

EFFECT OF LOW TEMPERATURE ON THE RICH FLAMMABILITY LIMITS OF SOME GASEOUS FUELS AND THEIR MIXTURES

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SUMMARY

The rich flammability limits in air of methane, ethane, propane, butane, ethylene and propylene at atmospheric pressure and for upward flame propagation were established consistently under isothermal initial conditions at low temperatures extending down to -60°C . In addition, the flammability limits of a range of binary combinations of their mixtures were also established. On the basis of the experimental data obtained, some guidelines for predicting the rich flammability limits are presented and discussed.

INTRODUCTION

The importance of the flammability limits in assessing the fire and explosion hazards involved in the storage, transport and use of fuels has long been recognized. At the present time, it is not possible to derive the flammability limits from an entirely theoretical basis and hence these limits need to be determined experimentally. The values of the flammability limits for any fuel are dependent on all the factors that can influence the mode of flame initiation and propagation. These factors include the temperature and pressure of the mixture, ignition energy employed, direction of flame propagation, the type of apparatus employed and whether quiescent or flowing mixtures are involved. Normally, the flammability limit values in the literature refer to quiescent and homogeneous mixtures when quoted using adequate amount of ignition energy in a well-specified apparatus.

The information available in the open literature about the flammability limits of common gaseous fuels and vapours is truly voluminous. It was obtained over a very protracted period of time by different workers in a variety of apparatus for a wide range of operating conditions. It is becoming increasingly evident that careful scrutiny of some of the reported

data, especially for the rich flammability limit values, is in order and more rigorous approaches to the determination of these limits would be necessary. For example, there are serious uncertainties relating to how to determine effectively the rich limits of fuel mixtures from the corresponding limits of the individual fuels making up the mixture. This determination becomes particularly troublesome when diluent gases, such as N_2 , CO_2 or H_2O are present within the fuel mixture. Moreover, for a further improvement to the fundamental understanding of the nature of the limits in general and the rich limit in particular, the contribution of changes in the mixture temperature, the important controlling parameter, needs to be established better. There has been a distinct tendency, that may be somewhat justified, to focus attention on the role of high mixture temperatures on the flammability limits of fuels in air. Accordingly, the corresponding role of low temperature environments received in comparison very much less attention. There is a need to rectify this deficiency, not only because of the common need to use fuels under very low ambient temperature conditions, but also because of the increasing use of liquified fuel components that produce on evaporation into air, fuel-air mixtures that are at temperatures lower than the bulk ambient temperature. A notable example is the fuel-air mixtures that result from the evaporation into air of liquified natural gas (LNG) or liquified petroleum gas (LPG).

The present contribution reports some experimentally determined rich flammability limits in air of some common fuels obtained consistently under isothermal initial mixture conditions at initial temperatures extending down to $-60^\circ C$. In addition, the flammability limits of a range of binary combinations of their mixtures were also examined. On the basis of these experimental data, some guidelines for predicting the rich flammability limits in air for the fuels and some of their mixtures at low temperatures are presented and discussed.

APPARATUS AND EXPERIMENTAL PROCEDURE

The flammability limits were established in a specially designed stainless steel smooth circular tube of 50 mm diameter that is just over one metre in length. These tests were carried out throughout for homogeneously prepared mixtures that were maintained at constant temperature and pressure. Upward vertical flame propagation following spark ignition was employed while the tube was kept closed at the top yet open at its lower end.

Since the work being reported here considers the effects of low temperatures on the rich flammability limits, there was a need to provide a flexible and effective facility for lowering the temperature of the mixture

to the low levels required while ensuring the temperature distribution within the mixture remains uniform throughout. This was achieved by the external chilling of the tube employing boiling liquid nitrogen. The whole tube was cooled uniformly by circulating liquid nitrogen around the flame tube. The liquid nitrogen was permitted to evaporate over the exterior of the tube wall. The annulus was divided into six chambers of equal length and the flow of the liquid nitrogen to each chamber could be controlled independently. A set of unsheathed thermocouples (K-type) was used to monitor the temperature of the flame tube wall in each chamber as well as the gas temperature at the top and bottom of the tube. Ignition of the test mixture was obtained by an electric spark discharge between two horizontal conical tungsten electrodes that were spaced, 6.5 mm apart and centred in the tube 35 mm from the lower end of the tube. The electric power was supplied by a 10 kV, 23 mA centre-tapped transformer with its primary hooked up to a 110V, 60 Hz supply. The spark duration was controlled by the use of an internal timer which was normally set at two seconds for the determination of the rich limits.

