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THE FLAMMABILITY LIMITS OF HYDROGEN AND METHANE IN AIR AT MODERATELY ELEVATED TEMPERATURES

B. B. Ale and I. Wierzba
Department of Mechanical Engineering
The University of Calgary
2500 University Drive, NW
Calgary, Alberta, T2N 1N4



ABSTRACT

The flammability limits of hydrogen and methane in air were determined experimentally at elevated initial mixture temperatures up to 350°C at atmospheric pressure for upward flame propagation in a conventional steel test tube apparatus. Additionally the extent to which a prolonged exposure (i.e., residence time) of the mixture to elevated temperatures before spark ignition and, consequently, the existence of pre-ignition reactions that may influence the value of the lean and rich flammability limits was also investigated. It was shown that the flammability limits for methane widened approximately linearly with an increase in the initial mixture temperature over the whole range of temperatures tested. These limits were not affected by the length of the residence time before spark ignition. Different behaviour was observed for flammability limits of hydrogen. They were also widened with an increase in the initial temperature but only up to 200°C. In this initial temperature range the limits were not affected by the length of the residence time. However, at initial temperature exceeding 200°C the flammability limits, especially, the rich limits narrowed with an increase in the temperature and were significantly affected by the residence time before spark ignition. The results of detailed chemical kinetic simulation showed that the gas phase reactions of hydrogen oxidation could not be responsible for the substantial drop in the value of the rich limit. It was therefore, suggested that this drop in the value of the rich limit with the increase in the residence time was caused by the relatively low temperature catalytic reactions on the stainless steel surface of the flame tube. Simple method for calculating the hydrogen conversion to water was proposed. The results of calculations are in fair agreement with the experimental evidence.

INTRODUCTION

Although much research has been conducted in the field of flammability limits, there are still many questions that cannot be answered adequately. For example, there are industrial processes conducted at elevated temperatures and a knowledge of the corresponding flammability limits is needed for safety considerations. Reference to the literature indicates that at present only very limited such data are available (Coward and Jones, 1952; Zabetakis, 1965; Bunev, 1997; Hustad and Sonju, 1988). Moreover often they were obtained for specific conditions, such as downward flame propagation, in small diameter or short flame tubes. Also for many rich fuel mixtures

a well known and widely used Le Chatelier's rule to estimate the flammability limits of fuel mixtures does not hold (Wierzba et al., 1987) and there is no information as to how changes in the mixture temperature will affect this deviation. There is also the possibility that at elevated temperatures fuel-air mixtures will undergo substantial pre-ignition reactions especially when the test fuel-air mixture is allowed to stand at this temperature a while before ignition. Additionally, for some fuel and temperature combinations there is the possibility of surface reactions taking place that effectively change the composition of the mixture with time. It was shown previously (Ale and Wierzba, 1997) that the rich flammability limits of ethylene in air determined experimentally in a conventional stainless steel test tube at elevated temperatures were affected very significantly by the time of exposure of the mixture to these elevated temperatures before the spark ignition. Similar observations were reported by Bunev (1972) during experiments conducted with hydrogen-air and methanol-air mixtures in a spherical stainless steel reactor with central ignition. In both studies the observed trends were attributed to the fact that stainless steel can act as a catalyst for enhancing low temperature oxidation reaction of hydrogen and ethylene in air.

The purpose of the present work was: (i) to establish the flammability limits, especially the rich limits, of hydrogen and methane in air for upward vertical flame propagation at elevated temperatures up to 350°C and atmospheric pressure in a conventional stainless steel test tube apparatus and (ii) to investigate the extent to which a prolonged exposure (i.e. residence time) of the mixture to elevated temperatures before ignition and, consequently, the existence of pre-ignition reactions may influence the value of the flammability limits.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus for the flammability limit tests was in general similar to that developed and used by the US Bureau of Mines in their flammability limits work. The flammability limits were established in a stainless steel smooth circular tube of 50.8 mm diameter and just over one metre in length. The tube was heated externally uniformly electrically. A set of unshielded thermocouples (K-type) was used to monitor the wall and gas temperatures along the whole length of the flame tube. The test tube temperature was maintained at the required level for the desired residence time using temperature controller. The pressure inside the flame tube was monitored

using a strain gage type pressure transducer (Validyne, Model DP 15-42) located at the top of the tube. Ignition of the test mixture was initiated by an electric spark discharge between two horizontal conical tungsten electrodes. The electric power for ignition was supplied by a 10 kV, 23 mA centre-tapped transformer with its primary hooked to a 110 V, 60 Hz supply. The ignition system was optimized with respect to the electrode gap and the spark duration to give the widest flammability limits.

