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THE FLAMMABILITY OF RICH GASEOUS FUEL MIXTURES INCLUDING THOSE CONTAINING PROPANE IN AIR

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ABSTRACT

A consistent set of rich flammability limit data was obtained for binary fuel combinations of propane with the other common fuels: methane, ethylene, carbon monoxide and hydrogen. In addition, some tertiary combinations of propane, hydrogen and carbon monoxide were investigated. The influence of the addition of the diluents nitrogen and carbon dioxide to the fuel mixtures was also considered.

Procedures for predicting the rich flammability limits of fuel mixtures involving propane are presented, and the extent of deviations from experimental values established. A correlation of the effect of the presence of the diluents nitrogen and carbon dioxide in the fuel or the fuel mixtures is proposed.

INTRODUCTION

An important characteristic of any fuel from the safety and the utilization points of view is its flammability limits representing the maximum, or minimum, of its concentration in air that can support flame propagation from an adequate ignition source. At the present time, it is not possible to calculate the flammability limits from entirely fundamental physicochemical data and the limits are determined experimentally.

There are many practical situations involving having to deal with complex fuel mixtures containing different gaseous fuels and diluents. Obviously, with the many different combinations of gaseous fuel mixtures that may be encountered, it would be clearly impossible to test routinely for all of them. Therefore, it is very important to develop guidelines to predict their limits on the basis of a knowledge of their composition and the flammability limits of the individual gases making up the fuel mixture under the same conditions. The rich flammability limit in general and for gaseous fuel mixtures in particular is not very well documented when compared to the corresponding lean limit.

One of the known and often used guidelines for predicting the flammability limit of fuel mixtures is the so called "Le Chatelier's Rule" which is based on the assumption that the mixture of limiting mixtures is itself a limiting mixture and can be expressed as follows:

$$L_m = \frac{100}{\sum_{i=1}^{n} \frac{Y_i}{L_i}}$$

where L_m is the flammability limit of the fuel mixture in air, % by volume; L_i is the corresponding flammability limit for the "i"th fuel component, % by volume; and Y_i is the corresponding volumetric fraction of the fuel component "i" in the fuel mixture.

This rule has been shown to give a reasonably good estimate of the lean flammability limits of many mixtures, containing common hydrocarbon fuels, hydrogen and carbon monoxide (1, 2). The nature of the rich flammability limit is somewhat different from that of the lean flammability limit. The rich flammability limit is associated with insufficient amounts of oxygen for complete combustion and hence the chemical kinetic aspects of the mixture become particularly important.

The purpose of the present work was to establish the rich flammability limits of common gaseous fuels and their mixtures in a consistent way in the same apparatus employing the same procedure and to establish guidelines for predicting the rich flammability limits of different fuel mixtures, particularly those containing propane.

APPARATUS AND EXPERIMENTAL PROCEDURE

A clean and internally smooth stainless steel flame tube was employed (3). The 50mm diameter flame tube was fitted at the bottom with spark ignition of adequate energy. The flame tube was normally closed at the top but open at the bottom so that ignition and subsequent upward flame propagation takes place at essentially atmospheric pressure throughout. Detection of the successful arrival of the flame at the top of the tube was made through the provision of a set of rapid response thermocouples, located in the central portion of the tube, and their output monitored on both an oscilloscope and a chart recorder.

The test mixture was prepared initially in a mixing chamber on the basis of the partial pressure of the components and then introduced gently and uniformly into the evacuated flame tube. Provision was made for four supply lines, for the fuels and diluent gas used, in addition to that of the dry air. Throughout, great care was taken to ensure very precise determination of the concentration of the components of the test mixture. It was shown earlier (2, 3, 4) that the flammability limits have a probabilistic nature. When tests were repeated carefully a large number of times with the same mixture (typically 25 times), a range of fuel concentrations could be obtained where the probability of flame propagation through the tested mixture is seen to vary between 0% and 100%. The extent of the relative deviation of the fuel concentration with the probability of flame propagation for mixtures around the rich limit for five common gaseous fuels is shown in Fig. 1.

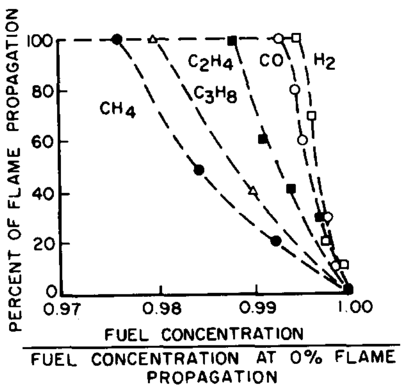

Fig. 1 The extent of deviation of the fuel concentration with the probability of upward flame propagation for mixtures around the rich limit for the five gaseous fuels, at 22° C and atmospheric pressure (3)

All data reported here relating to the rich flammability limits, whether for the individual fuels or their mixtures in air, correspond to the "zero probability of flame propagation value" at a temperature of 22° C and an atmospheric pressure of 89 kPa.