The fuel-air test mixture was prepared in a four litre stainless steel mixing chamber on the basis of partial pressures. The mixture was stirred by a propeller rotating at 500 rev/min for five minutes. When the tube temperature along the entire length stabilized to within $\pm 1^\circ\text{C}$ of the desired temperature, the mixture was admitted into the previously evacuated flame 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 flame tube was then maintained at the test temperature until the mixture was in thermal equilibrium with the tube walls and the turbulence had died down. This took usually around ten minutes to achieve. At this point the additional valve at the bottom of the tube was opened slowly so as to permit the test to be performed at atmospheric pressure (88 kPa). The spark timer was then activated to pass a spark through the mixture. The arrival of the flame front at the top of the tube for flammable mixtures was noted by observing the thermocouple readings at the top and bottom of the tube. 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 right to the top end. Once a limit mixture was found this was confirmed by repeating the test twice. Should a complete flame propagation be detected once in three identical testing attempts then the mixture was considered to be flammable. This consistently applied procedure ensured good repeatability of results.

EXPERIMENTAL RESULTS AND DISCUSSIONS

All experimental data reported were obtained for upward flame propagation at atmospheric pressure. They are quoted as the concentration of the fuel by volume (%) in the total mixture. The rich flammability limits for upward flame propagation are usually higher than the corresponding values obtained for downward flame propagation. Therefore, from the safety point of view it was more desirable to quote the limits for upward propagation, throughout.

The rich flammability limits that were established according to the procedure described earlier for methane, ethane, propane, butane, ethylene and propylene over a range of low mixture temperatures are presented in Fig. 1 and Fig. 2. It can be seen that with the lowering of the initial mixture

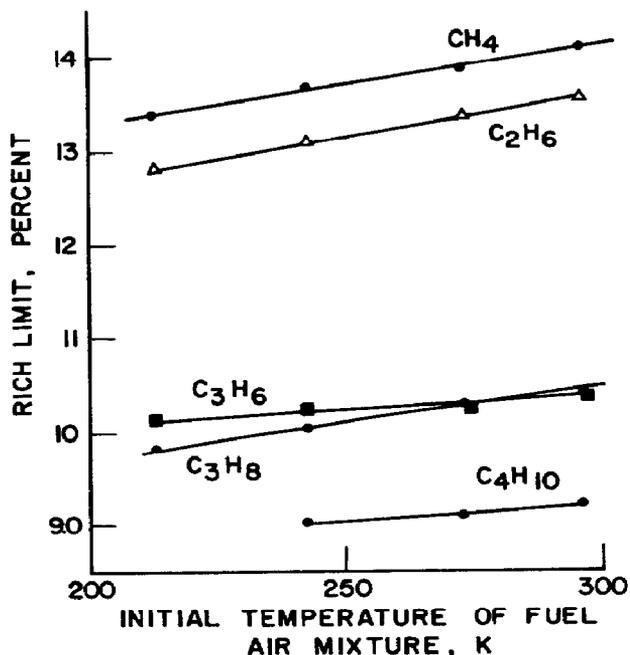


Fig. 1 Experimentally determined rich flammability limits in air of CH_4 , C_2H_6 , C_3H_6 , C_3H_8 and C_4H_{10} as a function of the initial temperature of the initial temperature of the fuel-air mixture.

temperature from 296 K to 213 K (-60°C), the rich flammability limit tends to decrease essentially linearly by about 5.0% for methane, 5.8% for propane and ethane, 2.9% for propylene, and 13.9% for ethylene. For butane the rich limit decreased linearly by about 2.2%, when the initial temperature of the mixture was lowered down to -30°C from 23°C . Throughout the results being reported, it was ensured that the fuel present in the mixture remained in the gaseous phase.

TABLE I

The Rich Flammability Limits of Fuel-Air Mixtures at the Initial Mixture Temperature of -60°C

| Fuel | Rich Limit (% by Volume) | |
|------------------------|--------------------------|---------------------|
| | Exp. | Burgess-Wheeler Law |
| CH_4 | 13.4 | 13.78 |
| C_2H_6 | 12.8 | 13.40 |
| C_3H_8 | 9.8 | 10.27 |
| C_3H_6 | 10.1 | 10.26 |
| C_2H_4 | 24.2 | 27.90 |

The rich flammability limits for various binary mixtures of methane-propane, propane-propylene and methane-ethylene were also established at mixture temperatures down to -60°C . These results are listed in Table II and plotted

