Thermal Autoignition Temperatures for Hydrogen-Air and Methane-Air Mixtures

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ABSTRACT

The autoignition temperature and ignition delay times for hydrogen-air mixtures and methane-air mixtures as a function of concentration were measured in the Bureau of Mines 1.2-L ignitability furnace. The data shows that the minimum autoignition temperature (MAIT) values obtained for hydrogen-air and methane-air mixtures are in excellent agreement with previously reported AIT values of other researchers. There is also good agreement in the gas concentrations at which the minimum AITs occurred.

Key words: Minimum Autoignition Temperatures (MAIT), Methane-Air mixture, Hydrogen-Air mixtures, ignition delay times.

IGNITION SOURCES CAN be characterized according to the type of energy they introduce into a flammable mixture; electrical, chemical, optical, or thermal ignition sources. For any given type of ignition source, a variety of geometric sizes and shapes are possible, as well as a variety of time-dependent profiles for its power density and energy delivery rate. For spatially concentrated sources such as electric sparks or chemical pyrotechnics that also deliver their energy into the mixture almost instantaneously, the total source energy, by itself, is usually sufficient to determine the effectiveness of the ignitor. A certain minimum ignition energy must be exceeded (in a static mixture) for ignition to occur.

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At the other end of the ignition source spectrum are sources that are spatially and temporally extended. The simplest such sources is a purely thermal one that is geometrically uniform in its spatial extension and is steady-state in time. The data to be presented here are for such thermal sources: ones that are spatially and temporally isothermal; it is only for such sources that the source temperature, by itself, is sufficient to determine the effectiveness of the ignitor. A minimum temperature must be exceeded for ignition to occur, and that temperature is defined as is the minimum autoignition temperature (MAIT).

Although the data to be reported here are for a system that is geometrically uniform in spatial extension, its dimensions are nevertheless limited to a furnace volume of 1.2-L. The detailed structure of the Bureau's 1.2-L ceramic furnace is shown in the perspective drawing in Figure 1. The furnace is essentially cylindrical in shape. The system was designed to study the autoignition properties of dusts in air and to provide for accurate control of the internal temperature. In that mode of operation a dust dispersion system injects and disperses a uniform dust cloud into the furnace. The same system can be used to inject only gas into the furnace. Temperature uniformity data and the dust and gas dispersion effectiveness have been published elsewhere [1,2]. The extensive data obtained for a variety of dusts have been described elsewhere [3,4]. The system was also modified to measure spark ignition energies of dusts at elevated temperatures [5].

There are four access holes in the side wall of the furnace, two of which are shown in Figure 1. One is used for the thermocouple near the furnace wall, which controls the initial temperature of the furnace. Another is used for a thermocouple in the center of the furnace, which monitors the temperature of the dust-air mixture or gas-air mixture. This thermocouple is a fine 25-μm platinum-rhodium thermocouple, whose time constant is fast enough to follow the thermal evolution of an explosion during ignition. The two remaining access ports in the side wall of the furnace are used for spark electrodes [1,5] or for gas sampling tubes [2].

In the dusts studies, the dust to be tested is placed in the disperser, which is placed into the bottom part of the furnace only moments before the sequence of ignition test events is started. A fiberglass rupture diaphragm covers the top part of the furnace in order to isolate the 1.2-L volume. The dispersion pulse which lasts for 30 ms disperses the dust as it releases about 0.066 L of room temperature air from a pressurized reservoir into the furnace. The time constant for heating the dispersed dust-air mixture to the initial temperature of the furnace is usually much shorter than the time constant for ignition. Autoigni-

