



THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS
345 E. 47th St., New York, N.Y. 10017

98-GT-179

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THE EFFECT OF TIME OF EXPOSURE TO ELEVATED TEMPERATURES ON THE FLAMMABILITY LIMITS OF SOME COMMON GASEOUS FUELS IN AIR.

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ABSTRACT

The flammability limits of methane, ethylene, propane and hydrogen were determined experimentally at elevated initial mixture temperatures up to 350°C at atmospheric pressure for upward flame propagation in a steel test tube apparatus. The existence of preignition reactions at these levels of temperatures that may influence the value of the flammability limits was also investigated. The fuel-air mixtures were exposed to elevated temperatures over different periods of time before spark ignition (up to 2 hours). It was shown that the flammability limits for methane widened approximately linearly with an increase in the initial mixture temperature over the entire range of temperatures tested and were not affected by the length of the exposure time to these temperatures before spark ignition. However, different behaviour was observed for the flammability limits of the other tested fuels - ethylene, propane and hydrogen. At higher temperatures the flammability limits narrowed and were very significantly affected by the exposure time. The longer was the exposure time of fuel-air mixtures to the elevated temperatures, the narrower were their flammability limits.

INTRODUCTION

Alternative gaseous fuels are increasingly employed in industrial gas turbines installations in a variety of applications such as the production of power and for gas compression. This is prompted by their increased availability at attractive prices as well as by their potential for reduced emissions in comparison to liquid fuels. It is essential to ensure in such applications the safety against the risk of fire

and explosion. The knowledge of the flammability limits is important in assessing these hazards. 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 many 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, 1972; Hustad and Sonju, 1988). The apparatus used to determine the flammability limits as well as some operational conditions (e.g., temperature, pressure, direction of flame propagation and ignition source) are usually described, while, the time of exposure of fuel-air mixtures to elevated temperatures before spark ignition is usually not specified. However, there is the possibility that at elevated temperatures fuel-air mixtures will undergo substantial preignition reactions, especially when the test fuel-air mixture is allowed to stand at this temperature for a while before ignition. It was reported by Bunev (1972) that the time of exposure of hydrogen-air and methanol-air mixtures to elevated temperatures before ignition influenced significantly the rich flammability limit determined in a relatively small spherical stainless steel reactor with central ignition. The limit decreased when the exposure time increased, this was attributed to existence of unspecified preignition reactions. Moreover, 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) before ignition is applied (Ale and Wierzba, 1997).

Presented at the International Gas Turbine & Aeroengine Congress & Exhibition
Stockholm, Sweden — June 2–June 5, 1998

This paper has been accepted for publication in the Transactions of the ASME
Discussion of it will be accepted at ASME Headquarters until September 30, 1998

The purpose of the present work was to determine the flammability limits of some common gaseous fuels at elevated temperatures for upward flame propagation associated with the widest flammable range. Additionally the extent to which time of exposure of fuel-air mixtures to the elevated temperatures before spark ignition influenced the limits was established. The existence of any preignition reaction activity under these conditions was also investigated.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus (Fig.1) was in general similar to that developed and used by the US Bureau of Mines in their flammability limits work. The 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 unsheathed 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 a temperature controller. The pressure inside the test tube was monitored using a strain gage type pressure transducer 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 (6.4 mm) and the spark duration to give the widest flammability limits.

The homogeneous mixture of desired composition was prepared on the basis of partial pressures in the stainless steel mixing chamber at room temperature. It was introduced into the previously evacuated test tube when its temperature along the entire tube 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 tube were then closed. The time for the gas mixture to reach thermal equilibrium with the tube wall usually did not exceed 30 seconds. 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 to exhaust just prior to passing the spark. Ignition was initiated by activating the interval timer, while the top and bottom thermocouples 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.

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. A number of experiments were also repeated to verify the repeatability of the results.

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

RESULTS

The flammability limits reported in this work relate to *upward flame propagation* at atmospheric pressure. The limits are quoted as the volumetric concentration of the fuel in the fuel air mixture.

The effect of the initial temperature on the flammability limits of methane, hydrogen, ethylene and propane in air is shown in Fig.2 for the residence time (i.e. time interval between the time of acquiring the desired initial temperature by the fuel-air mixture and initiation of spark ignition) of 10 minutes. It can be seen that the effect of the temperature depends on the type of the fuel.