TABLE II

Rich Flammability Limits of Binary Fuel Mixtures

| Fuel Composition % by Volume | | | | Initial Temperature of Fuel-Air Mixture, $^{\circ}\text{C}$ | | | | | | | |
|---------------------------------|------------------------|------------------------|------------------------|---|----------------------------|------------|----------------------------|------------|----------------------------|------------|----------------------------|
| | | | | 23 | | 0 | | -30 | | -60 | |
| CH_4 | C_3H_8 | C_3H_6 | C_2H_4 | Exp. Limit | $\frac{L_c - L_e}{L_e} \%$ | Exp. Limit | $\frac{L_c - L_e}{L_e} \%$ | Exp. Limit | $\frac{L_c - L_e}{L_e} \%$ | Exp. Limit | $\frac{L_c - L_e}{L_e} \%$ |
| 80 | 20 | | | 13.4 | -1.8 | 13.2 | -1.6 | 13 | -1.9 | 12.6 | -0.9 |
| 50 | 50 | | | 12.1 | -0.1 | 11.8 | 0.3 | 11.5 | 0.5 | 11.1 | 2.0 |
| 20 | 80 | | | 11.0 | -0.2 | 10.9 | -0.3 | 10.6 | -0.3 | 10.3 | 0.6 |
| | 20 | 80 | | 10.7 | -2.8 | 10.5 | -1.9 | 10.3 | -1.4 | 10.2 | -1.6 |
| | 50 | 50 | | 10.8 | -3.7 | 10.6 | -2.8 | 10.5 | -3.8 | 10.3 | -3.4 |
| | 80 | 20 | | 10.5 | -1.0 | 10.4 | -1.0 | 10.2 | -1.6 | 10.0 | -1.4 |
| 80 | | | 20 | 15.7 | -0.3 | 15.4 | -0.3 | 15.1 | 0 | 14.7 | 0.1 |
| 58 | | | 42 | 17.2 | 3.7 | 16.9 | 2.8 | 16.6 | 2.4 | 16.1 | 2.0 |
| 20 | | | 80 | 22.4 | 4.7 | 22.0 | 2.0 | 21.5 | 1.2 | 20.6 | 0.6 |

where L_c is the calculated limit according to Le-Chatelier's Rule (%)

L_e is the experimentally established limit (%).

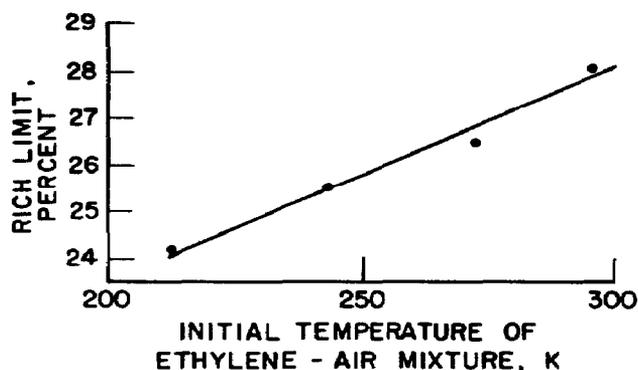


Fig. 2 Experimentally determined rich flammability limits in air of ethylene as a function of the initial temperature of the fuel-air mixture.

These experimentally established flammability data were checked against corresponding data that were calculated according to the modified "Burgess-Wheeler Law" (1) which relates the limit at any temperature to the value at a reference temperature (23°C) according to the following relationship:

$$L_{R,t} = L_{R,23^{\circ}\text{C}} + \frac{0.75}{\Delta H_c} (t - 23)$$

where

$L_{R,t}$ is the rich limit at an initial mixture temperature t ;
(% by volume).

$L_{R,23^{\circ}\text{C}}$ is the rich limit at an initial mixture temperature of
23°C (% by volume).

t is the initial mixture temperature, °C.

ΔH_c is the net energy release by combustion, kcal/mol.

The result of this comparison is shown in Table I. It can be seen that the calculated limits are higher than the corresponding experimental values. The difference varies from around 1.5% for propylene to 15% for ethylene. These differences can be larger where the initial mixture temperature is lowered beyond -60°C. Accordingly, the use of this simple predictive approach can be recommended only as a rough guide to the values of the rich limit at low mixture temperatures.

in Figs. 3, 4 and 5. The experimental data were then compared with the corresponding values calculated using the well-known Le-Chatelier's Rule (2), when using the corresponding limits for the individual fuels that we established at the same temperature. The deviation of the predicted values from the corresponding experimental values are listed in Table II. These deviations are also plotted in Fig. 6.

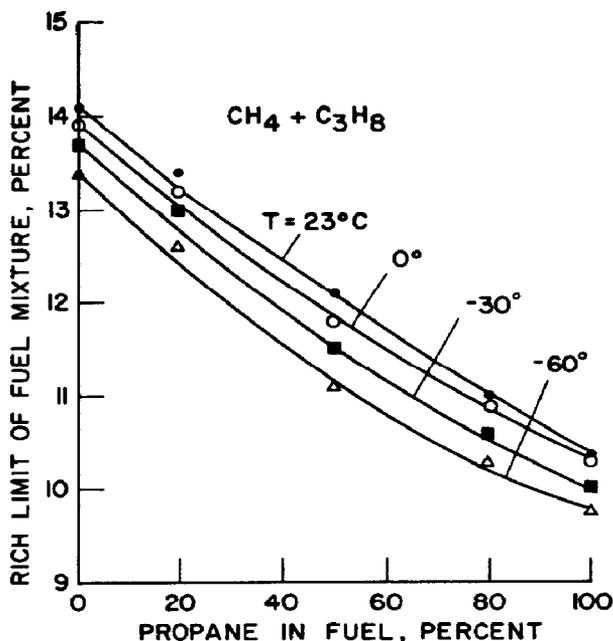


Fig. 3 Experimentally determined rich flammability limits in air of binary mixtures of methane and propane for a range of initial mixture temperature.

