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Thermodynamic Analysis of the Flammability Limits of Fuel, Oxygen and Inert Mixtures

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Abstract

In Sheldon's [1] presentation of the flammability limit of a methane-oxygen-nitrogen mixture, he did not consider the effect of other inert gases. In this paper, Sheldon's idea is generalized by considering the presence of inert gases. Three important parameters appear in the conservation of mass equation describing the mixture; the molar stoichiometric ratio of oxygen to fuel, the molar ratio of inert gases to oxygen and the molar ratio of the excess gases to the stoichiometric oxidizing mixture. Other literature data on the lower flammability limit for a number of hydrocarbon compounds in both oxygen and air was utilized to show that lean limit values are almost identical. The flammable envelope is defined by a region in a plot of the reciprocal of the molar fuel concentration versus the molar excess gases to stoichiometric oxidizing mixture ratio. A similar region is defined by a plot of the molar inert oxygen ratio versus the molar excess gases to stoichiometric oxidizing mixture ratio. It is shown that the flammable region of any fuel can be defined by considering the flammability limits of a fuel in pure oxygen.

Key words: Flammability Limits; Methane Combustion; Inert Additives.

Introduction

Fuels in general and hydrocarbon compounds in particular occupy an important place in our present way of life. They are used for the operation of our transportation systems as well as being used as solvents in many manufacturing processes. The safe handling of these compounds requires an understanding of the flammability characteristics for preventing fire and explosions. The safest method to prevent fires and explosions of flammable vapors is to prevent the existence of flammable mixtures in the first place. This method requires a detailed knowledge of the flammability region as a function of the fuel, oxygen and nitrogen concentrations as well as the effect of the addition of various diluents that can prevent ignition from happening. The flammability limits are defined by two important indices, the lower flammability limit (LFL) and the upper flammability limit (UFL). The information available in the literature is based on experimental results. The relationship between the flammability limits and the thermochemical parameters of combustion is still not well understood. There are still no theoretical based methods available for predicting the flammability limits for compound where experimental data are not available.

In order to support the development of the theoretical model that is to be discussed in this paper, some preliminaries will be discussed as a basis. Because a significant component of the discussion relates to the influence of inerts on the flammability limits of hydrocarbons, the data of Coward and Jones [2] will be used.

Flammability Limits and Ignition Temperature

The flammability limits are not a thermodynamic property of fuels and are dependent on the apparatus used for measurement. This is why a standard, e.g., ASTM E 681-79 Standard Method, must be followed for determination. Cullis and Foster [3] examined the applicability of the thermal ignition theory to the combustion of decane. They modified the Arrhenius rate equation to produce an agreement between the experimental results and their theory. Suzuki [4] on the other hand, using statistical methods, produced an empirical correlation between the standard enthalpy of combustion and the LFL for some 123 compounds. Sheldon [1] 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 a 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" Melhelm [5], in examining the combustion of methane in oxygen makes an almost identical assertion 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 theoritical flame temperature of 1500°K. At this temperature, the combustion reaction is able to generate enough heat to produce a self sustaining (propagating) reaction". He also states that: "The low flammability limit (LFL) and the upper flammability limit UFL do not change significantly over 500 degrees window (adiabatic temperature)". Hertzberg [6] noticed that the addition of an inert powder to a flame is equivalent to increasing the surface area of the tube confining the flame. In the same vein, the ignition temperature is not a thermodynamic property of any combustible mixture. However, it was defined by Shouman and El-Sayed [7] on the basis of the thermal explosion theory, as the temperature where the concentration versus temperature trajectory contains a single inflection point before the maximum temperature is reached. It is the premise of the present work that the ignition temperature so defined can be used to predict the flammability limits on theoritical basis.