Methane

The flammability limits of methane-air mixtures widen virtually linearly with an increase in the initial mixture temperature over the whole range of 21°C - 350°C . No data are available in the literature for comparison for upward flame propagation. However, the observed trends for both lean and rich limits were similar with what has been reported by others in the literature (Coward and Jones, 1952; Zabetakis, 1965), for downward flame propagation.

Hydrogen

The flammable range of hydrogen-air mixtures also widens essentially linearly with increasing initial temperature but only at the initial temperatures lower than 200°C . 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). No data are available for comparison of the rich limits of such mixtures for upward flame propagation.

Ethylene and propane

For these fuels in air the flammable range widens with an increase in the initial temperature from 21°C to 300°C with a much stronger dependence for the rich limit. The only data available in the literature for comparison appears to be for downward flame propagation. However our observed trends for upward flame propagation were similar with what has been reported in the literature for downward flame propagation (Coward and Jones, 1952; Zabetakis, 1965). However, when the initial temperature was higher than 300°C, the rich flammability limit for both of these fuels was sharply reduced. These limits were established in the absence of cool flames.

Effect of residence time

The effect of the residence time on the flammability limits depends on the type of fuel and the level of the mixture initial temperature.

The rich flammability limits of methane-air mixtures remained unchanged when the residence time was increased up to 2 hours at all the different temperatures tested (Fig. 3). Different behaviour was observed for the other fuels employed. The rich limits of ethylene and hydrogen were unaffected by the length of the residence time when the initial temperature was lower than about 200°C for hydrogen and 250°C for ethylene. When the temperature exceeded these values the rich flammability limits of both of these fuels were dependent of the duration of the residence time and the levels of the mixture temperature. The higher was the temperature and the longer was the time, the greater was the reduction in the limit (Figs. 4 and 5). Similar effect was also observed with propane-air rich mixtures as shown in Fig.6 for the initial temperature of 350°C.

The lean limits of hydrogen, ethylene and propane were also significantly affected by the duration of the residence time as shown in Fig.7 at the higher initial temperatures of 300°C and 350°C for hydrogen-air and ethylene-air mixtures respectively. The longer was the time, the higher was the lean limit.

Continuous measurements of the temperature of fuel-air mixtures within the test tube during the residence time showed that the temperature remained virtually constant during all experiments with all the fuels tested. However, the pressure within the test tube did not always remain constant during the residence time. The pressure remained constant for methane-air mixtures, decreased for hydrogen-air mixtures, increased for propane-air mixtures and very slightly for ethylene-air mixtures. Examples of pressure variations within the different fuel-air mixtures at the initial

temperature of 350°C are shown in Fig.8.

DISCUSSION

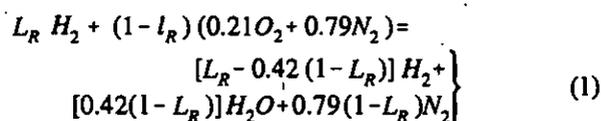
The independence of the flammability limits of methane-air mixtures of the residence time in the range of temperatures tested (up to 350°C) is indicative of the absence of significant preignition reaction activity whether due to gas-phase reactions or surface reactions. It was also confirmed by measuring the oxygen concentration within the mixture, which remained constant over the entire residence time.

On the other hand, the observed behaviour of the flammability limits of the other fuels tested - hydrogen, ethylene and propane - especially, at higher initial temperatures and longer residence times is not consistent with expectation in that it shows a reduction in the flammable range. This fact as well as the pressure variations within the fuel-air mixtures during the residence time is indicative of some chemical activity in the mixture taking place before spark ignition. The strong dependence of the rich limits of these fuels on the length of the residence time as well as the pressure variation within the tested mixtures supports this suggestion. The rich limits are associated with oxygen deficiency. A significant drop in the measured value of this observed limit would suggest the need for less fuel to consume the oxygen available or 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 original 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. Measurements of oxygen concentration in the rich fuel-air mixtures at the end of the residence time confirm that some oxygen has been consumed. As an example, measured oxygen concentrations at the end of the residence time for different hydrogen-air mixtures (corresponding to different residence times) at the initial temperature of 300°C are shown in Table I together with the corresponding calculated oxygen concentrations (Eq.(2)).