RESULTS

The experimental values for the rich flammability limit obtained for different binary mixtures of propane with methane, and with carbon monoxide, are shown in Fig. 2. The corresponding rich limits of these mixtures calculated according to Le Chatelier's Rule are also shown for comparison. It can be seen that binary mixtures of propane with methane and propane with carbon monoxide obey Le Chatelier's Rule quite well.

The flammability limits of propane-ethylene mixtures are shown in Fig. 3. Only mixtures containing less than 30% of propane obey reasonably well Le Chatelier's rule. The experimental flammability limits of the propane-ethylene mixtures containing less than 58% of propane are higher than the corresponding calculated values, while those of mixtures containing more than 58% of propane are lower than the calculated values. Moreover, significant deviation from Le Chatelier's Rule for propane-hydrogen mixtures containing relatively small amounts of propane can be observed from Fig. 4. The

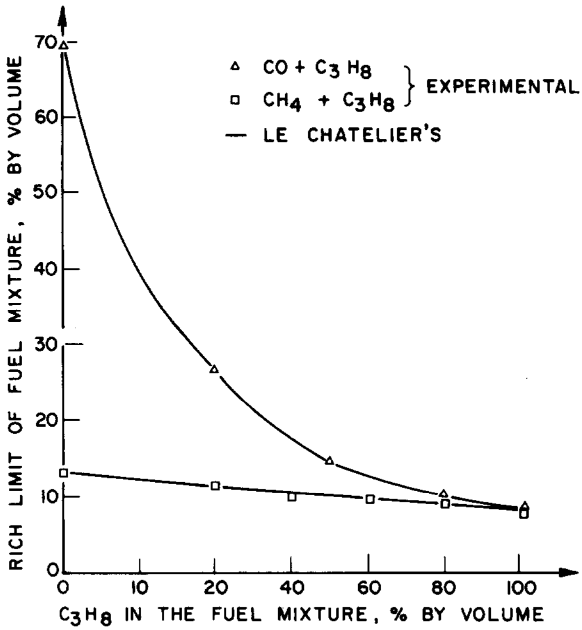

Fig. 2 The rich flammability limits for binary fuel mixtures involving propane in air at 22° C
— Calculated according to Le Chatelier's Rule

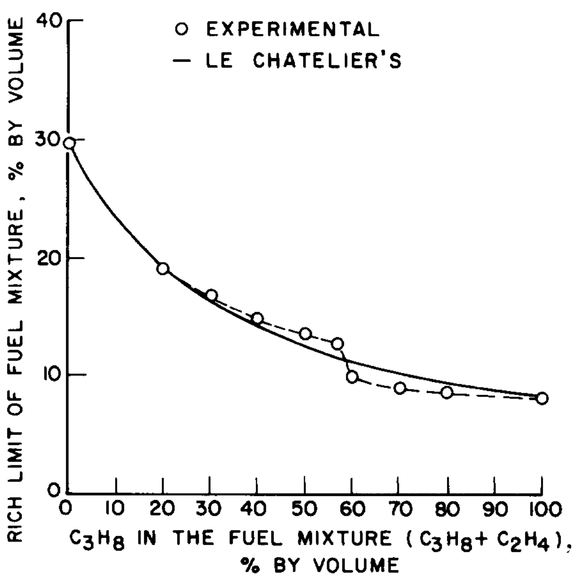

Fig. 3 The rich flammability limits for binary fuel mixtures of propane and ethylene at 22° C
— Calculated according to Le Chatelier's Rule

