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A METHOD OF MEASUREMENT FOR THE FLAMMABLE LIMITS OF HYDROGEN

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Abstract: The current method for determining the flammable limits for a gas in a closed spherical vessel is based on a specification of the maximum pressure increase during the combustion, usually from 5 to 10% of the initial ambient pressure. This approach is completely arbitrary and is not fundamentally based. For most hydrocarbons this pressure boundary and hence the flammable limit is easy to determine experimentally since an abrupt pressure drop occurs at the flammable limit as the fuel concentration in air is adjusted. However, for some species, particularly hydrogen mixed with air, the drop in maximum combustion pressure is not very abrupt and the fuel concentration can range several percentage points depending on the arbitrary criterion used for the flammable limit.

This paper will discuss a new approach for determining the flammable limits for a gas in a spherical vessel. The approach is based on the maximum second derivative of pressure rise. The second derivative is indicative of an acceleration of the combustion rate and is, hence, fundamentally based. Furthermore, we have identified a new approach to determine the downward propagating flammable limits based on the combustion time, that is, the time that the gas actually burns in the vessel.

Keywords: Flammability, Upward flammable limit, Downward flammable limit, Hydrogen,

1. INTRODUCTION

The flammable limits of combustible gases are very important to ensure the safety in industrial and domestic applications. The flammable limits are a critical design point used in an inerting procedure which is achieved by the partial or complete substitution of the flammable atmosphere by an inert. Inerting is normally only considered when the flammable or explosive hazards cannot be eliminated by other means, i.e. substitution of a flammable material with non-flammable, or adjustment of process conditions to ensure conditions are outside the flammable range. There is a minimum concentration of flammable gas in air below which propagation of flame does not occur on contact with a source of ignition. There is also a maximum concentration of the gas in oxidizer above which propagation of flame does not occur. These boundary mixtures of the gas with oxidizer are known as the lower and upper flammable limits (LFL and UFL) respectively, and they are usually expressed in terms of percentage by volume of the gas in oxidizer. The LFL and UFL are also known as the lower explosive limit (LEL) and the upper explosive limit (UEL), respectively.

There are several specific technical criteria and test methods for experimentally determining flammable limits of gases. However, observed values depend on the individual apparatus, criteria, and many other parameters. Several established standard methods for measuring the explosion limits [1, 2, 3, 4] are available. In these testing methods, the dimension of equipment and ignition energy must be specified to ensure the reproducibility of experiment data. The criteria for determining the flammable limits are classified into two classes: visual inspection of the flame kernel produced by the igniter, and measurement of the maximum pressure rise and application of a pressure rise criteria- usually from 5 to 10% of the initial ambient pressure.

If flammability limit measurements using the visual criterion are carried out, it is easier for a flame to propagate upward (in a tube) by igniting at the bottom than to propagate downward by igniting at the top. In this case easier propagation is reflected by a lower LFL in upward flame propagation than in downward flame propagation. For safety considerations it is universally agreed that the published LFL values must be conservatively determined for upward propagation since these concentrations are lower. However, within the concentration range from the upward to the downward flammable limit, the extent of combustion depends highly on the turbulence of the gas mixture or location of the ignition source [5]. The gas mixture will be burned entirely when the concentration of flammable gas is within the range of downward flammable limits. Therefore, the downward flammable limit may be also an important index for analyzing the consequences of gas explosion. However, a method to experimentally measure the downward flammable limits in a spherical vessel has not been developed, until this work.

For most hydrocarbons the maximum pressure rise changes abruptly near the flammable limits as the fuel concentration in air is adjusted. However, for some species, particularly hydrogen mixed with air, the drop in maximum combustion pressure is not very abrupt and the fuel concentration can range several percentage points depending on the arbitrary criterion used for the flammable limit [5]. Furthermore, the lower flammable limit of a hydrogen-air mixture determined using a pressure rise criterion is inconsistent with the visual criterion result with a visible flame observed well below the pressure rise criterion limit. The visual criterion is also difficult to place into practice when the flame of gas is non-visible or of very weak intensity.

This work proposes a fundamentally based method to experimentally determine the flammable limits in a closed combustion test cell. We believe this approach will result in much more consistent flammable limits than previously published.

We have also found an experimental method to determine the upward and downward flammable limits in a closed combustion vessel. A method for determining these limits in a closed vessel has not been proposed before and will result in increased data and understanding on combustion.