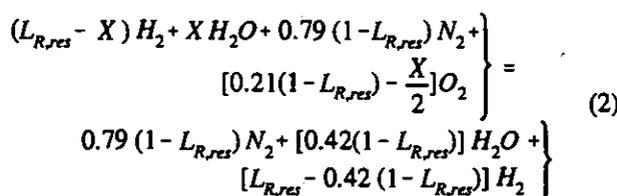
Calculations involving detailed chemical kinetic simulation conducted for the oxidation of hydrogen (21 reactions, 8 species), ethylene (137 reactions, 32 species) and propane (137 reactions and 32 species) at initial temperature of 350°C showed an insignificant progress in the gas phase reactions of oxidation of these fuels at residence times up to 4.5 hours (Fig. 9). However, a significant change in the value of their rich limit 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 these fuels over a period of time due to catalytic action on the stainless steel tube surface and not through gas phase oxidation. It is well-known that some metals, for example, steel and iron are active catalysts for the oxidation of hydrogen and ethylene in air at elevated temperatures (Pangborn and Scott, 1979; Baker, 1974; Krishnankutty et al., 1996).

Hydrogen conversion. For hydrogen oxidation with the simplest product, water, the extent of hydrogen conversion during the residence time due to 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 (Zabetakis, 1965; Wierzba et al. 1996; Ale and Wierzba, 1997). If all the 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.

For an ideal gas constant volume and temperature conditions changes in pressure are proportional to changes in the number of moles of the mixture or the pressure at the end of the residence time, P_2 , is expected to be lower than the initial pressure at the commencement of the residence time, P_1 , according to

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

Oxygen concentration in the mixture at the end of the residence time can also be calculated from Eq.(2) and compared with those determined experimentally. As it can be seen from Table 1, the calculated values of the final pressure and oxygen concentration are in fair agreement with the experimental values. This supports the validity of the proposed approach.

Similar approach can be used for ethylene and propane conversion on the steel surface if more information about products of their oxidation during the residence time is available.

CONCLUSIONS

- The residence time and the type of the test tube surface should be taken into consideration when determining the flammability limits at elevated temperatures.
- The flammability limits of methane in air widen with increasing the initial mixture temperature over the entire range of temperatures tested, i.e. from 21°C to 350°C. They are not affected by duration of the residence time and there is no chemical reaction activity during this time.
- The flammability limits of hydrogen, ethylene and propane widen with increasing temperature up to a certain temperature level. With further increase in temperature the limits are narrowed with a significant drop in the rich limit value. At this temperature level the flammability limit depend on the duration of the residence time (before spark ignition). The higher initial temperature of the fuel-air mixture and the longer residence time, the smaller is the value of the rich limit.
- The narrowing of the limits is suggested to be mainly due to catalytic reactions on the stainless steel surface of the test tube.
- A simple method was proposed that allows estimate of the hydrogen conversion to water due to surface reactions within the steel test tube during the residence time fairly accurately.

ACKNOWLEDGMENTS

The financial assistance of the Natural Sciences and Engineering Research Council of Canada (NSERC) and Canadian International Development Agency (CIDA) is gratefully acknowledged.

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Table 1. Hydrogen conversion to water in the rich limiting mixtures at different residence times at $T=300^{\circ}\text{C}$ and initial pressure, $P_1 = 105.0$ kPa.

Test No.	Residence time, min	$L_{R,lim}$ %	X %	Hydrogen depletion ($X/L_{R,lim}$), %	Pressure, P_2 measured, kPa	Pressure, P_2 calculated, kPa	Remained oxygen, calculated, %	Remained oxygen, measured, %
1	5	81	1.3	1.60	104.2	104.3	3.34	3.4
2	10	77	3.0	3.90	103.4	103.4	3.53	3.6
3	30	70	5.9	8.43	101.3	101.9	3.35	3.8
4	60	61	9.7	15.90	98.9	99.9	3.44	3.8
5	90	56	11.8	21.07	96.7	98.8	3.34	3.8
6	120	52	13.5	25.96	94.6	97.9	3.33	3.6