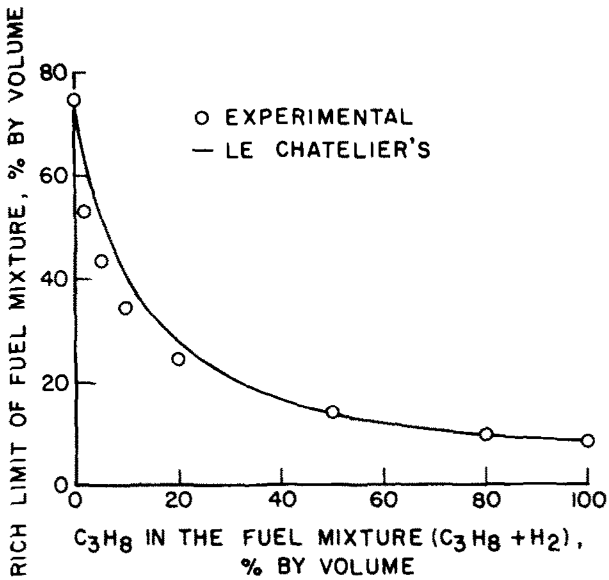

Fig. 4 The rich flammability limits for binary fuel mixtures of propane and hydrogen at 22° C
— Calculated according to Le Chatelier's Rule

extent of the deviation of the experimental results from the corresponding calculated values is shown in Fig. 5.

The deviation from Le Chatelier's Rule can be due to the chemical interaction of the fuels present and the available oxygen in the mixture, which is not accounted for in the simple physical basis for mixing the fuel components assumed by the Rule. As it was examined earlier for hydrogen-ethylene mixtures near the rich flammability limit (3, 4), combustion chemical kinetics

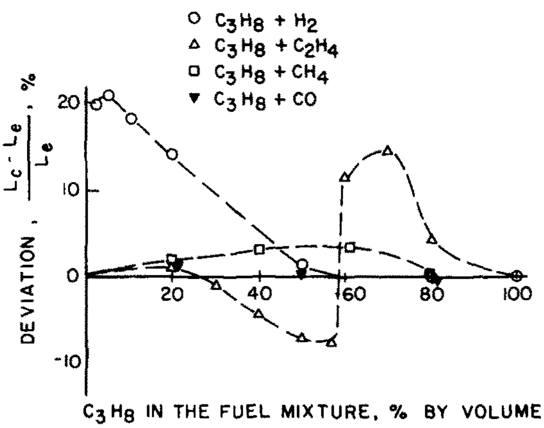

Fig. 5 The relative deviation of the calculated limit (L_c) according to Le Chatelier's Rule from the corresponding experimental limit (L_e) for various binary fuel mixtures involving propane

influence dramatically the overall reaction rates of the fuel mixture and its components and therefore the flammability limits. For example, the addition of 20% of ethylene to hydrogen decreases drastically the overall reaction rate of hydrogen. Similar effect can be observed for hydrogen-propane mixtures, Fig. 4, that can be checked similarly by examining in detail the chemical kinetics of those mixtures.

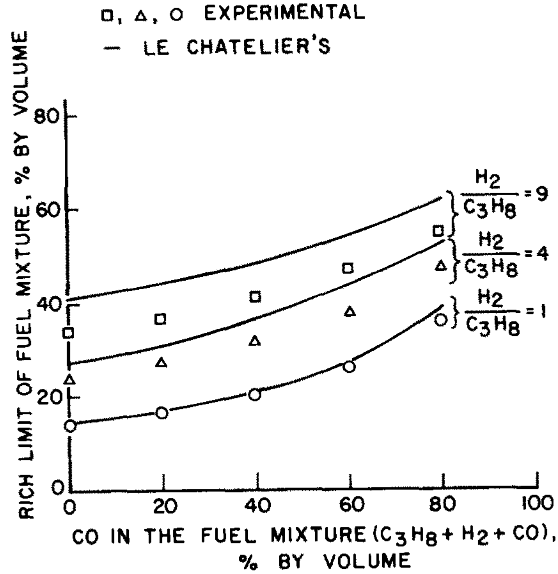

Fig. 6 The rich flammability limits for tertiary fuel mixtures of propane, hydrogen and cabon monoxide in air
— Calculated according to Le Chatelier's Rule using experimental limits of propane, hydrogen and carbon monoxide in air individually at 22° C

If a third gaseous fuel is added to a binary fuel mixture, which does not follow the Rule well, it is very probable that the resulting tertiary fuel mixture will also deviate from the Rule. For example, the presence of carbon monoxide in hydrogen-propane mixtures results in fuel mixtures that display significant deviation as shown in Fig. 6. Fig. 7 shows the deviation of the flammability limits of different fuel mixtures containing propane, hydrogen and carbon monoxide. The largest deviation is observed for the mixture in which hydrogen-propane ratio is 9 to 1 and 10 to 1 (with carbon monoxide content up to 80%); that is in agreement with the results presented in Fig. 5 on the deviation of propane-hydrogen mixtures. It can be seen also, Fig. 8, that the application of the Rule to such mixtures using the experimental limits of the binary mixtures of hydrogen and propane and that of carbon monoxide gives very good agreement with the experimentally determined limits of the tertiary fuel mixtures. This simple approach appears to be quite adequate since the