Thermodynamic Analysis

For any fuel, μ moles of oxygen are required per mole of fuel for stoichiometric combustion. No oxygen is considered for the oxidation of nitrogen for fuels containing nitrogen in their chemical structure. Nitrogen only oxidizes at high temperature by dissociation. The molar ratio between the inert gases and oxygen is defined as α. Under non-stoichiometric conditions, there is either excess oxygen or excess fuel in the mixture. The molar ratio of the excess gases to the stoichiometric mixture, excluding fuel, is defined by β where β is analogous to the excess air factor X used in dealing with combustion in atmospheric air. Utilizing the conservation of mass equation produces:

$$1/C_f = 1+ \mu\,(1+\alpha)(1+\beta) \quad (1)$$

This equation is valid for all mixtures whether flammable or not. For $\beta< 0$, a rich mixture is indicated, $\beta = 0$ represents a stoichiometric mixture and $\beta> 0$ defines a lean mixture. For $\beta=-1$, $C_f=1$. For any given μ (fuel), $1/C_f$ plotted versus β for a constant value of α produces a straight line with a slope of $\mu\,(1+\alpha)$. All lines intersect at $\beta = -1$ and $C_f =1$. This sets the theoretical foundation for the empirical correlation discovered by Wierzba et al. [8]. The line for $\alpha=0$ represents the combustion in an oxygen atmosphere while the line for $\alpha=3.762$ represents combustion in atmospheric air. On the line $\alpha=0$, $(\beta_0)_{LFL}$ defines the lower flammability limit and $(\beta_0)_{UFL}$ defines the upper flammability limit. The three sided inflammable region is bordered by the line $\alpha=0$ with $(\beta_0)_{LFL}$ and $(\beta_0)_{UFL}$ as two apexes. The third apex is defined by the intersection of the line $\alpha=\alpha_{st}$ and the β axis. Connecting the apexes with straight lines defines the flammability limit with a margin of safety as will be discussed later.

Application of the Results to Methane Combustion in Air

On examining the data by Coward and Jones [2] on the LFL of a number of hydrocarbon compounds in both oxygen and air, it was noticed that they are practically identical. This suggests that replacing the nitrogen in the air by oxygen did not affect the LFL and that the presence of excess oxygen is equivalent to the presence of the inert nitrogen since they both have almost same value of molar specific heats. Application of the results to the combustion of methane will now be discussed. The value of μ for methane is 2, its LFL in both oxygen and air is 0.053, its UFL in oxygen 0.61 and in air 0.14. Using these values produces $(\beta_0)_{LFL}= 7.934$,

$(\beta_0)_{UFL}$= - 0.68033, $(\alpha_{st})_{LFL}$= 7.9340 and $(\beta_{air})_{UFL}$ = - 0.3550. Figure 1 shows the flammability envelope for methane in the β - (1/ C_f) plane which is given by a triangular region. The base of the triangle is represented by the α=0 line between $(\beta_0)_{LFL}$ and $(\beta_0)_{UFL}$. The second side of the triangle is the UFL line which is constant and the third side is the line connecting $(\beta_0)_{UFL}$, $(\beta_{air})_{UFL}$ and $(\alpha_{st})_{LFL}$. The results in Figure 1, when transferred to the α - β plane, shows that the flammability envelope of any organic compound for an oxygen-nitrogen mixture is only controlled by α and β, as shown in Figure 2. It can be seen that connecting the apexes in Figure 2 with straight lines will define the flammable region with a margin of safety.

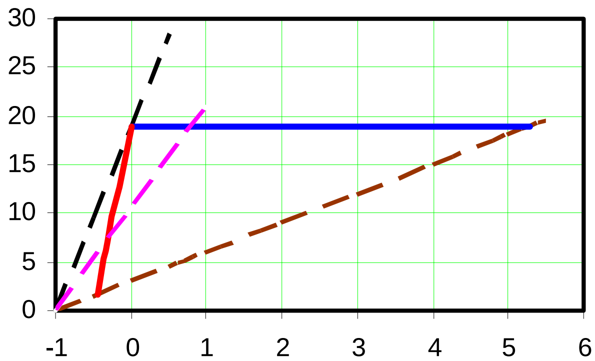

Figure 1. Flammability envelope for methane.

Figure 2. Flammability envelope for methane in a - b plane.

Effect of Inert Additives Different than Nitrogen

This approach will now be applied to the experimental data reported by Coward and Jones [2] showing the effect of various inert additives to air on the flammability limits of methane. In that study α was defined as the ratio of moles of inert to the sum of moles of air plus inert. The value of α according to this definition was evaluated and used here.

