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Correlation of the Flammability Limits of Hydrocarbons with the Equivalence Ratio

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Abstract

Correlation in the literature between lower flammability limit and enthalpy of combustion are examined in light of the thermal explosion theory. When the calculated average equivalence ratio was used to predict the LFL, the value obtained was found to be higher than the measured LFL by 7%. When a modified equivalence ratio (the ratio of the fuel mole fraction to the mole fraction of the fuel in the stoichiometric mixture) was used instead, the predicted LFL value was lower than the measured value by 22%. These observations allow estimation of bounds for flammability limits when data is not available. It was also found that the enthalpy of reaction of 113 of the compounds correlates linearly with number of moles of oxygen needed for stoichiometric combustion of the fuel.

Key Words: Lower Flammability Limit; Upper Flammability Limit; Thermal Explosion Theory.

Introduction

An observation of the evolution of understanding of a phenomenon is that empirical observation of interesting and perhaps quixotic behavior is made before the underlying principles are apparent. After substantial study and the public dissemination of observed empirical relationships has been made and the full set of influential independent variables has become identified, then the theoreticians have information from which to deduce the fundamental underlying principles. Flammability limits are such a phenomenon. Over the past one to two centuries, much data has been collected on flammability limits of various fuels. From this data, relationships with other properties of a fuel and the correlation between the variables for the various fuels have been observed. However, partly owing to the complexity of the combustion process, and in some cases, duplication or overlap in definition of various properties, there have been a very large number of publications relating these observations. It is recently that the theoreticians have begun to try and assimilate this information into a model that will allow extrapolation and interpolation of these findings to all fuels, whether or not they have been studied in the laboratory. In the spirit of adding to the empirical correlations, the present paper was written.

Burgess and Wheeler [1] found that the heat of combustion of one mole of fuel at the lean limit is nearly constant, for fuel air mixtures at room temperature and pressure. White [2] found that the adiabatic flame temperature was reasonably constant for many limit mixtures. Egerton and Powling [3] found that adiabatic temperatures for limit mixtures of hydrocarbons asymptotically approached 1600 C as molecular weight of the fuel increases. Hertzberg [4] noticed that the addition of an inert powder to a flame is equivalent to increasing the surface area of the tube confining the flame. Beside the flammability limits for single fuels, fuel experts are also interested in determining the same for mixtures of fuels in gaseous forms for domestic heating applications as well as in liquid forms for industrial and transportation application. Sheldon [5] states that: “As a general rule, although there are many exceptions, the lower flammability limit in air at 25°C is half the stoichiometric concentration, and the upper limit is 3.5 times the stoichiometric concentration”. He also states that: “It has been found that, at pressure of one bar, combustion is only self-sustaining when the exothermic reaction can generate 44 KJ per mole of products (including inert gases). In air this corresponds to a minimum flame temperature of 1500 K where the flame temperature is calculated by dividing the heat of combustion by the average heat capacity of the products and adding the initial temperature of the reactants”. Later, Melhelm [6] examined the combustion of methane in oxygen and made an almost identical statement to that of Sheldon by stating: “At the reported literature flammability limits (LFL of 5% and UFL of 60%), the methane-oxygen system has a threshold theoretical flame temperature of 1500K. At this temperature, the combustion reaction is able to generate enough heat to produce self sustaining (propagating) reaction”. He also states that: “The lower flammability limit (LFL) and the upper flammability limit (UFL) do not change significantly over 500 degrees window (of adiabatic combustion temperatures)”. Suzuki [7] using statistical methods produced an empirical correlation between the standard enthalpy of combustion and the LFL for some 123 compounds. Britton [8] and Britton and Frurip [9] observed behavior for hydrocarbon and halogen substitute hydrocarbons and codified their observation into a number of “rules” which could be used to correlate lower flammability limits. According to Britton [8], the most important predictive parameter is the quotient of the heat of oxidation of the fuel to the stoichiometric ratio of oxygen to fuel.