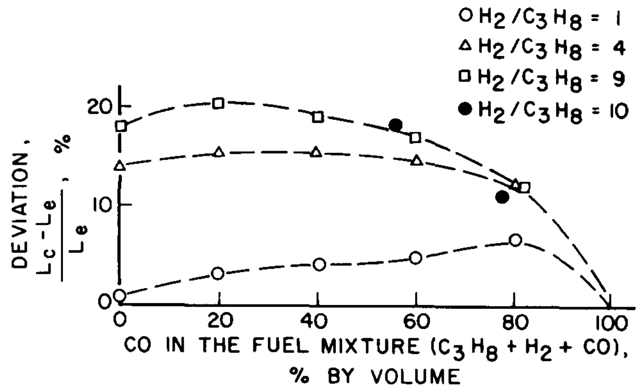

Fig. 7 The relative deviation of the calculated limit (L_c) according to Le Chatelier's Rule from the experimental limit (L_e) for tertiary fuel mixtures of propane, hydrogen and carbon monoxide

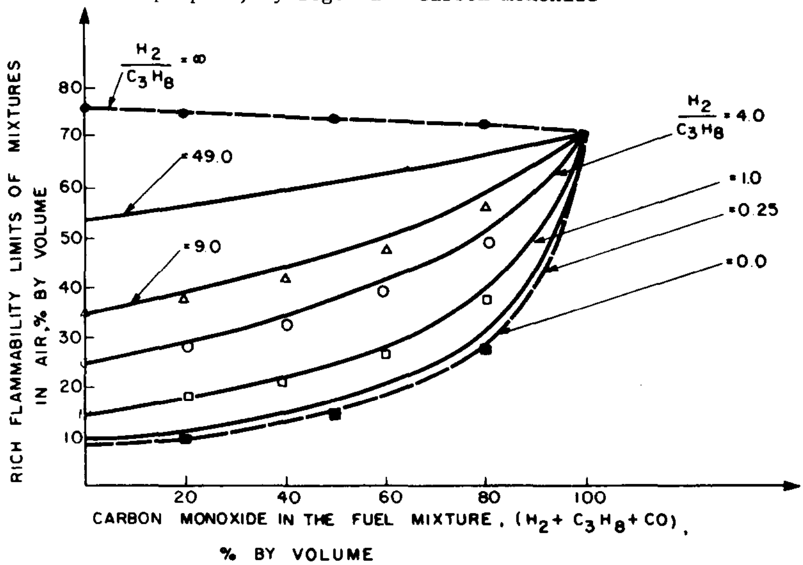

Fig. 8 The rich flammability limits for tertiary fuel mixtures of propane, hydrogen and carbon monoxide in air
— Calculated according to Le Chatelier's Rule using experimental limits of binary mixture of propane and hydrogen and the limit of carbon monoxide in air
--- Calculated according to Le Chatelier's Rule for binary mixtures of propane and carbon monoxide and for binary mixtures of hydrogen and carbon monoxide (3)

binary mixtures of carbon monoxide and propane, as well as carbon monoxide and hydrogen, on their own obey the Rule quite closely.

The effect of the presence of diluents such as nitrogen or carbon dioxide with propane or with fuel mixtures containing propane was also investigated. As was reported earlier (5, 6) the effect of the diluents in the fuel mixture can be correlated conveniently and well in the majority of the cases tested involving common gaseous fuels on the basis of the inverse of the measured flammability limit of the fuel and diluent mixture versus the percentage by volume of the combustible component in the fuel mixture. This is shown in Fig. 9 for mixtures involving nitrogen or carbon dioxide with propane in air; while the effect of the dilution with carbon dioxide or nitrogen for a binary mixture of propane and ethylene, in the volumetric proportion of 70% and 30% respectively, is shown in Fig. 10. Similarly, Fig. 11 shows the effect of the presence of nitrogen in two different mixtures containing the three gaseous fuels: propane, hydrogen and carbon monoxide.