Before each run, the entire system was evacuated and filled with air three times to ensure that the residual gas in the evacuated system consisted only of air. The mixture of desired composition was prepared on the basis of partial pressures in the stainless steel mixing chamber at room temperature. After the correct quantities of each gas had been added to the mixing chamber the gases were mixed for five minutes mechanically. When the test tube temperature along the entire length was stabilized within $\pm 3^\circ\text{C}$ of the nominal test temperature, the gas mixture was permitted to flow from the mixing chamber to the test tube through inlet valves located at the top and bottom ends of the tube until the pressure within the tube was slightly above atmospheric. The valves between the mixing chamber and the flame tube were then closed. The time for gas mixture to reach thermal equilibrium with the tube wall usually did not exceed 2 minutes. The fuel-air mixture was then kept inside the test tube for the desired residence time. To allow the flame propagation at constant pressure, the valve at the bottom of the test tube was slowly opened just prior to passing the spark. Ignition was initiated by activating the interval timer, while the top and bottom thermocouple readings were monitored. A sudden increase in the bottom thermocouple reading indicated the initiation of a flame kernel around the igniter, while a sudden rise in the top thermocouple reading marked arrival of the flame at the top of the tube. In the case of the flame arrival at the top of the tube, a new mixture with *less fuel for lean mixtures* or with *more fuel for rich mixtures* was prepared and tested again as described. In case when the flame did not arrive a new mixture with *more fuel for lean mixtures* or with *less fuel for rich mixtures* was prepared and tested. The entire procedure was repeated for various fuel-air mixture compositions until a mixture was found when the flame would not propagate the whole length of the tube, but propagation had been achieved in the mixture with a slightly modified composition. It can be seen from the experimental procedure in order to establish the single flammability limit value at the set conditions many different mixture compositions were prepared and tested. Once a limit mixture was found, this was confirmed by repeating the test three times in all the tests for a 10 min residence time and two times in the tests for longer residence times.

A mixture was considered to be non-flammable if a flame kernel formed in the immediate vicinity of the spark at the bottom of the tube did not propagate the whole length of the tube in any of the repeated tests while using the same mixture composition. An average testing time of few days was needed

to determine each flammability limit value especially at higher temperatures and longer residence times. A number of experiments were also repeated to verify the repeatability of the results.

Using this procedure the flammability limits of hydrogen and methane in air were determined for various initial temperatures of up to 350°C and various residence times of up to 2 hours.

RESULTS

The flammability limits reported in this work relate to upward flame propagation at atmospheric pressure of 88 kPa (Calgary). The limits are quoted as the volumetric concentration of the fuel in the fuel-air mixture.

Methane: The effect of the initial temperature on the flammability limits of methane in air, as established experimentally, is shown in Figure 1. The residence time, i.e., the time interval between the time of acquiring the desirable temperature by the methane-air mixture and initiation of spark ignition, was kept for these values at 10 minutes. It can be seen that the flammable range widens virtually linearly with an increase in the initial mixture temperature over the whole range of $21 - 350^\circ\text{C}$. The observed trends for both lean and the rich limits were similar with what has been reported by others in the literature (Coward and Jones, 1952; Zabetakis, 1965), although for different operating conditions, (e.g. downward flame propagation). Our experimental work showed that the limits remained unchanged when the residence time was increased up to 2 hours as it can be seen in Figure 2.

