

THE UNIVERSITY OF CALGARY

**Flammability Limits of Hydrogen-Carbon Monoxide-Methane Mixtures
in Air at Elevated Temperatures**

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

DEPARTMENT OF MECHANICAL AND MANUFACTURING ENGINEERING

CALGARY, ALBERTA

APRIL, 2004

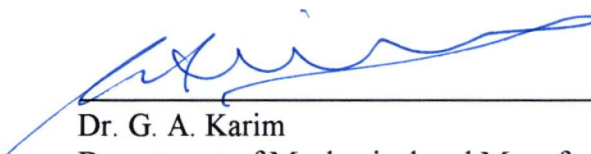
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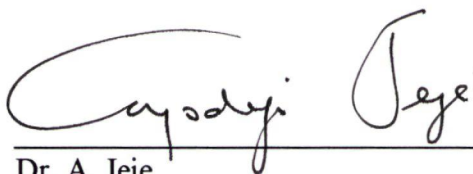
The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies for acceptance , a thesis entitled “Flammability Limits of Hydrogen-Carbon Monoxide-Methane Mixtures in Air at Elevated Temperatures” submitted by Qun Wang in the partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering.



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ABSTRACT

The flammability limits of H_2 , CH_4 , C_2H_4 , CO and various tertiary H_2 - CH_4 -CO mixtures were established at different initial temperatures in two different test tubes, quartz and stainless steel, of identical size and design with an identical ignition system. The effect of the duration of exposure (residence time) of the mixture to elevated temperatures prior to spark ignition was also investigated. It was found that the flammability limits of CH_4 were not affected by the duration of residence time or by the material of the test tube. However, the flammability limits of CO, H_2 , and CH_4 determined in the stainless steel apparatus were influenced significantly by the residence time. The limit values of CO established in the quartz test tube were independent of the residence time, while the flammability limits of H_2 and C_2H_4 obtained in the quartz test tube were significantly influenced by the duration of the residence time. It suggested that the variations in the flammability limits were the result of pre-ignition chemical activity, which effectively changed mixture composition prior to spark ignition. Measurement showed that oxygen was consumed during the residence time. The method of "constant adiabatic flame temperature" was employed to predict the flammability limits at different initial temperatures as well as oxygen consumption during the residence time. Calculated values were in a good agreement with the experimental data. The limits of the fuel mixtures (at short residence times) follow closely those calculated using Le Chatelier's Rule.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Wierzba, for her initiating this project and for her valuable suggestions and continuous encouragement.

I would also like to thank Dr. G. A. Karim for his support at various stages of the present work.

The financial support from the Natural Science and Engineering Research Council of Canada (NSERC) and from the Government of Alberta (Province of Alberta Graduate Scholarship and Alberta Learning's Achievement Scholarship) is highly acknowledged.

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CHAPTER 1

INTRODUCTION

1.1 Background

The flammability limits are important characteristics of a fuel from the point of safety and utilization. They divide fuel-air mixtures into a flammable and a non-flammable zones. When the composition of the mixture changes from the stoichiometrical to the rich or lean flammability limit, the flame temperatures and the flame speeds decrease. Eventually, when the energy released from the combustion reactions can not balance the heat dissipated to the surroundings, the mixture becomes non-flammable. Therefore, the rich and lean flammability limits are defined as the highest and lowest fuel concentration in the fuel-air mixture, correspondingly, at which the mixture is just unable to sustain the flame propagation through a fresh fuel-air mixture after its ignition.

Consequently, the values of the flammability limits are affected by the all factors, influencing the chemical reaction and heat dissipation rates, such as the nature of the fuel, temperature and pressure of the fuel-air mixture, and direction of the flame propagation. Although many theories have been suggested to predict the flammability limits, it is still impossible to establish the flammability limits on an entirely theoretical basis and, at present, the flammability limits have to be determined experimentally.

Although much research has been conducted in the field of the flammability limits, there are still many questions that cannot be answered adequately. For example,

the flammability limits of complex fuel mixtures are not readily available in the literature at the present time, especially at elevated temperatures and there is a lack of information about their prediction. The knowledge of the flammability limits of hydrogen, carbon monoxide and methane mixtures becomes particularly important to evaluate the fire and explosion hazards, because of the increasing use of these kind of mixtures in the hydrogen production process.

It was reported that the values of the flammability limits of some common gaseous fuels and their mixtures determined in a stainless steel test tube at moderately elevated temperatures could be affected by the duration of their exposure to these temperatures prior to spark ignition (Wierzba, I. and Ale, B. B., 1999; Wierzba, I. and Kilchyk, V., 2001). It was found that the flammable ranges narrowed with an increase of this waiting time (residence time). It was shown that some pre-ignition oxidation reactions were taking place during this time, which altered the initial composition of the test mixtures prior to ignition, and it was suggested that at this level of temperature the steel surface of the test tube might act as a catalyst to promote such reactions.

1.2 The objectives of the present study

The objectives of the present work were the following:

- To establish experimentally the flammability limits of mixtures of hydrogen, carbon monoxide and methane in air at elevated temperatures for the upward flame propagation.

- To investigate the effect of the test tube material on the values of the experimentally obtained flammability limits at elevated temperatures
- To check the effectiveness of some predictive methods in relation to such mixtures.

CHAPTER 2

LITERATURE SURVEY

The efforts for the establishment of flammability limits were initially made to improve safety conditions in mines. Since then, numerous experimental results have been published and some of them have been compiled in the excellent reviews by Coward and Jones (1952), Barnett and Hibbard (1957), Zabetakis (1965), Lovachev, et al (1973), Lovachev (1979), and Jarosinski (1986). Studies of these experimental data show that the values of the flammability limits reported by different researchers are strongly affected by the apparatus and the experimental methods used as well as by the initial conditions employed in their investigations.

The reported flammability limits were usually established for quiescent fuel-air mixtures in cylindrical tubes (Coward, H. F., et al, 1919; White, A.G., 1925; Coward, H. F. and Jones, G. W., 1952; Wierzbza, I., et al, 1985; Smedt, G. De. et al., 1999), spherical vessels (Bone, W. A., 1928; Bunev, V. A., 1972; Smedt, G. De., et al., 1999), or cubic vessels (Lovachev, L.A., 1979). The size of the vessel used in the experiments is considered an important factor affecting the values of flammability limits. It is widely believed that the flame quenching mechanism is governed by two processes, i.e. the heat generated due to the chemical reactions and heat loss to the surroundings. When the heat loss exceeds the heat generation, the flame temperature decreases, and eventually the flame quenches. In the larger vessels, for example, in the cylindrical tubes of larger diameter, with smaller surface to volume ratio, relatively less heat is lost, and

consequently, wider flammable ranges were obtained. The experimental data show that the effect of the test tube diameter is not significant when the tube diameter is larger than 50 mm. It was also recommended to use long tubes of 1 m plus to eliminate the effect of the ignition source. A tube of diameter 50.8mm and length 1.00 metre was chosen as a standard test tube by the U.S. Bureau of Mines. However, the experimental data also show that even when the test tube is longer than 1 metre, the flammability limits are strongly influenced by the tube length, if the tests are conducted in closed tubes and the pressure inside the tube increases during the flame propagation (Lovachev, L. A., et al, 1973). That is the reason that most recent investigations have been conducted in tubes open to atmosphere during the process of flame propagation after ignition.

The direction of the flame propagation in a flame tube is also an important factor affecting the values of the flammability limits. When a mixture is ignited at the top of a vertical flame tube, the flame will propagate downward, while, when a mixture is ignited at the bottom, the flame will propagate upward. Experiments show that the flammability range for the upward propagation is wider than that for the downward propagation (Lovachev, L. A., 1971; Andrews, G. E. and Bradley, D., 1973; Hertzberg, M., 1976; Macek, A., 1979; Kumar, R. K., 1985). The reason for this is that the heat transfer by free convection supports upward flame propagation. The values of the flammability limits determined in a horizontal tube lie somewhere between those for upward and those for downward flame propagation.

Many different methods were employed to detect the flame propagation in the test tube. Visual observation in a glass container was used by Levy, A. (1965); Andrews, G. E. and Bradley, D., (1973); as well as Jarosinski, J. and Strehlow, R. A., (1978). Other

researchers monitored the changes in the mixture temperature (Kumar, R. K., 1985; Hustad, J. E. and Sonju, O. K., 1988; Wierzba, I. and Ale, B. B., 1988), or mixture pressure (Bunev, V. A., 1972; Checkel, M. D., et al, 1995; Smedt, G. De. et al, 1999), or mixture composition (Bone, W. A., et al, 1928) for the flame propagation detection.

The experimental values of the flammability limits may be affected by the ignition source employed in the experiments. Although different ignition sources were used, such as pilot flame, hot rods or wires, fused wires, and plasma jets (Coward, H. F. and Jones, G. W., 1952; Zabetakis, M. G., 1965; Boston, P. M. et al, 1984; Vince, I. M. et al, 1984; Jarosinski, J., 1986), spark ignition is a preferred method, mainly because of its easy energy release control. The electrode gap, ignition voltage, and spark duration are the main factors in a spark ignition system. Investigations of spark ignition (Blank, M. V., et al, 1949; Barnett, H. C. and Hibbard, R. R., 1957) show that there is an optimum electrode gap allowing to obtain strongest initial flame kernel. If the gap is less than this optimum value, the flame kernel formed between the electrodes will quench because of the larger heat loss along the electrodes. On the other hand, with the larger gap between the electrodes, higher voltages are needed to ionize the gases and more energy is needed to heat the gases in a larger volume to reach a certain temperature level (Lewis, B. and Von Elbe, G., 1987).

In addition to experimental conditions mentioned above, the values of the flammability limits are affected by the parameters of the mixture initial state, which influence the heat and mass transfer process as well as the combustion reaction rate. These parameters may include temperature, pressure, gravity acceleration, turbulence, and a presence of diluents.

The effects of gravity acceleration on flammability limits of methane-air mixtures have been studied by conducting experiments under high acceleration conditions (Lovachev, L. A., et al, 1973). Experimental results show that with an increase in gravity acceleration more than 200 times that of the normal value, the flammability range of methane-air mixture narrows significantly especially for the downward propagation. Some researchers believed that the flammability limits obtained in the zero gravity condition may lie somewhere between those obtained at upward and downward propagation under the normal gravity condition (Coward, H. F. and Jones, G. W., 1952; Egerton, A., 1953; Von Dolah, R. W., et al, 1962; Zabetakis M. G., 1965). However, the experiments conducted in a micro-gravity environment showed that the flammable range is wider at the zero gravity than that at the normal conditions (Strehlow, R. A. and Reuss, D. L., 1980; Strehlow, R. A., et al, 1986; Jarosinski, J., 1986; Ronney, P. D., 1988).

The flammability limits are also affected by the turbulence level of the fuel-air mixtures. The earlier studies showed that whereas the flammability range narrows at high level of turbulence (Coward and Jones, 1952), in general, there is no significant change in the limit values under the condition of moderate turbulence. Moreover, it was also shown that the more intensive ignition energy is needed to form flame kernel in the presence of turbulence than that in quiescent mixtures, and if an adequate ignition source is provided, the flammability range widens as the turbulence level rises (Lovachev, L. A., et al., 1973).

The flammability limits of fuel mixtures containing diluents have increasingly gained interest because of increasing use in industry of low Btu gases, containing significant amounts of diluents (N_2 , CO_2). Adding inert diluents to the fuel-air mixtures

changes the mixture thermodynamic properties such as specific heat, thermal diffusivity, mass diffusivity, the oxidation reaction rates and, as result, their flammability limits (Zabetakis, M., et al., 1965; Coward, H. F. and Jones, G. W., 1952; Glassman, I., 1987). It was reported that an addition of such diluents as carbon dioxide and nitrogen to fuel-air mixture narrows the mixture flammability range. On the other hand, the experiments showed that the addition of argon to methane-air mixtures widens the lean limit because of argon's smaller specific heat in comparison with air (Coward, H. F. and Jones, G. W., 1952; Wierzba, I., et al, 1985). Some semi-empirical methods have been suggested to predict the limits changes due to the addition of diluents (Boon, S. L., 1982; Cheng, T. K. H., 1985; Heffington, W. M. and Gaines, W. R., 1981; Odgers, J., et al, 1980; Wierzba, I., et al, 1996).

The initial pressure of fuel-air mixture is another factor influencing the value of the flammability limits. Usually, the mixtures maintain unchanged flammability limits with the decrease of the pressure below atmospheric until the absolute pressure reaches about 8kPa. With the further decrease of the pressure, the flammable range narrows continuously until such a point is reached, at which the mixture eventually becomes totally non-flammable (Van Dolah, R. W., et al, 1962; Glassman, I., 1987; Lewis, B. and von Elbe, G., 1987). At pressures above the atmospheric, on the other hand, the pressure effect depends on the type of fuel-air mixtures. It was reported that the flammable range of carbon monoxide-air mixtures narrows with the increase in pressure, while that of hydrogen-air and methane-air mixtures narrow initially and then broaden with the further increase in the pressure (Bone, W. A., et al., 1928; Coward, H. F. and Jones, G. W., 1952). With the exceptions mentioned above, for the majority of gaseous fuels, the

flammable range widens with the increase of pressure, especially at the rich limit side (Zabetakis, M. G. and Richmond, J. K., 1953; Zabetakis, M. G., 1965). However, the usual changes in atmospheric pressure do not vary the flammability limits noticeably (Coward, H. F. and Jones, G. W., 1952).

The initial temperature of a fuel-air mixture (before the ignition) affects its flammability limits very significantly. The flammability limits broaden with an increase in the mixture initial temperature (Coward, H. F. and Jones, G. W., 1952; Zabetakis, M. G., 1965; Boon, S. L., 1982; Hustad, J. E. and Sonju, O. K., 1988; Harris, K. P., 1990; Wierzba, I., et al, 1992; Wierzba, I. and Ale, B. B., 1998). It is known that the flame propagation through a limit mixture is associated with a certain threshold flame temperature. Flame temperatures lower than the threshold result in the combustion reaction rate being too low to support the flame self-propagation. Higher initial temperatures enhance the reaction rates, and therefore widen flammability ranges. To predict the changes in the flammability limits caused by the variation in the initial temperatures, some researchers suggested that the adiabatic flame temperature, which is proportional to the threshold temperature in the reaction zone, remains almost constant at the limit when the initial temperature changes (Zabetakis, M. G., 1965; Bade Shrestha, S. O., 1992; Wierzba, I., et al, 1996). It was shown that this method, so called “constant adiabatic flame temperature approach”, allows to calculate flammability limits of fuels and fuel mixtures at elevated temperatures, which are in a good agreement with the corresponding experimentally obtained values.

Further investigations showed that at moderately elevated temperatures (up to 400°C), the values of the flammability limits determined in a stainless steel test tube

changed when the fuel-air mixtures were exposed to the elevated temperatures over different periods of time (residence time) before spark ignition. Gas analysis conducted in these experiments showed that during the residence time, the test mixtures underwent pre-ignition reactions, which effectively change the mixture composition before the spark ignition and as a result its flammability limits. It was suggested by Wierzba, I. and Ale, B. B (1998) that the stainless steel surface of the test tube acted as a catalyst to promote the pre-ignition reactions, since numerical simulations of the gas-phase reactions showed that these reactions are negligible at such moderate temperature levels. However, to confirm their suggestion about the nature of the pre-ignition reactions, it is necessary to repeat the tests in a tube made of a different (inert) material.

Many different fuel mixtures are increasingly used in industry. Their flammability limits in air are usually calculated using Le Chatelier's rule. The calculation are based on the mixture composition and the flammability limits of the individual fuel components in the mixture on its own in air, which assumes that a mixture of limiting fuel/air mixtures is also a limiting mixture. Experimental investigations have demonstrated that rule is fairly accurate in predicting mixtures' lean flammability limits, and relatively less accurate in predicting the rich limits for a rather wide range of various fuel mixtures (Boon, S. L., 1982; Cheng, T. K. H., 1985; Coward, H. F. and Jones, G. W., 1952; Heffington, W. M. and Gaines, W. R., 1981; Wierzba, I., et al, 1992; Zabetakis, M. G., 1965). However, it was also reported that there are fuel mixtures that do not obey the Le Chateliar's rule even at room temperatures (Coward, H. F. and Jones, G. W., 1952; Wierzba, I., et al, 1987; Wierzba, I., et al, 1989). For example, the calculated rich flammability limit of hydrogen-ethylene mixture may deviate from the experimental value significantly (up to

25%) (Wierzba, I., et al, 1987). The deviations were expected to be larger at higher initial temperatures. The significant deviations were reported in the rich limits of some hydrogen-carbon monoxide and hydrogen-methane mixtures at initial temperatures up to 300°C (Wierzba, I. and Ale, B. B., 1998; Wierzba, I. and Kilchyk, V., 2001).

In general, more experimental investigation is needed to meet the requirement for the knowledge of the flammability limit.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Experimental apparatus

The experimental apparatus used in this investigation to establish the flammability limits of some common gaseous fuels and their mixtures for upward flame propagation is shown in Fig. 3.1.1.

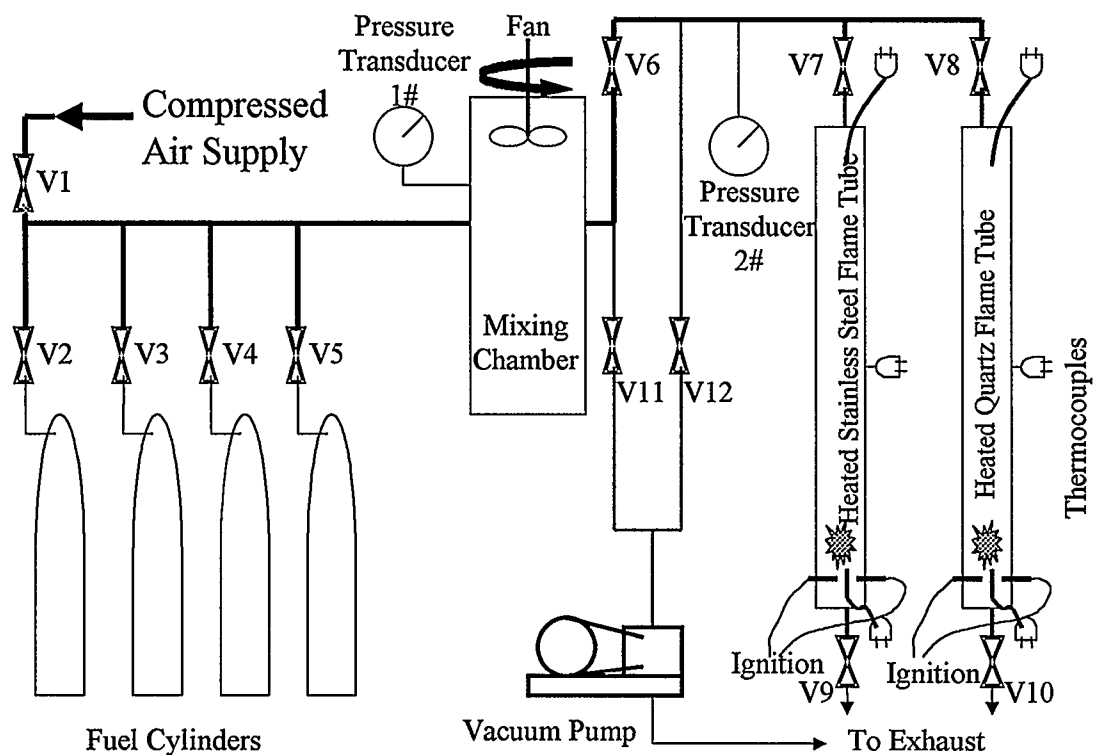


Figure 3.1.1 Schematic diagram of the experimental apparatus.