Figure 3 shows the data for all gases plotted in the β - 1/C_f plane that demonstrates the influence of different gases on the flammability limits. Figure 4 shows the data for all gases and Figure 5 shows the data of Figure 4 superimposed on Figure 2. Examining the data shows that the increase in the molar specific heat of the inert reduces α_{st}.

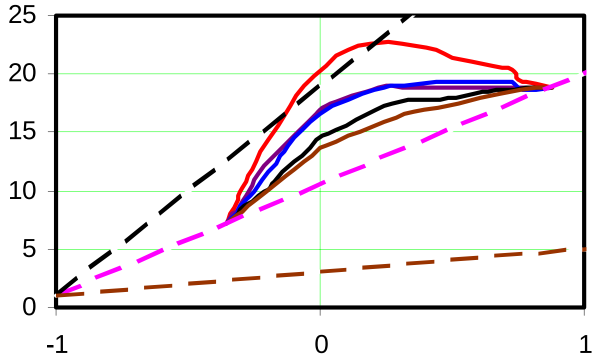

Figure 3. Effect of various inert additives on the flammability envelope of methane.

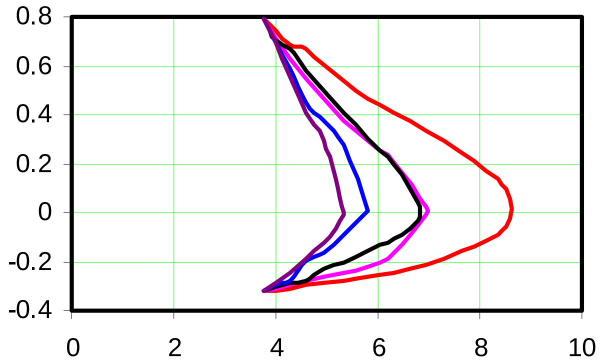

Figure 4. Effect of the various inert additives on the flammability envelope of methane

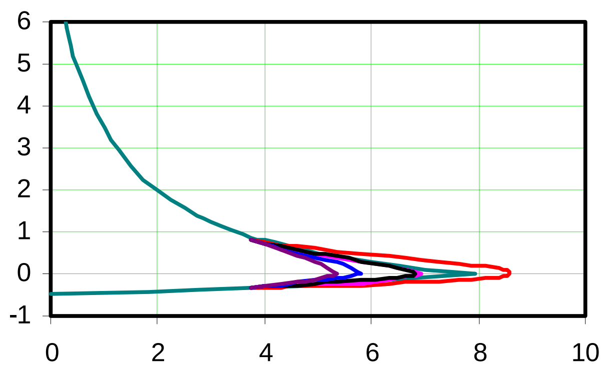

Figure 5. Superimpose of flammability envelope for methane and effect of the various inert additives on the envelope

Conclusions

In this study, it is shown that the flammability envelope for a mixture of an organic compound, oxygen and nitrogen is uniquely defined for each organic compound in the α - β plane as well as the β - $1/C_f$ plane. It is concluded that the flammability limit of any fuel can be determined by examining the combustion of the fuel in an oxygen atmosphere. Adding excess oxygen, excess fuel or an inert of choice to a stoichiometric fuel-oxygen mixture until it is impossible to ignite, produces the LFL, UFL and $\alpha_{st.}$ Connecting these three points with straight lines in the $\beta - 1/C_f$ plane defines the flammable region.

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).
LFL, UFL	lower and upper flammability limit of mixture respectively (mole/mole)
X	excess air factor for combustion in air.

Greek Symbols

α	ratio of number of moles of inert gases to the number of moles of oxygen in a reacting mixture.
β	ratio of number of moles of excess gas to number of moles of oxidizing gases in the stoichiometric mixture.
β_0	ratio of excess oxygen to the stoichiometric fuel – oxygen mixture.
β_α	ratio of excess gases to the stoichiometric fuel – gas mixture with inert to oxygen concentration 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 for nitrogen containing fuels.

Subscripts

st	stoichiometric.
LFL, UFL	upper and lower flammability limits, respectively

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