyleneimine	$C_6H_{13}N$	9.6
tert-Butylbenzene	$C_{10}H_{14}$	5.8	Tetramethylethylenediamine	$C_6H_{16}N_2$	9.0
p-Diethylbenzene	$C_{10}H_{14}$	6.1	Monoethanolamine	C_2H_7NO	13.1
m-Xylene	C_8H_{10}	6.4	Methyl Isocyanate	C_2H_3NO	26.0

Table E.10. Continued

Compound	Formula	UFL/vol%
m-Methylstyrene	C_9H_{10}	11.0
Ethanol	C_2H_6O	19.0
1-Pentanol	$C_5H_{12}O$	10.0
1-Nonanol	$C_9H_{20}O$	6.1
2-Pentanol	$C_5H_{12}O$	9.0
2-Methyl-1-Butanol	$C_5H_{12}O$	9.0
3-Methyl-1-Butanol	$C_5H_{12}O$	9.0
1,2-Propylene Glycol	$C_3H_8O_2$	12.5
1,4-Butanediol	$C_4H_{10}O_2$	15.6
Diethylene Glycol	$C_4H_{10}O_3$	37.0
trans-2-Butene-1,4-diol	$C_4H_8O_2$	13.3
Neopentyl Glycol	$C_5H_{12}O_2$	18.8
trans-Crotonaldehyde	C_4H_6O	15.5
Butanal	C_4H_8O	12.5
Pentanal	$C_5H_{10}O$	7.8
Acetone	C_3H_6O	13.0
Methyl Isopropenyl Ketone	C_5H_8O	9.0
Acetylacetone	$C_5H_8O_2$	11.4
2-Heptanone	$C_7H_{14}O$	7.9
Ethyl Formate	$C_3H_6O_2$	15.7
2-Ethylhexyl Acetate	$C_{10}H_{20}O_2$	8.14
Methyl Acetate	$C_3H_6O_2$	14.0
Ethyl Acetate	$C_4H_8O_2$	11.5
Isopropyl Acetate	$C_5H_{10}O_2$	7.2
Isopentyl Acetate	$C_7H_{14}O_2$	7.0
n-Pentyl Acetate	$C_7H_{14}O_2$	7.1
Isobutyl Isobutyrate	$C_8H_{16}O_2$	7.59
Acetic Anhydride	$C_4H_6O_3$	10.0
Phthalic Anhydride	$C_8H_4O_3$	9.2
tert-Butyl Ethyl Ether	$C_6H_{14}O$	6.75
Di-*n*-Butyl Ether	$C_8H_{18}O$	8.5
Acetal	$C_6H_{14}O_2$	10.4
Ethylene Oxide	C_2H_4O	100
1,3-Propylene Oxide	C_3H_6O	37.0
Isobutyl Acrylate	$C_7H_{12}O_2$	8.0
1,6-Hexamethylene Diisocyanate	$C_8H_{12}N_2O_2$	9.5
Acetonitrile	C_2H_3N	17.0
Methacrylonitrile	C_4H_5N	11.0
cis-Crotonitrile	C_4H_5N	8.8
Benzonitrile	C_7H_5N	12.0
2-Methoxyethanol	$C_3H_8O_2$	20.6
2-Ethoxyethanol	$C_4H_{10}O_2$	15.6
Propylene Glycol Monomethyl Ether	$C_4H_{10}O_2$	13.1
Propylene Glycol 1-*tert*-Butyl Ether	$C_7H_{16}O_2$	6.75
Dipropylene Glycol *n*-Propyl Ether	$C_9H_{20}O_3$	5.7
2-Butoxime	C_4H_9NO	12.3
4-Formylmorpholine	$C_5H_9NO_2$	8.2
N-Ethyl-Morpholine	$C_6H_{13}NO$	9.8
Pentafluoroethyl Methyl Ether	$C_3H_3F_5O$	13.5
Methyl Chloroacetate	$C_3H_5ClO_2$	18.5
Benzoyl Chloride	C_7H_5ClO	4.9
Vinyl Bromide	C_2H_3Br	13.5
1-Bromopropane	C_3H_7Br	9.1
Methyl Bromide	CH_3Br	16.0
1,1,2,2,3-Pentafluoropropane	$C_3H_3F_5$	11.5
Methyl Fluoride	CH_3F	19.9
Chlorofluoromethane	CH_2ClF	26.5
3-Chloropropene	C_3H_5Cl	11.9
2-Chloropropene	C_3H_5Cl	16.0
1,4-Dichloro-*trans*-2-Butene	$C_4H_6Cl_2$	4.0
3,4-Dichloro-1-Butene	$C_4H_6Cl_2$	12.2
Isobutyl Chloride	C_4H_9Cl	8.8
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	6.6
o-Dichlorobenzene	$C_6H_4Cl_2$	9.2
Monochlorobenzene	C_6H_5Cl	9.6
Benzyl Chloride	C_7H_7Cl	7.1
p-Chlorotoluene	C_7H_7Cl	8.3
cis-1,2-Dichloroethylene	$C_2H_2Cl_2$	15.5
1,1,2-Trichloroethane	$C_2H_3Cl_3$	14.6
Trichloroethylene	C_2HCl_3	29.0

Table E.11. Training set of upper flammability limit data from the Bureau of Mines

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Acetylene	C_2H_2	100	Triethylene Glycol	$C_6H_{14}O_4$	9.2
Ethylene	C_2H_4	36	Propanal	C_3H_6O	17
1-Butene	C_4H_8	10	*cis*-Crotonaldehyde	C_4H_6O	16
Isobutene	C_4H_8	9.6	Acetone	C_3H_6O	13
2-Methyl-2-Butene	C_5H_{10}	8.7	Methyl Ethyl Ketone	C_4H_8O	10
1,3-Butadiene	C_4H_6	12	Methyl Isopropenyl Ketone	C_5H_8O	9
Methane	CH_4	15	Isobutyl Formate	$C_5H_{10}O_2$	8.9
Propane	C_3H_8	9.5	*n*-Butyl Acetate	$C_6H_{12}O_2$	8
n-Butane	C_4H_{10}	8.4	Isopentyl Acetate	$C_7H_{14}O_2$	7
Neopentane	C_5H_{12}	7.5	Methyl Propionate	$C_4H_8O_2$	13
2,3-Dimethylpentane	C_7H_{16}	6.8	Acetic Anhydride	$C_4H_6O_3$	10
Cyclohexane	C_6H_{12}	7.8	Diethyl Ether	$C_4H_{10}O$	36
Methylcyclohexane	C_7H_{14}	6.7	Divinyl Ether	C_4H_6O	27
Ethylcyclopentane	C_7H_{14}	6.7	Acetal	$C_6H_{14}O_2$	10
Bicyclohexyl	$C_{12}H_{22}$	5.1	Ethylene Oxide	C_2H_4O	100
Benzene	C_6H_6	7.9	Dimethyl Sulfide	C_2H_6S	20
Ethylbenzene	C_8H_{10}	6.7	Carbon Disulfide	CS_2	50
n-Butylbenzene	$C_{10}H_{14}$	5.8	Ethyl Mercaptan	C_2H_6S	18
p-Xylene	C_8H_{10}	6.6	Trimethylamine	C_3H_9N	12
tert-Butylbenzene	$C_{10}H_{14}$	5.8	Triethylamine	$C_6H_{15}N$	8
Naphthalene	$C_{10}H_8$	5.9	Diethylamine	$C_4H_{11}N$	10
Methanol	CH_4O	36	Pyridine	C_5H_5N	12
Ethanol	C_2H_6O	19	Aniline	C_6H_7N	8.3
1-Propanol	C_3H_8O	14	Ethyleneimine	C_2H_5N	46
1-Butanol	$C_4H_{10}O$	12	N,N-Dimethylformamide	C_3H_7NO	14
1-Pentanol	$C_5H_{12}O$	10	Hydrogen Cyanide	CHN	40
2-Methyl-1-Propanol	$C_4H_{10}O$	11	Furfuryl Alcohol	$C_5H_6O_2$	16
2-Butanol	$C_4H_{10}O$	9.8	Acetone Cyanohydrin	C_4H_7NO	12
2-Methyl-2-Propanol	$C_4H_{10}O$	9	Methyl Bromide	CH_3Br	15
3-Methyl-1-Butanol	$C_5H_{12}O$	9	Vinyl Chloride	C_2H_3Cl	33
Allyl Alcohol	C_3H_6O	18	Trichloroethylene	C_2HCl_3	40

Table E.12. Test set of upper flammability limit data from the Bureau of Mines

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
cis-2-Butene	C_4H_8	9.7	Acrolein	C_3H_4O	31.0
trans-2-Butene	C_4H_8	9.7	*trans*-Crotonaldehyde	C_4H_6O	16.0
3-Methyl-1-Butene	C_5H_{10}	9.1	Diisobutyl Ketone	$C_9H_{18}O$	6.2
Methylcyclopentadiene	C_6H_8	7.6	Methyl Formate	$C_2H_4O_2$	23.0
Ethane	C_2H_6	12.4	Ethyl Formate	$C_3H_6O_2$	16.0
n-Pentane	C_5H_{12}	7.8	*n*-Butyl Formate	$C_5H_{10}O_2$	8.2
n-Hexane	C_6H_{14}	7.4	Methyl Acetate	$C_3H_6O_2$	16.0
n-Heptane	C_7H_{16}	6.7	Ethyl Acetate	$C_4H_8O_2$	11.0
n-Decane	$C_{10}H_{22}$	5.6	*n*-Propyl Acetate	$C_5H_{10}O_2$	8.0
Isobutane	C_4H_{10}	8.4	*n*-Pentyl Acetate	$C_7H_{14}O_2$	7.1
2,2-Dimethylbutane	C_6H_{14}	7.0	Ethyl Propionate	$C_5H_{10}O_2$	11.0
2,3-Dimethylbutane	C_6H_{14}	7.0	Phthalic Anhydride	$C_8H_4O_3$	9.2
Cyclopropane	C_3H_6	10.4	Dimethyl Ether	C_2H_6O	27.0
Cycloheptane	C_7H_{14}	6.7	Diisopropyl Ether	$C_6H_{14}O$	7.9
Toluene	C_7H_8	7.1	Ethyl Propyl ether	$C_5H_{12}O$	9.0