It includes two geometrically similar test tubes made of different material, a mixing chamber, a vacuum pump, a compressed air supply system, an ignition system,

fuel cylinders and the instrumentation for the temperature and pressure measurement, as shown in Fig.3.1.1.

The test tubes have the dimensions of 50.8 mm in diameter and 1 metre in length (as originally suggested by the U. S. Bureau of Mines and widely accepted as standard dimensions). One test tube is made of stainless steel (316) and the other is made of quartz. The new quartz test tube was designed and constructed in addition to the stainless steel tube in order to investigate the effect of the tube material on the flammability limits at elevated temperatures. The test tubes are arranged in parallel.

The stainless steel test tube can be heated by electrical cable heaters, directly wrapped around the tube. The main heater is controlled by an automatic temperature controller, whereas two additional small heaters at two ends of the tube are manually adjusted to obtain uniform temperature along the tube. The tube and its heaters are all covered with a ceramic insulation to reduce heat loss.

The quartz tube has stainless steel flanges at both ends for the connection to the system. The interior surfaces of the metallic flanges and tubes immediately connected to the flanges were coated with a layer of a ceramic material, a product of AREMCO, INC. which is stable at high temperatures up to 1760 °C. The coating was done to prevent catalytic reactions on the steel surface. Four semi-cylindrical high temperature ceramic radiation heaters were employed to heat the quartz tube to temperatures up to 300°C. To improve the heat conduction along the quartz tube, the tube is tightly encased by two copper semi-cylinders. As a result, a relatively uniform temperature profile was obtained, e.g. $300 \pm 3^\circ\text{C}$. In addition to the above measure, small heating tapes were mounted at the bottom part of the quartz test tube to compensate the conduction heat loss along the tube

supports at the bottom and the heat transfer along the test tube due to free convection. The radiation heaters were also insulated outside with a layer of ceramic fiber, as it has been done on the stainless steel tube.

Both test tubes are equipped with a set of thermocouples to monitor the wall and gas temperatures. Preliminary tests showed that there was almost no measurable difference between the temperatures of the inside and outside surfaces of the tubes under the experimental conditions. Therefore, the thermocouples for the measurement of the wall temperature at the middle of tubes were attached to the outside surface of the tubes to eliminate the possibility of fire quenching caused by the protrusion of the thermocouples inside the tubes. Inside the tube at their both ends, the thermocouples were installed to detect the sudden changes in the test mixture temperature.

Similar electric spark plugs were employed at the base of these two test tubes. An electric spark discharge between two horizontal conical electrodes with the gap of 6.4 mm was produced during ignition by 10 kV, 23 mA centre-tapped transformer with its primary hooked to 110V/60Hz.

Fuel-air mixtures were prepared in the 4.3 l mixing chamber at room temperature on the basis of partial pressures. A pressure transducer was employed to measure the pressure inside the mixing chamber so as to obtain the desired mixture composition. A fan installed at the top of the chamber and driven by an electric motor at a speed of 500 rpm was used to ensure the homogeneity of the test mixtures.

The pressure transducer installed in the pipe, connecting the mixing chamber with the test tubes was used to monitor the pressure inside either of the test tubes.

The gaseous fuels employed in this investigation are listed in table.3.1.1

Table 3.1.1 Gaseous fuels used

Gases	Purity, %
Hydrogen	99.9
Ethylene	99.9
Carbon monoxide	99.9
Methane	97.9

A mechanical vacuum pump was employed to evacuate the system before every test. The valves in the system allow the pump to evacuate different parts of the system to meet the requirements of every stage of the tests. Outlets of the vacuum pump and the test tubes are connected to the exhaust duct for removal of the waste gases out of the laboratory.

3.2 Experimental procedure

For tests conducted at elevated temperatures, the test tube was heated electrically up to the desired so-called initial temperature. It took approximately one hour to get a stable temperature profile along the tube for the maximum temperature used in the experiments (300°C). The first and the last steps of every test were evacuating the test tube being used, the mixing chamber and all connecting pipes. After the pressure inside the system drops to an acceptable level (zero indication at pressure transducers), the system was refilled with air and evacuated again. By this way, it was ensured that the residual gas in the system was mainly air. Then, the mixing chamber was separated from the test tube by closing valve 6 (Fig. 3.1.1). While the test tube continued to be evacuated

by the pump, the compressed air and the desired fuels were introduced into the mixing chamber on the basis of partial pressures measured by #1 pressure transducer (Fig. 3.1.1.) to establish a desired mixture composition. Air was introduced to the mixing chamber before any gaseous fuels were added to the chamber. Therefore, the effect of the level of vacuum in the mixing chamber on the accuracy of the mixture composition was eliminated, since any potential residual gas in the chamber was also air. After the air and fuels were added to the mixing chamber, the fan at the top of the chamber was switched on and run at least 10 minutes to produce a homogenous fuel-air mixture. After that, the vacuum pump was separated from the system and the homogenous mixture was introduced to the test tube until the pressure in the tube reached the level of slightly above the atmospheric pressure. After a pre-determined period of time, called as a residence time, the valve at the bottom of the tube was opened just before spark ignition to allow the flame propagation proceeding at constant atmospheric pressure.

A sudden increase in the reading of the thermocouple measuring the mixture temperature at the base of the test tube indicated that a flame kernel formed near the ignition source. The thermocouple at the top of the tube was used to check if the flame propagated through the whole length of the fuel-air mixture and reached the top of the tube. If there was a sudden increase in the reading of the thermocouple at the top, the mixture was considered flammable. On the other hand, if in any three repeated tests with mixtures of identical composition, the flame did not arrive at the top indicated by the thermocouple, the mixture was considered to be non-flammable. Finally, the amount of the fuel in the non-flammable mixture (% by volume) was considered as the value of the flammability limit, if with a slight (0.1 percent) change in the mixture composition, i. e.

slightly less fuel in rich mixtures or slightly more fuel in lean mixtures, the mixture became flammable.

In the present experimental investigation, the flammability limits were obtained by trial and error. An average of 3-5 days of experimental time was needed to determine one flammability limit value, especially at elevated temperatures and longer residence times. Therefore, the establishment of flammability limits values reported in this study was a very time consuming task.

To examine the existence of the pre-ignition chemical reactions leading to changes in the mixture composition, gas samples were withdrawn from the test tube for gas analysis. The continuous measurement of the temperature and pressure variations inside the test tube during the residence time provided another evidence of the existence of pre-ignition chemical activity within the test mixture.

CHAPTER 4

FLAMMABILITY LIMITS OF SOME COMMON GASEOUS FUELS

The flammability limits reported in this investigation were determined experimentally for upward flame propagation at atmospheric pressure. All established values are reported as volumetric concentration of the fuel in the fuel-air mixture. The maximum uncertainty is $\pm 0.1\%$ for the lean limit and $\pm 0.15\%$ for the rich limit.

As mentioned previously, one of the aims of this research was to investigate the effect of the test tube material on the values of the flammability limits. The flammability limits were obtained in the stainless steel and quartz test tube at various initial temperatures. The effect of the duration of the residence time (the time of exposure of the test mixture to the elevated temperature before spark ignition) on the values of the flammability limits was also investigated.

The determined flammability limits of individual fuels presented in this chapter were also used as the basis in examining the applicability of Le Chatelier's rule to fuel mixtures considered in this investigation.

4.1 Effect of initial temperature

4.1.1 Experimental results

The experimental values of the flammability limits of methane, hydrogen, ethylene and carbon monoxide in air, determined in the stainless steel flame tube at different initial temperatures and a short residence time of 0.5 minutes, are presented Table 4.1.1.1 and Fig 4.1.1.1-4.1.1.4. As expected, with an increase in the initial

temperature, the flammable ranges of fuel-air mixtures broaden. The same trend was observed earlier (Coward, H. F. and Jones G. W., 1952; Wierzba, I. and Kilchyk, V., 2001; Wierzba, I. and Ale, B. B., 1999).

Table 4.1.1.1 Flammability limits of hydrogen, carbon monoxide, ethylene and methane, (% by volume), obtained in the stainless steel tube at the residence time of 0.5 min

Fuel	Temperature (°C)	Flammability limits (% by volume)	
		Lean	Rich
Hydrogen	25	3.9	74.7
	200	2.8	80.3
	300	2.4	82.6
Carbon Monoxide	25	13.6	66.5
	200	11.5	74.4
	300	10.3	76.1
Ethylene	25	3.0	32.9
	200	2.6	42.6
	300	2.4	48.8
Methane	25	4.9	14.0
	200	4.1	15.4
	300	3.8	17.0

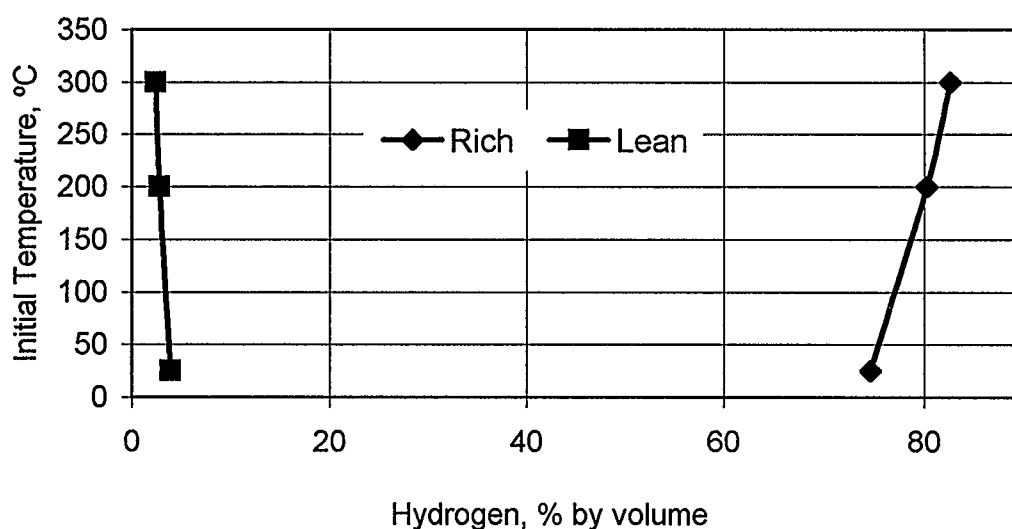


Figure 4.1.1.1 Flammability limits of hydrogen, established in the stainless steel tube at a residence time of 0.5 min

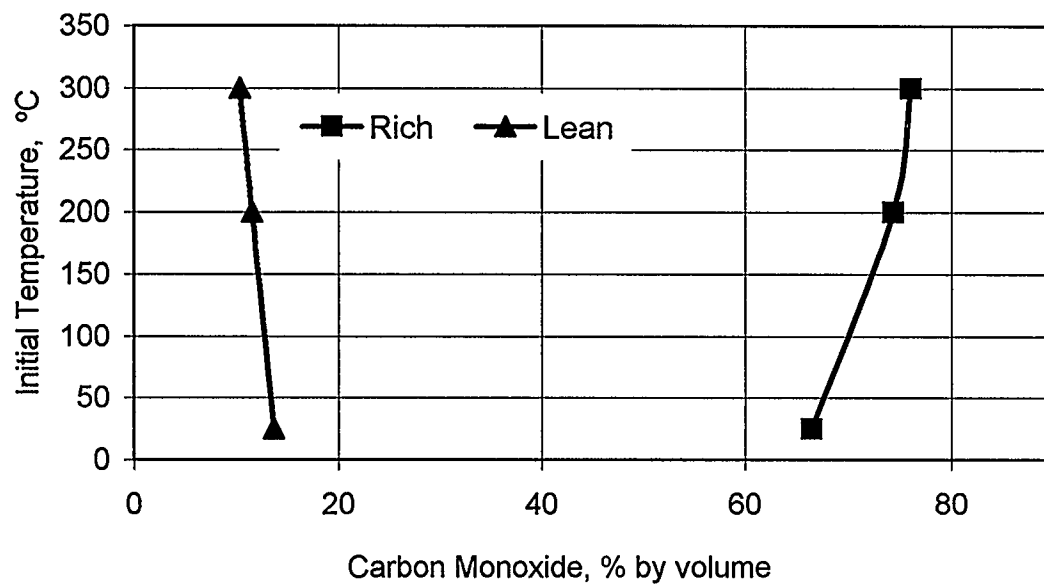


Figure 4.1.1.2 Flammability limits of carbon monoxide, established in the stainless steel tube at a residence time of 0.5 min

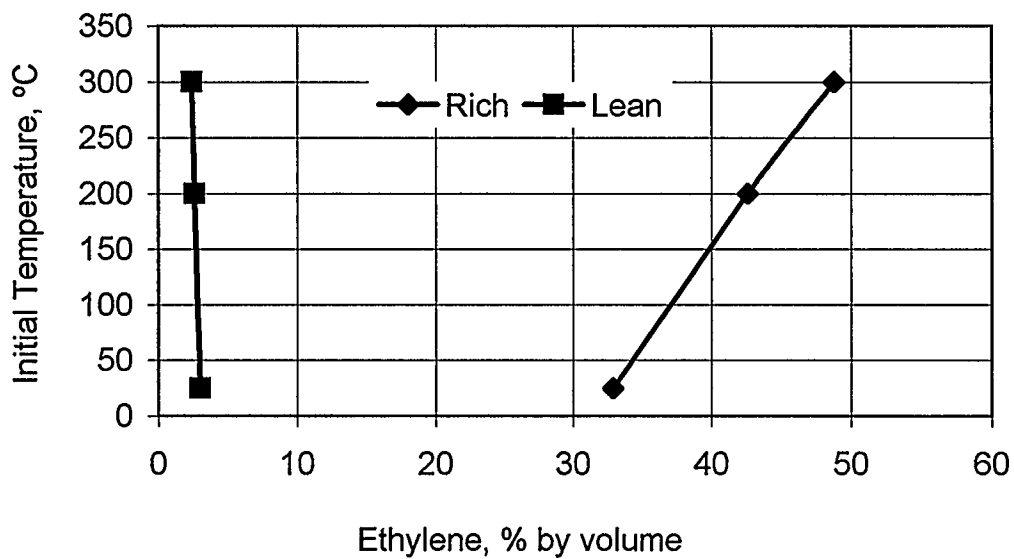


Figure 4.1.1.3 Flammability limits of ethylene established in the stainless steel tube at a residence time of 0.5 min.

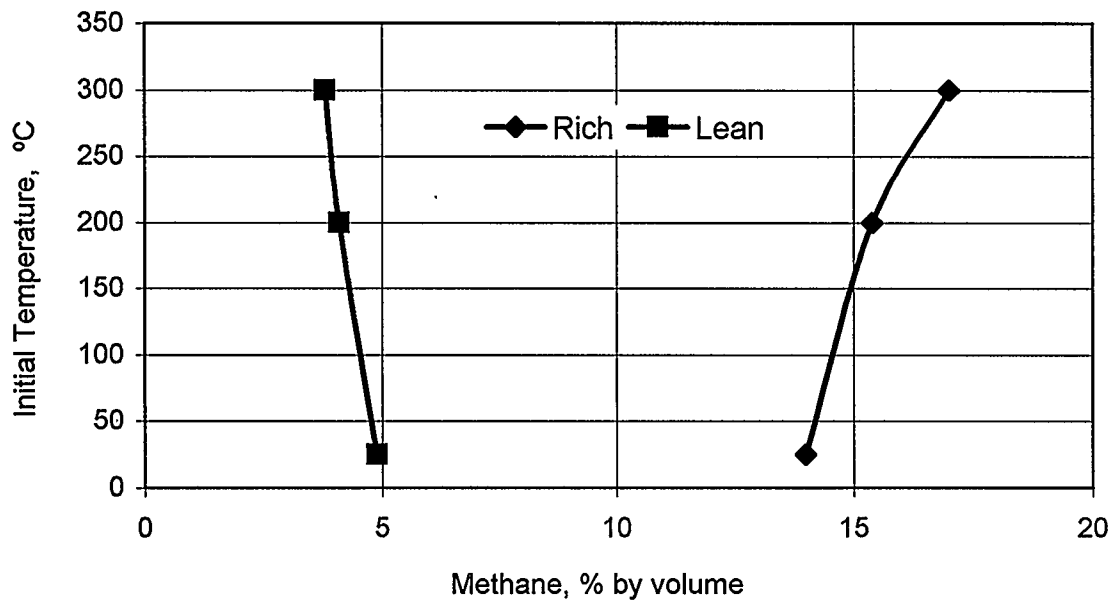


Figure 4.1.1.4 Flammability Limits of methane, established in the stainless steel tube at a residence time of 0.5min.

4.1.2 Prediction of values of the flammability limits at different initial temperatures

The flammability limits at an elevated initial temperature can be predicted according to the method of “the constant adiabatic flame temperature” (Bade Shrestha, S. O., et al., 1995). It is assumed that the adiabatic flame temperature has approximately the same value at the limit regardless of the initial temperature of the mixture. In this section, the limits calculated by this approach are compared with the corresponding experimental data.