Hydrogen: The effect of the initial temperature on the flammability limits of hydrogen-air mixtures is shown in Figure 3. The residence time, i.e., the time interval between the time of acquiring the desirable temperature by the hydrogen-air mixture and initiation of spark ignition, was kept for these values at 10 minutes. Over the temperature range from 21°C to 200°C the rich limit increased while the lean limit decreased essentially linearly with increasing initial temperature. The limits were somewhat narrowed when the initial temperature was higher than 200°C showing lower rich limits and approximately constant lean limits. This behaviour of the lean limit was unexpected and inconsistent with trends reported for lean flammability limit of hydrogen-air mixtures at similar elevated temperatures by Hustad and Sonju (1988). To our knowledge no data were available for comparison of the rich limits of such mixtures for upward flame propagation.

The effect of the residence time on the rich flammability limits at different initial temperatures is shown in Figures 4 and 5. Over the range of initial temperatures from 21°C to about 200°C , the rich limit was generally unaffected by the duration of residence time. When the initial mixture temperature exceeded 200°C a decrease in the value of the rich limit was observed for all different residence times employed in this work. The decrease was relatively small for residence time of

5 minutes. It was much more substantial for longer residence times. For example, an increase in temperature from 200°C to 325°C caused a drop in the value of the rich limit from 82% to 78% for a 5 minute residence time, while for a 120 minute residence time the corresponding drop was from 81% down to 47%.

Similar trend was also observed for the values of the lean flammability limit of hydrogen, as can be seen in Figure 6. At an initial temperature of 300°C the lean limit of 2.6% for the 10 minutes residence time increased to more than twice this value when the residence time was increased to 6 hours.

Continuous measurements of temperature and pressure inside the test tube during the residence time showed that the temperature remained virtually constant during all tests for both fuels, methane and hydrogen. The pressure in all tests with methane also remained unchanged. However, in tests with hydrogen the pressure was decreasing with longer residence time, which may be indicative of some low temperature oxidation activity taking place during the residence time and the associated decrease in the total number of moles in the mixture. The values of the pressure inside the test tube at the end of the residence time (just prior to ignition) for tests conducted with different residence times at the same temperature of 350°C are shown as an example in Table 1. The corresponding initial concentrations of hydrogen in the hydrogen-air mixtures which are the corresponding rich limits at these conditions are also included.

DISCUSSION

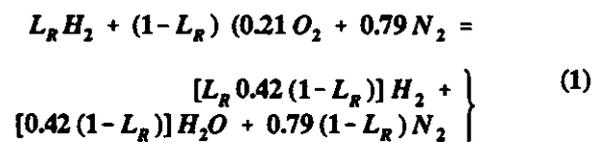
Methane: The independence of the flammability limits of methane-air mixtures from the residence time in the range of temperature tested is an evidence of absence of the pre-ignition reaction, whether they are gas-phase reactions or surface reactions.

Hydrogen: The observed behaviour of the flammability limits of hydrogen in air at initial temperatures higher than 250°C and at longer residence times is not consistent with expectation in that it shows a reduction in the limit. This may be indicative of some chemical activity in the mixture taking place before spark ignition. The strong dependence of the rich limit of hydrogen on the duration of the residence time supports this suggestion. The rich limits are associated with oxygen deficiency. A significant drop in the measured value of this observed limit would suggest a more acute oxygen deficiency existing for the fuel available at the time of passing the spark for ignition. Some of the oxygen in the mixture must have been consumed through oxidation of some fuel during the waiting period at higher temperature. Similarly, the lean limits are associated with fuel deficiency and an increase in the value of the limit could be indicative that some fuel could have also been oxidized before spark ignition.

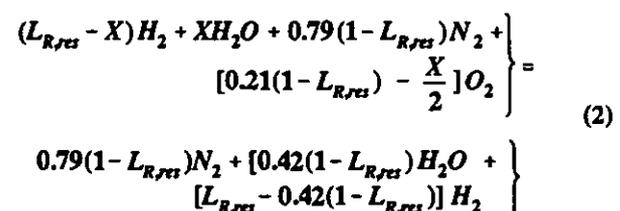
Calculations involving detailed chemical kinetic simulation for the oxidation of hydrogen were conducted for different hydrogen-air mixtures at initial temperature of 350°C. The program developed by Liu (1995) involving 21 reactions

with 8 species for hydrogen was adapted. The results of this calculation (Figure 7) showed a rather slow progress in the gas phase reactions of hydrogen oxidation at the initial temperature of 350°C at residence times up to 5 hours while a significant change in the value of the rich limit of hydrogen was observed experimentally at this temperature even for the short residence time of 10 minutes. Therefore, the observed changes in the flammability limits are most probably a result of the oxidation of hydrogen over a period of time mainly due to catalytic action on the stainless steel (316) tube surface and not through gas phase oxidation. It is known that some metals, for example, steels and iron are active catalysts for the oxidation of hydrogen and ethylene at elevated temperatures in air (Pangborn and Scott, 1979; Baker, 1974; Krishnankutty et al., 1996).