Table E.12. Continued

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
o-Xylene	C_8H_{10}	6.4	Methyl Vinyl Ether	C_3H_6O	39.0
m-Xylene	C_8H_{10}	6.4	*tert*-Butylamine	$C_4H_{11}N$	8.9
Cumene	C_9H_{12}	6.5	Allylamine	C_3H_7N	22.0
Isobutylbenzene	$C_{10}H_{14}$	6.0	2-Methoxyethanol	$C_3H_8O_2$	20.0
sec-Butylbenzene	$C_{10}H_{14}$	5.8	*n*-Butyl Chloride	C_4H_9Cl	10.0
1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	5.0	1-Chloropentane	$C_5H_{11}Cl$	8.6
Acetaldehyde	C_2H_4O	60.0			

Table E.13. Training set of upper flammability limit data from the European method

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Acetylene	C_2H_2	89	Diisopropyl Ether	$C_6H_{14}O$	21.2
Methylacetylene	C_3H_4	16.8	Methyl Ethyl Ether	C_3H_8O	10.1
Ethylene	C_2H_4	32.4	Methyl *tert*-Pentyl Ether	$C_6H_{14}O$	7.1
1-Pentene	C_5H_{10}	8.7	Ethyl Vinyl Ether	C_4H_8O	28.0
cis-2-Butene	C_4H_8	10	Methylal	$C_3H_8O_2$	16.9
Isobutene	C_4H_8	8.8	Acetal	$C_6H_{14}O_2$	10.4
3-Methyl-1-Butene	C_5H_{10}	9.1	1,4-Dioxane	$C_4H_8O_2$	22.5
d-Limonene	$C_{10}H_{16}$	6.1	1,2-Epoxy-2-Methylpropane	C_4H_8O	13.5
Propadiene	C_3H_4	17.0	Tetrahydrofuran	C_4H_8O	12.4
Isoprene	C_5H_8	9.7	Methyl Methacrylate	$C_5H_8O_2$	12.5
Methylcyclopentadiene	C_6H_8	7.6	Isobutyl Acrylate	$C_7H_{12}O_2$	8.6
Dicyclopentadiene	$C_{10}H_{12}$	6.3	Ethyl Lactate	$C_5H_{10}O_3$	11.4
Methane	CH_4	17.0	Formic Acid	CH_2O_2	45.5
Propane	C_3H_8	11.0	2-Ethyl Hexanoic Acid	$C_8H_{16}O_2$	6.7
n-Pentane	C_5H_{12}	7.8	Hexamethyldisiloxane	$C_6H_{18}OSi_2$	28.4
n-Hexane	C_6H_{14}	9.18	Tetramethylsilane	$C_4H_{12}Si$	37.9
n-Octane	C_8H_{18}	6.5	Methyl Dichlorosilane	CH_4Cl_2Si	87.0
n-Undecane	$C_{11}H_{24}$	6.5	Vinyltrimethoxysilane	$C_5H_{12}O_3Si$	28.2
2-Methylpentane	C_6H_{14}	7.0	Trimethyl Silanol	$C_3H_{10}OSi$	45.2
3-Methylpentane	C_6H_{14}	7.0	Carbon Disulfide	CS_2	60.0
2-Methylhexane	C_7H_{16}	6.0	Methyl Mercaptan	CH_4S	21.8
Neopentane	C_5H_{12}	7.7	Ethyl Mercaptan	C_2H_6S	18.0
2,3-Dimethylpentane	C_7H_{16}	6.7	*n*-Propylamine	C_3H_9N	13.6
2,2,4-Trimethylpentane	C_8H_{18}	6.0	Triethylamine	$C_6H_{15}N$	8.0
Cyclopropane	C_3H_6	10.4	Diethylamine	$C_4H_{11}N$	10.1
Cyclobutane	C_4H_8	10.0	Isobutylamine	$C_4H_{11}N$	10.8
Ethylcyclohexane	C_8H_{16}	6.6	Isopropylamine	C_3H_9N	15.0
Methylcyclopentane	C_6H_{12}	8.55	*tert*-Butylamine	$C_4H_{11}N$	9.2
cis-Decahydronaphthalene	$C_{10}H_{18}$	4.9	Tri-*n*-Butylamine	$C_{12}H_{27}N$	6.0
trans-Decahydronaphthalene	$C_{10}H_{18}$	4.9	Tripropylamine	$C_9H_{21}N$	5.6
Bicyclohexyl	$C_{12}H_{22}$	5.1	Pyridine	C_5H_5N	10.6
Benzene	C_6H_6	8.6	Aniline	C_6H_7N	11.0
Ethylbenzene	C_8H_{10}	7.8	N,N-Dimethylaniline	$C_8H_{11}N$	7.0
m-Xylene	C_8H_{10}	7.0	Ethyleneimine	C_2H_5N	46.0
Cumene	C_9H_{12}	6.5	Hexamethyleneimine	$C_6H_{13}N$	9.6

Table E.13. Continued

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Isobutylbenzene	$C_{10}H_{14}$	6.0	Tetramethylethylenediamine	$C_6H_{16}N_2$	9.0
sec-Butylbenzene	$C_{10}H_{14}$	6.9	Monoethanolamine	C_2H_7NO	13.1
2-Phenylbutene-1	$C_{10}H_{12}$	6.4	N,N-Dimethylformamide	C_3H_7NO	16.4
Styrene	C_8H_8	8.0	N-Methylformamide	C_2H_5NO	17.8
Styrene	C_8H_8	6.1	N,N-Dimethylacetamide	C_4H_9NO	11.5
α-Methylstyrene	C_9H_{10}	6.6	2-Aminoethoxyethanol	$C_4H_{11}NO_2$	15.5
Naphthalene	$C_{10}H_8$	5.9	1-Amino-2-propanol	C_3H_9NO	10.4
1-Methylnaphthalene	$C_{11}H_{10}$	6.5	*n*-Butyl Isocyanate	C_5H_9NO	10.0
1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	5.0	Hydrogen Cyanide	CHN	46.6
Methanol	CH_4O	37.5	Acetonitrile	C_2H_3N	17.0
Ethanol	C_2H_6O	15.0	Acrylonitrile	C_3H_3N	28.0
1-Propanol	C_3H_8O	19.2	Methacrylonitrile	C_4H_5N	13.2
1-Butanol	$C_4H_{10}O$	11.3	Cyanogen	C_2N_2	36.6
1-Pentanol	$C_5H_{12}O$	10.5	Tetrahydrofurfuryl Alcohol	$C_5H_{10}O_2$	9.7
2-Methyl-2-Propanol	$C_4H_{10}O$	8.1	Furfuryl Alcohol	$C_5H_6O_2$	16.3
2-Methyl-2-Butanol	$C_5H_{12}O$	10.2	2-Ethoxyethanol	$C_4H_{10}O_2$	15.7
3-Methyl-1-Butanol	$C_5H_{12}O$	10.3	2-Butoxyethanol	$C_6H_{14}O_2$	10.6
4-Methyl-2-Pentanol	$C_6H_{14}O$	5.5	2-(2-Methoxyethoxy)Ethanol	$C_5H_{12}O_3$	9.5
2,6-Dimethyl-4-Heptanol	$C_9H_{20}O$	7.7	Propylene Glycol Monomethyl Ether	$C_4H_{10}O_2$	13.7
Phenol	C_6H_6O	9.5	2-(2-Hexoxyethoxy)Ethanol	$C_{10}H_{22}O_3$	5.9
Ethylene Glycol	$C_2H_6O_2$	51.0	1-Ethoxy-2-Propanol	$C_5H_{12}O_2$	56.0
Ethylene Glycol	$C_2H_6O_2$	42.0	Propylene Glycol *n*-Butyl Ether	$C_7H_{16}O_2$	8.4
Diethylene Glycol	$C_4H_{10}O_3$	37.0	N-Methyl-2-Pyrrolidone	C_5H_9NO	9.5
Triethylene Glycol	$C_6H_{14}O_4$	9.2	Morpholine	C_4H_9NO	15.2
Hexylene Glycol	$C_6H_{14}O_2$	9.9	2-Mercaptoethanol	C_2H_6OS	18.0
Glycerol	$C_3H_8O_3$	11.3	Acetyl Chloride	C_2H_3ClO	19.0
1,4-Butanediol	$C_4H_{10}O_2$	15.6	Methyl Chloroformate	$C_2H_3ClO_2$	26.0
Formaldehyde	CH_2O	73.0	1-Chloro-2,4-Dinitrobenzene	$C_6H_3ClN_2O_4$	22.0
Acetaldehyde	C_2H_4O	57.0	Methyl Bromide	CH_3Br	20.0
2-Methylpropanal	C_4H_8O	11.0	Vinyl Bromide	C_2H_3Br	13.5
2-Ethylhexanal	$C_8H_{16}O$	6.6	1,1-Difluoroethylene	$C_2H_2F_2$	25.1
Acrolein	C_3H_4O	31.0	Fluorobenzene	C_6H_5F	8.9
trans-Crotonaldehyde	C_4H_6O	15.5	3,3,3-Trifluoropropene	$C_3H_3F_3$	16.9
Benzaldehyde	C_7H_6O	8.5	Vinyl Fluoride	C_2H_3F	28.9
Acetone	C_3H_6O	14.3	Methyl Iodide	CH_3I	66.0
3-Hexanone	$C_6H_{12}O$	8.0	1,1-Dichloro-1-Fluoroethane	$C_2H_3Cl_2F$	17.7
Cyclopentanone	C_5H_8O	10.8	Chlorotrifluoroethylene	C_2ClF_3	64.3
Cyclohexanone	$C_6H_{10}O$	9.4	1-Chloro-1,1-Difluoroethane	$C_2H_3ClF_2$	17.9
Methyl Formate	$C_2H_4O_2$	23.0	1,2-Dichloropropane	$C_3H_6Cl_2$	14.5
Ethyl Formate	$C_3H_6O_2$	16.5	1,2,3-Trichloropropane	$C_3H_5Cl_3$	12.6
Isobutyl Formate	$C_5H_{10}O_2$	8.0	Isobutyl Chloride	C_4H_9Cl	8.8
Ethyl Acetate	$C_4H_8O_2$	12.8	3-Chloropropene	C_3H_5Cl	11.2
n-Butyl Acetate	$C_6H_{12}O_2$	7.5	*n*-Butyl Chloride	C_4H_9Cl	10.1
Isobutyl Acetate	$C_6H_{12}O_2$	10.5	3,4-Dichloro-1-Butene	$C_4H_6Cl_2$	12.2
Isopropyl Acetate	$C_5H_{10}O_2$	8.0	Monochlorobenzene	C_6H_5Cl	11.0
Vinyl Acetate	$C_4H_6O_2$	13.4	*p*-Chlorotoluene	C_7H_7Cl	8.3