For any fuel-air mixture, its adiabatic flame temperature can be calculated by applying the first law of thermodynamics to the test mixture within the flame tube, expressed as the following:

$$\left[\sum_i H_{i,reactant} \right]_{T_0} = \left[\sum_i H_{i,product} \right]_{T_f} \quad (4.1.2.1)$$

where,

$H_{i,reactant}$ is the enthalpy of the i species of the reactants at initial temperature T_0

$H_{i,product}$ is the enthalpy of the i species of the products at adiabatic flame temperature T_f

At the lean limits, the combustion products are primarily carbon dioxide, water, oxygen and nitrogen. Then, the overall reaction can be expressed as the following equation:

$$\begin{aligned} L_{L,T_0} (C_n H_m O_l) + (1 - L_{L,T_0}) (0.21 O_2 + 0.79 N_2) = \\ L_{L,T_0} n (CO_2) + L_{L,T_0} \frac{m}{2} (H_2O) + \left[0.21 + \left(\frac{l}{2} - n - \frac{m}{4} - 0.21 \right) L_{L,T_0} \right] O_2 + 0.79 (1 - L_{L,T_0}) N_2 \end{aligned} \quad (4.1.2.2)$$

where,

L_{L,T_0} is the lean flammability limit of the fuel at the initial temperature of T_0

n , m , and l are the numbers of the atoms of carbon, hydrogen, and oxygen in the fuel, respectively

The adiabatic flame temperature can be calculated from eq. (4.1.2.1) and (4.1.2.2) for the known value of the lean limit at a certain initial temperature. Then, the lean limit at another initial temperature can be calculated by assuming the same value of the product adiabatic temperature. Based on the experimental limit value at room temperature obtained in this work (Table 4.1.1.1), the adiabatic flame temperatures were calculated, as shown in Table 4.1.2.1. Using these values, lean flammability limits at 200 °C and 300 °C were calculated and compared with the corresponding experimental data (Table

4.1.2.2 and Fig. 4.1.2.1). It can be seen that this method gives an accurate estimation for the lean limits of carbon monoxide, ethylene and methane with the exception of hydrogen. In the case of hydrogen, the experimental value of the lean limit at 25°C was 3.9%, and based on this value, the calculated adiabatic flame temperature was extremely low (619K). It was suggested (Goldmann, F., 1929) that the actual flame temperature in the flame zone was higher than the calculated value, because significant amount of hydrogen diffused from surrounding unburned area to the flame zone due to high hydrogen diffusivity. As a result, the method on the basis of the calculated adiabatic flame temperature gives very significant deviations.

Table 4.1.2.1 Calculated adiabatic flame temperature for the lean limit mixtures at the initial temperature $T_0=25^\circ\text{C}$

Fuel	Hydrogen	Carbon monoxide	Ethylene	Methane
Lean limit (% by volume)	3.9	13.6	3.0	4.9
Adiabatic flame temperature (K)	619	1480	1474	1462

Table 4.1.2.2 Calculated lean limits of hydrogen, carbon monoxide, methane and ethylene, based on the experimental values at room temperature, % by volume

Initial temp. $^\circ\text{C}$	Lean flammability limit											
	Hydrogen			Carbon monoxide			Ethylene			Methane		
	Cal.	Exp.	Dev.	Cal.	Exp.	Dev.	Cal.	Exp.	Dev.	Cal.	Exp.	Dev.
200	1.80	2.8	-35.7	11.8	11.5	2.61	2.59	2.6	-0.38	4.22	4.1	2.93
300	0.58	2.4	-75.8	10.7	10.3	3.88	2.34	2.4	-2.40	3.82	3.8	0.53

Relative deviation, $\text{Dev.} = (L_{R,\text{Cal.}} - L_{R,\text{Exp.}}) / L_{R,\text{Exp}}$

In rich limit mixtures, deficient in oxygen, the combustion products may contain some carbon monoxide and hydrogen as well as some non-reacted fuel. It was suggested by Wierzba, I., et al. (1996) that the available oxygen in the mixture is firstly consumed to oxidize the carbon atoms of the fuel to form carbon monoxide, then the remaining oxygen oxidizes the available hydrogen in the fuel to form water and finally the remaining oxygen, if there is any, may contribute to the conversion of some carbon monoxide into carbon dioxide.

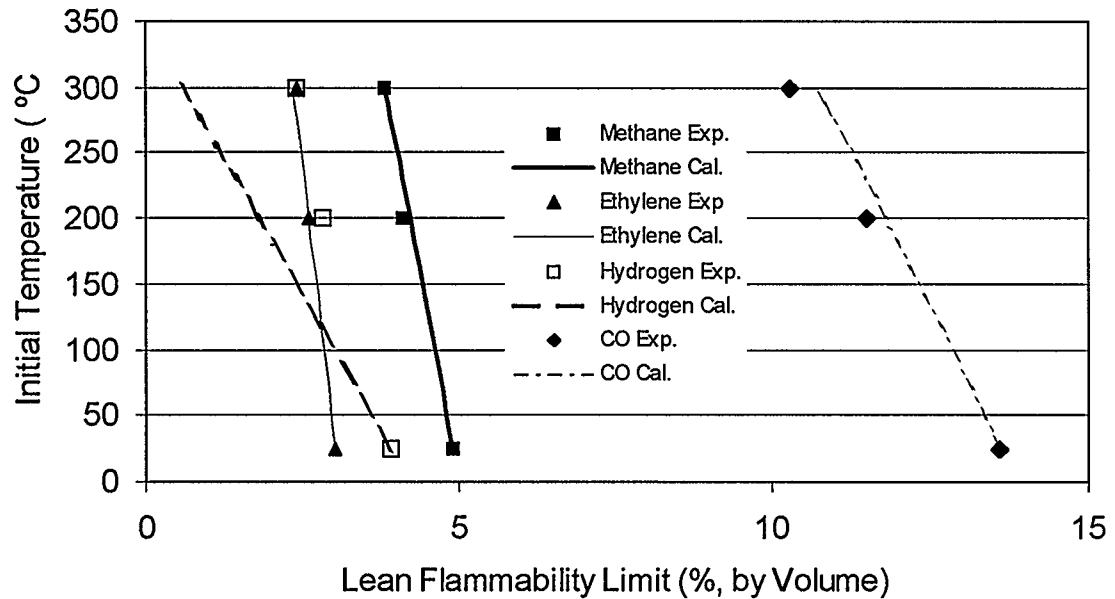


Figure 4.1.2.1 Experimental and calculated values of the lean flammability limits of hydrogen, carbon monoxide, methane and ethylene.

Applying these assumptions to the fuels investigated in this work and considering the range of the actual values of the rich limits, denoted as L_{R,T_0} in the equations, the overall reactions can be expressed as:

For hydrogen (L_{R,T_0} : 74%-83%):

$$\begin{aligned} L_{R,T_0} H_2 + (1 - L_{R,T_0})(0.21O_2 + 0.79N_2) = \\ 0.42(1 - L_{R,T_0})(H_2O) + (1.42L_{R,T_0} - 0.42)H_2 + 0.79(1 - L_{R,T_0})N_2 \end{aligned} \quad (4.1.2.3)$$

For carbon monoxide (L_{R,T_0} : 66%-77%):

$$\begin{aligned} L_{R,T_0} CO + (1 - L_{R,T_0})(0.21O_2 + 0.79N_2) = \\ 0.42(1 - L_{R,T_0})(CO_2) + (1.42L_{R,T_0} - 0.42)(CO) + 0.79(1 - L_{R,T_0})N_2 \end{aligned} \quad (4.1.2.4)$$

For methane (L_{R,T_0} : 13%-18%):

$$\begin{aligned} L_{R,T_0} (CH_4) + (1 - L_{R,T_0})(0.21O_2 + 0.79N_2) = \\ L_{R,T_0} (CO) + (0.42 - 1.42L_{R,T_0})(H_2O) + (3.42L_{R,T_0} - 0.42)H_2 + 0.79(1 - L_{R,T_0})N_2 \end{aligned} \quad (4.1.2.5)$$

For ethylene (L_{R,T_0} : 32%-52%):

$$\begin{aligned} L_{R,T_0} (C_2H_4) + (1 - L_{R,T_0})(0.21O_2 + 0.79N_2) = \\ 0.42(1 - L_{R,T_0})(CO) + 0.42(1 - L_{R,T_0})H_2 + (1.21L_{R,T_0} - 0.21)(C_2H_4) + 0.79(1 - L_{R,T_0})N_2 \end{aligned} \quad (4.1.2.6)$$

where,

L_{R,T_0} is the rich flammability limit of the fuel at the initial temperature of T_0

The flame adiabatic temperature can be calculated from eq. (4.1.2.1) and (4.1.2.3-4.1.2.6) for the known value of the rich limit at a certain initial temperature. Then, the rich limit at another initial temperature can be calculated by assuming the same value of the product adiabatic temperature. Based on the experimental limit value at room temperature obtained in this work (Table 4.1.1.1), the corresponding adiabatic flame temperatures for hydrogen, carbon monoxide, methane, and ethylene were calculated and are presented in Table 4.1.2.3. Using these temperatures values, the enthalpies of

products and the values of the rich flammability limits at 200 °C and 300 °C were calculated from Eq. 4.1.2.1 and the corresponding equation out of Eq. 4.1.2.3-4.1.2.6 and compared with the corresponding experimental data in Table 4.1.2.4 as well as Fig.4.1.2.2. The approach shows reasonable accuracy, when calculated values are compared with experimental data. The maximum relative deviation is around 6%, when the rich limits of ethylene were calculated.

Table 4.1.2.3 Calculated adiabatic flame temperature for the rich limit mixture at the initial temperature $T_0=25^\circ\text{C}$

Fuel	Hydrogen	Carbon monoxide	Ethylene	Methane
Rich limit (%, by volume)	74.7	66.5	32.9	14.0
Adiabatic flame temperature (K)	1179	1519	1105	1869

Table 4.1.2.4 Calculated rich limits of hydrogen, carbon monoxide, ethylene and methane, based on the experimental values at room temperature, % by volume

Initial temp. °C	Rich flammability limit											
	Hydrogen			Carbon monoxide			Ethylene			Methane		
	Cal.	Exp.	Dev.	Cal.	Exp.	Dev.	Cal.	Exp.	Dev.	Cal.	Exp.	Dev.
200	79.6	80.3	-0.87	70.8	74.4	-4.84	40.4	42.6	-5.16	15.3	15.4	-0.65
300	82.4	82.6	-0.24	73.3	76.1	-3.68	45.6	48.8	-6.56	16.1	17.0	-5.29

Relative deviation, $\text{Dev.} = (L_{R,\text{Cal.}} - L_{R,\text{Exp.}}) / L_{R,\text{Exp}}$

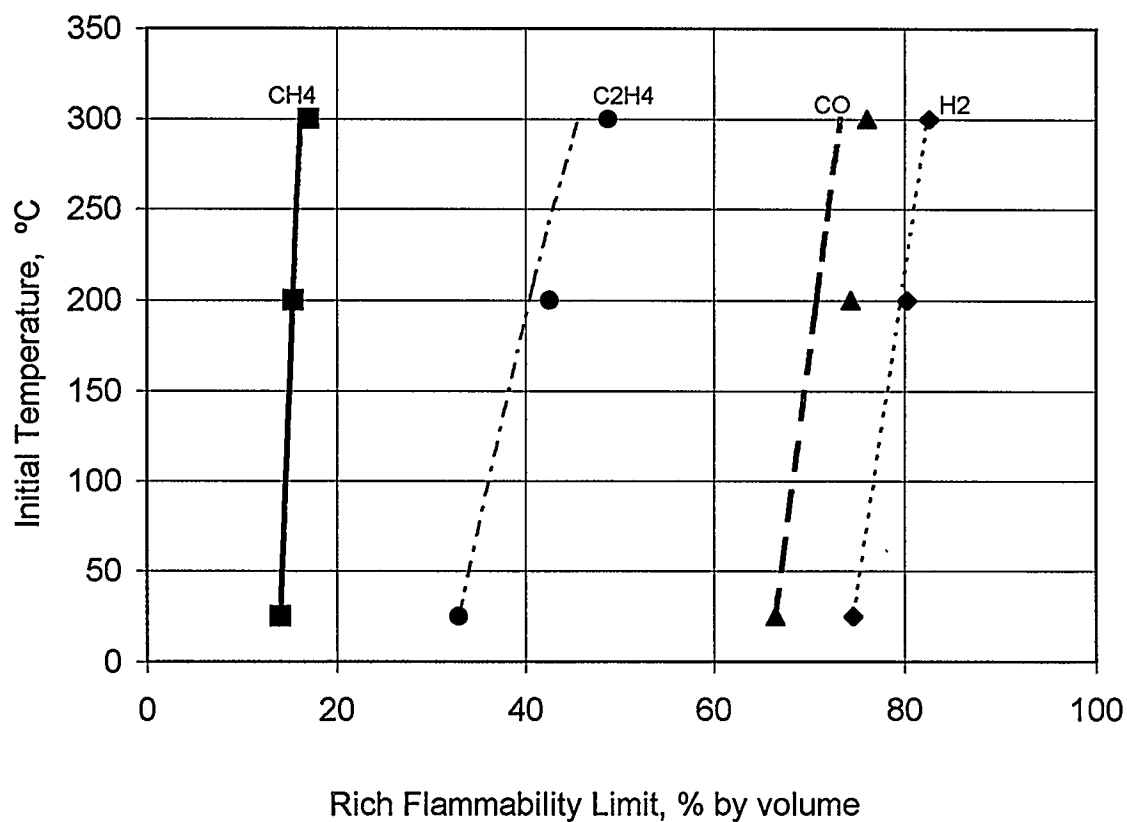


Figure 4.1.2.2 Experimental and calculated values of the rich flammability limits of hydrogen, carbon monoxide, ethylene and methane; symbols: experimental data; lines: calculated results.

4.2 Effects of the residence time and the material of the test tube on the rich flammability limit

It was reported earlier (Wierzba, I. and Ale, B. B., 1999; Wierzba, I. and Kilchyk, V., 2001) that the flammability limits of some gaseous fuels changed when the fuel-air mixtures exposed to elevated temperatures in the stainless steel tube for different periods of time before spark ignition. The effect was much stronger on the rich side than that on the lean side. The values of the rich flammability limits were found decreasing with an increase in the residence time. It was reported by Wierzba, I. et al. (1999, 2001) that there was some pre-ignition chemical activity in these situations and the existing pre-ignition reactions changed the initial mixture composition before spark ignition, and as a result, changed the value of the flammability limit. It was found that the oxygen concentration decreased during the residence time, and carbon dioxide was detected in the mixture. According to the previous studies involving the chemical kinetic simulation (Liu, Z., 1995), the gas-phase reactions at moderately elevated temperatures (up to 300°C) are very weak and could not cause significant changes in the mixture composition and the flammability limit values. Therefore, Wierzba, I. et al. (1999, 2001) concluded that the change in the value of the rich flammability limit is, probably, a result of surface oxidation reactions during the residence time with the stainless steel acting as a catalyst. To confirm this conclusion, the test were conducted in the new test tube made of quartz, a relatively inert material. As it was mentioned in the description of the experimental apparatus, the quartz test tube has the same dimensions as the stainless steel test tube and the same ignition system. The results obtained at the initial temperature of 300 °C and different residence times for both test tubes are presented and compared in this section.

The temperature of 300 °C was chosen, since the effect of the residence time and pre-ignition chemical activity are more pronounced at higher temperatures.

Methane. As it can be seen (Table 4.2.1), the rich flammability limit of methane was not affected either by the duration of the residence time or by the material of the test tube at this level of the initial temperature. The independence of the rich flammability limits from the residence time indicates that there was no pre-ignition chemical activity within these mixtures.

Table 4.2.1 Rich flammability limits of methane (% by volume), as a function of the residence time, at 300 °C.

Tube material	Residence time (min)		
	0.5	10	30
Quartz	17.0	17.0	17.0
Stainless steel	17.0	17.0	17.0

Carbon Monoxide. The rich flammability limits of carbon monoxide in air established for different residence times in both test tubes are presented in Table 4.2.2 and Fig. 4.2.1. It can be seen that the values of the rich limits established in the stainless steel test tube were affected by the duration of the residence time, which confirms previously reported results (Wierzba, I. and Ale, B. B. 1999; Wierzba, I. and Kilchyk, V., 2001). However, the values of the rich limits established in the quartz test tube were independent of the residence time at this initial temperature. This would suggest that pre-ignition chemical activity detected in the stainless steel test tube was the result of the surface reactions, and not that of gas-phase reactions.

Table 4.2.2 Rich flammability limits of carbon monoxide (% by volume), as a function of the residence time, at 300 °C.

Tube material	Residence time (min)		
	0.5	10	30
Quartz	76.8	76.8	76.8
Stainless steel	76.1	74.5	74.3

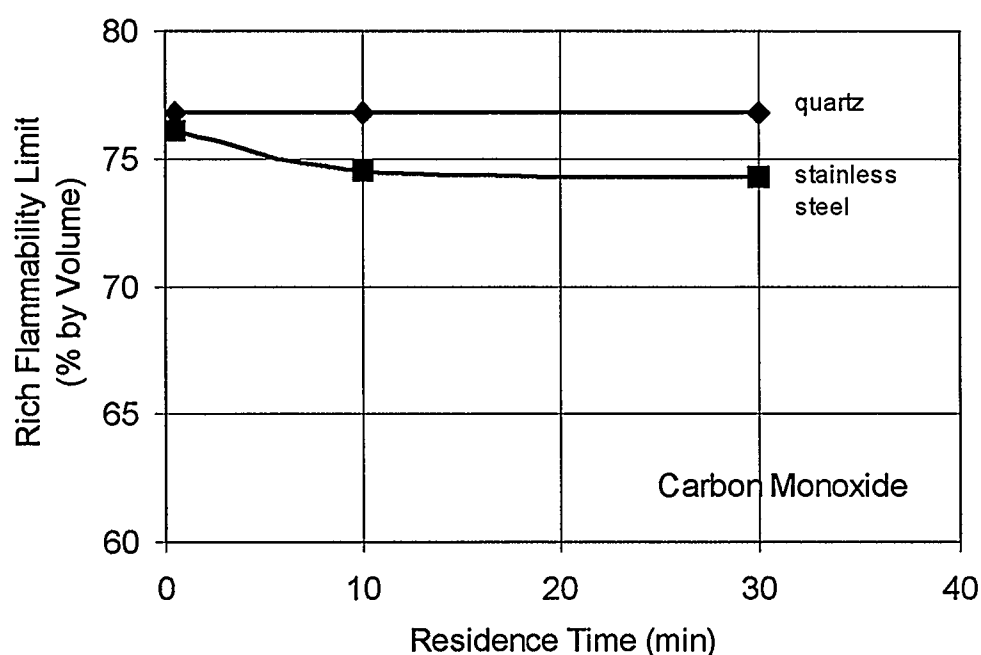


Figure 4.2.1 Rich flammability limits of carbon monoxide (% by volume), as a function of the residence time, at 300 °C.