In the work presented here the flammability of fuels in atmospheric air will be considered to produce a useful correlation for Suzuki's list of hydrocarbons. It is quite desirable to be able to predict the flammability limits merely on theoretical basis. Based on work for thermal explosion theory, the partitioning of combustion mixtures to be composed of two separate segments is suggested: the reacting segment and the inert segment. The reacting segment is composed of the stoichiometric mixture of fuel and oxygen in the lean mixture and all the oxygen and the fuel needed to react stoichiometrically in the rich mixture case. This represents the active heat source element of the mixture. The second segment is composed of the inert elements acting as a heat sink which is composed of the excess oxygen and any added diluents in the lean mixture and excess fuel and any added diluents in the rich mixture. This indicates that the combustion in air is a special case of combustion with oxygen where nitrogen is added as diluent. Heat energy is exchanged between the active elements and the inert elements by diffusion, conduction, convection and radiation. Combustion will be sustained if the temperature of the reacting mixture is maintained at or above the ignition (critical) temperature. This would be regardless of the heat losses to the inert elements as well as the losses to the surroundings of the reaction vessel for constant volume combustion or the surroundings of the burner for combustion in a flow system. This was demonstrated by showing that the excess gases are an important parameter in controlling flammability.

One of the difficulties in examining flammability limit data and its correlation to fuel properties is the scatter in the data. Kueffer and Donaldson [10] discuss some of the many reasons why this is the case. Some of the more apparent reasons are that apparatus, with different geometry has been used in various studies, and that flame propagation can be in the upward, downward, or horizontal direction. For upward propagation, the buoyancy of product gases augments the propagation, and hence, lower fuel energy release is required, i.e., flammability limit is expanded as compared to downward propagation.

In addition to correlations of flammability limits versus properties of fuel-air mixtures, the mass balance relating all of the factors in a reaction can be expressed in various ways. It is convenient to use customary expressions when they exist for such terminology. For example, at the lean flammability limit in pure oxygen, the excess oxygen behaves very nearly as nitrogen would behave because the effect would be simply dilution of thermal energy. So, fuel-air mixtures could be treated as a fuel + oxidizer + inert. However, much of the literature data treats air as the oxidizer for the general case, and oxygen only, as a special case.

Because of the number of mass variables, e.g., specifying concentration of fuel, oxidizer, and inert, it is not easy to represent how these mass quantities each contribute to the flammability. The plots shown by Coward and Jones [11] show flammability envelopes relating ratio of fuel to mixture versus ratio of diluent to mixture, and also shows a family of curves for each diluent. Other researchers report flammability envelops using three coordinate flammability diagrams, e.g., see [12].

While none of these methods provides for easy visualization of flammability for any diluent, they do represent various attempts for presentation of data.

The Flammability Limits in Air

For any fuel containing nitrogen without including any oxygen needed for oxidizing nitrogen, μ moles of oxygen are required per mole of fuel for stoichiometric combustion. The ratio of the number of moles of inert gases to the number of moles of oxygen as α is equal to 3.762 for air. In all studies of combustion of fuel-air mixtures, two parameters play major roles in the outcome of the combustion process. The first parameter is the equivalence ratio which is defined as:

$$\Phi = 4.762\ \mu\ C_f/(1-C_f) \tag{1}$$

The second parameter is the excess air factor defined by:

$$X = [1-C_f\ (1+4.762\mu)]/(4.762\ \mu\ C_f) \tag{2}$$

Combining equations (1) and (2) produces:

$$1/\ \Phi = 1+ X \tag{3}$$

This equation is applicable to all compounds and all mixtures whether they are flammable or not. The range of $0<X<\infty$ designates the lean mixture range, while $-1<X<0$ designates the rich mixture range. Considering Sheldon statement, comparing the flammability limits concentration with that of the stoichiometric mixture suggests the definition of a modified equivalence ratio Φ` which is given by:

$$\Phi` = C_f\ [1+ 4.762\mu] \tag{4}$$

Writing these equations for the general case considered in (1) where α is the ratio of inert to oxygen gives:

$$\Phi_\alpha = \mu\ (1+ \alpha)C_f/\ (1-C_f) \tag{5}$$

$$\beta_\alpha = [1- C_f\ \{1+\mu(1+\alpha)\}]/[C_f\ \mu\ (1+\alpha)] \tag{6}$$

$$\Phi_\alpha = 1/(1+\beta_\alpha) \tag{7}$$

$$\Phi_\alpha` = C_f\ [1+ \mu(1+\alpha)] \tag{8}$$

Applying equation (3) to the flammability limits produces:

$$(1/\Phi)_{LFL,\ UFL} = 1+ (X)_{LFL,\ UFL} \tag{9}$$

If the values of $(\Phi)_{LFL,\ UFL}$ and $(X)_{LFL,\ UFL}$ were the same for all compounds, our task would be made very easy and the problem would be neatly solved.

Suziki's Data Revisited

Suzuki listed in his paper [7], one hundred and twenty four different organic compounds giving for each one of them the chemical formula, the enthalpy of combustion and the $(C_f)_{LFL}$ for combustion in atmospheric air at standard pressure and temperature. This will also be considered to represent $(C_f)_{LFL}$ in oxygen atmosphere. Figure 1 shows a correlation between the heat of reaction Δ H of any of the compounds listed and the number of oxygen moles μ needed for the stoichiometric reaction of the compound.

The correlation produces a linear relationship between the heat of reaction and the number of moles of oxygen needed. The fit is nearly perfect for one hundred and thirteen of the compounds and differs very slightly for the other eleven compounds.

This correlation indicates that for any reaction, 424.48 KJ of heat energy is produced for each mole of oxygen consumed. With the knowledge that Suzuki obtained a good correlation between the $(C_f)_{LFL}$ and ΔH, substituting for ΔH in terms of μ would produce another useful empirical correlation. Our objective in this study is to gain a better understanding of the flammability limits in light of the discussion presented above. However, empirical correlation renders very useful functions. Statistical analysis was applied to various parameters obtained for the different compounds on Suzuki's list and Table 1 summarizes the statistical findings.

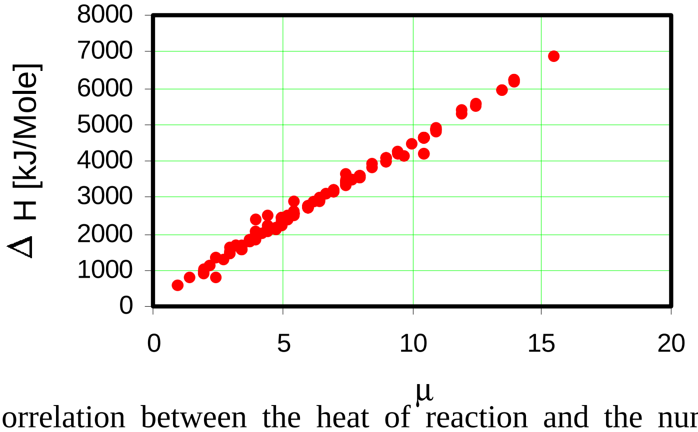

Figure 1. Correlation between the heat of reaction and the number of moles of oxygen needed for the stoichiometric combustion of one mole of fuel.

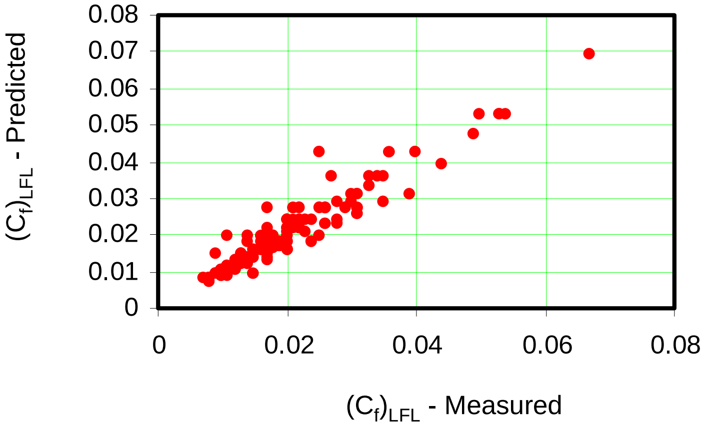

Figure 2. Correlation between the measured and predicted values of $(Cf)LFL$ using the average of equivalence ratio $(\Phi_0)_{LFL}$