Table E.13. Continued

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
n-Pentyl Acetate	$C_7H_{14}O_2$	7.5	Methyl Chloride	CH_3Cl	19.0
Glyceryl Triacetate	$C_9H_{14}O_6$	7.7	Ethyl Chloride	C_2H_5Cl	14.8
1-Methylvinyl Acetate	$C_5H_8O_2$	10.0	Vinyl Chloride	C_2H_3Cl	31.0
Methyl Propionate	$C_4H_8O_2$	13.0	Dichloromethane	CH_2Cl_2	22.0
Acetic Anhydride	$C_4H_6O_3$	10.2	1,1-Dichloroethane	$C_2H_4Cl_2$	16.0
Butyric Anhydride	$C_8H_{14}O_3$	7.6	1,2-Dichloroethane	$C_2H_4Cl_2$	16.2
Phthalic Anhydride	$C_8H_4O_3$	10.5	1,1,1-Trichloroethane	$C_2H_3Cl_3$	15.5
Dimethyl Ether	C_2H_6O	32.0	*cis*-1,2-Dichloroethylene	$C_2H_2Cl_2$	16.0

Table E.14. Test set of upper flammability limit data from the European method

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Propylene	C_3H_6	11.1	1,2-Epoxybutane	C_4H_8O	18.3
1-Butene	C_4H_8	10.0	Ethyl Acrylate	$C_5H_8O_2$	13
trans-2-Butene	C_4H_8	10.0	*n*-Butyl Acrylate	$C_7H_{12}O_2$	8.0
Isobutene	C_4H_8	10.0	Dioctyl Phthalate	$C_{24}H_{38}O_4$	2.4
Cyclohexene	C_6H_{10}	7.7	Diisooctyl Phthalate	$C_{24}H_{38}O_4$	2.7
1,2-Butadiene	C_4H_6	18.3	2-Ethoxyethyl Acetate	$C_6H_{12}O_3$	10.7
1,3-Butadiene	C_4H_6	16.3	Methyl Acetoacetate	$C_5H_8O_3$	14.2
Ethane	C_2H_6	15.5	Acetic Acid	$C_2H_4O_2$	19.9
n-Butane	C_4H_{10}	9.3	Propionic Acid	$C_3H_6O_2$	12.0
n-Heptane	C_7H_{16}	6.7	*n*-Butyric Acid	$C_4H_8O_2$	10.0
n-Nonane	C_9H_{20}	5.6	*n*-Pentanoic Acid	$C_5H_{10}O_2$	7.3
n-Decane	$C_{10}H_{22}$	5.4	Trimethyl Silane	$C_3H_{10}Si$	44.0
Isobutane	C_4H_{10}	9.8	Dimethyl Sulfide	C_2H_6S	19.7
2,2-Dimethylbutane	C_6H_{14}	7.0	Thiophene	C_4H_4S	12.5
2,2-Dimethylpentane	C_7H_{16}	6.8	Tetrahydrothiophene	C_4H_8S	12.3
3,3-Diethylpentane	C_9H_{20}	5.7	Methylamine	CH_5N	20.7
Cyclohexane	C_6H_{12}	8.3	Ethylamine	C_2H_7N	13.9
Ethylcyclopentane	C_7H_{14}	6.7	*n*-Butylamine	$C_4H_{11}N$	10.0
Toluene	C_7H_8	7.8	Dimethylamine	C_2H_7N	14.4
n-Propylbenzene	C_9H_{12}	6.5	Trimethylamine	C_3H_9N	11.6
n-Butylbenzene	$C_{10}H_{14}$	5.8	Diisopropylamine	$C_6H_{15}N$	8.5
o-Xylene	C_8H_{10}	7.6	Quinoline	C_9H_7N	7.0
p-Xylene	C_8H_{10}	7.0	2-Methylpyridine	C_6H_7N	8.6
1,2,4-Trimethylbenzene	C_9H_{12}	7.3	Isoquinoline	C_9H_7N	7.0
Mesitylene	C_9H_{12}	7.3	3-Methylpyridine	C_6H_7N	8.7
tert-Butylbenzene	$C_{10}H_{14}$	5.6	4-Methylpyridine	C_6H_7N	8.7
m-Divinylbenzene	$C_{10}H_{10}$	6.2	Ethylenediamine	$C_2H_8N_2$	16.3
Biphenyl	$C_{12}H_{10}$	5.8	1,2-Propanediamine	$C_3H_{10}N_2$	11.1
Isopropanol	C_3H_8O	13.4	Pyrrolidine	C_4H_9N	10.6
2-Methyl-1-Dutanol	$C_5H_{12}O$	10.3	3-Amino-1-Propanol	C_3H_9NO	10.6
Allyl Alcohol	C_3H_6O	18.0	2,4-Toluene Diisocyanate	$C_9H_6N_2O_2$	9.5
Cyclohexanol	$C_6H_{12}O$	11.1	1,6-Hexamethylene Diisocyanate	$C_8H_{12}N_2O_2$	9.5
1,2-Propylene Glycol	$C_3H_8O_2$	12.6	Propionitrile	C_3H_5N	14.0
Propanal	C_3H_6O	21.0	Isobutyronitrile	C_4H_7N	12.7
Butanal	C_4H_8O	12.5	*trans*-Crotonitrile	C_4H_5N	8.8
Octanal	$C_8H_{16}O$	6.15	Benzonitrile	C_7H_5N	12.0

Table E.14. Continued

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Methyl Ethyl Ketone	C_4H_8O	11.5	*cis*-Crotonitrile	C_4H_5N	8.8
Methyl Isobutyl Ketone	$C_6H_{12}O$	8.0	Nitromethane	CH_3NO_2	63.0
2-Hexanone	$C_6H_{12}O$	8.0	Furfural	$C_5H_4O_2$	19.3
5-Methyl-2-Hexanone	$C_7H_{14}O$	8.8	2-Methoxyethanol	$C_3H_8O_2$	20.6
Diisobutyl Ketone	$C_9H_{18}O$	6.2	Dimethyl Sulfoxide	C_2H_6OS	27.0
Isophorone	$C_9H_{14}O$	3.8	α-Epichlorohydrin	C_3H_5ClO	34.4
n-Propyl Formate	$C_4H_8O_2$	7.8	2-Chloroethanol	C_2H_5ClO	16.1
n-Butyl Formate	$C_5H_{10}O_2$	8.0	Bromoethane	C_2H_5Br	11.3
Methyl Acetate	$C_3H_6O_2$	16.0	1-Bromopropane	C_3H_7Br	9.1
n-Propyl Acetate	$C_5H_{10}O_2$	8.0	1-Bromobutane	C_4H_9Br	6.6
Isopentyl Acetate	$C_7H_{14}O_2$	9.0	Tetrafluoroethylene	C_2F_4	59.0
Allyl Acetate	$C_5H_8O_2$	9.3	1,1-Difluoroethane	$C_2H_4F_2$	20.2
Ethyl Propionate	$C_5H_{10}O_2$	11.0	Isopropyl Chloride	C_3H_7Cl	10.7
n-Propyl *n*-Butyrate	$C_7H_{14}O_2$	7.5	Chloroprene	C_4H_5Cl	20.0
Diethyl Ether	$C_4H_{10}O$	36.0	*n*-Propyl Chloride	C_3H_7Cl	10.5
Di-*n*-Butyl Ether	$C_8H_{18}O$	8.5	*n*-Propyl Chloride	C_3H_7Cl	11.1
Methyl *tert*-Butyl Ether	$C_5H_{12}O$	8.4	1-Chloropentane	$C_5H_{11}Cl$	8.6
1,2-Dimethoxyethane	$C_4H_{10}O_2$	10.4	2-Chloropropene	C_3H_5Cl	16.0
Diphenyl Ether	$C_{12}H_{10}O$	15.0	*o*-Chlorotoluene	C_7H_7Cl	8.3
Trioxane	$C_3H_6O_3$	28.7	*trans*-1,2-Dichloroethylene	$C_2H_2Cl_2$	12.8
1,2-Propylene Oxide	C_3H_6O	15.0			

Table E.15. Training set of upper flammability limit data from the ASHRAE apparatus

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Acetylene	C_2H_2	100	α-Epichlorohydrin	C_3H_5ClO	21.0
Propylene	C_3H_6	11.2	2-Chloroethanol	C_2H_5ClO	15.9
1-Butene	C_4H_8	10.0	Methyl Chloroacetate	$C_3H_5ClO_2$	18.5
trans-2-Butene	C_4H_8	9.7	Bromoethane	C_2H_5Br	8.0
3-Methyl-1-Butene	C_5H_{10}	9.1	1-Bromobutane	C_4H_9Br	6.6
1,3-Butadiene	C_4H_6	16.0	Vinyl Bromide	C_2H_3Br	13.5
Methylcyclopentadiene	C_6H_8	7.6	Vinyl Bromide	C_2H_3Br	15.0
1,4-Hexadiene	C_6H_{10}	7.9	Difluoromethane	CH_2F_2	29.3
Methane	CH_4	15.8	Tetrafluoroethylene	C_2F_4	50.0
Ethane	C_2H_6	12.5	1,1-Difluoroethane	$C_2H_4F_2$	17.5
Propane	C_3H_8	9.5	1,1,2-Trifluoroethane	$C_2H_3F_3$	22.6
n-Butane	C_4H_{10}	8.4	Vinyl Fluoride	C_2H_3F	25.0
n-Pentane	C_5H_{12}	7.8	Isobutyl Chloride	C_4H_9Cl	8.8
n-Heptane	C_7H_{16}	6.7	3-Chloropropene	C_3H_5Cl	11.9
n-Nonane	C_9H_{20}	2.9	Chloroprene	C_4H_5Cl	20.0
Isobutane	C_4H_{10}	8.4	2,3-Dichloropropene	$C_3H_4Cl_2$	11.0
Isopentane	C_5H_{12}	7.6	Ethyl Chloride	C_2H_5Cl	15.4
3-Methylpentane	C_6H_{14}	7.0	Dichloromethane	CH_2Cl_2	22.0
Neopentane	C_5H_{12}	7.5	1,2-Dichloroethane	$C_2H_4Cl_2$	16.0
2,3-Dimethylbutane	C_6H_{14}	7.0	1,1,1-Trichloroethane	$C_2H_3Cl_3$	12.5
Cyclopropane	C_3H_6	10.4	Trichloroethylene	C_2HCl_3	29.0
Methylcyclohexane	C_7H_{14}	6.7	*trans*-1,2-Dichloroethylene	$C_2H_2Cl_2$	15.3
Methylcyclopentane	C_6H_{12}	8.4	1,1-Dichloroethylene	$C_2H_2Cl_2$	15.5
Pentafluoroethyl Methyl Ether	$C_3H_3F_5O$	13.5			