Hydrogen: It can be seen (Table 4.2.3 and Fig. 4.2.2) that the rich flammability limit of hydrogen determined at 300 °C in either test tube was dependent on the duration of the residence time. Such behaviour indicates the presence of pre-ignition chemical activities even in the quartz test tube, which was rather unexpected. However, the effect of the residence time was less significant for the limits determined in the quartz test tube, which

would indicate that pre-ignition chemical activity is weaker in the quartz tube than that in the stainless-steel test tube. Assuming that catalytic properties of quartz are very weak, this would indicate the existence of gas-phase reactions within hydrogen-air mixtures at this relatively low temperature of 300°C. However, on the basis of these data alone, it is difficult to draw the final conclusion on the type of the reactions taking place during the residence time prior to the spark ignition.

Table 4.2.3 Rich flammability limits of hydrogen (% by volume), as a function of the residence time, at 300 °C.

Tube material	Residence time (min)		
	0.5	10	30
Quartz	82.9	77.1	75.5
Stainless steel	82.6	76.0	67.0

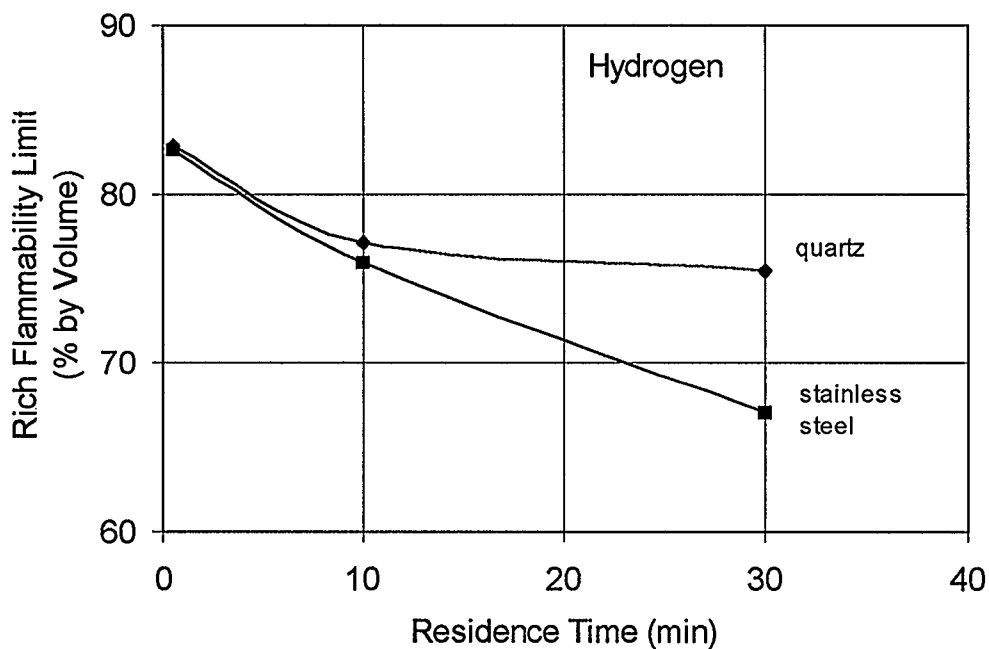


Figure 4.2.2 Rich flammability limits of hydrogen (% by volume), as a function of the residence time, at 300 °C.

Ethylene. The values of the rich flammability limits of ethylene established in the stainless steel and quartz test tubes for different residence times at the initial temperature of 300 °C are shown in Table 4.2.4 and Fig. 4.2.3.

Table 4.2.4 Rich flammability limits of ethylene, % by volume, as a function of the residence time, at 300 °C.

Tube material	Residence time (min)					
	0.5	10	20	30	60	120
Quartz	48.5	47.9	32.0	28.6	20.6	14.3
Stainless steel	48.8	48.6	35.1	26.3	17.1	—

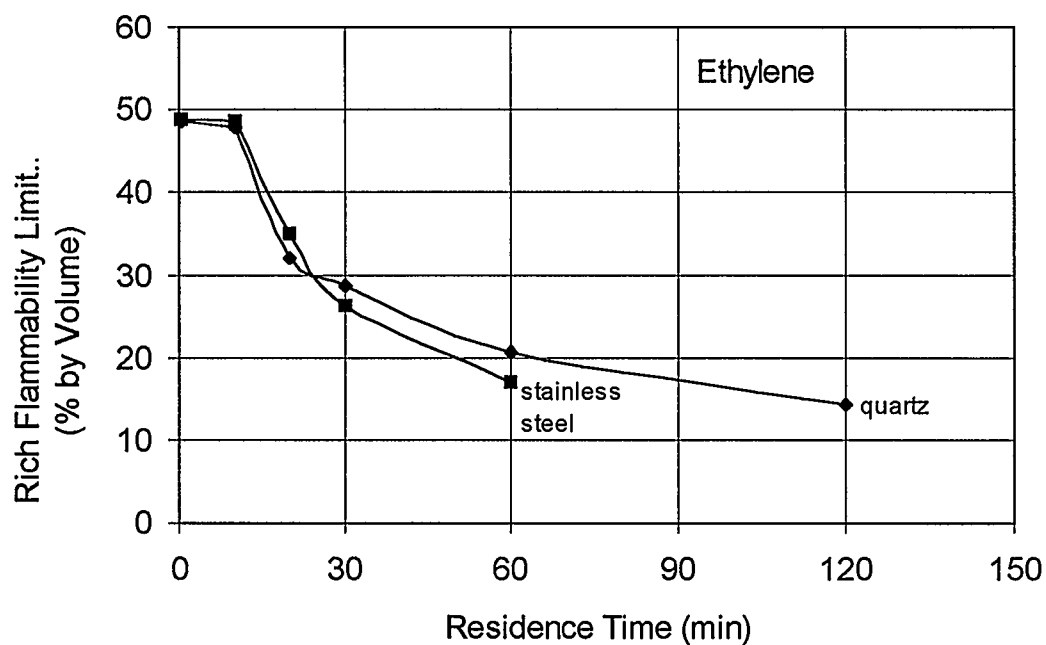


Figure 4.2.3 Rich flammability limits of ethylene (% by volume), as a function of the residence time, at 300 °C.

It can be noticed that the values of the rich flammability limits established in the two different test tubes behave very similarly within the range of the residence time from 0.5 minutes to 60 minutes, continuously decreasing, with the more significant change in the range of the residence time from 10 min. to 20 min. It can also be seen that the differences between the limit values obtained in the stainless steel tube and the quartz tube at the same conditions are not very significant. These results are rather unexpected and further investigation is needed to explain what was happening in the ethylene-air mixture during their exposure to the temperature of 300°C before spark ignition. There is a possibility that gas-phase reactions are dominant in the ethylene air mixture at this temperature.

If pre-ignition reactions occur in the mixture during the residence time, oxygen is consumed and at the moment of spark ignition, the mixture could be much richer than that initially prepared. Therefore, to be still flammable after a certain residence time, initial mixture has to have more oxygen and less fuel, i.e. the rich limit value decreases with an increase in the residence time. The changes in the flammability limits are related to the pre-ignition reactions, during which some oxygen is consumed. The temperature of all fuel-air mixtures tested remained constant during the waiting time in both test tubes, while the pressure varied depending on the type of the fuel used. At the conditions of constant volume and temperature, the variations in pressure were directly related to the changes in the total number of moles of the mixture, due to the pre-ignition chemical activity. In this research, the pressure variations during the residence time were monitored to verify the presence of some oxidation reactions. Moreover, the oxygen concentration in the test mixture was directly measured during the residence time by

Orsat apparatus. The results of oxygen concentration measurement are presented in Tables 4.2.5, 4.2.7, 4.2.9, and 4.2.10 as well as in Figs.4.2.4, 4.2.7,4.2.9 and 4.2.10. The results of the continuous monitoring of the test mixture pressure during the residence time are shown in Table 4.2.6 and 4.2.8 as well as Figs.4.2.5, 4.2.6, and 4.2.8.

Hydrogen. The variations of the oxygen concentration measured in various hydrogen-air mixtures at the end of different periods of residence times in both stainless steel and quartz tubes are presented in Table 4.2.5 and Fig. 4.2.4. The initial mixture composition corresponded to the rich limit for the duration of the residence time shown in the brackets in Table 4.2.5.

Table 4.2.5 Oxygen concentration within the hydrogen-air mixtures (% by volume), at the end of different residence times at 300 °C

Initial test mixture composition (Rich limit at residence time, τ , min)	Tube material	Residence time, min			
		0	10	30	60
77.1% H_2 +22.9%Air ($\tau=10$)	Quartz	4.81	3.98	3.70	—
75.5% H_2 +24.5%Air ($\tau=30$)		5.15	4.33	4.02	3.74
76% H_2 +24%Air ($\tau=10$)	Stainless steel	5.04	3.71	2.63	—
67% H_2 +33%Air ($\tau=30$)		6.93	5.61	3.97	2.96

It can be seen that the oxygen concentrations decrease much more rapidly in the stainless steel tube than that in the quartz tube. The value of the oxygen concentration, for example, drops from 5.15% to 4.02% after 30 minutes in the quartz flame tube, while at

the same conditions, the concentration decreases dramatically from 5.04% to 2.63% in the stainless steel test tube. This result is consistent with the corresponding changes in the value of the rich flammability limits. Although the initial compositions were different (Fig. 4.4.1), the variations in oxygen concentration have a similar trend in the same test tube.

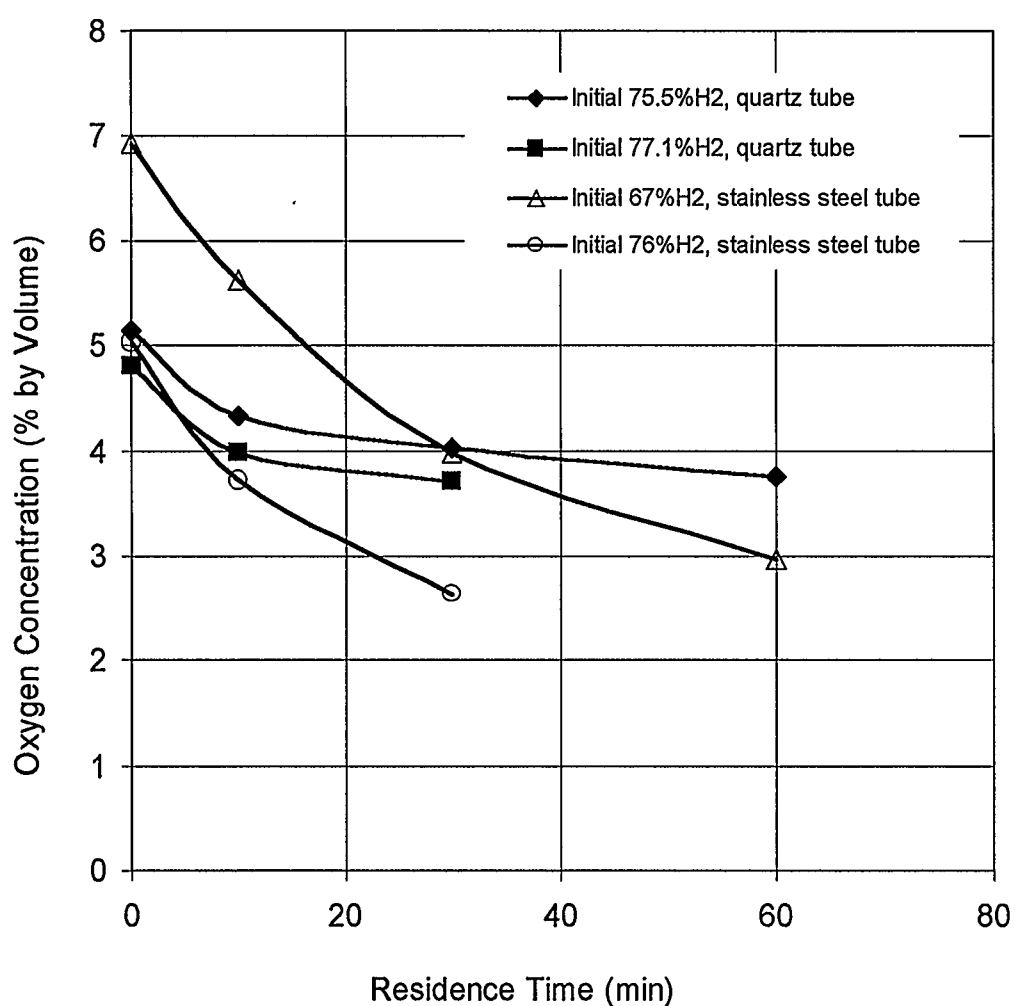


Figure 4.2.4 Oxygen concentration within hydrogen-air mixtures, as a function of the residence time at 300 °C

It can be seen that the rich limiting mixtures had approximately the same oxygen concentration at the end of the corresponding residence time just prior to the ignition. For example, the oxygen concentration of the limiting mixture established at the residence time of 30 min in the quartz test tube is 4.02% at the end of the residence time and the corresponding value of the mixture for the 10 min residence time is 3.98%.

Pre-ignition chemical activity can result in a gradual change of the total moles in the mixture with an increase in the duration of the residence time. Under constant temperature and constant volume conditions, for perfect gas, the pressure ratio is equal to the ratio of total moles of the mixture:

$$\frac{P_2}{P_1} = \frac{n_2}{n_1} \quad \text{or} \quad P_2 = P_1 \frac{n_2}{n_1} \quad (4.2.1)$$

where

P_1 is the initial pressure of the mixture

P_2 is the final pressure of the mixture, at the end of the residence time τ

n_1 is the initial total moles of the mixture

n_2 is the final total moles of the mixture, at the end of the residence time τ

The experimentally measured pressures during the residence time for different test mixtures are presented in Table 4.2.6 and Figs. 4.2.5 and 4.2.6. It can be seen that the pressure drop in the stainless steel test tube is much steeper than that in the quartz test tube. This phenomenon is consistent with the fact that oxygen consumption within the test mixture in the stainless steel tube was higher than that in the quartz tube.

Table 4.2.6 Pressure (kPa), within the test hydrogen-air mixtures, at different residence times, at 300°C.

Test tube	Initial test mixture composition (Rich limit at residence time, τ , min)	Residence time (min)						
		0	5	10	15	20	25	30
Quartz	77.1% H_2 ($\tau=10$)	100	99.8	99.5	99.3	99.1	98.8	98.6
	75.5% H_2 ($\tau=30$)	100	99.8	99.7	99.6	99.5	99.4	99.3
Stainless steel	76% H_2 ($\tau=10$)	100	99.3	98.7	98.3	97.8	97.4	97.0
	67% H_2 ($\tau=30$)	100	99.4	98.8	98.3	97.8	97.3	97.0

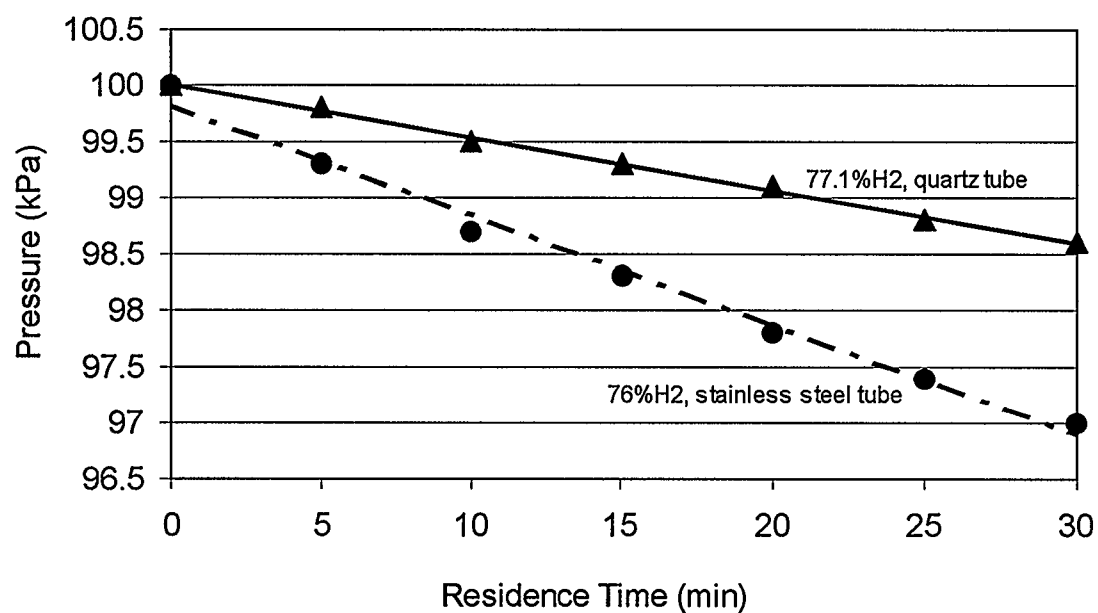


Figure 4.2.5 Pressure variations, within limiting hydrogen-air mixtures, as a function of the residence time at 300°C

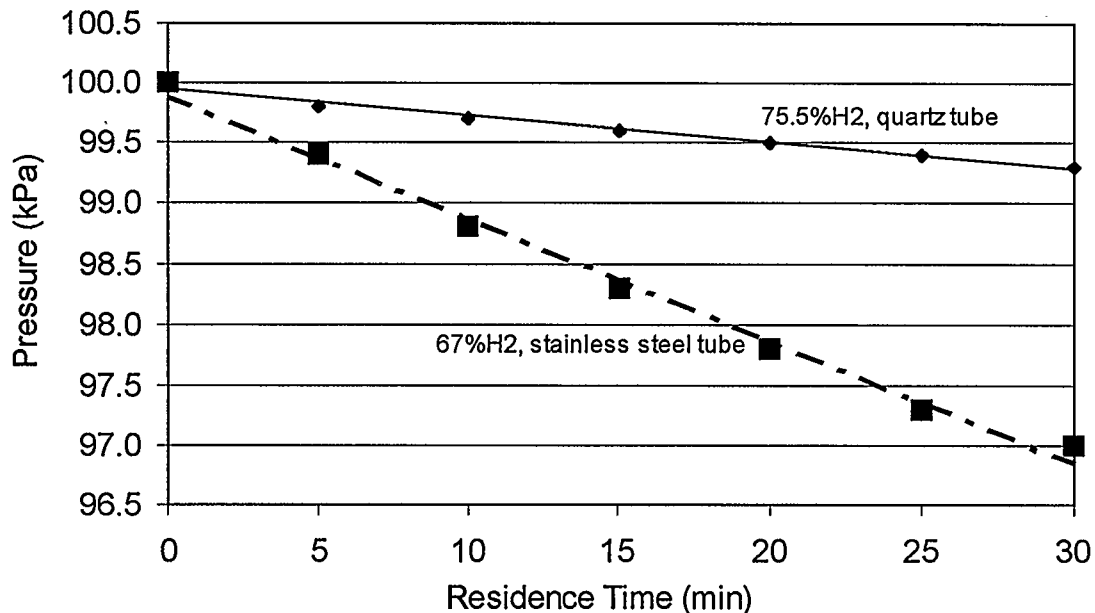


Figure 4.2.6 Pressure variations, within limiting hydrogen-air mixtures, as a function of the residence time at 300°C

Carbon Monoxide. The oxygen concentrations within carbon monoxide-air mixtures at the end of different residence times are presented in Table 4.2.7 and Fig. 4.2.7 for both stainless steel and quartz test tubes. The tested mixtures are the rich limiting for the residence times indicated in brackets in Table 4.2.7.