Table 1. Various parameters derived for Suzuki's list of compounds

Parameter	Mean	Standard deviation
$(\Phi_0)_{LFL}$	0.111369	0.000306
$(\Phi_{3.762})_{LFL}$	0.530339	0.006928
$(\Phi`_0)_{LFL}$	0.129693	0.000393
$(\Phi`_{3.762})_{LFL}$	0.540034	0.006665
$(\beta_0)_{LFL}$	8.224859	2.71128
$(\beta_{3.762})_{LFL}$	0.937182	0.092365

Examining the equivalence ratios $(\Phi_0)_{LFL}$ and $(\Phi_{3.762})_{LFL}$ indicates that they came from normally distributed domains. This then confirms that, it is possible on a statistical basis to estimate the lower flammability limit for any fuel by using the average equivalence ratio. Figure 2 compares the predicted values of $(C_f)_{LFL}$ using the average of $(\Phi_0)_{LFL}$ with the measured values which produces an excellent correlation except for the fact that the predicted values are overestimated by 7%.

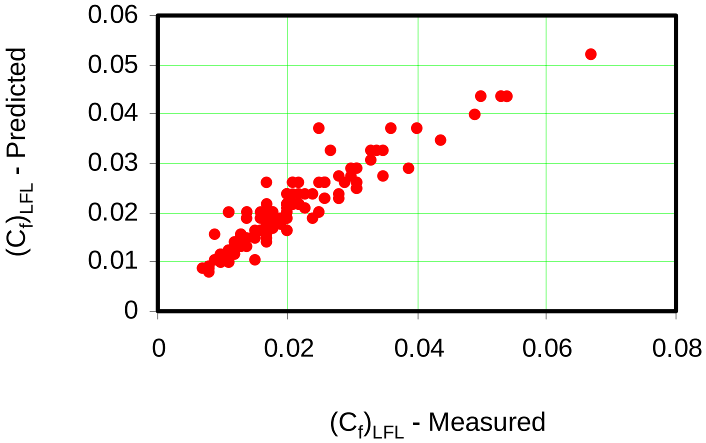

Figure 3: Correlation between the measured and predicted values of $(C_f)_{LFL}$ using the average of modified equivalence ratio $(\Phi'_0)_{LFL}$

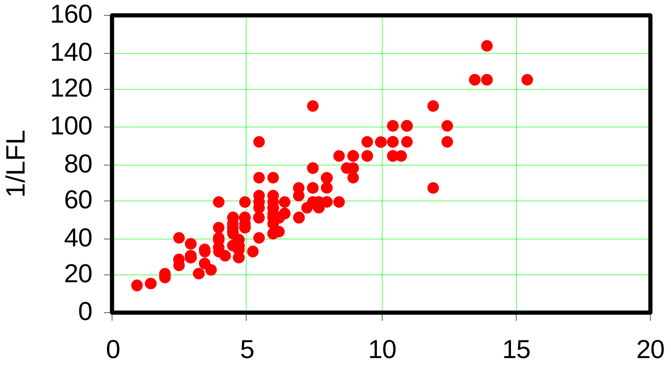

Figure 4. Correlation between 1/LFL and μ for Suzuki's compounds.

Figure 3 uses the average value of $(\Phi`_0)_{LFL}$ instead for predicting $(C_f)_{LFL}$ and produces an excellent correlation as well except that it underestimates the values by 22%. This can serve as a means of producing both an upper and lower limit for estimating the lower flammability limit. This will offer the designer the choice of parameters that will maximize the safety of a design.