Table E.16. Test set of upper flammability limit data from the ASHRAE apparatus

Compound	Formula	UFL/vol%	Compound	Formula	UFL/vol%
Ethylene	C_2H_4	36	Ethylcyclopentane	C_7H_{14}	6.7
Propylene	C_3H_6	11.1	Methyl Bromide	CH_3Br	16
1-Pentene	C_5H_{10}	8.7	Methyl Fluoride	CH_3F	19.9
cis-2-butene	C_4H_8	9	1,1,1-trifluoroethane	$C_2H_3F_3$	17
Isobutene	C_4H_8	9.6	1,1-difluoroethylene	$C_2H_2F_2$	21.5
Isoprene	C_5H_8	8.9	Chlorofluoromethane	CH_2ClF	26.5
n-Hexane	C_6H_{14}	7.5	1,1-dichloro-1-fluoroethane	$C_2H_3Cl_2F$	15.4
n-Octane	C_8H_{18}	6.5	Chlorotrifluoroethylene	C_2ClF_3	16
n-Decane	$C_{10}H_{22}$	5.4	1-Chloro-1,1-difluoroethane	$C_2H_3ClF_2$	18.2
2-Methylpentane	C_6H_{14}	7	1,2-dichloropropane	$C_3H_6Cl_2$	10.7
2-Methylhexane	C_7H_{16}	6	Isopropyl Chloride	C_3H_7Cl	10.7
2,2-dimethylbutane	C_6H_{14}	7	*n*-Propyl Chloride	C_3H_7Cl	11.1
2,3-dimethylpentane	C_7H_{16}	6.7	*n*-Butyl Chloride	C_4H_9Cl	10.1
3,3-diethylpentane	C_9H_{20}	5.7	1-Chloropentane	$C_5H_{11}Cl$	8.6
Cyclohexane	C_6H_{12}	8	Methyl Chloride	CH_3Cl	17.4
Cycloheptane	C_7H_{14}	6.7	Vinyl Chloride	C_2H_3Cl	33
Ethylcyclohexane	C_8H_{16}	6.6	*cis*-1,2-dichloroethylene	$C_2H_2Cl_2$	15.5
1,1-diethylcyclohexane	$C_{10}H_{20}$	6			

Table E.17. Flash point training and data sets from DIPPR® 801 database

Compound	FP/K	Reg. Set		Compound	FP/K	Reg. Set	
		1	2			1	2
n-Pentane	224.15	x	x	1,4-Dichloro-*trans*-2-Butene	326.15	x	x
n-Hexane	250.15	x	x	*cis*-1,3-Dichloropropene	294.15		
n-Heptane	269			*trans*-1,3-Dichloropropene	300.15	x	x
2-Methylhexane	263.15			1,4-Dichlorobutane	325.15		
n-Octane	287.15	x	x	1,1-Dichloroethane	263.15		
2-Methylheptane	279.15	x		1,2-Dichloroethane	286		
3-Methylheptane	279.15			1,2-Dichloropropane	286.15		
4-Methylheptane	279.15	x	x	Isopropyl Chloride	238.15		
3-Ethylhexane	278	x		Propargyl Chloride	259		
2,3-Dimethylhexane	280.15	x		1,2,3-Trichloropropane	347	x	x
2,4-Dimethylhexane	276.15	x		1,2-Dichlorobutane	298.65		
2,5-Dimethylhexane	275.15			2,3-Dichlorobutane	291.15		
3,4-Dimethylhexane	280.65			3-Chloropropene	244.15		
3-Methyl-3-Ethylpentane	276	x	x	Chlorocyclohexane	305.15	x	x
2,2,3-Trimethylpentane	272.65			Benzyl Chloride	333.15		
2,3,3-Trimethylpentane	275.65			3-Chloro-*o*-Xylene	346	x	
2,3,4-Trimethylpentane	277.15	x		4-Chloro-*o*-Xylene	340.15		
2,2,3,3-Tetramethylbutane	281			Monochlorobenzene	301.15	x	x
n-Nonane	304.15			*o*-Dichlorobenzene	339		
2,2,5-Trimethylhexane	282.15	x	x	*m*-Dichlorobenzene	336.15		
3,3,5-Trimethylheptane	304	x		*p*-Dichlorobenzene	339		
2,4,4-Trimethylhexane	283.15			Hexachlorobenzene	515	x	x
3,3-Diethylpentane	294			Benzotrichloride	364		
2,2,3,3-Tetramethylpentane	294.65	x	x	*o*-Chlorotoluene	316.15		
2,2,3,4-Tetramethylpentane	284			*p*-Chlorotoluene	322.15		
2,2,4,4-Tetramethylpentane	278.15			2,4-Dichlorotoluene	352.15		

Table E.17. Continued

Compound	FP/K	Reg. Set		Compound	FP/K	Reg. Set	
		1	2			1	2
2,3,3,4-Tetramethylpentane	294.15			*cis*-1,2-Dichloroethylene	277	x	x
Squalane	490			*trans*-1,2-Dichloroethylene	267.15	x	x
n-Decane	322.85			Chloroprene	253.15	x	x
iso-Butylcyclohexane	315.65			*n*-Propyl Chloride	242.15	x	
tert-Butylcyclohexane	315.15	x		*n*-Butyl Chloride	263.75	x	
n-Undecane	339.05	x		*sec*-Butyl Chloride	258.15	x	
n-Tridecane	363.15			1-Chloropentane	284.15	x	x
n-Tetradecane	382.45	x	x	1-Chloronaphthalene	394.15		
n-Hexadecane	407.05	x	x	1,1-Dichloroethylene	248.15		
n-Heptadecane	421.15			1,2,4-Trichlorobenzene	378.15		
n-Nonadecane	441	x		1,4-Dichloro-*cis*-2-Butene	328.15		
3-Methylnonane	319.15			2-Chloropropene	239.15		
2-Methylnonane	314			3,4-Dichloro-1-Butene	301.15	x	
4-Methylnonane	317.15	x	x	1,3-Dichloro-*trans*-2-Butene	300.15	x	x
5-Methylnonane	312	x	x	Benzyl Dichloride	361.15	x	x
2,2,4,4,6,8,8-Heptamethylnonane	368.15	x	x	Bromoethane	250.15	x	x
2-Methyloctane	299.15	x		1-Bromobutane	283		
3-Methyloctane	298.65	x	x	1-Bromoheptane	334.15	x	
4-Methyloctane	296.15			*m*-Dibromobenzene	366.15	x	x
3-Ethylheptane	296.15	x	x	Bromobenzene	324.26		
2,2-Dimethylheptane	292.15			Isopropyl Iodide	293.15		
Ethylcyclopentane	273.15			Dimethylamine	223.15		
Cyclohexane	255.93	x	x	Triethylamine	262.15		
Methylcyclohexane	269.15	x	x	Di-*n*-Propylamine	280.65		
Ethylcyclohexane	291.15			N,N-Dimethyl-*n*-Butylamine	270.15	x	x
1,1-Dimethylcyclohexane	280.15			N,N-Diethylmethylamine	250.15	x	x
cis-1,2-Dimethylcyclohexane	288.15			Diethylamine	245.15	x	x
cis-1,3-Dimethylcyclohexane	283.15			*n*-Butylamine	266.15		
cis-1,4-Dimethylcyclohexane	284.26			*n*-Pentylamine	280.15		
trans-1,4-Dimethylcyclohexane	284.26	x		Isobutylamine	260.15	x	x
1-*trans*-3,5-Trimethylcyclohexane	292.15	x	x	Cyclopropylamine	248.15	x	x
n-Propylcyclohexane	308.15			Hydrazine	313.15		
Isopropylcyclohexane	308.15	x	x	Diisobutylamine	297.35		
n-Butylcyclohexane	325.65			Isopropylamine	236.15	x	x
cis-Decahydronaphthalene	334.15			Pyrrole	312		
trans-Decahydronaphthalene	327.15	x	x	Methyl Diethanolamine	399.82	x	x
Bicyclohexyl	358.15	x	x	Monoethanolamine	366.55		
1,1-Diethylcyclohexane	322.15	x		Diethanolamine	445.15	x	x
Cycloheptane	280.15			Triethanolamine	463.15		
Cyclooctane	303.15			*sec*-Butylamine	254.15		
2,6-Dimethylheptane	290.65			Cyclohexylamine	299.65		
2,4-Dimethyl-3-Ethylpentane	291.15			Dehydroabietylamine	464		
Isobutene	197.04			Hexamethylenediamine	354.15		
1-Pentene	222			Benzylamine	338.15		
trans-2-Pentene	228	x	x	*o*-Toluidine	358.15		
3-Methyl-1-Butene	217.15			*m*-Toluidine	359	x	x
2-Methyl-2-Butene	228.15			*p*-Toluidine	360		
1-Hexene	247.15			Triethylenetetramine	408.15	x	
trans-3-Hexene	248.15	x		Ethylenediamine	311		
3-Methyl-1-Pentene	245.15	x	x	Ethyleneimine	262.04	x	x