Table 4.2.7 Oxygen concentration within CO-air mixtures (% by volume), at the end of different residence times at 300 °C

Initial test mixture composition (rich limit at residence time, τ , min)	Tube material	Residence time (min)		
		0	10	30
76.8%CO+23.2%Air	Quartz	4.87	4.84	4.86
74.5%CO+25.5%Air ($\tau=30$)	Stainless steel	5.36	5.18	5.01

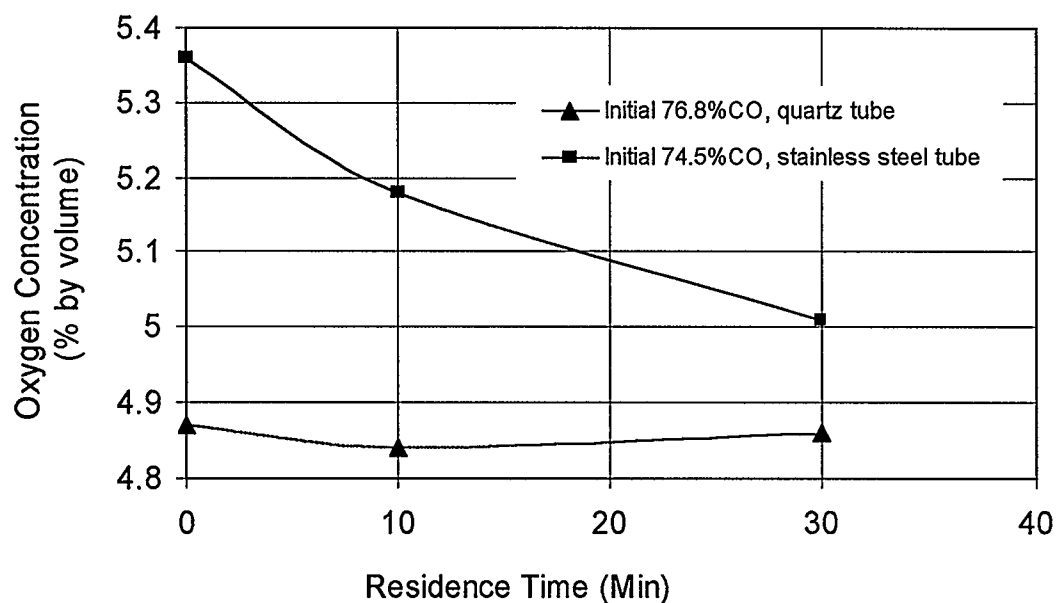


Figure 4.2.7 Oxygen concentration within CO-air mixtures, as a function of the residence time at 300 °C

As expected, the oxygen concentrations within the CO-air mixture in the quartz test tube remained unchanged for different durations of the residence times (small numerical difference are within the experimental error). This would indicate that there was no pre-ignition chemical activity. This is also consistent with the corresponding behaviour of the values of the rich limit, which is also unaffected by the duration of the residence time. However, in the stainless steel test tube, the mixture oxygen concentration decreased during the residence time, implying that there was pre-ignition chemical activity, which was probably promoted by the surface of the stainless steel test tube, acting as a catalyst.

The experimentally measured pressures during the residence time for different test mixtures are presented in Table 4.2.8 and Fig. 4.2.8. It can be seen that the pressure decreased in the stainless steel test tube, while it remained unchanged in the quartz test

tube. This phenomenon is consistent with the fact that oxygen was consumed within the test mixture in the stainless steel tube and was unchanged in the quartz tube.

Table 4.2.8 Pressure (kPa), within the test CO-air mixtures, at different residence times, at 300°C.

Test tube	Initial test mixture composition	Residence time (min)						
		0	5	10	15	20	25	30
Quartz	76.8%CO ($\tau=10$)	100	100	100	100	100	100	100
Stainless steel	74.5%CO ($\tau=10$)	100	99.9	99.7	99.6	99.5	99.4	99.3

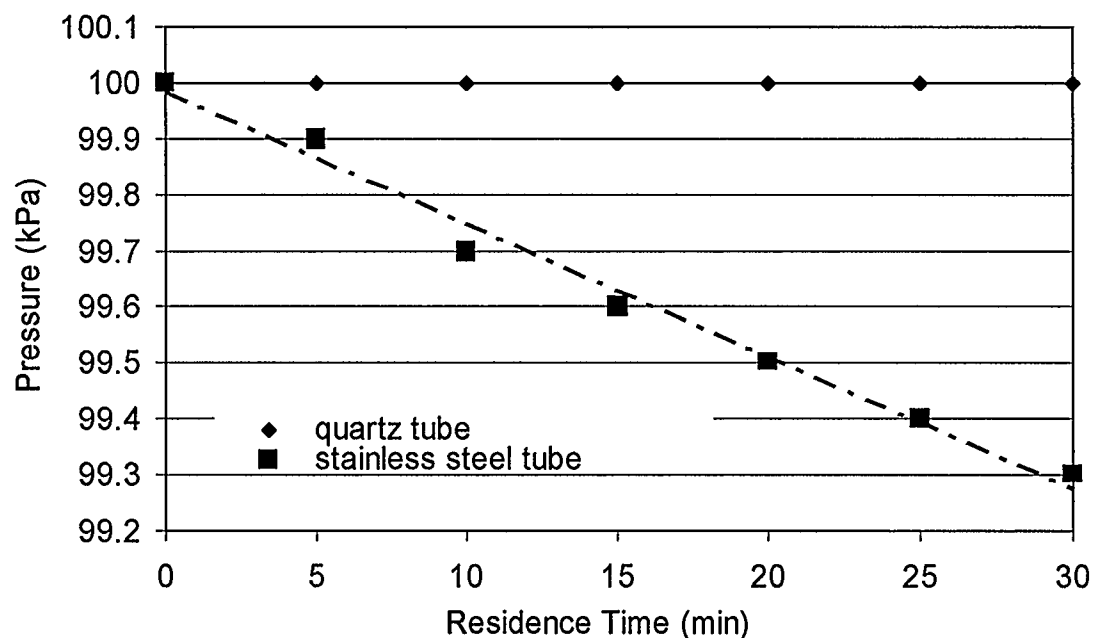


Figure 4.2.8 Pressure variations, within limiting CO-air mixtures, as a function of the residence time at 300°C

Ethylene. Table 4.2.9 and Fig. 4.2.9 show the variation of the oxygen concentration within the ethylene-air mixture with the initial composition of 32% C_2H_4 +68%air, at the residence time up to 60 min. and 300°C in the quartz test tube. It can be seen that the oxygen concentration decreases significantly with the duration of the exposure of the mixture to this temperature.

Table 4.2.9 Oxygen concentration within the ethylene-air mixture in the quartz test tube, at different residence times and 300 °C.

Initial mixture composition (% by volume)	Residence time, min				
	Initial	10	20	30	60
32% C_2H_4 +68%air	14.2	14.2	9.7	5.3	2.6

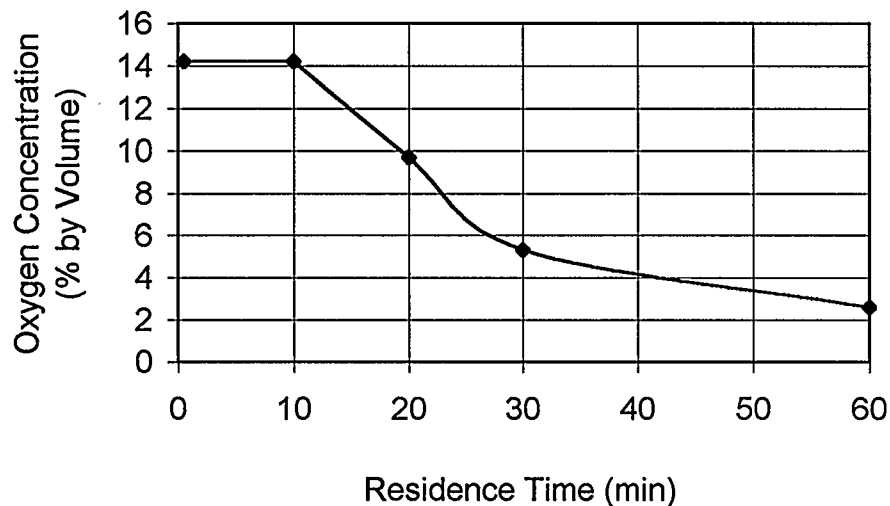


Figure 4.2.9 Oxygen concentration, as a function of the residence time at 300 °C in the quartz test tube. Initial mixture composition: 32% C_2H_4 +68%Air

This mixture was the rich limiting mixture at the residence time of 20 min, i.e. it was flammable for all residence times less than 20 min, and non-flammable for residence

time longer than 20 min. It appears that for the mixture to be flammable the oxygen concentration should be greater than the value measured at 20 min (9.7%). To check this, additional measurements were conducted. The oxygen concentrations were measured for the mixtures with the initial concentrations of ethylene in air of 48.5%, 47.9%, 32.0%, 28.6%, 20.6%, being the rich limiting mixtures at the residence time of 0.5, 10, 20, 30, 60 min respectively. The measurements were conducted at the end of corresponding residence time and the results are shown in Table 4.2.10

Although the initial oxygen concentration in limiting test mixtures increases with an increase in the residence time, the values of the oxygen concentrations at the end of the residence time, i.e. at the time of spark ignition, are very close for flammable mixtures (Table 4.2.10 and Fig. 4.2.10). This suggests that there is the minimum value of the oxygen concentration in the mixture at the moment of spark ignition required to sustain the flame propagation through the mixture.

Table 4.2.10 Oxygen concentration (% by volume), in the rich limiting ethylene-air mixtures, at the end of different residence times at 300 °C in the quartz test tube.

Concentration (% by volume)	Residence time, (min)				
	Initial	10	20	30	60
Initial C ₂ H ₄ Concentration (Rich Limit)	48.5	47.9	32.0	28.6	20.6
Initial O ₂ concentration	10.8	10.9	14.3	15.0	16.7
Final O ₂ concentration	10.8	10.8	9.7	9.4	9.2

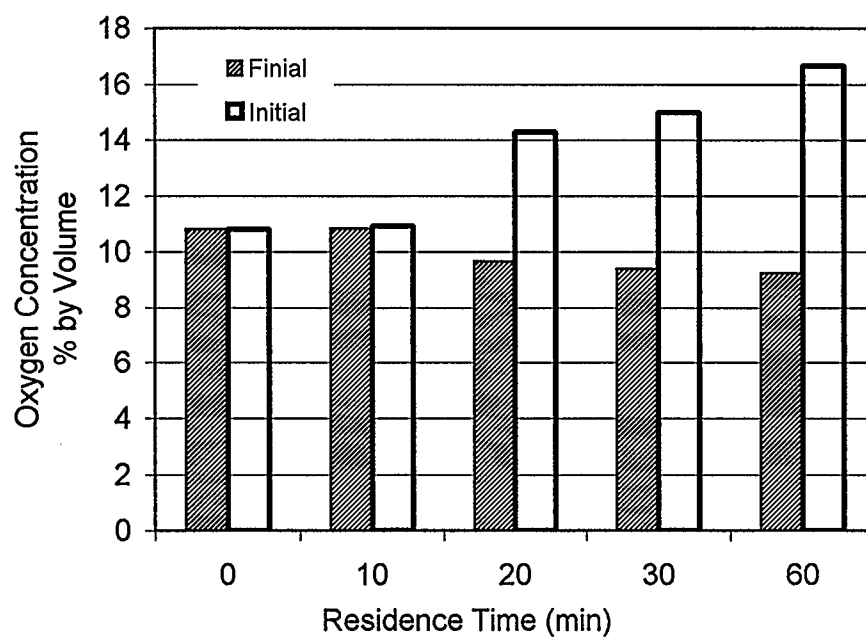


Figure 4.2.10 Oxygen concentrations of the C₂H₄-air mixtures with the compositions at the rich limits in the quartz tube at 300°C.

4.3 Prediction of fuel and oxygen consumption during the residence time

The concept of “the constant adiabatic flame temperature” at limit conditions, which was already discussed in the section 4.2, was employed again to predict the amount of fuel oxidized during the residence time. It can be assumed that the products of the pre-ignition fuel oxidation are primarily CO₂ and H₂O, which can be considered as diluents added to the fuel-air mixture. It was shown earlier that the concept of “the constant adiabatic flame temperature” allows to predict accurately the flammability limits of fuel-diluent-air mixtures (Wierzba, I., et al, 1996). In the present calculation, it was assumed that the adiabatic flame temperatures of the rich limiting mixtures were the same at the same initial temperature in the same apparatus, irrespective of the duration of the residence time. The adiabatic flame temperatures were calculated using the experimental value of the rich flammability limits established for very short residence time (0.5 minutes) and otherwise the same conditions. At a very short residence time, there was no pre-ignition chemical activity observed and the initial reactants remained the same at the time of spark ignition.

Hydrogen-air mixture. The adiabatic flame temperature was calculated on the basis of the following equations:

$$\left[\sum_i H_{i,reactant,l} \right]_{T_0} = \left[\sum_i H_{i,product,l} \right]_{T_f} \quad (4.3.1)$$

$$L_{R1}H_2 + (1 - L_{R1})(0.21O_2 + 0.79N_2) = 0.42(1 - L_{R1})(H_2O) + (1.42L_{R1} - 0.42)H_2 + 0.79(1 - L_{R1})N_2 \quad (4.3.2)$$

where,

L_{R1} is the experimentally determined rich limit with the very short residence time

($\tau = 0.5$) at the initial temperature T_o

$H_{i,reactant,1}$ is the enthalpy of the i species of the reactants at the initial temperature T_o and very short residence time ($\tau = 0.5$)

$H_{i,product,1}$ is the enthalpy of the i species of the products at adiabatic flame temperature T_f

The calculated adiabatic flame temperatures at $T_o=300^\circ\text{C}$ are 1172K in the stainless steel test tube and 1162K in the quartz test tube, correspondingly based on $L_{R1} = 82.6\%$ for stainless steel tube and $L_{R1} = 82.9\%$ for the quartz test tube.

When the mixture was exposed to the elevated temperature for a certain period of residence time τ , some hydrogen reacted and the mixture could contain some water vapour prior to spark ignition. It is proposed that the amount of hydrogen reacted during the longer residence time can be calculated assuming that the adiabatic flame temperature T_f for limiting mixture remains constant irrespective of the duration of the residence time. For such a limiting mixture the corresponding reaction equations are:

$$\left[\sum_i H_{i,reactant,2} \right]_{T_o} = \left[\sum_i H_{i,product,2} \right]_{T_f} \quad (4.3.3)$$

$$(L_{R2} - X)H_2 + X(H_2O) + [0.21(1 - L_{R2}) - 0.5X]O_2 + 0.79(1 - L_{R2})N_2 = 0.42(1 - L_{R2})(H_2O) + (1.42L_{R2} - 0.42)H_2 + 0.79(1 - L_{R2})N_2 \quad (4.3.4)$$

where,

L_{R2} is the experimentally determined rich limit at the residence time τ and the initial temperature T_0

$H_{i,reactant,2}$ is the enthalpy of the i species of the reactants at the end of the residence time under investigation and initial temperature T_0

$H_{i,product,2}$ is the enthalpy of the i species of the products at adiabatic flame temperature T_f

X is the amount of hydrogen converted to water, %,by volume

The parameter X , the amount of hydrogen reacted during the residence time, was directly calculated by solving Eqs. 4.3.3 and 4.3.4 and was not experimentally measured in this work. To check the validity of the method and its accuracy, the values of the reacted hydrogen were employed to calculate oxygen concentrations and the mixture pressure variations, which can be compared with corresponding experimental results. The concentration of the remaining oxygen in the fuel-air mixtures just before the spark ignition $O_{2\tau}$ is:

$$O_{2\tau} = \frac{0.21(1 - L_{R2}) - 0.5X}{1 - 0.5X} \quad (4.3.5)$$

The overall pre-ignition chemical reaction during the residence time can be described as the following:

$$L_{R2}H_2 + (1 - L_{R2})(0.21O_2 + 0.79N_2) = (L_{R2} - X)H_2 + X(H_2O) + [0.21(1 - L_{R2}) - 0.5X]O_2 + 0.79(1 - L_{R2})N_2 \quad (4.3.6)$$

As described earlier, the pre-ignition chemical activity can result in a gradual change of the total moles in the mixture with an increase in the duration of the residence time. Under constant temperature and constant volume conditions, for a perfect gas, the pressure ratio is equal to the ratio of total moles of the mixture. From the equations 4.2.1 & 4.3.6, the pressure variation is related to the hydrogen conversion as the following:

$$P_2 = \left(1 - \frac{X}{2}\right)P_1 \quad (4.3.7)$$

where

P_1 is the initial pressure of the mixture

P_2 is the final pressure of the mixture, at the end of the residence time τ

The calculated oxygen concentrations and final pressure values at different residence time are presented in Table 4.3.1. For comparison the corresponding measured oxygen concentrations and final pressures are also shown. It can be seen that the method allows to predict the consumption of oxygen due to the pre-ignition oxidation of hydrogen fairly well. It can also be noted that the method predicts a constant concentration of the remaining oxygen before spark ignition for the mixture to be flammable.

Table 4.3.1 Fuel conversion, oxygen concentration and pressure variation within the hydrogen-air mixture during the residence time at 300°C; initial pressure, $P_1=100\text{kPa}$

Material of test tube	Adiabatic flame temperature (K)	Rich limits (% by volume)	Res. time (min)	Hydrogen conversion X (% by volume)	Initial oxygen concentration %	Oxygen concentration (% by volume)			Final Pressure (kPa)		
						Cal.	Exp.	Dev. %	Cal.	Exp.	Dev. %
Stainless steel	1172	76.0	10	2.783	5.04	3.70	3.71	-0.27	98.61	98.7	-0.09
		67.0	30	6.568	6.93	3.77	3.97	-5.04	96.72	97.0	-0.29
Quartz	1162	77.1	10	2.447	4.81	3.63	3.98	-8.79	98.78	99.5	-0.72
		75.5	30	3.124	5.15	3.64	4.02	-9.45	98.44	99.3	-0.89

Relative deviation, $\text{Dev.} = (\text{Cal.} - \text{Exp.}) / \text{Exp.}$.