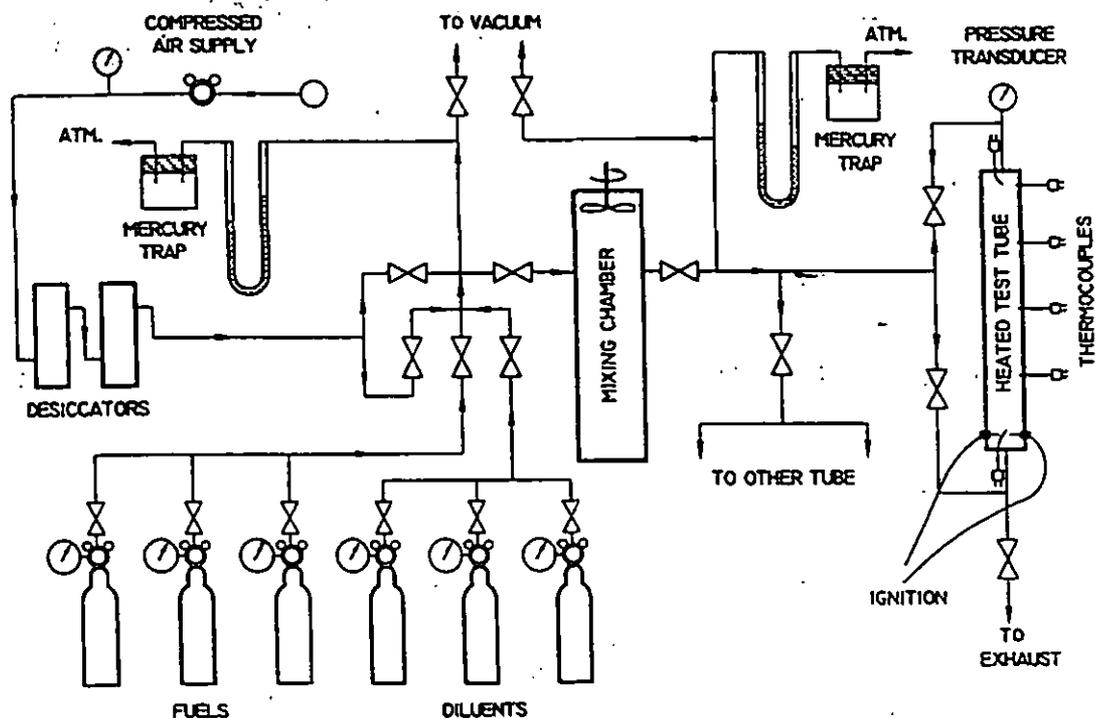


Figure 1. Schematic diagram of the apparatus

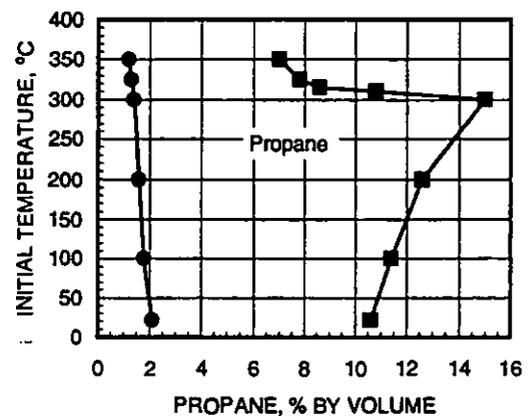
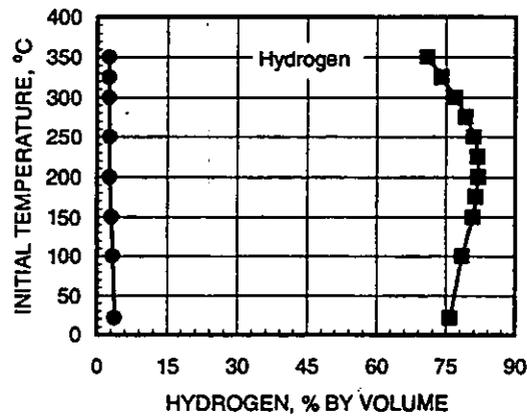
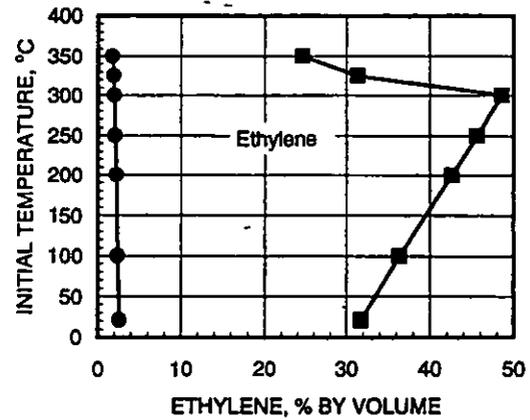
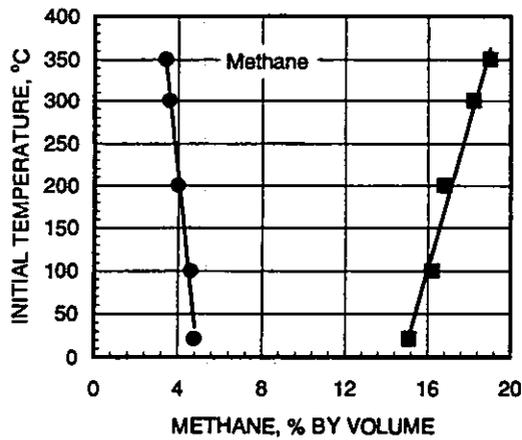