Table E.17. Continued

Compound	FP/K	Reg. Set		Compound	FP/K	Reg. Set	
		1	2			1	2
3-Methyl-*cis*-2-Pentene	246.15			Diisopropylamine	266.15	x	x
2-Ethyl-1-Butene	247.15	x	x	Di-*n*-Butylamine	315	x	x
3,3-Dimethyl-1-Butene	241.15	x	x	Piperidine	280.15	x	x
2,3-Dimethyl-2-Butene	257.15			*p*-Aminodiphenylamine	466.5		
1-Heptene	265.15			Quinoline	374		
cis-2-Heptene	270.95	x	x	N-Aminoethyl Piperazine	372.15		
trans-2-Heptene	272	x	x	1,2-Propanediamine	306.15	x	x
trans-3-Heptene	267.15			N,N-Diethylaniline	358.15	x	
2-Methyl-1-Hexene	267.15	x		N-Methylpyrrole	288.15		
3-Methyl-1-Hexene	267.15	x		Diphenylamine	426	x	x
trans-2-Nonene	305.15	x		Quinaldine	383.15		
2,3,3-Trimethyl-1-Butene	256.15			Nitromethane	308.15		
1-Octene	284.65	x	x	Nitroethane	303.15	x	x
trans-2-Octene	287.15	x	x	1-Nitropropane	308.15	x	x
2,4,4-Trimethyl-1-Pentene	269.1	x		2-Nitropropane	301	x	x
2,4,4-Trimethyl-2-Pentene	272.15			Hydracrylonitrile	402.15	x	x
1-Nonene	299.15	x		Morpholine	308.15	x	x
1-Decene	320.15	x	x	Pyrrolidine	276	x	x
1-Dodecene	346.15			N-Methylpyrrolidine	259		
1-Tridecene	365.15	x	x	1-Nitrobutane	320.15	x	x
1-Pentadecene	385.15	x		Hydrogen Cyanide	255		
1-Hexadecene	402.15	x		Acetonitrile	275.15	x	x
1-Octadecene	421.15	x	x	Acrylonitrile	268.15		
Cyclopentene	244			Methacrylonitrile	274.25	x	x
Cyclohexene	256.15	x	x	Succinonitrile	405		
Cycloheptene	280.65	x	x	*p*-Nitrotoluene	379		
Cyclooctene	298.15			*m*-Nitrotoluene	375	x	x
cis-2-Octene	290.65			*n*-Butyronitrile	291.15	x	x
trans-3-Octene	287.15			Valeronitrile	307.15	x	x
cis-4-Octene	285.65	x	x	Malononitrile	385.15		
trans-4-Octene	285.65			Hexanenitrile	316.15	x	x
cis-3-Octene	290			Isobutyronitrile	281.48		
Vinylcyclohexene	288.15			Benzonitrile	348.15		
1-Methylcyclopentene	256			Pyridine	293.15		
2,3-Dimethyl-1-Hexene	281	x		Aniline	344.15	x	x
d-Limonene	321	x	x	2,4-Toluene Diisocyanate	400.15	x	x
Terpinolene	329.15	x	x	Hexamethyleneimine	301.15	x	x
1,3-Butadiene	197.15	x	x	N-Methylaniline	351		
Isoprene	225			N,N-Dimethylaniline	348.15		
1,5-Hexadiene	246.15			2-Methylpyridine	299.15		
1,4-Hexadiene	248.15	x	x	*Cis*-Crotonitrile	288.65		
trans,*trans*-2,4-Hexadiene	266.15	x	x	*n*-Propyl Mercaptan	253.15	x	x
Dicyclopentadiene	318.15	x	x	Isobutyl Mercaptan	264.15		
α-Phellandrene	322	x	x	*n*-Hexyl Mercaptan	305.65	x	x
β-Phellandrene	322.15			*n*-Nonyl Mercaptan	351.15		
2,3-Dimethyl-1,3-Butadiene	251.15			*n*-Octyl Mercaptan	341.15		
Cis,*trans*-2,4-Hexadiene	266.15			Isopropyl Mercaptan	239		
1,5,9-Cyclododecatriene	360.15			Cyclohexyl Mercaptan	312.15		
2,5-Dimethyl-1,5-Hexadiene	280	x		Benzyl Mercaptan	343.15		
2,5-Dimethyl-2,4-Hexadiene	297.15	x	x	Methyl Ethyl sulfide	258.15	x	x
1,3-Cyclohexadiene	265.15	x		Methyl *t*-Butyl Sulfide	270.15		
1,4-Cyclohexadiene	267.15			Di-*n*-Propyl Sulfide	305.15		

Table E.17. Continued

Compound	FP/K	Reg. Set	
		1	2
1,5-Cyclooctadiene	308.15	x	
trans-1,3-Hexadiene	254.15	x	x
trans-2-Methyl-1,3-Pentadiene	255.15		
1,9-Decadiene	314.15	x	x
1,3,5,7-Cyclooctatetraene	299.26		
2-Hexyne	262.15		
2-Pentyne	243	x	x
1-Hexyne	252		
1-Octyne	289.15		
1-Nonyne	306.15	x	x
1-Decyne	315.65		
Benzene	262		
Toluene	279.15		
Ethylbenzene	296.15		
o-Xylene	305.15	x	x
m-Xylene	298.15		
p-Xylene	299		
n-Propylbenzene	312.15	x	
Cumene	309.15		
o-Ethyltoluene	316.15		
m-Ethyltoluene	311.15	x	x
p-Ethyltoluene	312.15		
1,2,3-Trimethylbenzene	324.15	x	
1,2,4-Trimethylbenzene	318.65	x	
Mesitylene	317.55		
Isobutylbenzene	325.15		
sec-Butylbenzene	325		
tert-Butylbenzene	317.15		
p-Cymene	320.15		
o-Diethylbenzene	330.37	x	x
m-Diethylbenzene	329	x	
p-Diethylbenzene	330	x	x
1,2,3,4-Tetramethylbenzene	347.15		
1,2,4,5-Tetramethylbenzene	346.15		
1,3,5-Triisopropylbenzene	359.82		
Pentamethylbenzene	364.15		
m-Diisopropylbenzene	349.82	x	x
p-Diisopropylbenzene	349.82		
1,2,4-Triethylbenzene	356.15	x	x
n-Heptylbenzene	370.65	x	x
Cyclohexylbenzene	372	x	x
Biphenyl	383.15		
p-Terphenyl	480		
m-Terphenyl	464	x	x
o-Terphenyl	436	x	x
Diphenylmethane	400		
1,2-Diphenylethane	398.15	x	x
n-Pentylbenzene	339.15		
n-Hexylbenzene	356.15	x	x
n-Octylbenzene	380.15	x	x
Diethyl Sulfide	263.15	x	
Dimethyl Sulfide	237.15		
Thiophene	266.45	x	x
Benzothiophene	364.15		
Diethyl Disulfide	313.15	x	
n-Decyl Mercaptan	371.15		
n-Pentyl Mercaptan	291.15		
Dimethyl Disulfide	288.15		
Di-*n*-propyl Disulfide	339.15	x	x
2-Methyl Benzothiophene	386.15		
n-Dodecyl Mercaptan	393	x	x
tert-Octyl Mercaptan	304		
n-Heptyl Mercaptan	323.65		
Diallyl Sulfide	298.65	x	
n-Butyl Mercaptan	274.15		
Phenyl Mercaptan	328.15	x	
Tetrahydrothiophene	291		
Dimethyl Sulfoxide	361		
Sulfolane	438.15	x	x
Sulfolene	386		
Di-*n*-Propyl Sulfone	399.15	x	x
Di-*n*-Butyl Sulfone	416.15		
Acetyl Chloride	269.15	x	x
Dichloroacetyl Chloride	339		
Benzoyl Chloride	345	x	
p-Chlorobenzotrifluoride	316	x	x
o-Chloroaniline	363.71		
Chloromethyl Methyl Ether	265.15	x	x
1,3-Dichloro-2-Propanol	358.15	x	
2,3-Dichloro-1-Propanol	366.15		
Di(2-Chloroethyl)Ether	348.15		
3-(Methylmercapto)Propanal	334.15		
3-Mercaptopropionic Acid	366.15	x	x
o-Chlorobenzoic Acid	446	x	x
N,N-Dimethylformamide	330.15	x	x
ε-Caprolactam	412.65		
α-Epichlorohydrin	304	x	x
Acetone Cyanohydrin	347.15	x	x
Triphenylphosphine	453.15		
Nitrobenzene	361		
Acetaldol	355.93	x	x
Furfural	333.15		
Acetomethoxane	356.15		
Ethylene Glycol Diacrylate	373.15		
Propylene Glycol Monomethyl Ether Acetate	316	x	x
Dipropylene Glycol Monomethyl Ether Acetate	359		
Methoxydihydropyran	299.15		
Trichlorosilane	259.15		
Carbon Disulfide	243.15	x	x
Hexamethyldisilazane	284.15	x	