The extent of hydrogen conversion during the residence time due to the catalytic activity at the steel wall can be approximately estimated from the following considerations. It has been shown that the flammability limits are associated with a certain critical level of reaction temperature that is assumed to be proportional to the calculated adiabatic flame temperature which has the same value under the same operating conditions (Bade Shrestha et al., 1995; Zabetakis, 1965). If all other operating conditions remain the same this temperature should remain constant for limiting mixtures irrespective of the residence time length, i.e. any catalytic activity at the wall before ignition. Such temperature can be estimated on the basis of the known flammability, L_R , measured with very short residence time, i.e. before the onset of any catalytic activity. For the rich limiting hydrogen-air mixtures the following overall reaction applies:



At the surface of the stainless steel test tube some of the hydrogen is converted to water catalytically and at the end of the residence time the overall reaction for the limiting mixture becomes the following:



where $L_{R, res}$ is the experimentally obtained rich limit at the corresponding residence time and X is the amount of the hydrogen converted to water (volume percent in total mixture) during the residence time.

Some calculated values of X are shown in Table 1. For an ideal gas at constant volume and temperature conditions changes in pressure are proportional to changes in the number of moles of the mixture. Accordingly, the pressure at the end of the residence time, P_2 , (just before ignition) can be calculated on the basis of derived value of X , i.e.

$$P_2 = P_1 \left(1 - \frac{X}{2} \right) \quad (3)$$

where, P_1 is the initial pressure in the test tube at the commencement of the residence time.

The results of these calculations are also shown in the Table 1. The calculated values of the final pressure P_2 are close to those measured experimentally. This would support the validity and applicability of the concept used.

Table 1. Hydrogen conversion to water in the rich limiting mixtures at different residence times at $T=350^\circ\text{C}$ and initial pressure, $P_1 = 106.3$ kPa.

Test No.	Residence time, min	$L_{R, \text{res}}$ %	X %	Hydrogen depletion ($X/L_{R, \text{res}}$), %	Pressure, P_2 measured, kPa	Pressure, P_2 calculated, kPa
1	5	76	4.0	5.26	105.9	104.17
2	10	71	6.1	8.59	104.9	103.06
3	30	61	10.3	16.88	102.4	100.82
4	60	49	15.4	31.43	99.5	98.11
5	90	44	17.5	39.77	97.2	96.99
6	120	21	18.3	43.57	95.1	96.57

CONCLUSIONS

- Waiting time and the type of the test tube surface should be taken into consideration when determining the flammability limits.
- At initial temperatures lower than 200°C the experimentally determined flammability limits of hydrogen in air were widened with an increase in the temperature. They were not affected by the length of the residence time before spark ignition.
- At the initial temperatures higher than 200°C the values of the flammability limits of hydrogen in air when determined experimentally in a conventional flammability limit stainless steel tube apparatus were significantly affected by the length of the residence time before ignition. The longer the residence time, the smaller was the rich limit and the higher was the lean limit.
- The narrowing of the limits is suggested to be mainly due to catalytic reactions on the stainless steel surface of the test tube.
- The experimentally determined flammability limits of methane in air were widened with an increase in the initial temperature over the whole range of temperatures employed and were not affected by the changes in the residence time.

