Temperature Influence on the Flammability Limits of Heat Treating Atmospheres

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Abstract

The flammability limits of gas constituents commonly used in heat treating atmospheres will be discussed in this paper. The upper and lower flammability limits, with respect to temperature, will be explored. A method will be described for determining these limits using CAFT Theory. This temperature factor and its impact on safe furnace practices will be addressed.

Introduction

The science of flammability of fuel gases within metal heat treating operations has its roots in the work of the pioneer flammability scientists Humphrey Davy and Robert Bunsen nearly two hundred years ago. This early work was in response to methane explosions that too often accompanied early coal mining in Europe. Today, although flammability science is fairly well developed – and especially in its application to heat treating – explosion accidents do occur. Often operators, for whatever reason, are not familiar with how close their operation may be to the flammable limit. Alternatively, operators may operate within a flammable region but assume that an ignition source is very unlikely. This paper provides the fundamentals on the subject as well as a means of evaluating the relative closeness to a flammability envelope. This paper does not provide information on controls and alarms. The material provided herein is only an example and should not be utilized for design or operation of safety systems. Practitioners should provide their own but perhaps similar analyses for their specific applications.

Background

Heat treating atmospheres are used to perform a variety of thermal processes including annealing, carburizing, neutral hardening, sintering and brazing among others. The role of the atmosphere varies depending on the specific heat treating application being performed. The material to be heat treated and final properties of the material are key considerations in determining the type of atmosphere used.

The most common atmospheres used are endothermic and exothermic gases that are both generated from the partial combustion of natural gas or other hydrocarbons with air. Another common atmosphere is generated via the dissociation of ammonia. Collectively, the above atmosphere types are referred to as generated atmospheres. Over the past 30 years or so, synthetic atmospheres utilizing nitrogen or hydrogen as the primary constituent, have gained popularity due to the purity and consistency of the feedstock gases. These atmospheres are typically nitrogen-based with hydrogen, natural gas or other hydrocarbons added as needed based on the specific application.

All heat treating atmospheres consist of both flammable and inert components regardless of how they are produced. The types and amount of flammables present is a function of many factors including; type of feedstock used, air-to-fuel ratio in the case of exothermic and endothermic gas, hydrocarbon or air additions for carbon control and inert gas additions.

Fundamentals of Combustion

Figure 1 is the familiar fire triangle with some additional text for fuel vapors or gases. The fuel vapor that is required must have the proper mixture ratio with air – that is, between the lower flammable limit (LFL) and the upper flammable limit (UFL) at the source of ignition. In flammability work the term lower explosive limit can also be used for the LFL. Similarly the term upper explosive limit can be used for the UFL.

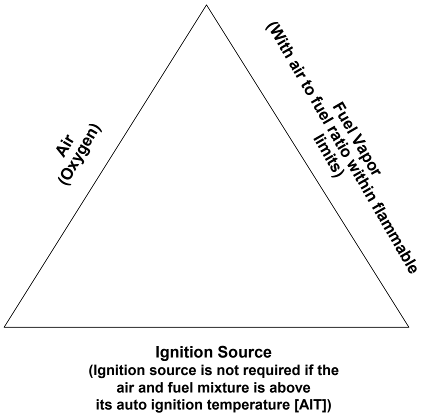

Figure 1: Fire Triangle – The three requirements for a fuel vapor fire to occur.

A schematic of the LFL and UFL concepts for hydrogen and methane fuels is given in Figure 2. For example, when the methane content in a mixture of methane and air is below 5% (by volume) there is too little methane (too much air) present to propagate a flame <u>if ignited</u>. Similarly if the methane

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content is greater than 15% there is too much methane (too little air) present to propagate a flame if ignited. Note the stoichiometric or chemically correct ratio of methane in air is 9.5%. At this ratio there is just sufficient air present to produce CO_2 and water vapor with no oxygen remaining.