Figure 2. Flammability limits of fuel-air mixtures as a function of initial temperature at residence time of 10 minutes.

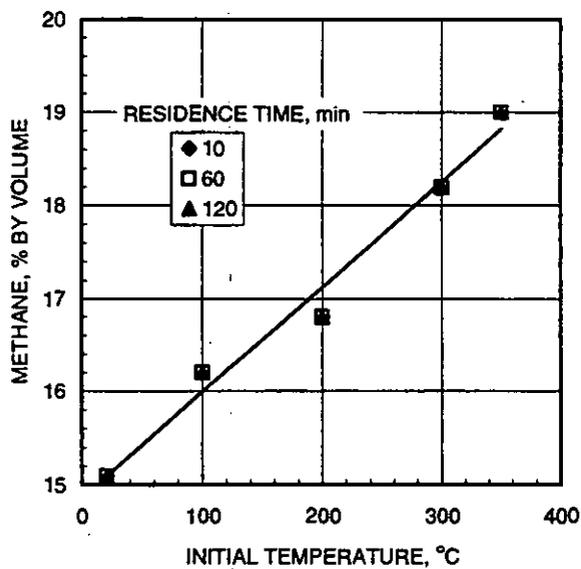


Figure 3. Rich flammability limits of methane in air as a function of initial temperature at different residence times.

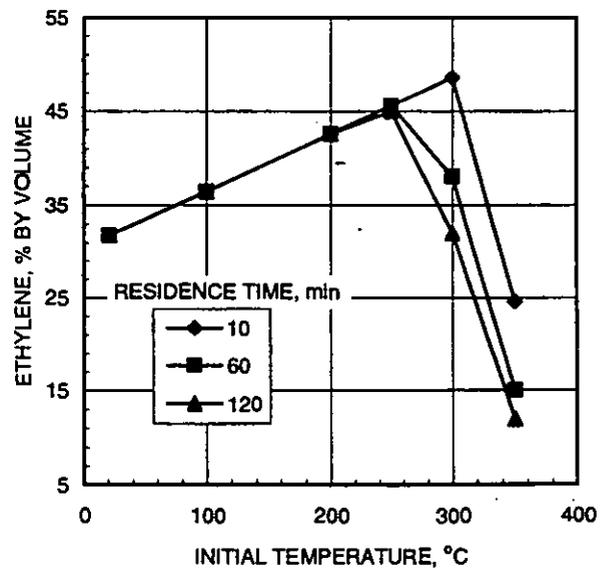


Figure 4. Rich flammability limits of ethylene in air as a function of initial temperature at different residence times.