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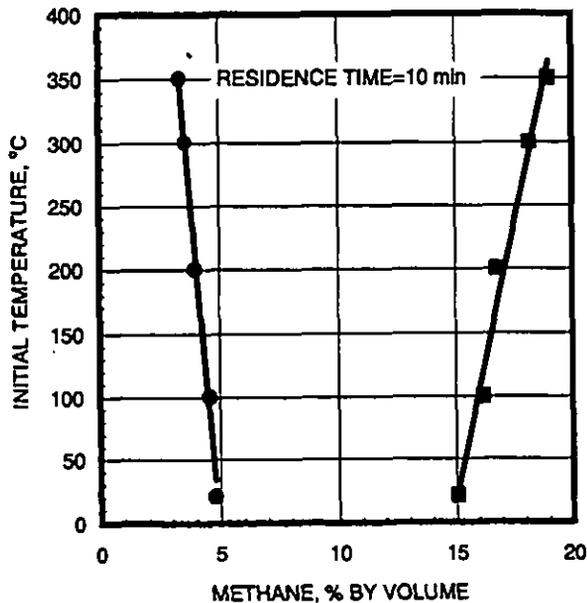


Fig.1. The flammability limits of methane-air mixtures as a function of temperature at residence time of 10 minutes.

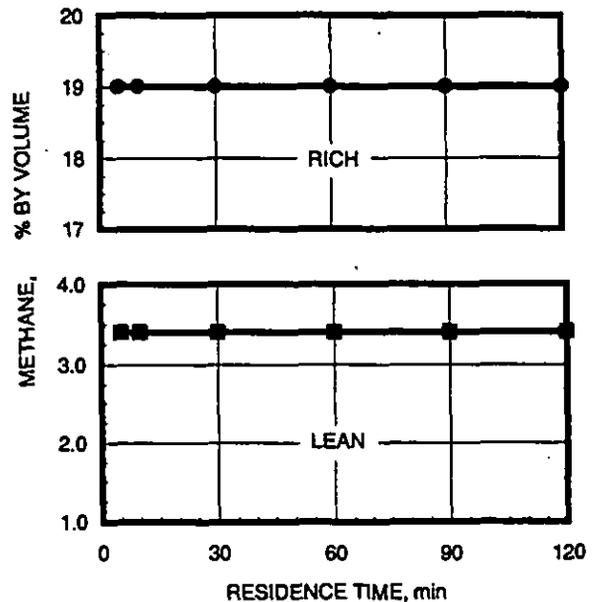


Fig.2. The flammability limits of methane in air as a function of residence time at 350°C.

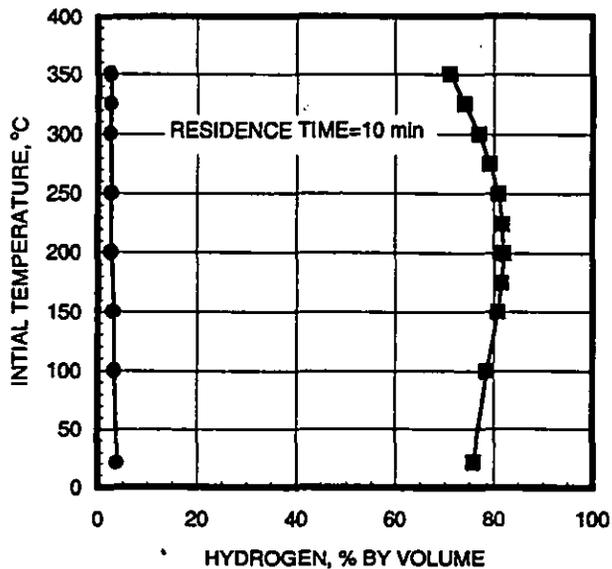


Fig. 3. The flammability limits of hydrogen-air mixtures as a function of temperature at residence time of 10 minutes.