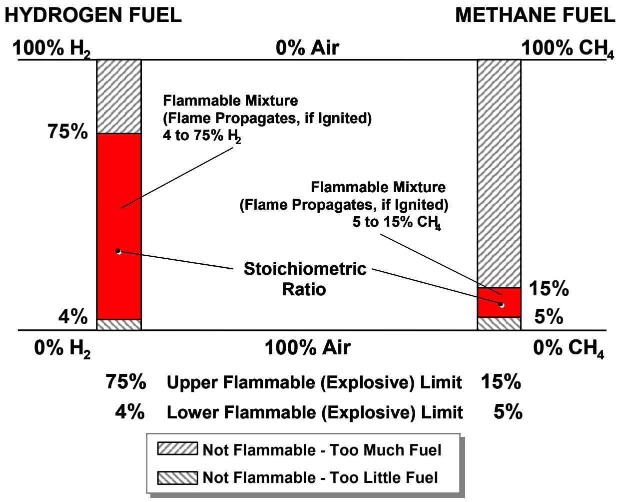

Figure 2: Concept of flammable limits for fuels in air.

Two other flammability concepts are important to understand:

Measuring Flammable Mixtures

A measured fuel vapor content in an air-fuel mixture only represents the fuel content at the location of the measurement and does not represent the fuel content throughout a volume unless the volume is well mixed. Fuel vapors and air do not mix well on their own. For example, in still air both hydrogen and natural gas are buoyant and initially rise to the upper region of the volume. Many industrial explosions have taken place, even though flammability measurements were taken at a specific location, because the fuel and air mixture was not uniform throughout a volume.

Upward propagation of flames

When flammability limit measurements are carried out it is easier for a flame to propagate upward (in a tube) when ignited at the bottom than to propagate downward when ignited at the top. In this case easier propagation is reflected in having a lower LFL in upward flame propagation than in downward flame propagation. For example at ambient conditions the listed LFL for methane in upward propagation is 5% and for downward propagation it is 6%. The LFL value is typically more conservative for upward propagation. For safety considerations it is universally agreed that the published measured LFL values be for upward propagation.

The addition of inert gases influences the LFL and UFL of a fuel-air mixture. Figure 3 reveals the effect of added inerts on the flammability of methane and air. The left side is the same as the methane side of Figure 2 but the right side of Figure 3 shows the effect of, for example, added nitrogen on the LFL and UFL and how a flammability envelope is generated. The far right portion of the envelope is termed the nose. At this location the amount of nitrogen added is such that the LFL and UFL merge (at the nose) and methane-air-nitrogen mixtures to the right of the nose are not flammable. Inside the envelope the methane-air-nitrogen mixtures are flammable. Such envelopes are published for many individual fuels with several individual inerts (e.g., N_2, Ar, CO_2) at ambient conditions. Each inert has a unique envelope. The envelopes may be used for flammability prediction if they directly match the conditions present.

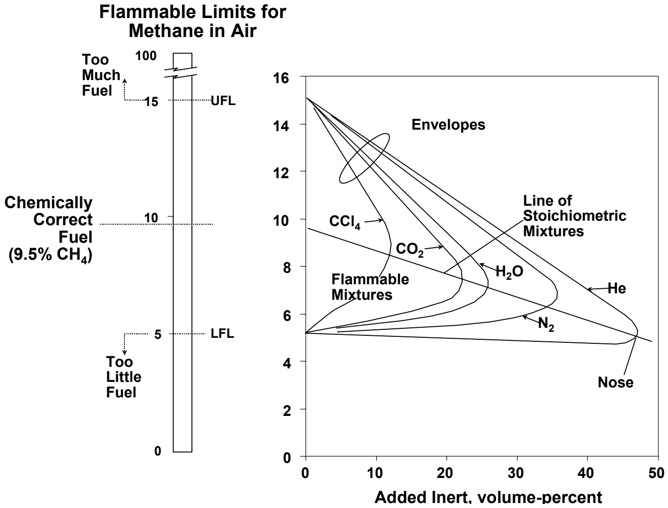

Figure 3: Flammable limits of methane in air with and without added inert gases.