Table E.17. Continued

Compound	FP/K	Reg. Set	
		1	2
2-Phenylbutene-1	325.15	x	
Styrene	305		
o-Methylstyrene	320.15		
m-Methylstyrene	324.15		
1,2,3,6-Tetrahydrobenzaldehyde	320.15		
o-Ethylstyrene	333.15		
m-Ethylstyrene	335.65		
p-Ethylstyrene	338.15		
p-Methylstyrene	320.65	x	
α-Methylstyrene	315.65		
m-Divinylbenzene	340.15		
Ethynylbenzene	304.15		
cis-1-Propenylbenzene	320.65		
trans-1-Propenylbenzene	325.15	x	x
Naphthalene	353.15	x	x
1-Methylnaphthalene	367.15		
2-Methylnaphthalene	370.15	x	x
1-Ethylnaphthalene	384.15		
1,2,3,4-Tetrahydronaphthalene	344	x	x
1-*n*-Decylnaphthalene	450.15		
2-Ethylnaphthalene	377.15	x	x
Methylcyclopentadiene Dimer	326.15		
Indene	331.15	x	x
Anthracene	458.15		
Phenanthrene	444	x	x
Pyrene	472		
Adamantane	359.6		
Vinylnorbornene	295.15		
1,3-Dimethyladamantane	325.15	x	
Indane	321.65	x	
α-Terpinene	319.15		
γ-Terpinene	325.65		
2-Norbornene	258.15	x	x
5-Ethylidene-2-Norbornene	298.15	x	x
sec-Butylcyclohexane	323.65	x	x
Bicyclo[2.2.2]Octane	313.15		
Camphene	307.15		
α-Pinene	305	x	
β-Pinene	310.65		
Acetaldehyde	233		
Propanal	247.15	x	x
5-*o*-Tolyl-2-Pentene	361	x	x
Butanal	262.15	x	
2-Methylpropanal	254.15	x	
Pentanal	279.15	x	x
Heptanal	308.15		
Hexanal	298.15		
Octanal	327.15	x	x
2-Ethylhexanal	317.59	x	
2-Methyl-2-Pentenal	304.15	x	
2-Ethyl-2-Hexenal	329.65	x	x
Hexamethyldisiloxane	271.15	x	x
Hexamethylcyclotrisiloxane	308.15		
Dodecamethylpentasiloxane	352.15	x	
Methyl Vinyl Dichlorosilane	276.15	x	x
[3-(Mercapto)Propyl]Triethoxysilane	360.93		
3-(trimethoxysilyl)-1-Propanethiol	347	x	
Octamethylcyclotetrasiloxane	330.15		
3-Nonanone	339.15	x	x
2-Cyclohexene-1-one	329.15	x	
2,6,8-Trimethyl-4-Nonanone	364.15	x	
2,3-Dimethyloctane	314		
2,7-Dimethyloctane	310.927	x	x
2,6-Di-*tert*-Butyl-*p*-Cresol	390.15	x	x
2-Phenylethanol	375	x	x
2,6-Dimethyl-4-Heptanol	339.15	x	
1-Phenyl-1-Propanol	363.15	x	
2-Phenyl-1-Propanol	381.15		
3-Phenyl-1-Propanol	382.15	x	
α-Methylbenzyl Alcohol	358.15	x	x
o-Tolualcohol	377.15	x	x
m-Tolualcohol	378.15	x	x
p-*tert*-Amylphenol	393.15		
p-Cumylphenol	444	x	x
2,4-Pentanediol	371.15		
3-Methyl-*trans*-2-Pentene	246.15	x	
Decan-1,10-Diol	425.15	x	x
1,4-Cyclohexanedimethanol	434.15		
2-Methyl-1-Octene	296.65	x	x
2-Methyl-1-Heptene	283.15		
Azelaic Acid	488.15	x	x
Neopentanoic Acid	337.15	x	
2-Ethyl Hexanoic acid	383.15	x	
n-Heptanoic Acid	388.15		
Neohexanoic Acid	352.15		
Suberic Acid	483.15	x	
Sebacic Acid	493.15	x	x
2-Ethyl Butyric Acid	360		
Methyl Maleic Anhydride	374.15		
tert-Butyl Formate	264.15		
n-Hexyl Formate	320	x	
1,2-Hexadiene	254.15		
Cyclohexyl Formate	324.15		
tert-Butyl Acetate	276.95	x	x
Methyl Isobutyrate	276.15	x	x
Ethyl Isobutyrate	287		
Benzyl Formate	355		
Allyl Methacrylate	306.15		
Cyclohexyl Acetate	331.15		
Propylene Carbonate	408.15		
Glyceryl Triacetate	411	x	x
Diethyl Phthalate	423.15	x	

Table E.17. Continued

Compound	FP/K	Reg. Set	
		1	2
Decanal	356.15	x	x
Undecanal	366		
Dodecanal	374.15	x	x
Tridecanal	386	x	x
2-Methylbutyraldehyde	269.15		
3-Methylbutyraldehyde	270.15	x	x
Acrolein	247.15	x	x
cis-Crotonaldehyde	285.93	x	x
trans-Crotonaldehyde	286.15		
Methacrolein	258.15	x	
2-Phenylpropionaldehyde	342		
o-Tolualdehyde	340.15		
p-Tolualdehyde	353	x	x
Benzaldehyde	337	x	x
Salicylaldehyde	349.15		
m-Tolualdehyde	351.15	x	x
Paraldehyde	298.71	x	x
Acetone	253.15		
Methyl Ethyl Ketone	264.15	x	x
3-Pentanone	280.15	x	x
Methyl Isobutyl Ketone	286.15	x	x
3-Methyl-2-Pentanone	285.15	x	x
5-Hexen-2-one	296.15		
3-Heptanone	310.15		
4-Heptanone	307.15		
2-Pentanone	280	x	
Methyl Isopropyl Ketone	272.15	x	x
2-Hexanone	296.15	x	
2-Heptanone	312.15		
5-Methyl-2-Hexanone	308.15		
Mesityl Oxide	301		
3,3-Dimethyl-2-Butanone	282.15	x	x
Diisobutyl Ketone	322.15	x	x
Diisopropyl Ketone	288.15		
2-Pyrrolidone	411.15	x	x
N-Methyl-2-Pyrrolidone	359.15	x	x
5-Nonanone	338.15		
2-Nonanone	345.5	x	
Anthraquinone	469.5	x	x
Acetylacetone	307.15		
Isophorone	350.65		
Cyclopentanone	299	x	
Cyclohexanone	316.15		
2-Octanone	329.15	x	x
Acetophenone	350.15		
β-Propiolactone	343.15		
γ-Butyrolactone	367.15		
ε-Caprolactone	382.15	x	x
γ-Valerolactone	369.26		
Ethyl Isopropyl Ketone	286.15		
Methyl Isopropenyl Ketone	278.15		
Di-*n*-Butyl Phthalate	444.26	x	x
Dimethyl Phthalate	419	x	
Diethyl Succinate	369.15		
Dihexyl Adipate	464		
Ethylidene Diacetate	343.15		
Dibutyl Maleate	413		
Isobutyl Acrylate	304.26		
Diethyl Maleate	366.15	x	x
Dimethyl Maleate	368.15		
Vinyl Pivalate	282.15		
Dimethyl Carbonate	289.85		
n-Propyl Benzoate	371.15		
Diisobutyl Ether	287.65		
1-Heptyne	271		
1,3-Dioxane	288.15		
Ethylal	268.15	x	x
1,2-Diethoxyethane	295		
2,3-Dihydrofuran	249.15		
1,1-Dichloropropane	280		
1,3-Dichloropropane	305.15	x	x
2,3-Dichloropropene	288.15		
1,2,3-Trichlorobenzene	386	x	x
1,3,5-Trichlorobenzene	380.15		
Benzotrifluoride	285	x	x
2-Bromobutane	279.15		
p-Bromotoluene	343.15	x	x
n-Hexyl Iodide	334.15	x	x
n-Butyl Iodide	304.15		
n-Hexylamine	300.15	x	x
n-Heptylamine	317.15		
n-Octylamine	333	x	
n-Nonylamine	343.15		
n-Decylamine	358.15	x	x
N-Ethyl-2-Methylallylamine	280.15		
Triallylamine	312.15	x	x
Tri-*n*-Butylamine	353.15		
Diethylenetriamine	367.15	x	x
Tetraethylenepentamine	436	x	
Tripropylamine	314	x	x
Vinylacetonitrile	296.15	x	x
n-Butyl Isocyanate	295.65	x	x
Cyclohexyl Isocyanate	326		
o-Ethylaniline	358.15		
o-Phenylenediamine	409	x	
Propyleneimine	263.15	x	x
m-Phenylenediamine	411.15	x	x
Cyclopentylamine	284.65	x	x
Dicyclohexylamine	372.65		
N-Methylcyclohexylamine	308.15		
N-Aminoethyl Ethanolamine	417.15	x	x
Diphenylmethane-4,4'-Diisocyanate	472		

Table E.17. Continued

Compound	FP/K	Reg. Set		Compound	FP/K	Reg. Set	
		1	2			1	2
Quinone	350.15			Diallylamine	289	x	x
Diketene	307	x	x	*m*-Dinitrobenzene	423.15	x	x
Methanol	284.15	x	x	*o*-Dinitrobenzene	423.15		
Ethanol	286.15			2,4-Dinitrotoluene	442	x	x
1-Propanol	297.59	x	x	2,6-Dinitrotoluene	433.15		
Isopropanol	285.15			*p*-Phenylenediamine	428.7		
1-Butanol	310.5			Phenyl Isocyanate	324.15	x	x
2-Methyl-1-Propanol	302.32			Piperazine	338.15	x	
2-Butanol	296.15			Pyridazine	358.15		
2-Methyl-2-Propanol	284.26	x	x	Pyrimidine	304.15	x	x
1-Pentanol	322.15			Pyrazole	355.65		
2-Pentanol	307.15	x	x	*o*-Nitroaniline	441.15		
2-Methyl-2-Butanol	292.15			*p*-Nitroaniline	486.15	x	x
2-Methyl-1-Butanol	316.15	x	x	*m*-Nitroaniline	469.15		
2,2-Dimethyl-1-Propanol	303.15	x	x	Isoquinoline	380.15	x	x
1-Hexanol	333.15			*p*-Aminodiphenyl	426.15	x	x
2-Hexanol	318.15			Nicotinonitrile	357.15	x	x
3-Hexanol	314.15			2,6-Diethylaniline	382.15		
2-Methyl-1-Pentanol	323.15			2,4,6-Trimethylpyridine	327.15	x	
3-Methyl-1-Pentanol	331.15	x	x	2,6-Dimethylpyridine	306	x	x
3-Methyl-3-Pentanol	297.15	x		3-Methylpyridine	309.15		
3-Pentanol	303.15			Methylglutaronitrile	388		
2-Ethyl-1-Hexanol	346			4-Methylpyridine	312.15	x	x
2-Methyl-1-Hexanol	333.65	x	x	1,6-Hexamethylene Diisocyanate	408.15		
3-Methyl-1-Butanol	316			Isophorone Diisocyanate	428.15	x	x
3-Methyl-2-Butanol	299.15	x	x	Methyl *n*-Butyl Sulfide	291.15	x	x
1-Heptanol	346.15			Trimethylene Sulfide	271.15	x	x
2-Heptanol	332.15			*tert*-Dodecyl Mercaptan	370.15	x	
3-Heptanol	327.15			*tert*-Nonyl Mercaptan	338.15		
5-Methyl-1-Hexanol	338.15	x		2-Methylthiophene	288.15	x	x
4-Methyl-2-Pentanol	314	x		3-Methylthiophene	285.15		
1-Octanol	359.7	x	x	Camphor	338.7		
2-Octanol	344.15			Formamide	423.15		
1-Nonanol	369.15			N-Methylformamide	384.15	x	x
2-Nonanol	355.15			Diacetone Alcohol	334		
1-Decanol	377.15	x	x	Furfuryl Alcohol	348.15		
1-Undecanol	386.15	x	x	N,N-Dimethylacetamide	336.15	x	
8-Methyl-1-Nonanol	370.65			*p*-Methoxyphenol	398	x	x
1-Dodecanol	400	x		2-Methoxyethanol	312		
1-Tetradecanol	421.15			2-Ethoxyethanol	316	x	x
1-Hexadecanol	443			2-Butoxyethanol	334.15		
1-Octadecanol	458.15	x		2-(2-Methoxyethoxy)Ethanol	360.15	x	x
2-Ethyl-1-Butanol	326.15			2-(2-Ethoxyethoxy)Ethanol	363.15	x	x
1-Eicosanol	468.15			2-Aminoethoxyethanol	397		
Cyclohexanol	334.15	x	x	Ethylchloroacetate	327.15		
cis-2-Methylcyclohexanol	331.15			Acetaldoxime	313.15	x	x
trans-2-Methylcyclohexanol	331.15	x	x	2-(2-(2-Methoxyethoxy)Ethoxy)Ethanol	391.48	x	x
cis-4-Methylcyclohexanol	343.15			Thioglycolic Acid	399.15	x	x
trans-4-Methylcyclohexanol	343.15			2-Hydroxyethyl Methacrylate	374.15		
l-Menthol	366.15	x	x	2-Acetoacetoxy Ethyl Methacrylate	407.05		