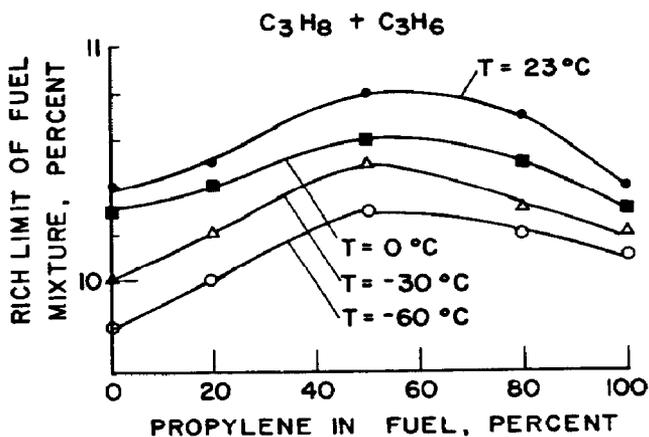


Fig. 4 Experimentally determined rich flammability limits in air of binary mixtures of propane and propylene for a range of initial mixture temperature.

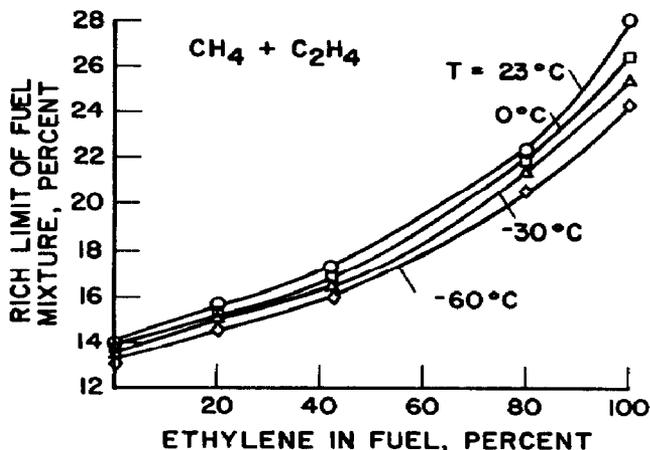


Fig. 5 Experimentally determined rich flammability limits in air of binary mixtures of methane-ethylene mixtures for a range of initial mixture temperature.

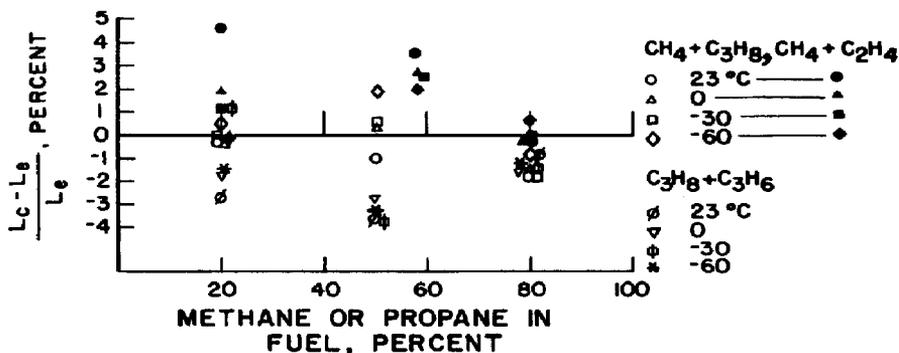


Fig. 6 The extent of the relative deviation of the calculated rich limit according to Le Chatelier's Rule for a range of binary fuel mixtures involving CH₄, C₂H₄, C₃H₆ and C₃H₈.

It is interesting to note that the extent of these deviations tends to be relatively small. The deviation is larger for mixtures such as propane-propylene and methane-ethylene involving mixtures of saturated and unsaturated hydrocarbons but smaller for the saturated hydrocarbons methane-propane mixture. The largest deviation for propane-propylene and methane-ethylene mixtures is observed for the mixtures containing fuels in approximately equal concentrations.

It can also be noted that for methane-ethylene mixtures the extent of deviation decreases significantly with the lowering of the initial temperature of the mixtures. The deviation of the experimentally obtained rich flammability limit of the mixture containing 20% of methane and 80% of ethylene is 4.7% at the initial temperature of 23°C and is only 0.6% at the initial temperature of -60°C.

ACKNOWLEDGEMENT

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