Carbon monoxide-air mixtures. Similarly to the case of hydrogen-air mixture, the approach of constant adiabatic flame temperature was employed for CO-air mixtures to calculate the changes in fuel and oxygen concentrations in the stainless steel test tube. A similar procedure was followed. For a short residence time of 0.5 min, the overall reaction is:

$$L_{R1}CO + (1 - L_{R1})(0.21O_2 + 0.79N_2) = 0.42(1 - L_{R1})(CO_2) + (1.42L_{R1} - 0.42)CO + 0.79(1 - L_{R1})N_2 \quad (4.3.8)$$

where,

L_{R1} is the experimentally determined rich limit with the very short residence time

($\tau = 0.5$) at the initial temperature T_0 .

For the rich limit of 76.1% CO obtained at the initial temperature of 300°C and residence time of 0.5 min, the adiabatic flame temperature T_f calculated on the basis of this equation and Eq. 4.3.1 is 1428K. This value was also assumed for the other residence times of 10 & 30 min. Assuming that for these residence times of 10 & 30 min, there is some pre-ignition chemical activity, the following equation can be written:

$$(L_{R2} - X)CO + X(CO_2) + [0.21(1 - L_{R2}) - 0.5X]O_2 + 0.79(1 - L_{R2})N_2 = 0.42(1 - L_{R2})(CO_2) + (1.42L_{R2} - 0.42)CO + 0.79(1 - L_{R2})N_2 \quad (4.3.9)$$

where

X is the amount of CO oxidized into CO₂ during the residence time, % by volume

L_{R2} is the experimentally determined rich limit at the residence time τ and the initial temperature T_o

From the above equation, the oxygen concentration is:

$$O_{2\tau} = \frac{0.21(1 - L_{R2}) - 0.5X}{1 - 0.5X} \quad (4.3.10)$$

And the pressure variation during the residence time is:

$$P_2 = \left(1 - \frac{X}{2}\right)P_1 \quad (4.3.11)$$

The calculated values of the fuel conversion, oxygen concentrations and mixture pressure variation are presented in Table 4.3.2. The corresponding experimental data are also shown for comparison.

Table 4.3.2 Fuel conversion, oxygen concentration and pressure variation within the CO-air mixtures during the residence time at 300°C; initial pressure, $P_1=100\text{kPa}$

Residence time (min)	Rich limit (% by volume)	CO conversion, X (% by volume)	Initial oxygen concentration %	Oxygen concentration (% by volume)			Final pressure (kPa)		
				Cal.	Exp.	Dev. %	Cal.	Exp.	Dev. %
10	74.5	0.6634	5.36	5.040	5.18	-2.70	99.67	99.7	-0.03
30	74.3	0.7477	5.40	5.042	5.05	-0.16	99.63	99.3	0.07

Relative deviation, $\text{Dev.}=(\text{Cal.}-\text{Exp.})/\text{Exp.}$

It can be seen that the method accurately predicts oxygen consumption within the CO-air mixture during the residence time. The calculation also shown that at the moment of spark ignition the minimum oxygen concentration in the flammable CO-air mixtures at 300°C should be above 5.04%.

Ethylene-air mixtures. The approach of “constant adiabatic flame temperature” was employed to calculate the changes in oxygen concentration of the ethylene-air mixtures in the quartz test tube. A similar procedure was followed in the calculations as that described for hydrogen and carbon monoxide.

The adiabatic flame temperature was calculated on the basis of the value of the rich flammability limit of C_2H_4 -air mixture, established at the initial temperature of $300^\circ C$ and residence time of 0.5 min, using Eq 4.3.1 and the following reaction equation:

$$L_{R1}(C_2H_4) + (1 - L_{R1})(0.21O_2 + 0.79N_2) = 0.42(1 - L_{R1})(CO) + 0.42(1 - L_{R1})H_2 + (1.21L_{R1} - 0.21)(C_2H_4) + 0.79(1 - L_{R1})N_2 \quad (4.3.12)$$

For the rich limit of 48.5% at $300^\circ C$, the calculated adiabatic flame temperature for this condition is 1068K. Assuming that a certain amount of the ethylene (X) was reacted during the residence time, producing CO_2 and H_2O , the following equation can be written:

$$(L_{R2} - X)(C_2H_4) + 2X(CO_2) + 2X(H_2O) + (0.21 - 0.21L_{R2} - 3X)O_2 + 0.79(1 - L_R)N_2 = 2(0.21 - 0.21L_{R2} - 3X)(CO) + 2(0.21 - 0.21L_{R2} - 3X)H_2 + (1.21L_{R2} + 2X - 0.21)(C_2H_4) + 2X(CO_2) + 2X(H_2O) + 0.79(1 - L_R)N_2 \quad (4.3.13)$$

This equation allows to calculate the value of X at the end of the residence time on the basis of the known value of the corresponding rich limit L_{R2} , and the adiabatic flame temperature at the initial temperature T_0 .

From the above equation, the concentration of O_2 and CO_2 can be derived as follows.

$$O_{2\tau} = 0.21(1 - L_{R2}) - 3X \quad (4.3.14)$$

$$CO_{2\tau} = 2X \quad (4.3.15)$$

The calculated fuel conversion X as well as the concentrations of O_2 and CO_2 are presented in Table 4.3.3. For comparison, the corresponding experimental data are also shown.

Table 4.3.3 Fuel conversion and the concentrations of O_2 and CO_2 within the C_2H_4 -air mixtures in the quartz test tube at $300^\circ C$ for different residence times

Residence time (min)	Rich limits (% by volume)	Ethylene conversion, X , %	Initial oxygen concentration %	O ₂ concentration (% by volume)			CO ₂ concentration (% by volume)		
				Cal.	Exp.	Dev. %	Cal.	Exp.	Dev. %
10	47.9	0.06	10.94	10.757	10.83	-0.67	0.12	0	
20	32.0	1.70	14.28	9.182	9.66	-4.95	3.40	3.64	-6.59
30	28.6	2.05	14.99	8.845	9.38	-5.70	4.10	4.56	-10.09
60	20.6	2.88	16.67	8.053	9.22	-12.66	5.75	6.45	-10.85

Relative deviation, $Dev. = (Cal. - Exp.) / Exp.$

It can be seen that in the case of C_2H_4 -air mixtures the oxygen concentration at the time of ignition does not remain constant. As it was mentioned before that the behaviour of the rich flammability limit of C_2H_4 with respect to the residence time is almost identical in the both test tubes: stainless steel and quartz tubes. It would indicate that gas-phase reactions are the dominant pre-ignition reactions and in this case the assumption that the C_2H_4 is oxidized to CO_2 and H_2O may not be valid. The products of C_2H_4 conversion during the residence time could contain some CO.

CHAPTER 5

FLAMMABILITY LIMITS OF H_2 , CO AND CH_4 MIXTURES IN AIR

Hydrogen has increasingly drawn attention recently because of its potential as a fuel in the future. The mixtures of hydrogen, carbon monoxide and methane may appear in the hydrogen production process. The knowledge of the flammability limits of such mixtures is necessary to evaluate the hazards of fire and explosion in such circumstances.

Although much research has already been conducted on the flammability limit of fuel mixtures (Coward, H.F. and Jones, G.W., 1952; Zabetakis, M.G., 1965; Wierzba, I., et al, 1985; Hustad, J.E. and Sonju, O.K., 1988; Shebeko, Yu.N., et al, 1995), there are still many questions that cannot be answered adequately. For example, there is lack of information on the flammability limits of fuel mixtures at elevated temperatures or pressures and lack of a reliable method to predict the flammability limits under such conditions.

As discussed in Chapter 4, the flammability limits of individual fuels such as hydrogen, carbon monoxide and methane are affected by the initial temperature and in some extent by the residence time and material of the test tube. The effects of these above parameters on the flammability limits of some H_2 -CO- CH_4 mixtures were investigated and are discussed in this Chapter. Also in this Chapter, the experimentally obtained flammability limits of H_2 -CO- CH_4 mixtures are compared with the corresponding predicted values calculated from the well known and widely used Le Chatelier's rule.

Moreover, the limits were also calculated using the “constant adiabatic flame temperature” approach.

5.1 Flammability limits of H₂-CO-CH₄ mixtures in air with a short residence time

5.1.1 Effect of initial temperature

As expected, the flammability limits of H₂-CO-CH₄ mixtures exhibit a similar behaviour to that of individual fuels making up the fuel mixtures i.e. H₂, CO, or CH₄. Table 5.1.1.1 and Figs. 5.1.1.1-5.1.1.2 present the experimental values of the lean and rich limits of the various fuel mixtures, containing H₂, CO, and CH₄, obtained at a short residence time of 0.5 min in the stainless steel test tube. It can be seen that the flammable ranges of these mixtures widen with an increase in the initial temperature.

Table 5.1.1.1 Flammability limits of some H₂-CO-CH₄ mixtures, stainless steel tube, residence time of 0.5 min.

Fuel composition %			Temp. °C	Lean limit %	Rich limit %
H ₂	CO	CH ₄			
20	40	40	25	6.0	27.0
			200	5.0	29.5
			300	4.4	31.5
50	25	25	25	5.0	34.8
			200	3.8	39.0
			300	3.1	43.2
80	10	10	25	4.2	48.1
			200	3.2	54.4
			300	2.6	58.6

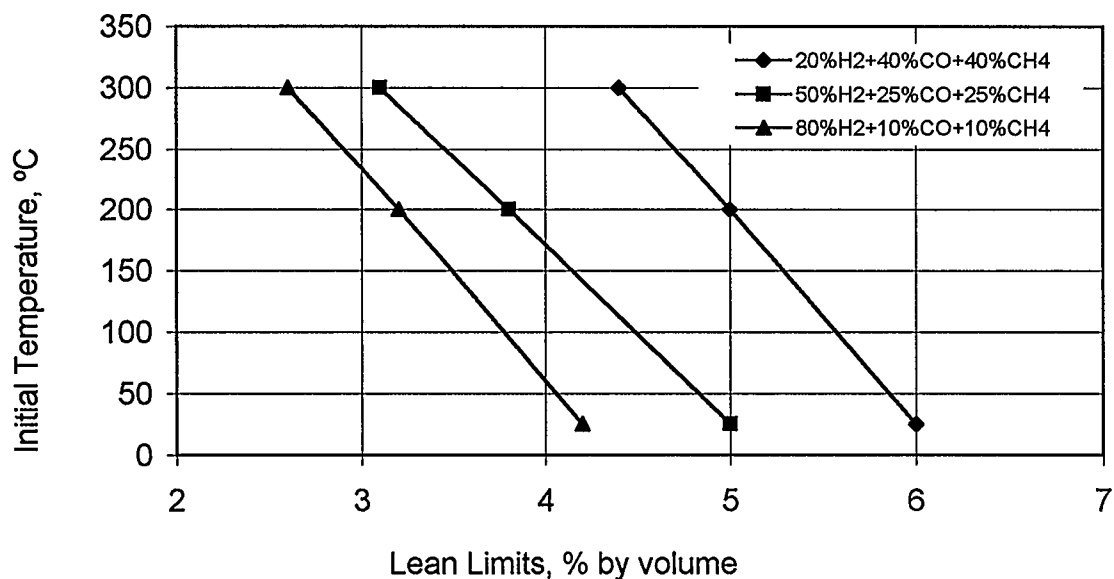


Figure 5.1.1.1 Lean flammability limits of H₂-CO-CH₄ mixtures in the stainless steel test tube as a function of the initial temperature at a residence time of 0.5 min.

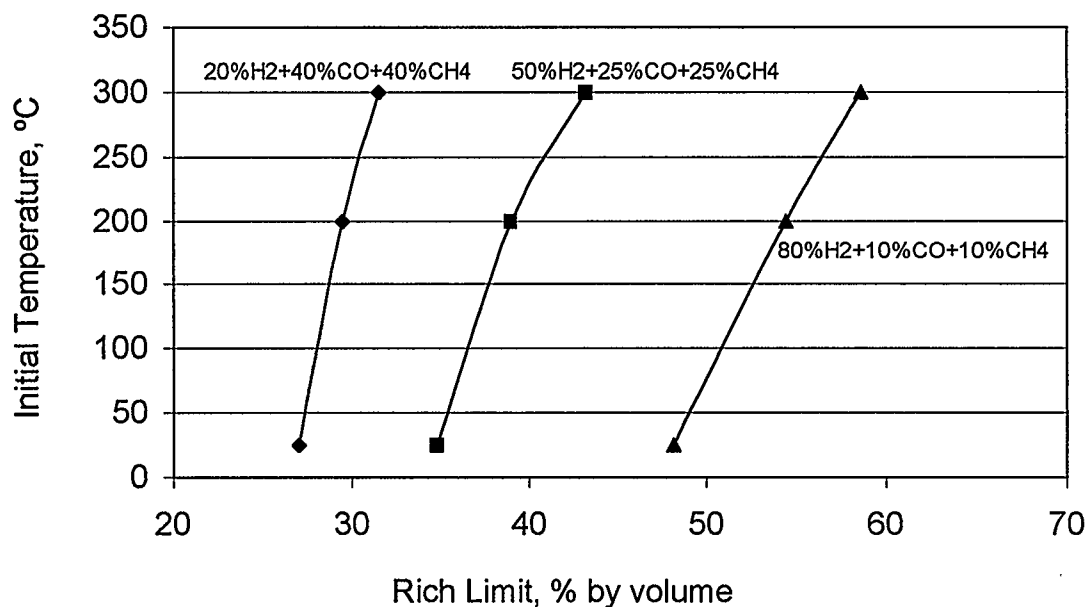


Figure 5.1.1.2 Rich flammability limits of H₂-CO-CH₄ mixtures in the stainless steel test tube as a function of the initial temperature at a residence time of 0.5 min.

It can be seen that at short residence times the flammable ranges of all tested fuel mixtures widen with an increase in the initial temperature.

5.1.2 Prediction of the flammability limits of H₂-CO-CH₄ fuel mixtures in air- the application of Le Chatelier's rule

Le Chatelier's rule is the commonly used method to predict the flammability limits of fuel mixtures. The rule suggests that a mixture of limiting fuel-air mixtures is also a limiting mixture. It is based on the mixture composition and the flammability limits of each component in the mixture on its own in air at the same conditions. It may be expressed as:

$$L_m = \left(\sum_{i=1}^n \frac{Y_i}{L_i} \right)^{-1} \quad (5.1.2.1)$$

where

L_m is the calculated flammability limit of the mixture, (vol. %).

L_i is the flammability limit of the i^{th} fuel component, (vol. %).

Y_i is the volumetric fraction of the i^{th} fuel component in the fuel mixture, (vol. %).

The objective of this section is to examine the validity of this rule in the prediction of the flammability limits of H₂-CO-CH₄ mixtures. The values of the lean flammability limits of fuel mixtures of H₂, CO, and CH₄ calculated using Le Chatelier's rule are compared with the corresponding experimental values in Table 5.1.2.1 and Fig. 5.1.2.1. It

can be seen that Le Chatelier's rule allow to predict the values of the lean limit reasonably well for short residence time of 0.5 min. It was noted that the largest deviations were observed at higher temperatures for the mixture with higher hydrogen concentration and relatively small amount of methane (10%) and carbon monoxide (10%). A similar trend was reported for hydrogen-methane mixtures with small concentrations of methane (Wierzba, I. et al, 1986).

Table 5.1.2.1 Lean flammability limits of H₂-CO-CH₄ mixtures in air, calculated and experimental, stainless steel test tube, residence time of 0.5 min.

Composition %			Initial temperature (°C)	Calculated limit (L _C) %	Experimental limit (L _E) %	Relative deviation (L _C -L _E)/L _E %
H ₂	CO	CH ₄				
20	40	40	25	6.16	6.0	2.67
50	25	25		4.91	5.0	-1.80
80	10	10		4.40	4.4	0
20	40	40	200	5.06	5.0	1.20
50	25	25		3.83	3.8	0.79
80	10	10		3.35	3.1	8.06
20	40	40	300	4.29	4.2	2.14
50	25	25		3.14	3.2	-1.88
80	10	10		2.71	2.6	4.23

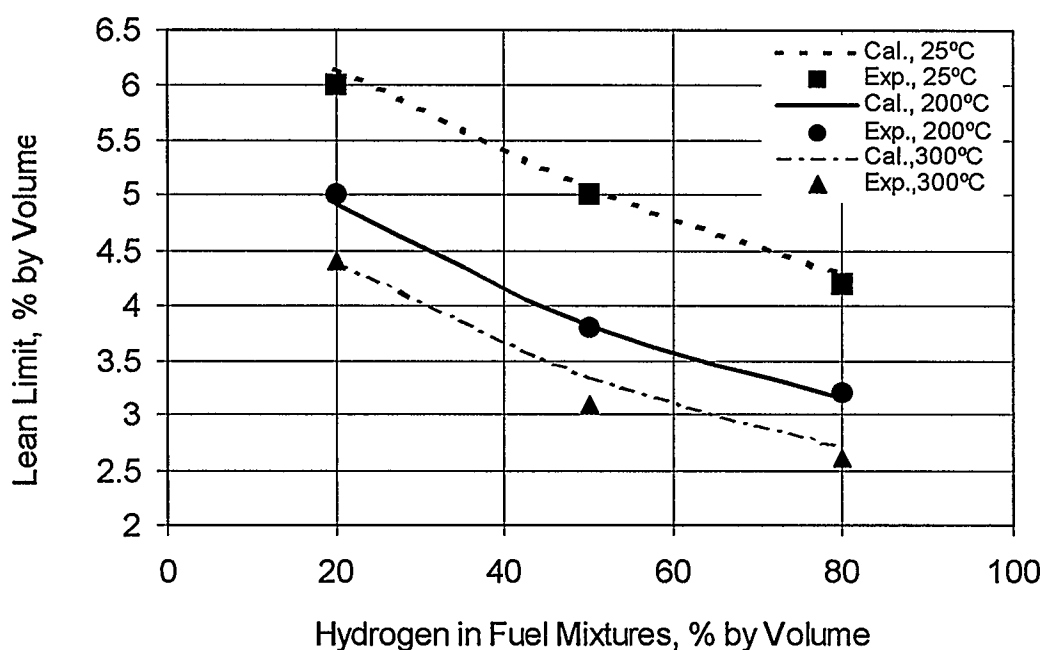


Figure 5.1.2.1 Lean flammability limits of $\text{H}_2\text{-CO-CH}_4$ mixtures in air, calculated and experimental, stainless steel test tube, residence time of 0.5 min.