Table E.17. Continued

Compound	FP/K	Reg. Set	
		1	2
α-Terpineol	364		
Tetrahydrofurfuryl Alcohol	343.15		
Allyl Alcohol	294		
2-Phenyl-2-Propanol	360.15		
2-Butyl-Octan-1-ol	382.15		
2,3-Xylenol	368.15		
2,4-Xylenol	368.15		
4-Methyl-Cyclohexane-Methanol	354		
2,5-Xylenol	368.15	x	x
2,6-Xylenol	358.15	x	
Propargyl Alcohol	305.15		
Benzyl Alcohol	366.15		
Phenol	352.15		
o-Cresol	354	x	x
m-Cresol	359.15		
p-Cresol	359.15	x	
o-Ethylphenol	358.15	x	x
p-Hydroquinone	438	x	x
p-Ethylphenol	373.15		
p-*tert*-Butylphenol	386	x	x
Bisphenol A	500.15	x	x
2,2,4-Trimethyl-1,3-Pentanediol	382.65		
Ethylene Glycol	384.15		
Diethylene Glycol	413.15		
Triethylene Glycol	429.15	x	
Tetraethylene Glycol	469	x	
1,2-Propylene Glycol	372		
Dipropylene Glycol	391		
Neopentyl Glycol	380.15		
2-Butyne-1,4-Diol	425		
Tripropylene Glycol	413.15		
2-Methyl-1,3-Propanediol	393.5	x	x
1,2-Butanediol	366.55		
1,3-Butanediol	382		
Hexylene Glycol	366		
Glycerol	464.15		
1,2,4-Butanetriol	461	x	x
p-*tert*-Butylcatechol	425		
Nonylphenol	424.65	x	x
2-Methyl-1,3-Pentanediol	383.15		
2,3-Butanediol	358.15	x	x
cis-2-Butene-1,4-Diol	401.15		
trans-2-Butene-1,4-Diol	401.15		
1,4-Butanediol	407.15	x	
1,5-Pentanediol	409.15	x	x
1,6-Hexanediol	420.15	x	x
1,2-Benzenediol	400		
1,3-Benzenediol	444		
Methyl Lactate	324.15		
2-Methoxy Propanol-1	314.15	x	x
m-Chloronitrobenzene	388	x	
2-Hydroxyacetophenone	371.15	x	x
4-Hydroxyacetophenone	447	x	x
p-Phenetidine	389		
Acetol	329	x	x
o-Chlorophenol	336.15	x	x
m-Chlorophenol	370.15		
p-Chlorophenol	389		
Pentafluorophenol	345.37	x	x
1-Isopropoxy-2-Propanol	313.15		
2-Chloroethanol	328.15		
Isophthaloyl Chloride	453.15	x	
4-Formylmorpholine	386.15	x	x
Octamethyltrisiloxane	308.15		
Octadecamethyloctasiloxane	417.15		
Tetraethyl Silane	305.15		
Hexadecamethylheptasiloxane	406.15		
Diamyl Ketone	361.48		
Thymol	374.15	x	x
1-Methyl-3-Hydroxy-6-Isopropyl Benzene	392		
7-Methyl-1-Octene	289.65		
m-Toluic Acid	419.15		
Dodecanedioic Acid	503		
Cyclopropane Carboxylic Acid	360.15	x	x
Malonic Acid	474.82		
Isobutyric Anhydride	340.15		
2,2,4-Trimethyl-1,3-Pentanediol Diisobutyrate	394		
Ethyl Trimethyl Acetate	288.15	x	
Di(2-Ethylhexyl)Terephthalate	511.15		
Phthalide	425.15		
Diallyl Phthalate	431.15		
Ethyl Phenyl Acetate	372.15	x	x
Dimethyl Succinate	358.15		
Dioctyl Adipate	500.15		
Di(2-Ethylhexyl)Adipate	469.15		
Dimethylmalonate	358.15		
1,3,5-Triethylbenzene	354.15		
Dodecyl Bromide	417.15	x	x
Cyclopropyl Cyanide	305.15	x	x
1,5-Pentanediamine	335.15		
2,4-Dimethylaniline	363.15	x	
3-(N,N-Dimethylamino) Propylamine	308.15	x	
8-Methylquinoline	378.15	x	x
Tri-*n*-Octylamine	444.5		
2-Butoxime	335.15	x	x
N-Methylpiperidine	276.15		

Table E.17. Continued

Compound	FP/K	Reg. Set		Compound	FP/K	Reg. Set	
		1	2			1	2
Pentaerythritol	533.15			Diamylamine	345.65	x	
Trimethylolpropane	449.15	x	x	Triamylamine	370.15	x	
Formic Acid	323.15			Undecylamine	365.15	x	
Acetic Acid	312.04	x	x	Di-2-Ethylhexylamine	401.15	x	
Propionic Acid	330			Tetramethylethylenediamine	290.15	x	x
n-Decanoic Acid	421.15	x		1,3-Propanediamine	322.15	x	x
n-Butyric Acid	345.15			N-Ethylaniline	358.15		
n-Pentanoic Acid	359.15	x	x	Di-*tert*-Butyl Disulfide	335.15	x	x
n-Nonanoic Acid	413.15			Di-*tert*-Butyl Sulfide	304.15		
Isobutyric Acid	333.15			2-Methylthiacyclopentane	300.65	x	
Isovaleric Acid	351.15			2-Pentanethiol	282.46		
n-Hexanoic Acid	375.15	x	x	2-Ethylthiophene	300.15	x	x
2-Methylhexanoic Acid	370.65	x	x	2-*n*-Propylthiophene	317.59		
n-Octanoic Acid	400.15	x	x	2,5-Dimethylthiophene	297.04		
Cyclopentylacetic Acid	382.15	x	x	Ethyl Propyl Disulfide	325.65	x	x
n-Dodecanoic Acid	437	x	x	Methyl Phenyl Sulfide	345.15		
cis-Crotonic Acid	353.15			Di-*n*-Butyl Sulfide	333.15		
trans-Crotonic Acid	363.15			Diisopentylsulfide	357.04	x	
n-Octadecanoic Acid	469	x		Ethyl Propyl Sulfide	285.65	x	x
Acrylic Acid	324			Diisopropyl Sulfide	280.15		
Methacrylic Acid	340	x		Ethylene Glycol 2-Ethylhexyl Ether	371.15		
Oleic Acid	462	x	x	Propylene Glycol Monomethyl Ether	305	x	x
Benzoic Acid	394.26	x	x	Dipropylene Glycol Monomethyl Ether	347.15		
Salicylic Acid	430	x	x	Propylene Glycol 1-*tert*-Butyl Ether	318.15		
Adipic Acid	469.26			Tripropylene Glycol Monomethyl Ether	394.15	x	x
Phthalic Acid	441.15			Diethylene Glycol Monopropyl Ether	372	x	x
Terephthalic Acid	533.15	x		*p*-Chloroaniline	386	x	x
Peracetic Acid	313.15			2-(2-(2-Butoxyethoxy)Ethoxy)Ethanol	416		
Acetic Anhydride	322.594	x		2-(2-(2-Ethoxyethoxy)Ethoxy)Ethanol	408.15		
Propionic Anhydride	336			Propylene Glycol Monoallyl Ether	327.55	x	x
Butyric Anhydride	355	x	x	2,3-Epoxy-1-Propanol	344.15		
Succinic Anhydride	425	x	x	2-Hexoxyethanol	363.15	x	x
Glutaric Anhydride	446.15			2-(2-Hexoxyethoxy)Ethanol	408.15	x	
Phthalic Anhydride	425	x	x	Dipropylene Glycol *n*-Propyl Ether	361.15	x	x
Maleic Anhydride	375.15	x	x	Propylene Glycol *n*-Propyl Ether	321.15	x	x
Trimellitic Anhydride	522.5	x	x	Diethylene Glycol Monobutyl Ether Acetate	389.15		
Ethyl Formate	254.15	x	x	Phenylacetonitrile	374.15		
n-Propyl Formate	270.15	x	x	N,N-Diethylhydroxylamine	318.15	x	x
n-Butyl Formate	286.15			Dipropylene Glycol Monoethyl Ether	364		
Isobutyl Formate	283.15	x		Tripropylene Glycol Monoethyl Ether	405	x	