LFL and UFL values are published [1] for a significant number of fuels for ambient conditions [i.e. 20°C (68°F) and 760 mm Hg (14.7 psia)] because room conditions are the easiest conditions to create for flammability testing.

There are up to four classic (and complicating) conditions that typically arise in many combustion applications. When any one or more of these occur published LFL/UFL values alone are not of direct help in predicting flammability. Two of the four can typically occur in heat treating. The four conditions are:

•**Multiple Fuels.** When multiple fuels are present and this is the only one of the four possible complications present, LeChatelier's [2] rule may be used to predict the LFL of the mixtures based upon the LFL values of the individual fuels.

•**Multiple Inerts.** This is a significant complication to predicting the flammability envelope since each inert has a different envelope. Fortunately all inerts except helium [due to its low molecular weight (hence buoyancy)] follow the calculated adiabatic flame temperature (CAFT) theory. A single envelope incorporating all the inerts present can be developed using this theory. The CAFT approach is described in the next section.

•**Elevated or Depressed Temperatures.** Air and fuel mixtures, which are above or below ambient temperature, require LFL, UFL and envelope data at those same temperatures. With few exceptions this data does not exist in the literature. Fortunately the effects of elevated or depressed temperatures follow the CAFT theory (assuming that all fuels and inerts remain as vapors and that the fuels do not decompose or self ignite at elevated temperatures).

•**Elevated Pressures.** This is a difficult complication for several reasons. The effect of pressure on LFL's, UFL's and envelopes does not follow CAFT theory. Some simple hydrocarbons tend to follow a logarithmic theory [3]. Further, published data on LFL's, UFL's and envelopes at elevated pressures tend to be rare. Fortunately almost all metal heat treating applications occur at essentially ambient pressure.

Flame Temperature as a Tool for Flammability Prediction

Since flame temperature is a measure of the combustion energy of a fuel-air-inert mixture it must contain sufficient energy to propagate. CAFT of a mixture may be used to help predict if a mixture is flammable. The theory is simple. CAFT values are calculated for a variety of fuels at their published LFL, UFL, and nose locations. These CAFT values may be termed CAFT reference. If one then has an actual mixture of a fuel, inert and air that is in the vicinity of the published LFL, UFL or nose, one can calculate the adiabatic flame temperature, termed CAFT mixture. The following criteria are then used to predict the unknown flammability of the mixture.

If $\mathrm{CAFT}_{mix} > \mathrm{CAFT}_{ref} \rightarrow$ mixture is flammable
(has sufficient energy)
If $\mathrm{CAFT}_{mix} < \mathrm{CAFT}_{ref} \rightarrow$ mixture is non-flammable
(has insufficient energy)

CAUTION: A factor of safety must always be applied in any CAFT comparison.

The calculation of adiabatic flame temperatures is accomplished via software programs based upon equilibrium achieved through minimization of the Gibbs free energy in the fuel-oxygen reaction. The first published recognition of the CAFT theory as a means to help predict flammable limits was by Edgerton and Powling in 1948[4]. Hansel [5] developed the CAFT theory into a comprehensive package involving over fourty fuels (single or multiple), multiple inerts, elevated pressures and temperatures. Subsequent publications by others [6, 7] are also based upon the CAFT theory.

The changes in the flammability envelope at, for example, elevated temperatures or the use of multiple inerts is essentially automatically compensated for in CAFT theory. The reason for the automatic compensation is simple: As the mixture temperature changes or the species of inerts change, it has been found that the CAFT reference valves are essentially unchanged. For the 5% LFL of methane as an example, if the methane-air mixture temperature increases from 70˚F to 300°F, and the CAFT reference remains the same at 2212°F, the actual LFL will decrease to 4.5% because the higher starting temperature means that less combustion energy (i.e. fuel concentration in the mixture) is required to reach the same CAFT reference.