The calculated and experimental values of rich flammability limits of $\text{H}_2\text{-CO-CH}_4$ mixtures with the concentration ratio of $\text{CO/CH}_4=1$ at 200°C and very short residence time (0.5 min) are presented in Table 5.1.2.2 and Fig. 5.1.2.2.

Table 5.1.2.2. Rich flammability limits of $\text{H}_2\text{-CO-CH}_4$ mixtures in air, calculated and experimental, stainless steel test tube, at 200°C , residence time of 0.5 min. $\text{CO/CH}_4=1$

Composition %			Calculated rich limit (L_C) %	Experimental rich limit (L_E) %	Relatively deviation (L_C-L_E)/ L_E %
H_2	CO	CH_4			
4	48	48	26.2	25.7	1.95
20	40	40	29.6	29.5	0.34
50	25	25	38.7	39.0	-0.77
80	10	10	56.2	54.4	3.31

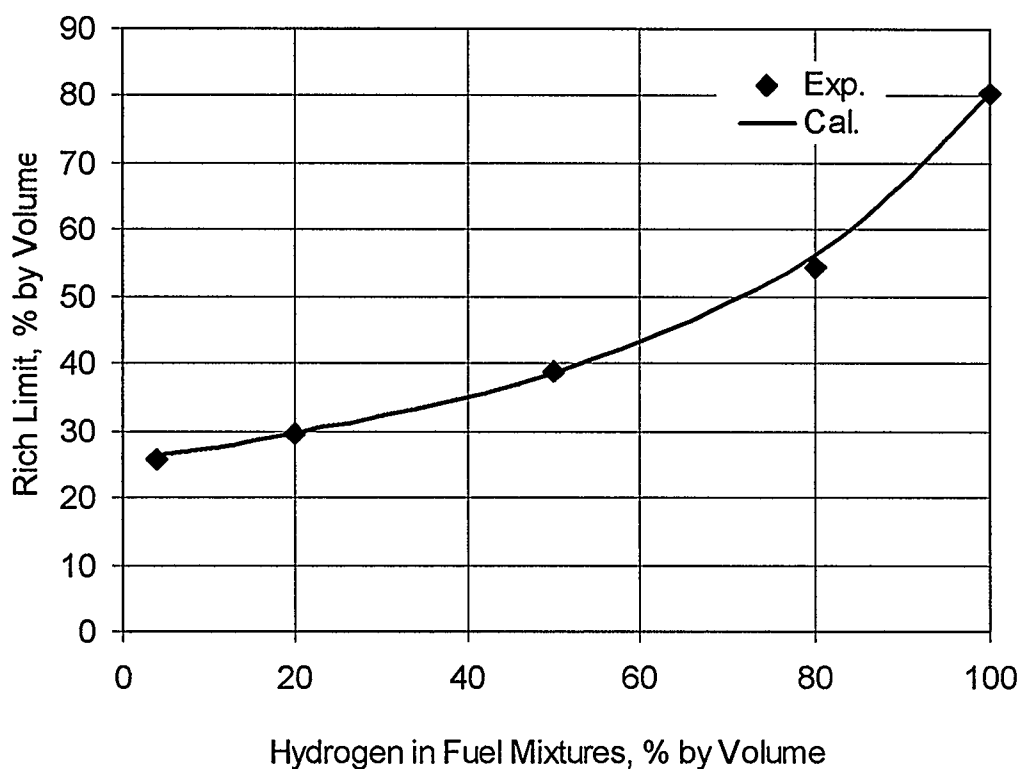


Figure 5.1.2.2 Rich flammability limits of H_2 -CO- CH_4 mixtures in air, calculated and experimental, stainless steel test tube, at $200^\circ C$, residence time of 0.5 min. $CO/CH_4=1$

It can be seen that the deviations of the calculated limits from the corresponding experimental values were very small. Relatively larger deviations occurred at very high and very low hydrogen concentration.

In the above fuel mixtures the concentration ratio of CO/CH_4 was 1. To investigate the effect of CO/CH_4 ratio on the rich flammability limit and the accuracy of the Le Chatelier's rule, the rich flammability limits of other H_2 -CO- CH_4 mixtures with various CO/CH_4 ratio were experimentally determined. Table 5.1.2.3 and Fig. 5.1.2.3 present the rich flammability limits of H_2 -CO- CH_4 mixtures with a fixed hydrogen concentration of

80% at 200 °C. The largest deviation was observed at the highest CO concentration in this case.

Table 5.1.2.3. Rich flammability limits H_2 -CO- CH_4 mixtures of 80% hydrogen, calculated and experimental, stainless steel test tube, at 200°C, residence time of 0.5 min.

Composition %			Calculated rich limit (L_C) %	Experimental rich limit (L_E) %	Relatively deviation (L_C-L_E)/ L_E %
H_2	CO	CH_4			
80	2.5	17.5	46.2	46.3	-0.22
80	5	15	49.1	49.0	0.20
80	10	10	56.2	54.4	3.31
80	15	5	65.7	61.9	6.14

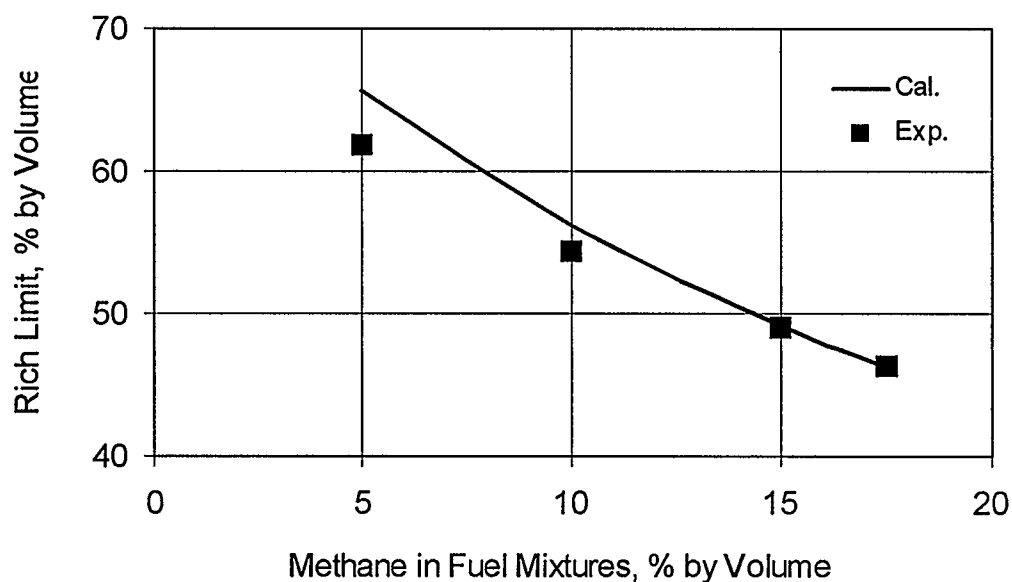


Figure 5.1.2.3. Rich flammability limits of H_2 -CO- CH_4 mixtures of 80% hydrogen, calculated and experimental, stainless steel test tube, at 200°C, residence time of 0.5 min.

Further investigation was conducted at a higher temperature. The calculated and experimental rich limits of different H_2 -CO- CH_4 mixtures at 300°C and a very short

residence time (0.5 min) are presented in Table 5.1.2.4 and Figure 5.1.2.4. It can be seen that the largest deviation was less than 8%.

Table 5.1.2.4. Rich flammability limits of H₂-CO-CH₄ mixtures in air, calculated and experimental, stainless steel test tube, at 300°C, residence time of 0.5 min.

Fuel Composition % by volume			Rich limit % by volume		
H ₂	CO	CH ₄	L _{R,Cal}	L _{R,Exp}	D _R [*] , %
20	20	60	24.8	24.0	3.33
20	40	40	32.0	31.5	1.59
20	60	20	45.3	45.1	0.44
50	12.5	37.5	33.6	36.5	-7.95
50	25	25	41.6	43.2	-3.70
50	37.5	12.5	54.5	54.1	0.74
80	5	15	52.2	52.5	-0.57
80	10	10	59.2	58.6	1.02
80	15	5	68.5	66.9	2.44

*Relative deviation, $D_R = (L_{R,Cal} - L_{R,Exp}) / L_{R,Exp}$

In general, Le Chatelier's rule predicts reasonably well the flammability limits of the tertiary H₂-CO-CH₄ fuel mixtures at moderate elevated temperatures up to 300°C.

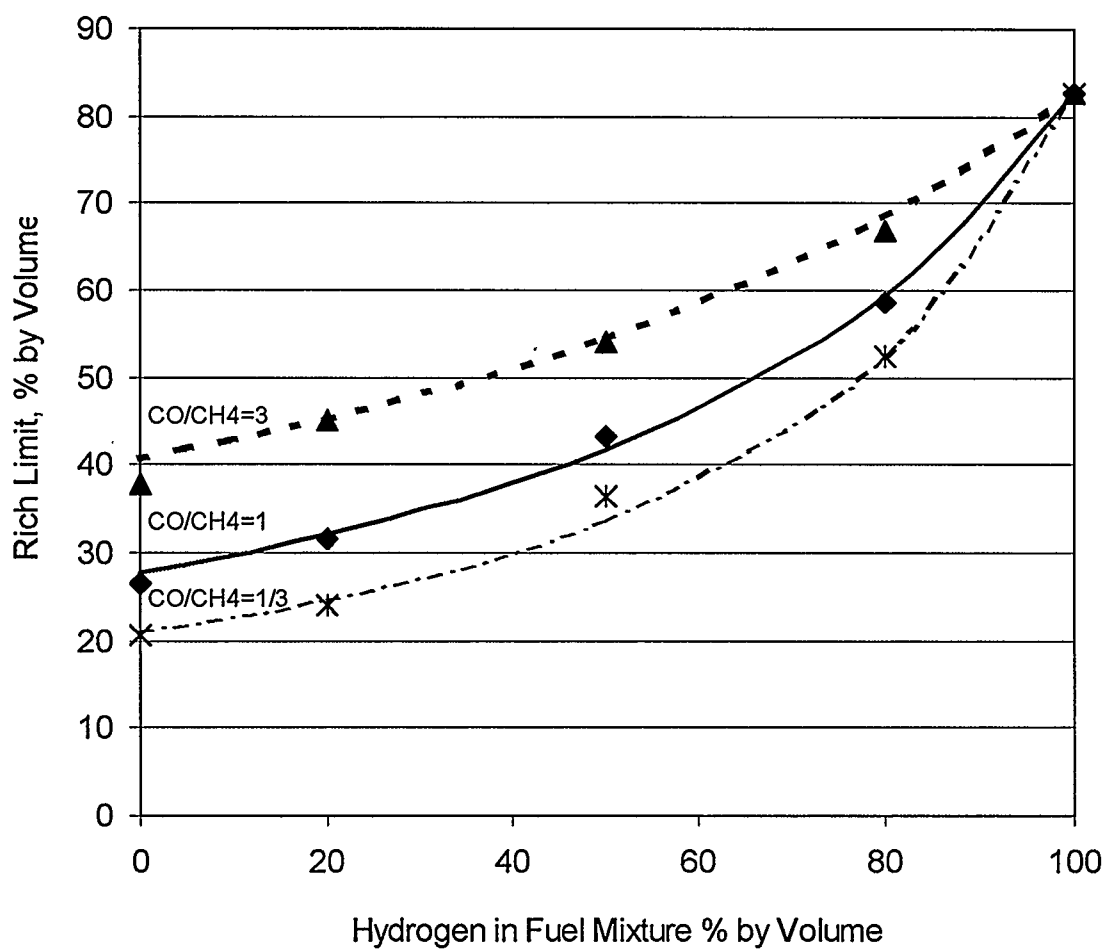


Figure 5.1.2.4. Rich flammability limits of H₂-CO-CH₄ mixtures in air, calculated and experimental, stainless steel test tube, at 300°C, residence time of 0.5 min; symbols: experimental data; lines: calculated values.

5.2 Effect of residence time and the material of test tube on the rich flammability limits

It was shown earlier (Chapter 4) that at elevated temperatures the duration of the residence time had an effect on the value of the rich flammability limits of H_2 and CO and this effect was dependent on whether the limits are determined in the stainless steel or quartz test tube. The limits of hydrogen were affected most significantly. The rich limit of hydrogen, established either in the stainless steel test tube or in the quartz tube decreased with an increase in the residence time and the decrease was much more significant in the stainless steel tube. The rich limit of carbon monoxide established in the stainless steel test tube was affected by the duration of the residence time to a lesser extent than hydrogen, while the value of the limit determined in the quartz tube was independent of the residence time. The rich limits of methane established in either of these two test tubes were unaffected by the residence time duration. As discussed in the last Chapter, the variation of the limit value with the residence time was caused by the pre-ignition chemical activity and the intensity of this chemical activity was influenced by the type of the fuel and the material of the test tube. Consequently, it can be expected that the duration of the residence time and the material of the test tube would also have an effect on the values of the rich limits of the fuel mixtures made up of these three fuels.

The rich flammability limits of two different mixtures, one containing high hydrogen concentration of 80% and the other containing relatively small hydrogen concentration of 20%, determined experimentally for various residence times at 300°C in both two test tubes, are presented in Table 5.2.1 and Fig. 5.2.1. As expected, the more of hydrogen was in the fuel mixture, the stronger was the effect of the residence time on rich

limit. In the stainless steel test tube, the value of the rich limit of the fuel mixture containing 80% of H_2 , 15% of CO and 5% of CH_4 dropped from 65.4% at $\tau = 0.5$ min to 58.1% at $\tau = 30$ min. Under the same conditions, the rich limit of the fuel mixture containing 20% of H_2 , 60% of CO and 20% of CH_4 decreased only from 44.6% to 42.8%. Moreover, it can be seen that the rich limit was much less affected by the residence time in the quartz test tube than that in the stainless steel tube, especially of the mixtures with higher hydrogen concentration (Fig. 5.2.1). For example, the value of the rich limit of the mixture with 80% of hydrogen established in the quartz test tube decreased by only 2.3% when the residence time increased from 0.5 min to 30 min, while the corresponding decrease in the value determined in the stainless steel tube was 7.3%.

Table 5.2.1 Rich flammability limits of H_2 - CO- CH_4 mixtures in air at 300°C with different residence times.

Fuel composition, % by volume			Residence time, min	Rich limit, % by volume					
				Quartz test tube			Stainless steel test tube		
H_2	CO	CH_4		$L_{R,Cal}$	$L_{R,Exp}$	$D_R^*, \%$	$L_{R,Cal}$	$L_{R,Exp}$	$D_R^*, \%$
80	15	5	0.5	68.8	67.8	1.47	68.5	65.4	4.74
			10	65.5	66.6	-1.65	64.6	63.2	2.22
			30	64.6	65.5	-1.37	59.2	58.1	1.89
20	60	20	0.5	45.5	45.5	0	45.3	44.6	1.57
			10	45.1	45.5	-0.88	44.5	44.1	0.91
			30	45.0	45.3	-0.66	43.8	42.8	2.34

*Relative deviation, $D_R = (L_{R,Cal} - L_{R,Exp})/L_{R,Exp}$

It is of interest to check whether Le Chatelier's rule is applicable to predict the rich limit of H_2 -CO- CH_4 mixture at different residence times, using corresponding limit

values for individual fuels in air at the same residence time. The results of such calculations are also presented in Table 5.2.1 and Figure 5.2.1 for comparison. It can be seen that the deviations were below 5 % for the tested mixtures.

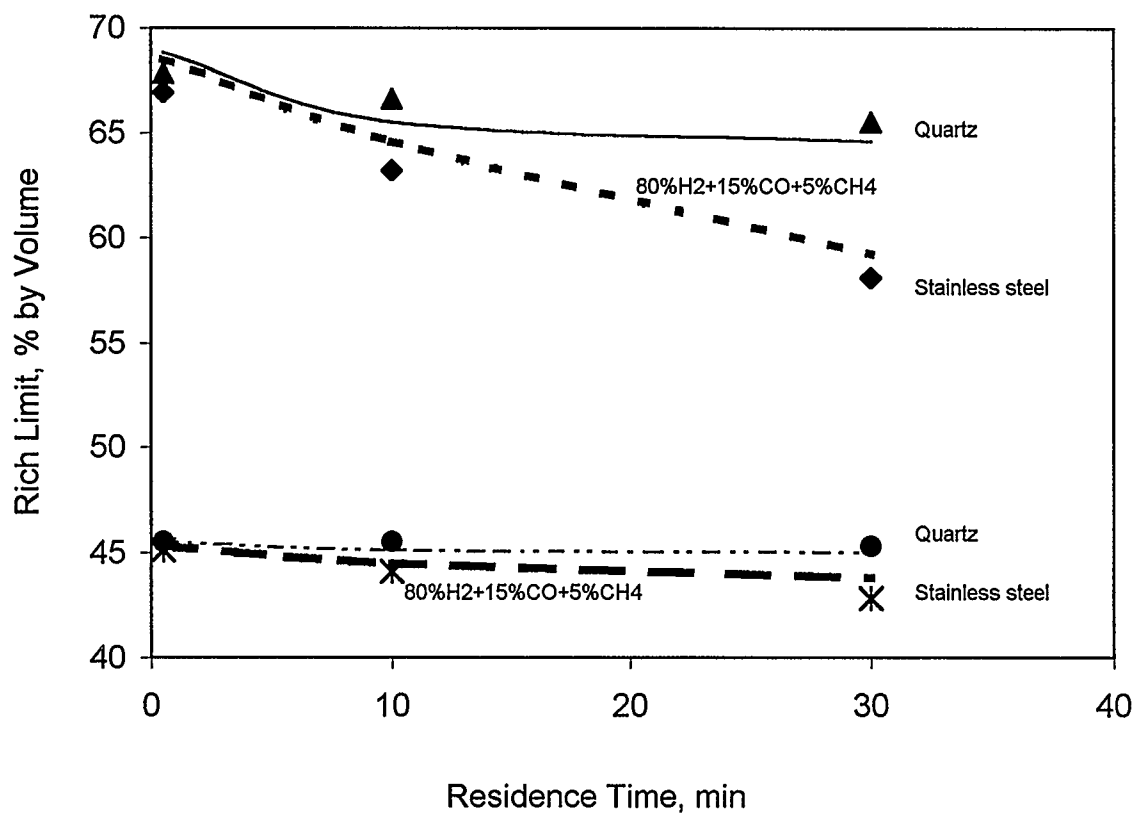
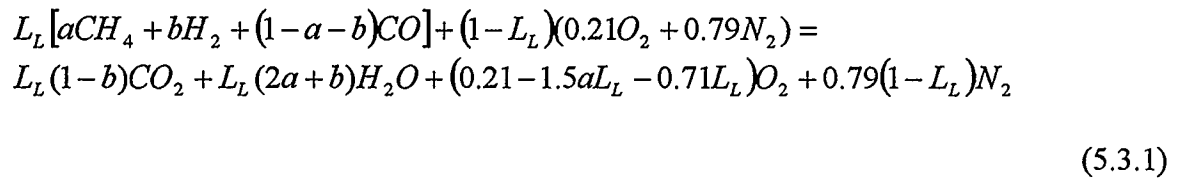


Figure 5.2.1 Rich flammability limits of H_2 -CO- CH_4 mixtures in air as a function of residence time at 300°C ; symbols: experimental data, lines: calculated values

5.3 Prediction of the rich limits using the concept of “constant adiabatic flame temperature”

The concept of the constant adiabatic flame temperature, as described in Chapter 4 for the individual fuels, was also employed to predict the limits of H₂-CO-CH₄ fuel mixtures at different initial temperatures.