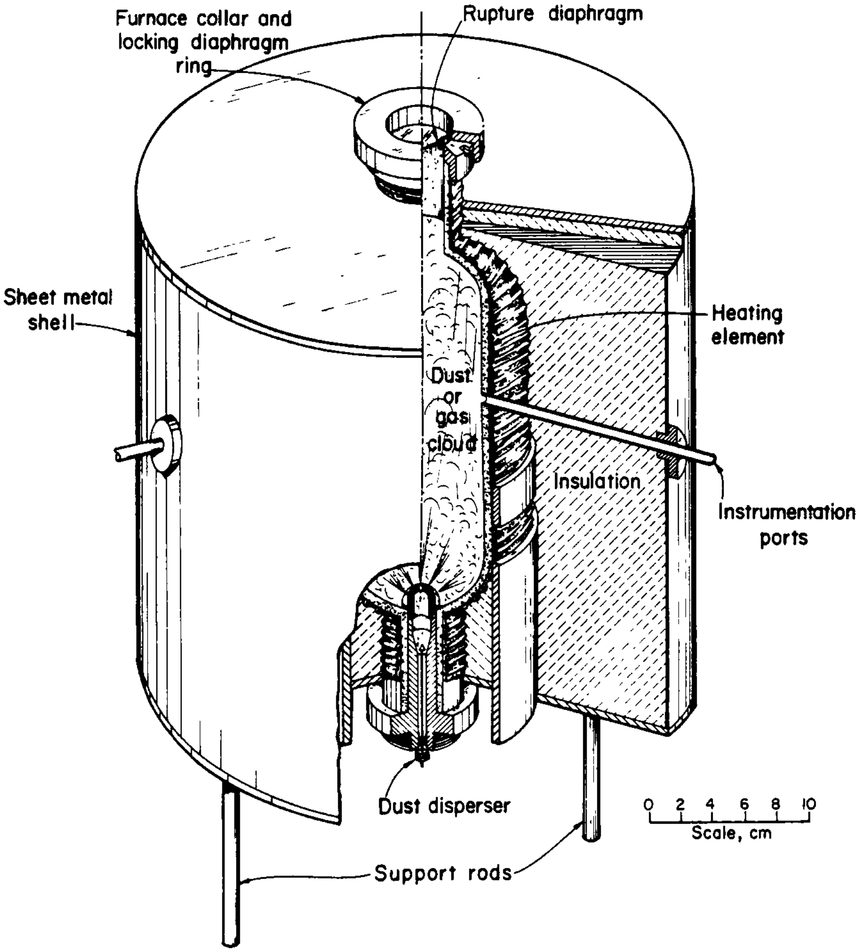

Figure 1. Perspective schematic of Bureau's 1-2-L ignitability furnace.

tion is accompanied by a rupture of the fiberglass diaphragm at an overpressure of 0.1 to 0.3 bar. The criterion for ignition is the rupture of the diaphragm with the simultaneous emission of flame from the top of the furnace. Such ignition is always associated with a temperature rise within the reacting volume of at least 1,000°C above the initial oven temperature.

The purpose of this report is to describe the additional modifications made to measure the autoignition temperatures of hydrogen-air and methane-air mixtures. For AIT measurements of such gases, a fuel gas reservoir (disperser) of fixed volume (V_0) at ambient temperature (T_0), is attached to the bottom of the furnace and pressurized to some initial overpressure. The furnace is then set to some specific elevated temperature (T_f) in order to test whether autoignition will occur at that temperature. A solenoid valve is then opened for a preset time and a predetermined volume of fuel gas is injected into the furnace. If we let the difference in the pressure of the fuel reservoir before and after gas delivery be Δp, then the volume of fuel gas delivered at the ambient temperature T_0 and the ambient pressure p_0 is thus:

$$v(T_0) = V_0 \Delta p / p_0 \tag{1}$$

That volume at ambient temperature T_0 occupies a larger volume when it is injected into the furnace as it heats to the furnace temperature T_f. That larger volume is given by

$$v(T_f) = V_0 \frac{\Delta p}{p_0} \frac{T_f}{T_0} \tag{2}$$

The heated volume mixes rapidly with the preheated air in the furnace to give a final fuel mole fraction of