Tertiary Diagrams

The type of diagram shown in the right side of Figures 3 can be used for flammability determinations. The fact that it is based upon a mixture of fuel, air and a variable amount of some inert is usually not as useful as a tertiary diagram which can handle any percentages of a fuel, oxygen and an inert (i.e. the diagram is not locked into the ratio of oxygen to nitrogen that is in air). Figure 4 is such a tertiary diagram for any ratio of hydrogen, oxygen and nitrogen at ambient conditions. Figure 4 is read as follows: The top (apex) of the triangle represents 100% hydrogen and the base of the triangle represents 0% hydrogen. A horizontal line representing 30% hydrogen, as an example, is shown as Line A. The lower left corner is 100% oxygen and the lower right corner is 100% nitrogen. A 30% oxygen mixture is shown as Line B and a 30% nitrogen mixture is shown as Line C. The center of the triangle is 33% hydrogen, 33% oxygen and 33% nitrogen. As an example Point D is 30% hydrogen, 27% oxygen and 43% nitrogen. Point E is air (0% hydrogen, 21% oxygen and 79% nitrogen).

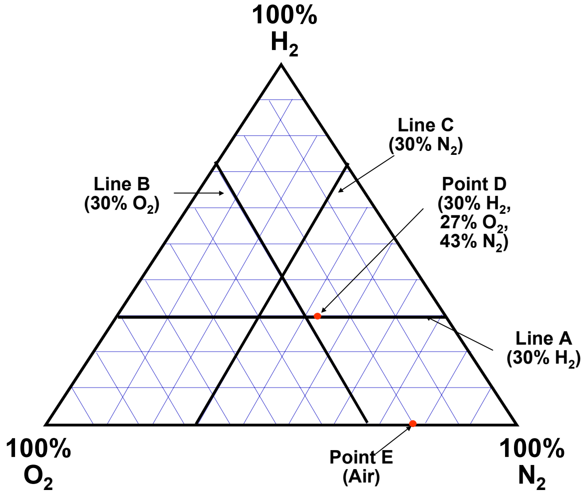

Figure 4: Tertiary diagram for hydrogen, oxygen and nitrogen (without flammability envelope).

Figure 5 provides the full tertiary diagram for hydrogen, oxygen and nitrogen including the flammability envelope for ambient conditions. Mixtures inside the envelope are flammable. Line F is drawn from air (Point E in Figure 4) to 100% hydrogen and thus any mixture of hydrogen and air alone must lie on Line F. Note the conventional LFL and UFL points for hydrogen in air (4% hydrogen and 75% hydrogen, respectively). Note also the LFL and UFL of hydrogen in oxygen (4% hydrogen and 94% hydrogen, respectively).

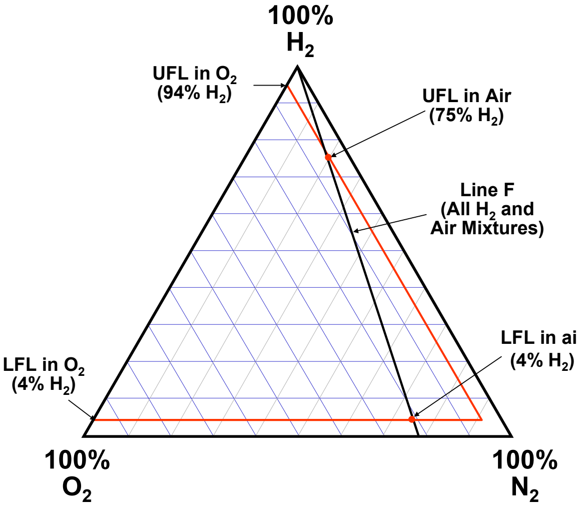

Figure 5: Tertiary diagram for hydrogen, oxygen and nitrogen (with flammability envelope for ambient conditions).