Lean limit. It can be assumed that the products of the combustion of lean mixtures are water, carbon dioxide, oxygen and nitrogen. Then the overall reaction can be written as:



where

a and b are fractions of methane and hydrogen in the fuel mixture, respectively.

L_L is the lean limit of fuel mixture in air expressed as a fraction.

The adiabatic flame temperature can be calculated applying the first law of thermodynamics:

$$\left[\sum_i H_{i,reactant} \right]_{T_0} = \left[\sum_i H_{i,product} \right]_{T_f} \quad (5.3.2)$$

where

T_0 is the initial mixture temperature

T_f is the adiabatic flame temperature

$H_{i,\text{reactant}}$ is the enthalpy of the i species of the reactants at initial temperature T_0

$H_{i,\text{product}}$ is the enthalpy of the i species of the products at adiabatic flame temperature T_f

Using Eqs. 5.3.1 and 5.3.2, the adiabatic flame temperatures were calculated for different lean limiting mixtures at the initial temperature of 25°C on the basis of the known corresponding experimental values of the lean limit determined in the stainless steel test tube at the residence time of 0.5 min. These values are shown in Table 5.4.1. It can be seen that the value of the adiabatic flame temperature depends on the fuel mixture composition and decreases with an increase of the hydrogen concentration in the fuel mixture as expected. For example, the adiabatic flame temperature of the fuel mixture containing 20% hydrogen is approximately 1198K, while that of the mixture with 80% hydrogen in the fuel is 723K. This is due to the fact that adiabatic flame temperatures of lean hydrogen-air mixtures are much lower than those of methane and carbon monoxide.

Table 5.3.1 The adiabatic flame temperatures of lean limiting $\text{H}_2\text{-CO-CH}_4$ mixtures with initial temperature of 25°C .

Composition %			Lean limit $L_{L,\text{Exp}}$ (% by volume)	Adiabatic flame temperature (K)
H_2	CO	CH_4		
20	40	40	6.0	1198
50	25	25	5.0	934
80	10	10	4.2	723

Assuming that the adiabatic flame temperature remains constant for the limiting mixtures at other initial temperatures, the lean limits of various tertiary $\text{H}_2\text{-CO-CH}_4$ mixtures were calculated using Eqs. 5.3.1 & 5.3.2 and the values of T_f in Table 5.3.1. The

results are presented in Table 5.3.2. For comparison, the corresponding experimental values of the lean limit are also shown. It can be seen that the agreement of the calculated and experimental values of the lean limits for mixtures with hydrogen concentration less than 80% is very good, but the deviations are very significant for the mixtures with 80% hydrogen. This was expected because hydrogen has shown much bigger deviation than that of the other two fuels when the same calculation approach was used (Chapter 4).

Table 5.3.2 Lean flammability limits of H₂-CO-CH₄ mixtures, experimental and calculated using the method of “constant adiabatic flame temperature”

Composition %			Initial Temp. (°C)	Lean flammability limit		Relative deviation (L _C -L _E)/L _E (%)
H ₂	CO	CH ₄		Calculated L _C (% by volume)	Experimental L _E (% by volume)	
20	40	40	200	4.91	5.0	-1.8
			300	4.27	4.4	-2.95
50	25	25	200	3.68	3.8	-3.16
			300	2.92	3.1	-5.81
80	10	10	200	2.51	3.2	-21.56
			300	1.52	2.6	-41.54

Rich limit. There is not enough available oxygen in rich mixtures to convert all fuels into water and carbon dioxide. Similar to the approach described in Chapter 4, it was proposed that the priority of the oxidization reactions can be assumed as follows. First, methane is converted into carbon monoxide and hydrogen; next, if there is still free

oxygen available, hydrogen is oxidized into water; and if after this, there is still some free oxygen left, carbon monoxide will be oxidized into carbon dioxide. Assuming that a fuel mixture of $a\text{CH}_4 + b\text{H}_2 + (1-a-b)\text{CO}$ has the rich limit L_R , with a , b and L_R all expressed as fractions, the general overall reactions can be written as follows:

If $L_R \geq \frac{42}{100a + 42}$, there is not enough oxygen to oxidize all the methane and some

methane is left in the products.

$$\begin{aligned} L_R [a\text{CH}_4 + b\text{H}_2 + (1-a-b)\text{CO}] + (1-L_R)(0.21\text{O}_2 + 0.79\text{N}_2) = \\ [(a+0.42)L_R - 0.42]\text{CH}_4 + [(b-0.84)L_R + 0.84]\text{H}_2 + \\ [(0.58-a-b)L_R + 0.42]\text{CO} + 0.79(1-L_R)\text{N}_2 \end{aligned} \quad (5.3.3)$$

If $\frac{42}{100a + 42} > L_R \geq \frac{42}{300a + 100b + 42}$, there is not enough oxygen to oxidize all the

hydrogen (initial plus produced by methane oxidization) and some hydrogen is left in the products.

$$\begin{aligned} L_R [a\text{CH}_4 + b\text{H}_2 + (1-a-b)\text{CO}] + (1-L_R)(0.21\text{O}_2 + 0.79\text{N}_2) = \\ [(3a+b+0.42)L_R - 0.42]\text{H}_2 + L_R(1-b)\text{CO} + \\ [0.42 - L_R(0.42+a)]\text{H}_2\text{O} + 0.79(1-L_R)\text{N}_2 \end{aligned} \quad (5.3.4)$$

If $L_R < \frac{42}{300a + 100b + 42}$, there is not enough oxygen to oxidize all the carbon monoxide

(initial plus produced by methane oxidization) and some carbon monoxide is left in the products.

$$\begin{aligned}
&L_R[aCH_4 + bH_2 + (1-a-b)CO] + (1-L_R)(0.21O_2 + 0.79N_2) = \\
&[(3a+1.42)L_R - 0.42]CO + [0.42 - L_R(3a+b+0.42)]CO_2 + \\
&L_R(2a+b)H_2O + 0.79(1-L_R)N_2
\end{aligned} \tag{5.3.5}$$

where

a and b are fractions of methane and hydrogen in the fuel mixture, respectively.

L_R is the rich limit, i.e. fuel mixture fraction in the fuel-air mixture.

Using Eqs 5.3.1 and 5.3.3-5.3.5, the adiabatic flame temperatures T_f of the rich limiting mixtures at 25°C were calculated and are shown in Table 5.3.3. Based on these values, the rich limits at 200°C and 300°C were calculated from the same equations. The results are presented in Table 5.4.4. For comparison, the corresponding experimental values are also shown in the same table. It can be seen that the agreement of calculated and experimental values is very fair.

Table 5.3.3 The adiabatic flame temperatures of rich limiting H_2 -CO- CH_4 mixtures with initial temperature of 25°C.

Composition %			Rich limit $L_{L,Exp}$ (% by volume)	Adiabatic flame temperature (K)
H_2	CO	CH_4		
20	40	40	27.0	1731
50	25	25	34.8	1680
80	10	10	48.1	1607

Table 5.3.4 Rich flammability limits of $\text{H}_2\text{-CO-CH}_4$ mixtures, experimental and calculated using the method of “the constant adiabatic flame temperature”

Composition %			Initial Temp. (°C)	Rich flammability limit		Relative deviation $(L_C - L_E)/L_E$ (%)
H_2	CO	CH_4		Calculated L_C (% by volume)	Experimental L_E (% by volume)	
20	40	40	200	29.5	29.5	0
			300	31.0	31.5	-1.59
50	25	25	200	37.9	39.0	-2.82
			300	39.7	43.2	-8.10
80	10	10	200	52.1	54.4	-4.23
			300	54.5	58.6	-7.00

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

- The values of the flammability limits experimentally determined at moderately elevated temperatures were influenced by the type of the test tube surface and the duration of the exposure of the test mixture to elevated temperatures prior to spark ignition (residence time).
- The flammability limit of individual fuels (H_2 , CO, CH_4 and C_2H_4) widened with an increase in the initial temperature of the fuel-air mixture.
- The value of the rich limit of methane was not affected by the duration of the residence time or by the material of the test tube at initial temperatures up to $300^\circ C$.
- The value of the rich limit of carbon monoxide at $300^\circ C$ decreased with an increase in the duration of the residence time when determined in the stainless steel test tube and remained constant at different residence times when established in the quartz tube.
- The rich flammability limits of hydrogen and ethylene at $300^\circ C$ determined in either test tube - stainless steel or quartz – were affected significantly by the duration of the residence time prior to spark ignition. The longer the residence time the smaller was the value of the rich limit. This behaviour was the result of chemical activity within the mixture prior to spark ignition.

- The pre-ignition chemical activity effectively changed the mixture composition prior to spark ignition and the existence of the pre-ignition chemical activity was confirmed by the results of gas analysis.
- The trends observed for the flammability limits of tertiary mixtures of H_2 , CO and CH_4 with respect to the variation in their initial temperature and the duration of the residence time were consistent with the corresponding trends observed for the individual fuels on their own in air.
- At a short residence time (0.5 min), the flammable range for all tested fuel mixtures widened with an increase in their initial temperature up to $300^\circ C$.
- The rich flammability limit of tested fuel mixtures decreased significantly with an increase in the duration of the residence time due to pre-ignition chemical activity.
- The effect of the duration of the residence time on the rich flammability limit was much stronger when the values of the limit were established in the stainless steel test tube as opposed to those determined in the quartz test tube.
- It was found that Le Chatelier's Rule can be applied with fair accuracy to determine the flammability limits of these tertiary mixtures, when based on the fuel composition and the corresponding limit values of the individual fuel components in air on their own at the same conditions (initial temperature and residence time).
- The method of "constant adiabatic flame temperature" as well as the correlation proposed by Wierzbka et al. can be employed to predict the flammability limits of H_2 , CO, CH_4 and C_2H_4 as well as H_2 -CO- CH_4 mixtures at different initial temperatures and different residence times with reasonable accuracy.

6.2 Future work

- To investigate the nature of pre-ignition chemical activity within the fuel-air mixtures during the residence time at moderately elevated temperature.
- To develop guidelines to predict the corresponding changes in the test mixture composition due to this activity.
- To validate these guidelines by determining the experimental values of the flammability limits of other important complex fuel mixtures, such as coal gas, producer gas, synthetic gas etc.

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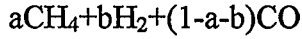
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APPENDIX A

Calculation of the rich flammability limit of 80% H_2 +10% CO +10% CH_4 mixture using “constant adiabatic flame temperature” concept

In the Eqs.5.3.3-5.3.5, a fuel mixture is expressed in a general expression:



In the case under consideration, the 80% H_2 +10% CO +10% CH_4 mixture has the rich limit of 48.1% at 25°C. The corresponding parameters can be written as:

$$a=0.1$$

$$b=0.8$$

$$L_R=0.481$$

Step 1. Choosing the correct overall reaction:

From $a=0.1$ and $b=0.8$, we have:

$$\frac{42}{100a + 42} = 0.8077 \quad \text{and} \quad \frac{42}{300a + 100b + 42} = 0.2961$$

It was known that $L_R=0.481$. The condition $\frac{42}{100a + 42} > L_R \geq \frac{42}{300a + 100b + 42}$ was satisfied. Eq. 5.3.4 was chosen as the expression of the overall reaction, as following:

$$\begin{aligned} L_R [aCH_4 + bH_2 + (1-a-b)CO] + (1-L_R)(0.21O_2 + 0.79N_2) = \\ [(3a+b+0.42)L_R - 0.42]H_2 + L_R(1-b)CO + \\ [0.42 - L_R(0.42+a)]H_2O + 0.79(1-L_R)N_2 \end{aligned} \quad (5.3.4)$$

Step 2. Calculation for the total enthalpy of the reactants at initial temperature $T_o=25^\circ C$.

Refer to data tables. The value of the enthalpy was written as follows;

$$H_{CH_4, T_o} = -74875 \text{ kJ/kmol}$$

$$H_{H_2, T_o} = -4.292 \text{ kJ/kmol}$$

$$H_{CO, T_o} = -110534 \text{ kJ/kmol}$$

$$H_{O_2, T_o} = -4.425 \text{ kJ/kmol}$$

$$H_{N_2, T_o} = -4.376 \text{ kJ/kmol}$$

The total enthalpy for the reactants was written as:

$$H_{R,T_o} = L_R [aH_{CH_4,T_o} + bH_{H_2,T_o} + (1-a-b)H_{CO,T_o}] + (1-L_R)(0.21H_{O_2,T_o} + 0.79H_{N_2,T_o}) \quad (A-1)$$

$$H_{R,T_o} = -8922 \text{ kJ/kmol}$$

Step 3. Calculation for adiabatic flame temperature. According to Eq. 5.3.2 (first law of thermodynamics), The total enthalpy of the products at the adiabatic flame temperature T_f is equal to that at the initial temperature T_o .

$$H_{P,T_f} = H_{R,T_o} = -8922 \text{ kJ/kmol}$$

By trial and error, the adiabatic flame temperature was found: $T_f=1607\text{K}$. At this temperature, the values of the enthalpy of the products are:

$$H_{H_2,T_f} = 39799 \text{ kJ/kmol}$$

$$H_{CO,T_f} = -67929 \text{ kJ/kmol}$$

$$H_{H_2O,T_f} = -188624 \text{ kJ/kmol}$$

$$H_{N_2,T_f} = 42160 \text{ kJ/kmol}$$

The total enthalpy for the products was written as:

$$H_{P,T_f} = [(3a+b+0.42)L_R - 0.42]H_{H_2,T_f} + L_R(1-b)H_{CO,T_f} + [0.42 - L_R(0.42+a)]H_{H_2O,T_f} + 0.79(1-L_R)H_{N_2,T_f} \quad (A-2)$$

$$H_{P,T_f} = -8910 \text{ kJ/kmol}$$

This value is close enough to that calculated for reactants at T_o .

Step 4. Calculation for the rich limit with initial temperature of 200°C . Assuming that the same value of the adiabatic flame temperature T_f will be reached, it was found that the rich limit was 52.1%.

At the initial temperature $T_1=200^\circ\text{C}$, the values of the enthalpy of the reactants are:

$$H_{CH_4,T_1} = -67872 \text{ kJ/kmol}$$

$$H_{H_2,T_1} = 5090 \text{ kJ/kmol}$$

$$H_{CO,T_1} = -105412 \text{ kJ/kmol}$$

$$H_{O_2,T_1} = 5247 \text{ kJ/kmol}$$

$$H_{N_2, T_1} = 5109 \text{ kJ/kmol}$$

Assuming the same adiabatic flame temperature was reached, the value of the enthalpy for each product was rewritten as follows:

$$H_{H_2, T_f} = 39799 \text{ kJ/kmol}$$

$$H_{CO, T_f} = -67929 \text{ kJ/kmol}$$

$$H_{H_2O, T_f} = -188624 \text{ kJ/kmol}$$

$$H_{N_2, T_f} = 42160 \text{ kJ/kmol}$$

According to Eq. 5.3.2 (first law of thermodynamics), the total enthalpy of the products at the adiabatic flame temperature T_f is equal to that at the initial temperature T_1 .

$$H_{P, T_f} = H_{R, T_1}$$

The detailed heat balance can be written as:

$$\begin{aligned} L_R [aH_{CH_4, T_1} + bH_{H_2, T_1} + (1-a-b)H_{CO, T_1}] + (1-L_R)(0.21H_{O_2, T_1} + 0.79H_{N_2, T_1}) = \\ [(3a+b+0.42)L_R - 0.42]H_{H_2, T_f} + L_R(1-b)H_{CO, T_f} + \\ [0.42 - L_R(0.42+a)]H_{H_2O, T_f} + 0.79(1-L_R)H_{N_2, T_f} \end{aligned} \quad (A-3)$$

The only unknown parameter in this equation is L_R . Solving this equation, rich limit can be obtained: $L_R = 0.521 = 52.1\%$

Step 5. Calculation for the rich limit with initial temperature of 300°C . Assuming that the same value of the adiabatic flame temperature T_f will be reached, it was found that the rich limit was 54.5% .

At the initial temperature $T_2=300^\circ\text{C}$, the values of the enthalpy of the reactants are:

$$H_{CH_4, T_2} = -63100 \text{ kJ/kmol}$$

$$H_{H_2, T_2} = 8009 \text{ kJ/kmol}$$

$$H_{CO, T_2} = -102409 \text{ kJ/kmol}$$

$$H_{O_2, T_2} = 8386 \text{ kJ/kmol}$$

$$H_{N_2, T_2} = 8077 \text{ kJ/kmol}$$

Assuming the same adiabatic flame temperature was reached, the value of the enthalpy for each product was rewritten as follows:

$$H_{H_2, T_f} = 39799 \text{ kJ/kmol}$$

$$H_{CO, T_f} = -67929 \text{ kJ/kmol}$$

$$H_{H_2O, T_f} = -188624 \text{ kJ/kmol}$$

$$H_{N_2, T_f} = 42160 \text{ kJ/kmol}$$

According to Eq. 5.3.2 (first law of thermodynamics), the total enthalpy of the products at the adiabatic flame temperature T_f is equal to that at the initial temperature T_2 .

$$H_{P,T_f} = H_{R,T_2}$$

The detailed heat balance can be written as:

$$\begin{aligned} L_R [aH_{CH_4,T_2} + bH_{H_2,T_2} + (1-a-b)H_{CO,T_2}] + (1-L_R)(0.21H_{O_2,T_2} + 0.79H_{N_2,T_2}) = \\ [(3a+b+0.42)L_R - 0.42]H_{H_2O,T_f} + L_R(1-b)H_{CO,T_f} + \\ [0.42 - L_R(0.42+a)]H_{H_2O,T_f} + 0.79(1-L_R)H_{N_2,T_f} \end{aligned} \quad (A-4)$$

The only unknown parameter in this equation is L_R . Solving this equation, rich limit can be obtained: $L_R = 0.545 = 54.5\%$