2. EXPERIMENTAL

Experiments were completed for the hydrogen/oxygen/nitrogen and methane/oxygen/nitrogen mixtures – comprising a database of several hundred runs. The apparatus used in this study is a spherical explosion vessel of 20 L. All experiments were carried out at room temperature and an initial pressure of 1 atm. First, the vessel is purged with ultra high purity (UHP) nitrogen and evacuated several times to remove combustion impurities in the reactor, and then UHP oxygen, UHP nitrogen and UHP flammable gas are filled sequentially to the desired partial pressures. The partial pressure gas filling is controlled by feedback control from a high precision pressure transducer, manufactured by Sensotec. Gases are mixed using Burkert solenoid valves,. The precision of the pressure transducer is estimated at less than 0.005 psia. The valves are controlled by LabVIEW software.

Once the gases are mixed homogeneously and a temperature requirement is satisfied, the gas mixture is ignited by a 40-gauge tinned copper fuse wire located at the center of the vessel. The fusing wire has a length of 10 mm and delivers a measured 10 J at ignition. The uncertainty of the ignition time by the fusing wire is less than about 10 msec due to using an alternating current electric source, heating of the fusing wire, and stabilization of the flame kernel in the gas mixture.

After ignition, pressure signals from the pressure transducer located on the reactor wall are monitored to characterize the explosion of flammable gas mixture. The occurrence of ignition is also observed visually through two sight glasses. The pressure rise history is saved on the computer – the equipment can achieve sampling rate of up to 50,000 samples per second. The vessel is evacuated to 0.3 psia at the end of the daily testing and the pressure is monitored before testing the next day to test for leaks in the vessel. The testing procedures are controlled automatically by computer. Details of the apparatus and procedures are described elsewhere [6].

3. UPWARD FLAMMABLE LIMITS

It is well known that the flammability limits are dependent upon the experimental apparatus and the conditions used for their measurement. With the criteria of 7% and 5% pressure rise according to ASTM E 918-83 and EN 1839(B), the upward LFL for hydrogen-air mixtures is about 5.7 vol. %, 5.5 vol. %, respectively as shown in Figure 1.

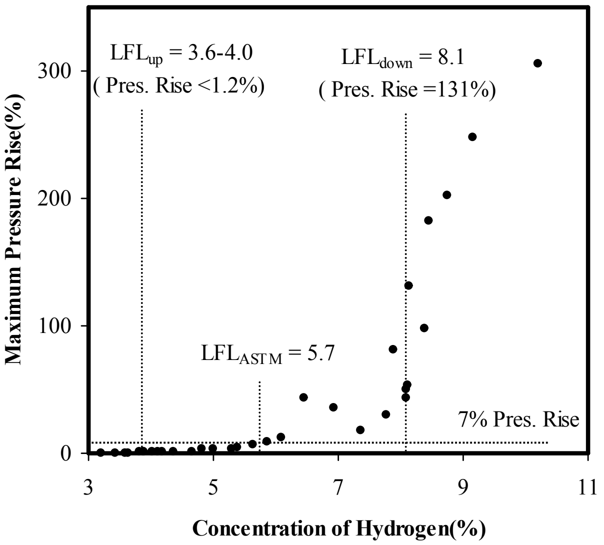

Figure 1. Maximum pressure rise of hydrogen-air mixture near lower flammable limit

A flame can still be observed visually rising up from the igniter below these concentrations. The flammability limit obtained using the pressure rise criterion is not consistent with literature data obtained using the visual test. Therefore, a new criterion for the flammable limit in a spherical vessel must be investigated which should be consistent with other methods. In this experiment, the combustion time, maximum explosion pressure, and type of pressure-time curve change across the different flammability limits. Some properties are changed abruptly crossing the boundaries of the flammability limits. For most hydrocarbons in air, the maximum explosion pressure shows a dramatic increase at the flammability limits. Therefore, the maximum pressure rise in the explosion vessel has been used as the criteria to determine the flammability limit. This criterion is not workable for hydrogen-air mixtures because there is no dramatic change in maximum explosion pressure near the LFL. A new criterion of the flammability limit of flammable gas is needed to determine the LFL of hydrogen in air with a spherical explosion vessel.

The peaks of the combustion time appear near upward LFL and downward LFL published in literature as shown in Figure 2. The peak near the upward LFL is about 3.63 vol. % in air. It is lower than 4.0 vol. % published in literature. The flame rising up can be observed dimly as low as 3.59 vol.%. This means that the concentration at peak on the curve of the combustion time verse the concentration of flammable gas is slightly higher than the concentration where the flame kernel can be observed visually. This gap, 0.04% (3.63-3.59), is in the error range for the gas mixing. Therefore, the peak of combustion time can be used as a criterion for the flammable limit.