Table E.17. Continued

Compound	FP/K	Reg. Set		Compound	FP/K	Reg. Set	
		1	2			1	2
n-Pentyl Formate	301.15	x	x	1-Ethoxy-2-Propanol	313.15		
n-Octyl Formate	349.5			Methyl Glycolate	339.15		
Methyl Acetate	260.15	x	x	*tert*-Butyl Methacrylate	300.15	x	
Ethyl Acetate	269			Tetraethoxysilane	324.82		
n-Propyl Acetate	283.706			γ-Aminopropyltriethoxysilane	369.26		
n-Butyl Acetate	298.15	x		Hexadecamethylcyclooctasiloxane	405		
Isobutyl Acetate	291	x		Eicosamethylnonasiloxane	432.04	x	x
Isopentyl Acetate	306.15			Hexacosamethyldodecasiloxane	471	x	x
Allyl Acetate	286.15			Methyl Dichlorosilane	241.15		
Isopropyl Acetate	274.816			Methyl Trichlorosilane	276.15	x	x
sec-Butyl Acetate	289	x		Vinyltrichlorosilane	283.15		
Vinyl Acetate	265.37	x	x	3-(Triethoxysilyl)Propionitrile	373.15		
Methyl Propionate	271			Tris(2-Methoxyethoxy)Vinylsilane	388.15		
Ethyl Propionate	285			Methyl Silicate	294.15		
n-Propyl Propionate	294.15			(3-Chloropropyl)Trimethoxy-Silane	351.48		
n-Butyl Propionate	313.15	x	x	[3-(2,3-Epoxyproxy)Propyl]Trimethoxy Silane	408.15		
n-Propyl *n*-Butyrate	310.15			Trichloro(3-Chloropropyl)Silane	357.15		
Vinyl Propionate	281	x	x	Ethylsilanetriol Triacetate	377.15		
Methyl *n*-Butyrate	287			Triethyl Ester Phosphorous Acid	317.15	x	
Ethyl *n*-Butyrate	297.15			(3-Chloropropyl)Dimethylchlorosilane	313.15		
n-Propyl Isobutyrate	300.15			Dimethylchlorosilane	245.15		
Trioctyl Trimellitate	523.15	x	x	Trimethylchlorosilane	245		
Methyl Acrylate	270			Dimethyldichlorosilane	264.15	x	x
Ethyl Acrylate	280.93	x	x	Decamethylcyclopentasiloxane	350.15	x	x
n-Butyl Acrylate	310.15			Dodecamethylcyclohexasiloxane	366.15		
n-Butyl Valerate	340	x	x	Diphenyldichlorosilane	415.15	x	
Ethyl Isovalerate	299.15			Ethyltrichlorosilane	288.15		
Methyl Methacrylate	284.15			Dichlorodiethylsilane	297.15		
Ethyl Methacrylate	292.15	x	x	Diglycolic Acid	500	x	x
n-Propyl Methacrylate	306.15			Levulinic Acid	410	x	x
Dioctyl Phthalate	489			Guaiacol	355		
Diisooctyl Phthalate	505.15	x	x	Ethylene Glycol Monopropyl Ether	322.15	x	x
n-Pentyl Acetate	310.15	x		2-(2-Butoxyethoxy)Ethanol	378.15	x	x
2-Ethylhexyl Acetate	344.15			4-Chloro-3-Nitrobenzotrifluoride	374.15		
Benzyl Acetate	363.15	x	x	3,4-Dichlorophenyl Isocyanate	383.15		
Isobutyl Isobutyrate	311.15			3-Nitrobenzotrifluoride	361	x	
Isopentyl Isovalerate	333.15	x		Trichloroacetaldehyde	348		
Benzyl Benzoate	431			1-Chloro-2,4-Dinitrobenzene	467	x	x
n-Butyl Benzoate	379.15	x		*p*-Dimethylaminobenzaldehyde	420.15	x	x
Ethylene Carbonate	425			Ethyl Chloroformate	289.15	x	x
n-Octyl Acetate	356.15			Methyl Chloroformate	285.15		
n-Nonyl Acetate	372.15	x	x	3,4-Dichloroaniline	408.15		
n-Decyl Acetate	386.5			1,2-Dichloro-4-Nitrobenzene	396.15	x	x
Methyl Salicylate	369			*o*-Chloronitrobenzene	397.15	x	x
Diisobutyl Phthalate	444.5			*p*-Chloronitrobenzene	397.15		
Dimethyl Isophthalate	411.15			Triethyl Phosphate	372	x	
Di-*n*-Hexyl Phthalate	466.15			Trimethyl Phosphate	358.15	x	
Dimethyl Terephthalate	414.15			Cyclohexanone Oxime	362.15	x	x

Table E.17. Continued

Compound	FP/K	Reg. Set		Compound	FP/K	Reg. Set	
		1	2			1	2
n-Butyl Stearate	433.15			Vinyltrimethoxysilane	296.15		
Dibutyl Sebacate	470.15			Trimethoxysilane	269.15	x	x
n-Butyl *n*-Butyrate	323.15			Dimethyldimethoxysilane	263.15		
2-Ethylhexyl Acrylate	355.15	x		Phenyltrichlorosilane	364.15		
Ethylene Glycol Diacetate	361.15	x		Phenylmethyldichlorosilane	353.15	x	x
Isobutyl Methacrylate	314.15			Tetradecamethylhexasiloxane	375.15	x	
n-Butyl Methacrylate	322	x	x	Decamethyltetrasiloxane	336.15	x	x
Methyl Benzoate	352.5	x	x	Pyruvic Acid	355.15	x	x
Ethyl Benzoate	361.15			3-Amino-1-Propanol	374.15	x	x
Diethyl Carbonate	298.15	x		1-Amino-2-Propanol	347.04	x	x
Diethyl Oxalate	348.15	x	x	Methyl Chloroacetate	324.82		
Diethyl Malonate	358.15	x	x	Acetoacetanilide	423.15	x	x
Methyl Decanoate	367.15	x	x	Oxazole	292	x	x
Isopropyl Myristate	424.5	x	x	Acetanilide	434.15	x	x
Diethyl Ether	228.15			Lactonitrile	350.15		
Diisopropyl Ether	245			Ethyl Lactate	331	x	x
Methyl *tert*-Butyl Ether	244.15	x	x	2-Ethoxyethyl Acetate	327.15	x	x
Di-*sec*-Butyl Ether	285.65	x	x	Diethylene Glycol Ethyl Ether Acetate	368.15	x	x
Methyl Ethyl Ether	236	x	x	Methyl Acetoacetate	343	x	x
Di-*n*-Hexyl Ether	354.65	x	x	Ethyl Acetoacetate	343.15		
Divinyl Ether	226.15	x		Methyl Cyanoacetate	380.65		
Ethyl Propyl Ether	253.15	x		Ethyl Cyanoacetate	383.15	x	x
Anethole	362.15			3-Methoxypropionitrile	338.15	x	x
1,4-Dioxane	284.15			Isoxazole	285		
Trioxane	318.15			Terephthaloyl Chloride	453.15		
Di-*tert*-Butyl Ether	275.65			1-Chloro-2-Propanol	324.82	x	x
Di-*n*-Octyl Ether	412	x	x	*tert*-Butylformamide	355.15	x	x
Di-*n*-Pentyl Ether	330.15			N-Methylacetamide	381.15	x	
Methyl *sec*-Butyl Ether	243	x	x	Thiodiglycol	433.15	x	x
Methyl *tert*-Pentyl Ether	262.15			Dimercaptoethyl Ether	371.15	x	x
tert-Butyl Ethyl Ether	253.15			2-Mercaptoethanol	340.15		
Methylal	241.15			Ethylthioethanol	350.15		
Acetal	286.15			1,2-Ethanedithiol	318.15	x	x
1,2-Epoxy-3-Phenoxypropane	387			Diethylethanolamine	330.15	x	x
Triethyl Orthoformate	308.15			Methylethanolamine	345.15	x	x
Ethyl Hydroperoxide	305.65			Dimethylethanolamine	312.15	x	x
1,2-Epoxy-2-Methylpropane	241.15	x	x	Diisopropanolamine	408.15		
1,2-Propylene Oxide	236			N-(2-Hydroxyethyl)Piperazine	397.15		
Butyl Vinyl Ether	272	x		3-Methoxyisopropylamine	281.15		
Bis(α-Methylbenzyl) Ether	408.15	x	x	Ethylene Glycol Monobutyl Ether Acetate	344.15	x	x
Triethylene Glycol Dimethyl Ether	383.15	x		2-Hydroxyethyl Acrylate	378	x	x
1,2-Dimethoxyethane	271.48			2-Hydroxypropyl Methacrylate	374.15		
Diethylene Glycol Dimethyl Ether	330.15			Ethyl-3-Ethoxypropionate	331.15		
Tetraethylene Glycol Dimethyl Ether	414.15			2-Hydroxypropyl Acrylate	372.15	x	
1,2-Dimethoxyethane	271.48			2-Hydroxypropyl Methacrylate	374.15		
Diethylene Glycol Dimethyl Ether	330.15			Ethyl-3-Ethoxypropionate	331.15		

Table E.17. Continued

Compound	**FP/K**	**Reg. Set**		**Compound**	**FP/K**	**Reg. Set**	
		1	**2**			**1**	**2**
1,2-Dimethoxyethane	271.48			2-Hydroxypropyl Methacrylate	374.15		
Diethylene Glycol Dimethyl Ether	330.15			Ethyl-3-Ethoxypropionate	331.15		
Tetraethylene Glycol Dimethyl Ether	414.15			2-Hydroxypropyl Acrylate	372.15	x	
Diethylene Glycol Diethyl Ether	344.15	x	x	Di-(2-Chloroethoxy)Methane	383.15		
Diethylene Glycol Di-*n*-Butyl Ether	391.15	x		1-Methylvinyl Acetate	283		
Anisole	318.65	x	x	2-Pentoxyethanol	348.15		
Phenetole	328	x	x	1-Chloro-3-Propanol	346.15	x	x
Dibenzyl Ether	408.15			Methoxyacetone	297.15		
Allyl Glycidyl Ether	321.15	x		2-(2-Pentoxyethoxy)Ethanol	383	x	
Diphenyl Ether	388.15			Methyl *para*-Toluate	363.71	x	x
1,1-Dimethoxyethane	256.15			Phenyl Acetate	349.15	x	x
Methyl Vinyl Ether	217.15			Propylene Glycol *n*-Butyl Ether	332.15	x	x
1,2-Epoxybutane	258.15	x	x	Dipropylene Glycol *n*-Butyl Ether	373.55		
Cumene Hydroperoxide	356.15	x	x	Triethylene Glycol bis(2-Ethylhexanoate)	480.15		
t-Butyl Hydroperoxide	299.82			4,6-Dinitro-*o*-*sec*-Butylphenol	450.15	x	x
2,5-Dihydrofuran	257.15	x	x	Trimethyl Borate	260.15	x	
Furan	237			*t*-Butyl Acetoacetate	339.15	x	
Tetrahydrofuran	259.15	x	x	1,3-Dimethyl Urea	430.15		
Dibenzofuran	403.15			4-(2-Aminoethyl) Morpholine	359.15	x	x
Di-*t*-Butyl Peroxide	277.15			N-Ethyl-Morpholine	304.15		
2-Methylbenzofuran	340.15	x		Methyl-3-Mercaptopropionate	333.15		
1,2-Dimethoxypropane	273.15	x		2-Propanol-1-Methoxy-Propanoate	327.15		
2-Methyl-1,3-Dioxolane	270.93	x		Ethyl Levulinate	363.15		
Ethyl Chloride	223.15			4-(2-Hydroxyethyl) Morpholine	380.15	x	x