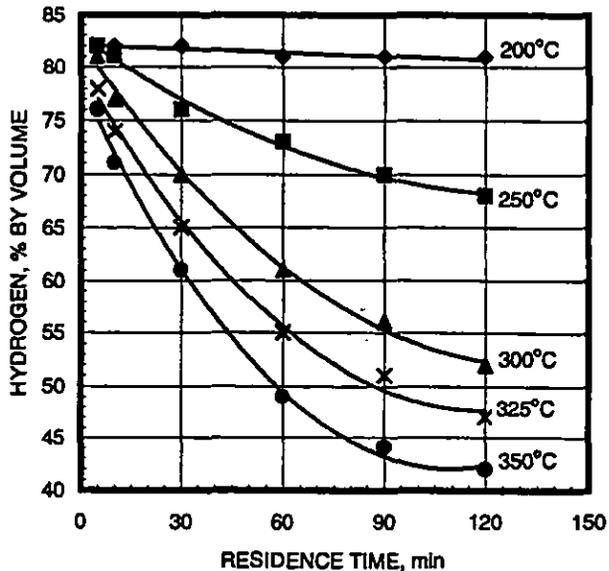


Fig. 4. The rich flammability limits of hydrogen in air as a function of residence time for different initial temperatures.

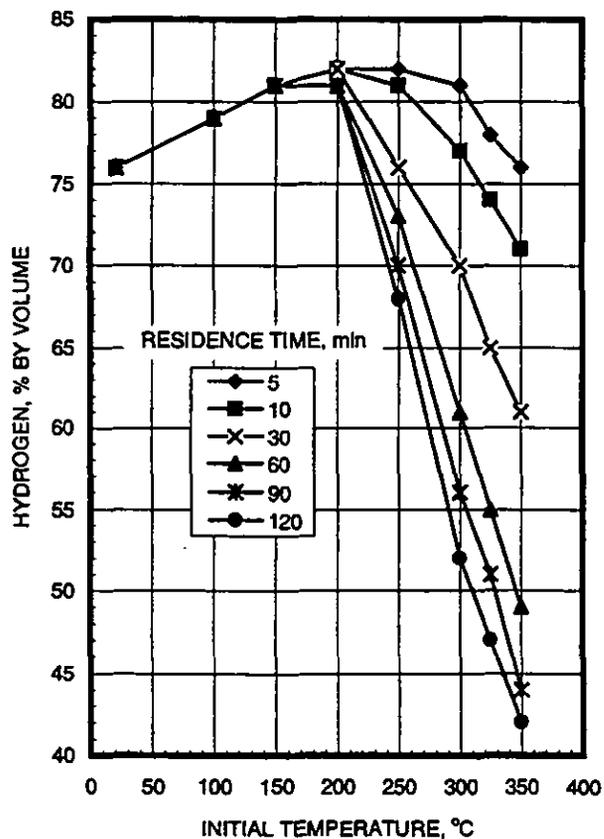


Fig. 5. The rich flammability limits of hydrogen in air mixtures as a function of temperature at different residence time.

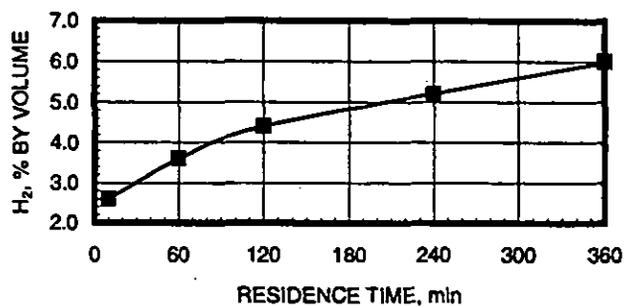


Fig. 6. The lean flammability limit of hydrogen in air as a function of residence time at 300°C.

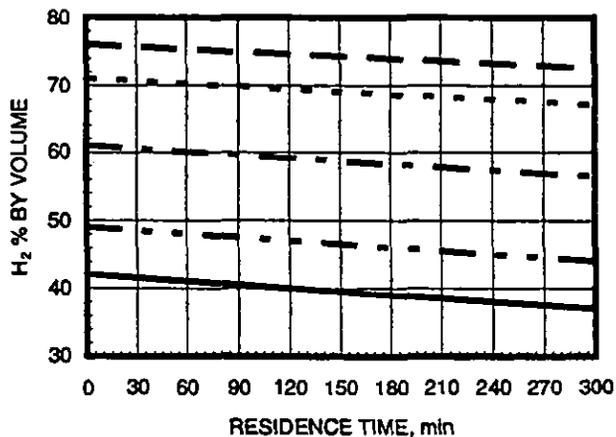


Fig. 7. The calculated concentration of hydrogen at 350°C for different initial hydrogen concentrations.