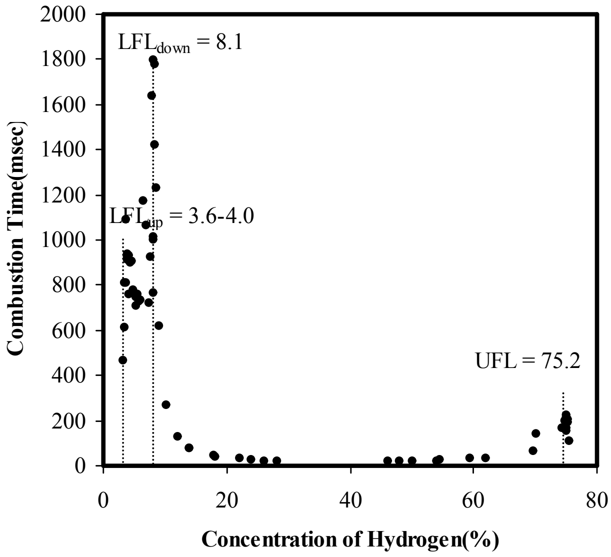

Figure 5. Combustion time of hydrogen-air mixture in spherical vessel.

The sign of the maximum second derivative of the pressure-time curve is shown in Table 1. The positive sign means that the surface area of the flame is growing with time. And the negative sign means that the surface of flame is diminishing with time and the flame is extinguished. Therefore, the change of the sign of the maximum second derivative of the pressure-time curve can be also used as a criterion for the flammable limit. The second derivative criteria of a flammable range of hydrogen in air result in 3.6 to 75.2% which is consistent with literature data.

The criterion using the sign change is more fundamentally based on physical phenomena of combustion than that using the combustion pressure change. Therefore, we would like to recommend that the sign change of the second derivative of the pressure-time curve be used as a criterion to determine the upward flammable limit instead of the pressure rise criterion of ASTM. The combustion time and the second derivative of pressure-time curve are conservative criteria to determine flammability limits comparing to 7% pressure rise criterion of ASTM in a closed vessel.

4. DOWNWARD FLAMMABLE LIMITS

Downward flammable limits have not been studied as much as upward flammable limits. If the concentration of flammable gas is inside the range of the downward flammable limits, then the flame can travel through the entire flammable gas mixture and the maximum explosion pressure can be approximated by thermodynamic calculations [7].

Table 1. Sign of maximum second derivative of Pressure Rise of hydrogen-air mixture near flammable limits.

Concentration of Hydrogen (%)	Sign of maximum second derivative of Pressure Rise [$\left(\frac{d^2P}{dt^2}\right)_{Max}$]
3.16	-
3.35	-
3.57	-
3.59	+
3.63	+
3.66	+
3.76	+
4.02	+
4.08	+
4.30	+
4.74	+
5.15	+
5.51	+
5.77	+
5.98	+
74.51	+
74.69	+
74.84	+
75.07	+
75.08	+
75.15	+
75.19	-
75.19	-
75.29	-
75.37	-
75.51	-

When the concentration is between the upward and downward flammable limits, the flame travel through part of the flammable gas mixture and the maximum explosion pressure depends on the location of the ignition source and the turbulence of the gas mixture. Therefore, the downward limits are also very important for analyzing consequences of explosions or fires. Unfortunately, there is no criterion for the downward flammable limits in a closed vessel experiment until this work. Near the downward flammable limit, as described above, the flame propagates very slowly near the bottom of combustion vessel and the combustion time is a maximum. The combustion time can be used as a criterion for the downward flammable limit. For hydrogen-air mixtures, the combustion time criteria resulted in a downward flammable range from 8.1 to 75.1% hydrogen. For methane, these limits are about 5.7 to 15.1%. These downward flammable limits are consistent with published values [7].

4. CONCLUSIONS

This paper focuses on combustion phenomena near the flammable limits in a spherical vessel and new criteria for flammable limits. The pressure-time curves, maximum explosion pressure, and combustion time all change with fuel concentration. Generally, the maximum explosion pressure is changes suddenly near the flammable limits for most hydrocarbon-air mixtures, but for hydrogen it changes gradually at the LFL. The traditional methods to determine the flammable limit, based mostly on a pressure rise, do not work very well for hydrogen. This implies that a new criterion for the flammable limits in a spherical vessel is required that would be applicable to a wider variety of fuels.

The combustion time, that is, the time from ignition to the maximum pressure peak, reaches a maximum value near the flammable limits. However, t a flame is still visible at slightly lower concentrations than the LFL obtained using the peak combustion time. This difference is within the gas mixing error range for our apparatus. Therefore, we believe the criterion of the combustion time can be used to determine the upward flammable limits. This criterion can also be used to determine the downward flammable limits in spherical vessel.

The second derivative of the pressure-time curve can also be used to determine the upward flammable limit. However, it is a conservative criterion for the flammable limits. The flammable limits obtained using the second derivative criterion in a spherical vessel has good agreement with the values obtained visually. This result strongly suggests that the second derivative criterion can be used as a new criterion of upward flammable limit in closed vessel.

5. REFERENCES

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