$$x_f = \frac{v(T_f)}{V_f + v(T_f)} \tag{3}$$

where V_f is the furnace volume. The fiberglass filter paper at the top of the furnace that serves to fix that final volume also serves as a rupture diaphragm if ignition occurs. The criterion for ignition for gases is the same as that for dusts. It is the rupture of the diaphragm, at an overpressure of 0.1 to 0.3 bar, with the simultaneous emission of flame from the top of the furnace. The mixing of fuel gas with air is rapid, and although the additional fuel volume initially pressurizes the system slightly, there is a rapid flow through small leaks in the various furnace connections so that ambient pressure is rapidly reestablished after mixing. Combining Equations (2) and (3) gives:

$$x_f = \left[\frac{1}{\frac{V_f}{V_0} \frac{p_0}{\Delta p} \frac{T_0}{T_f} + 1} \right] \tag{4}$$

where x_f is the mole fraction of fuel in the fuel-air mixture. Direct sampling [2] of the mixture compositions confirmed the validity of Equation (4) and the assumptions implicit in its derivation. Mixing times

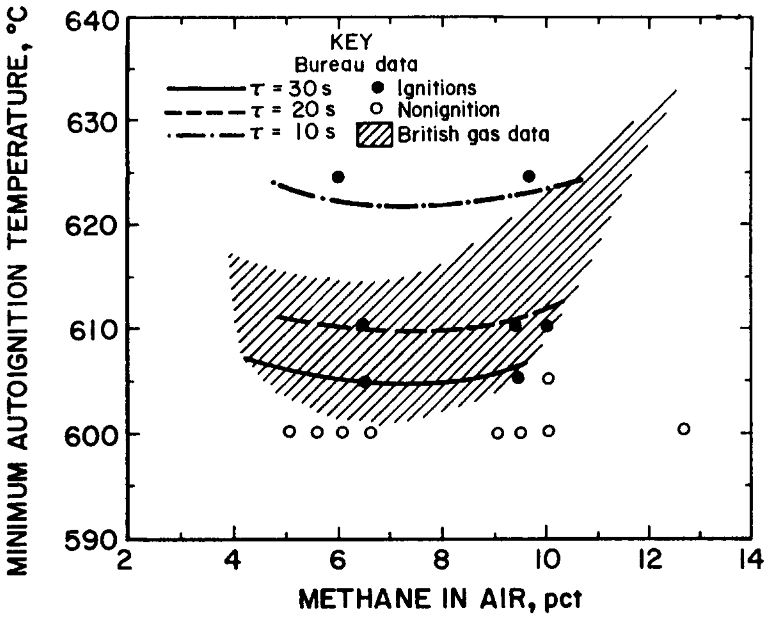

Figure 2. Comparison of 1.2-L furnace data with British Gas Corporation data [6,7] for methane-air mixtures.

were much shorter than autoignition times and that was confirmed by the sampling data.

The data obtained for methane-air mixtures are summarized in Figure 2. Data points are shown for ignition and nonignition cases at the temperatures and concentrations indicated. If ignition occurred it could also be characterized by a finite ignition delay time which could be measured to within an accuracy of a tenth of a second. The Bureau of Mines data obtained in the 1.2-L furnace are also presented in Figure 2 as contours for fixed ignition delay times (τ). The lowest autoignition boundary curve corresponds to the contour with the longest ignition delay times observed (30 s). The 1.2-L data are compared with the most recent measurements of Reid, Robinson and Smith [6,7] at the British Gas Corporation using stainless steel vessels of 0.8 to 1.0-L volumes. Their data are summarized in Figure 2 as the shaded area. Their range of values for the autoignition temperature of methane reflect variations in vessel volume and shape, stirring conditions, and whether or not the stainless steel surface was treated or untreated with a boric acid coating. The comparison between Bureau and British Gas data shows reasonably good agreement in the absolute