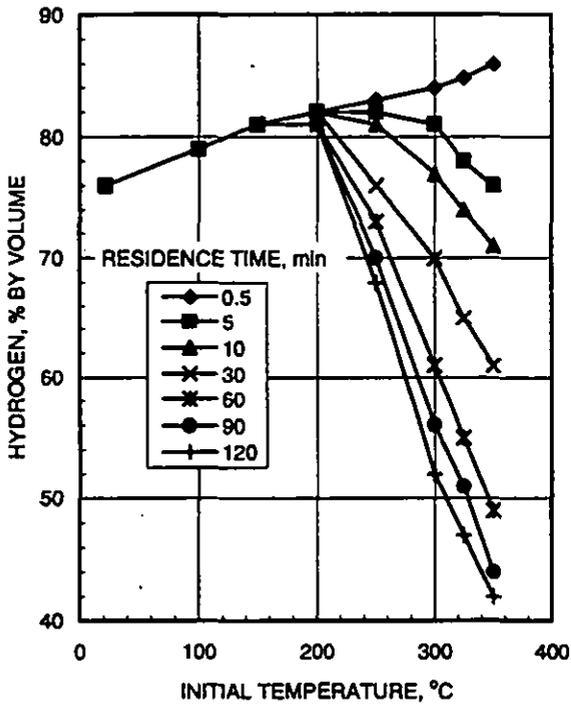


Figure 5. Rich flammability limits of hydrogen in air as a function of initial temperature at different residence times.

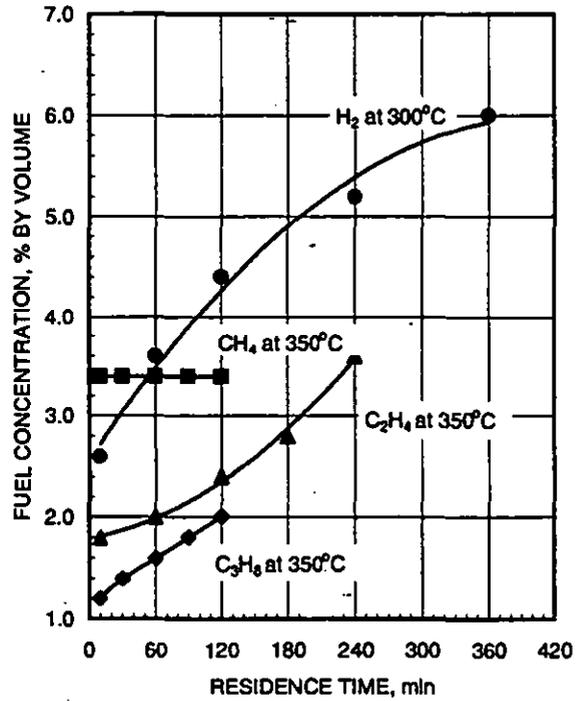


Figure 7. Lean flammability limits of fuel in air as a function of the residence time at 300°C and 350°C.

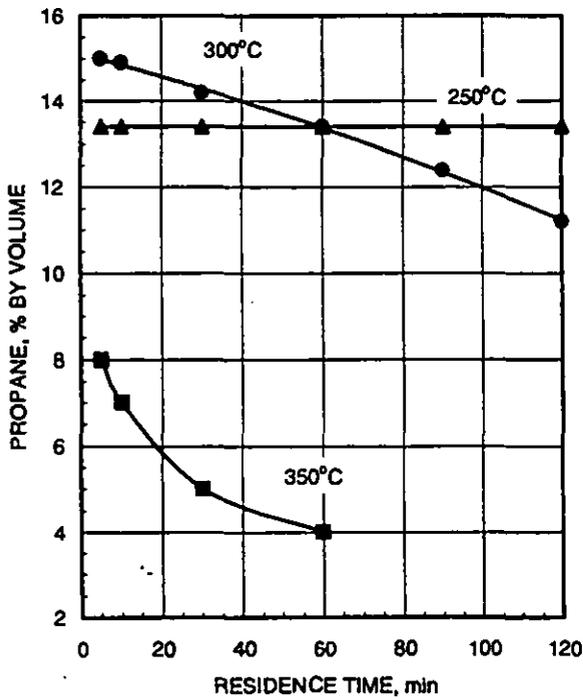


Figure 6. Rich flammability limits of propane in air as a function of the residence time at different initial temperatures.