Heat Treating Application of the Tertiary Diagram

Virtually all heat treating applications are at atmospheric or ambient pressure. Thus the available ambient pressure flammability envelopes may be utilized. The main factors therefore are the composition of the gas and the temperature. If there is a single fuel, a single inert, and oxygen then the ambient pressure tertiary diagram can be adjusted for temperature. Figure 6, and specifically the 70°F envelope, represents the right hand portion of Figure 5 for hydrogen, nitrogen and oxygen, assuming that oxygen is the contaminant.

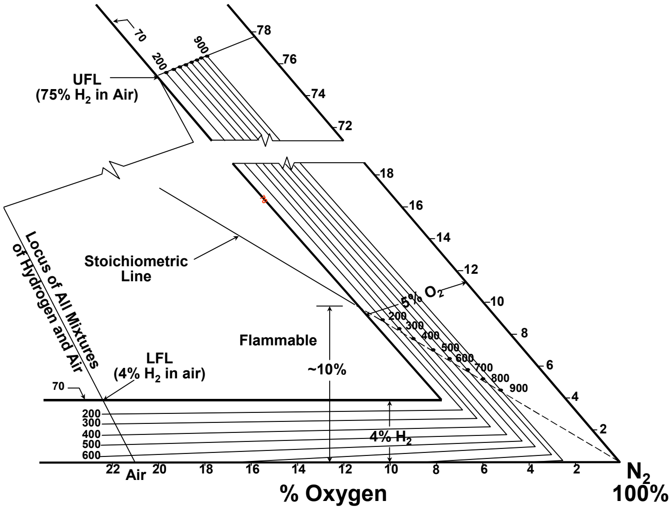

Figure 6: Portion of right side of tertiary diagram for hydrogen, oxygen and nitrogen at elevated temperatures.

Temperature is the factor to be corrected for and this may be accomplished using the elevated or depressed temperature description above. Three CAFT reference temperatures are known. The LFL in air is 676°F, the UFL in air is 1760°F, the nose is 824°F and the stoichiometric point on the envelope is 1621°F. Working first at the LFL in air the temperature rise (energy) to reach 676°F from 70°F is 676 – 70 = 606°F. If the initial temperature was 200°F, as an example, the temperature rise necessary would be 676 – 200 = 476˚F and the fraction of the 4% LFL required would only be 476/606 x 4 = 3.1%. Thus the LFL at 200°F would be approximately 3.1% as shown on the diagram. Similarly the 300˚F through 800°F lines may be drawn.

For the nose the CAFT reference is 824°F and the rise is 824 – 70 = 754°F. The 200˚F through 700°F points may be calculated as fractions of 4% hydrogen in the ratio, similar to the LFL case. A note of caution is necessary. The minimum auto ignition temperature of hydrogen in air is 968°F. This usually corresponds to roughly stoichiometric mixtures in air for most fuels. Thus at or near 968°F one has to assume that the hydrogen-nitrogen-oxygen mixture may self-ignite. At or about this temperature it may be assumed that any mixture of hydrogen, oxygen and nitrogen react until either the hydrogen or the oxygen is completely consumed. Thus mixture temperatures at or above 968°F in the figure are not relevant. CAUTION: Self-ignition is not guaranteed at the minimum AIT. Consult NFPA 86C for guidance on assuring self-ignition.

For the UFL the CAFT reference is 1760˚F and the 200˚F through 900°F points may be plotted as shown. They are based upon an **oxygen** concentration of 5% for the ratio. Finally, the stoichiometric CAFT reference is 1621°F. The 200˚F through 900˚F points are shown. They were based upon either 10% hydrogen or 5% oxygen since the stoichiometric ratio is $H_2 + ½ O_2$.

Summary and Conclusion

The flammability limits for numerous fuels, including those typically found in heat treating atmospheres, are very well understood and documented in the literature. Unfortunately, the data available almost always applies to ambient temperature and pressure conditions. The method described in this paper can be used for predicting flammability at elevated (or depressed) temperatures utilizing CAFT Theory.

With few exceptions, the flammability envelope is expanded as temperature increases. The most important consequence this has for heat treating applications is the suppression of the lower flammability limit (LFL).

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