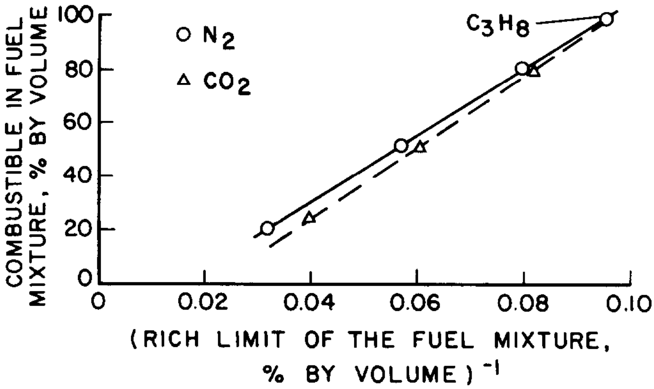

Fig. 9 A correlation of the observed rich flammability limits for propane with the addition of nitrogen or carbon dioxide

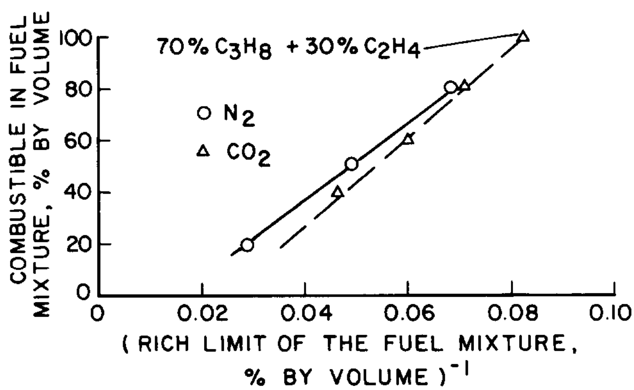

Fig. 10 A correlation of the observed rich flammability limits for a binary fuel mixture of propane and ethylene (70% C_3H_8 + 30% C_2H_4) with the addition of nitrogen or carbon dioxide

In all the cases considered, the correlation can be expressed by the simple equation:

$$\frac{100}{L_m} = \frac{Y_f}{L_f} + a(1 - Y_f) \qquad (2)$$

where

L_m - the rich limit of the "fuel + diluent" mixture in air, % by volume

Y_f - the fuel fraction in the "fuel + diluent" mixture, % by volume

L_f - the rich limit of the fuel component in air, % by volume

a - a constant

The value of the constant "a" depends on both the nature of the fuel and the diluent. As an example, for propane-nitrogen mixtures, "a" is equal to 0.0159, while for propane-carbon dioxide mixtures, "a" has the value of 0.0206.

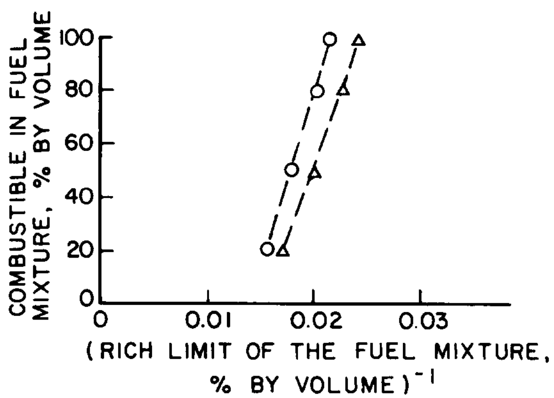

Fig. 11 A correlation of the observed rich flammability limits for tertiary fuel mixtures of propane, hydrogen and carbon monoxide with the addition of nitrogen.

o - fuel mixture is 4% C_3H_8 + 36% H_2 + 60% CO

Δ - fuel mixture is 6% C_3H_8 + 54% H_2 + 40% CO.

It is always important to remember that the flammability limit is a function of the many factors that influence the initiation and propagation of a flame within the mixture, such as temperature, pressure, flame propagation direction, level of turbulence, ignition energy, size of apparatus, etc. Accordingly, the numerical values obtained for the flammability limits are valid only for the conditions considered. The present contribution was involved primarily with establishing the tendencies for the behaviour of the rich flammability limit of fuel mixtures including those containing some common diluents.

CONCLUSIONS

i) The rich limits of binary fuel mixtures in air involving propane should be examined carefully as it was found that predicted values according to Le Chatelier's Rule, even for some common fuels, may lead to significant deviations from the corresponding experimental values.

ii) The flammability limit of tertiary mixtures can be estimated by applying the Rule to the experimental values of the binary mixture of the two fuels showing the most deviation from predicted values according to the Rule, with the remaining third fuel component. This approach will yield a better estimate than when using the limits of the individual fuels making up the mixture on their own.

iii) The influence of the presence of diluents, such as nitrogen and carbon dioxide in the fuel mixtures considered, on the rich flammability limits can be correlated well using the simple relationship of equation (2).

ACKNOWLEDGEMENT

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