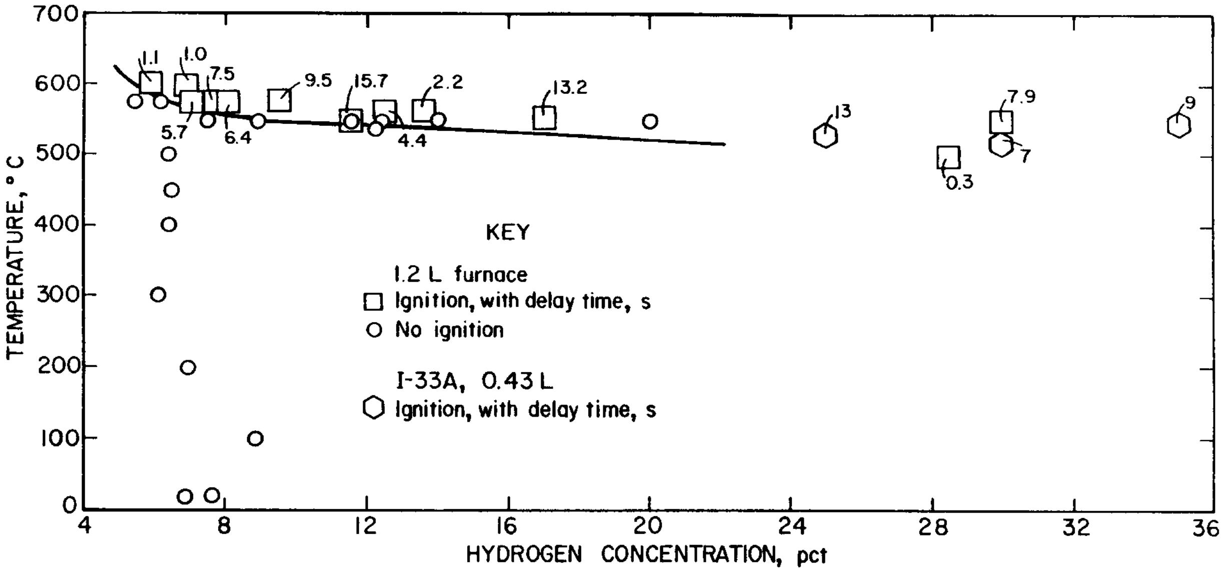

Figure 3*. Thermal autoignition delay times for hydrogen-air mixtures. A comparison of the 1.2-L data with the data of Zabetakis [8].*

values of the MAIT, which are in the range of 600° to 605°C. There is also good agreement in the methane concentration at which the MAIT occurs (6–8 volume percent). For some reason, a value of 537°C is often listed in the handbooks for methane [8], but as the data show here, the measured values for these volumes is from 600° to 605°C.

Despite the good agreement of the recent data, it should be realized that both sets of measurements were made in relatively small volumes, and, accordingly, it is likely that still larger test volumes could give lower MAITs. Such lower MAITs would be consistent with still longer ignition delay times, and the lowest MAIT would, ideally, coincide with the value measured in the limits of large test volumes, for which $\tau \rightarrow \infty$.

The data for hydrogen in air obtained in the 1.2-L furnace are shown in Figure 3. Individual data points are shown with the square data points representing ignitions and open circles representing nonignition. Also indicated within the square data points are the measured ignition delay times, in seconds, for those concentrations and temperatures that give ignitions. Although it cannot be proven conclusively, on the basis of audio and visual evidence, the operator of the 1.2-L system suggests that the one datum point at 28 1/2 pct H_2 with an ignition delay time of 0.3 s may have been a detonation. In addition to the 1.2-L furnace data, hexagonal data points are shown as reported by Zabetakis [9] using a 0.43-L stainless steel I-33A apparatus [10]. The latter apparatus was also used to measure the pressure dependence of the MAIT for H_2-air mixtures. The measured MAIT values reported by Zabetakis were essentially invariant in the pressure range of 1 to 8 bar although ignition delay times decreased somewhat at the elevated mixture pressures [9]. For the 1-atm data shown in Figure 3, there is fair agreement between the 1.2-L data reported here and those reported earlier by Zabetakis. Again, for some reason, 400°C is listed in the literature [8] as the value for hydrogen. Those previously published values for methane and hydrogen are in error, and the values reported in a recent Bureau of Mines Bulletin 680 [11] are in better agreement with the data presented here. In either case, despite the good agreement, all measurements were made in relatively small volumes. Accordingly, the extent to which the values of 600° to 630°C for methane and 500° to 520°C for hydrogen are sensitive to system volume remains to be determined.

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