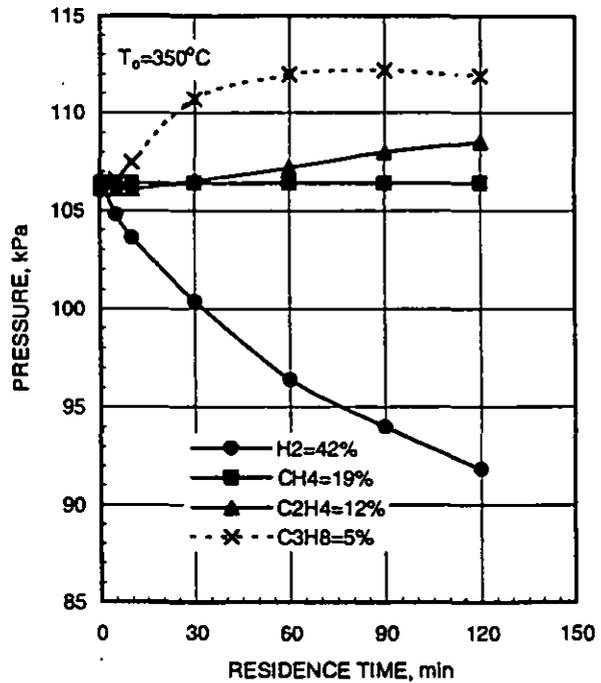


Figure 8. Pressure variation within fuel-air mixtures as a function of the residence time at 350°C.

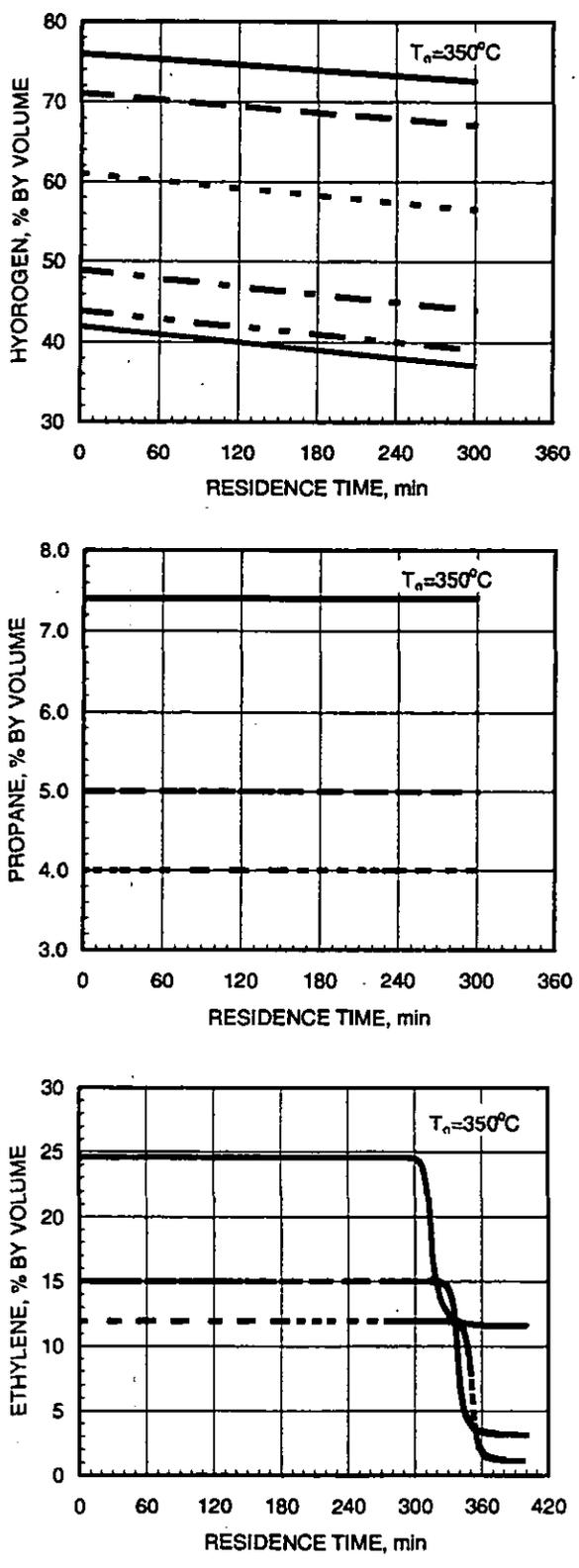


Figure 9. Fuel concentration variation due to gas phase reaction activity at 350°C for different initial fuel-air mixtures.