One last remark on correlation for LFL and UFL; 1/LFL was correlated versus μ, as shown in Figure 4 and produced the following relationship:

$$1/LFL = 5.2114 + 8.2069\,\mu \qquad (13)$$

and applies to a large number of the compounds on Suzuki's list. The UFL for the compounds considered by Suzuki were obtained from the literature and the correlation between 1/UFL and μ as shown in Figure 5 produces the following approximate relationship for predicting the UFL:

$$1/UFL = 1.2773 + 1.213\,\mu \qquad (14)$$

These relationships can be used for estimation of both LFL and UFL based on the number of moles of oxygen.

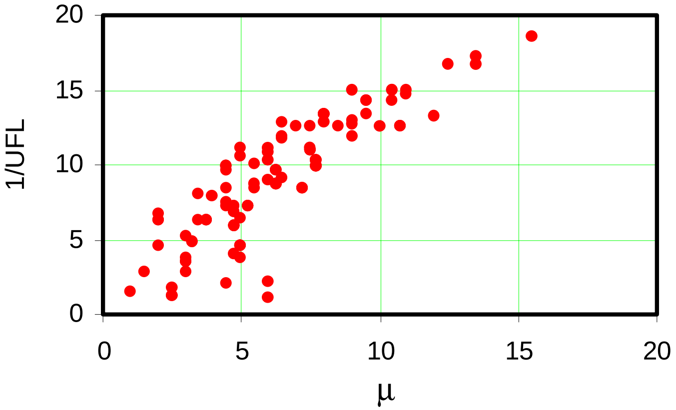

Figure 5: Correlation between 1/UFL and μ for Suzuki's compounds.

Conclusions

This study was completed to take a look at the flammability limits of the compounds studied by Suzuki [7]. It was discovered that the enthalpy of combustion of all hydrocarbon compounds correlates linearly with the number of moles of oxygen required for the stoichiometric combustion of any compound. For compounds containing nitrogen, the oxygen required for the oxidation of nitrogen was not taken into consideration. Approximate correlation for both the LFL and the UFL as functions of the number of moles of oxygen were obtained. These relationships can be used for estimation of both LFL and UFL.

Statistical analysis was completed on the LFL of all the compounds that showed that an average equivalence ratio as well as an average modified equivalence ratio at the LFL exists for all compounds. Using the average equivalence ratio to predict the LFL gives values less than the measured by 7% while using the average modified equivalence ratio gives a value higher than the measured by 22%. This allows the designer to bracket the LFL and consider the effect of either value on his system and decide on the safest design.

Nomenclature

C_f	mole fraction of fuel in mixture (mole/mole)
$(C_f)_{LFL}$	mole fraction of fuel in mixture at LFL (mole/mole)
$(C_f)_{UFL}$	mole fraction of fuel in mixture at UFL (mole/mole)
ΔH	heat of reaction (kJ mole^{-1})
LFL	lower flammability limit
X	excess air factor
UFL	upper flammability limit

Greek Symbols

α	ratio of number of moles of diluent gas to the number of moles of oxygen in a reacting mixture.
β_0	ratio of excess oxygen to the stoichiometric fuel – oxygen mixture in a reacting mixture.
β_α	ratio of excess gases to the stoichiometric fuel – gas mixture with inert to oxygen concentration ratio of α.
Φ_0	equivalence ratio for fuel reacting in an oxygen atmosphere.
Φ_α	equivalence ratio for fuel reacting in a gas mixture with an inert to oxygen ratio of α.
Φ_0'	modified equivalence ratio for fuel reacting in an oxygen atmosphere.
Φ_α'	modified equivalence ratio for fuel reacting in a gas mixture with an inert to oxygen ratio of α.
μ	the number of moles of oxygen needed for stoichiometric combustion of the fuel without including the oxygen needed for oxidizing the nitrogen in nitrogen containing fuels.

Subscripts

pr	predicted
st	stoichiometric.
LFL	lower flammability limit
UFL	upper flammability limit

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