

THE UNIVERSITY OF CALGARY

**FLAMMABILITY LIMITS OF CARBON MONOXIDE AND CARBON
MONOXIDE – HYDROGEN MIXTURES IN AIR AT ELEVATED
TEMPERATURES**

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ABSTRACT

The flammability limits of carbon monoxide in air were established at elevated temperatures (up to 300°C) for different concentrations of water vapor in the mixture. Results of the experiments confirmed high sensitivity of the flammability limits of carbon monoxide to the presence of water vapor in the mixture. The determined limit values were affected by the residence time duration (i.e. time of exposure to elevated temperatures before spark ignition). Additionally the flammability limits of different carbon monoxide – hydrogen mixtures were established at elevated temperatures (up to 300°C). It was shown that the lean flammability limits of such mixtures can be predicted reasonably well by applying the well-known LeChatelier's Rule, while the rich limits deviate significantly from the values calculated using the Rule. The determined limit values of these mixtures were also affected by the residence time duration. It was concluded that the observed changes in the limit values were most probably the result of surface reactions on stainless steel test tube.

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TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF SYMBOLS	xiii
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Objectives of the Present Work	2
CHAPTER 2 LITERATURE SURVEY	5
2.1 Experimental Investigations of the Flammability Limits	5
2.2 Theoretical Studies of the Flammability Limits	14
CHAPTER 3 EXPERIMENTAL APPARATUS AND PROCEDURE	18
3.1 Experimental Apparatus	18
3.2 Experimental Procedure	23
CHAPTER 4 FLAMMABILITY LIMITS OF CARBON MONOXIDE IN AIR	25
4.1 Effect of Initial Temperature and Water Vapor Concentration	25
4.2 Prediction of the Flammability Limits of Carbon Monoxide	35
4.3 Effect of the Residence Time/ Preignition Chemical Activity	41

CHAPTER 5 FLAMMABILITY LIMITS OF CARBON MONOXIDE – HYDROGEN MIXTURES IN AIR	57
5.1 Effect of Mixture Composition	57
5.2 Effect of Initial Temperature	68
5.3 Effect of Water Vapor	71
5.4 Effect of Residence Time	76
CHAPTER 6 CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK	81
6.1 Conclusion	81
6.2 Recommendations For Future Work	83
References	84

LIST OF TABLES

Table 3.1 Purity of Gases Used	22
Table 4.1 Rich Flammability Limits of Carbon Monoxide in Air	26
Table 4.2 Lean Flammability Limits of Carbon Monoxide in Air	26
Table 4.3 Activation Energies of Carbon Monoxide Oxidation Reactions	29
Table 4.4 Flammability Limits of Carbon Monoxide in Air as a Function of the Water Vapor Concentration at Two Different Temperatures	33
Table 4.5 Calculated Adiabatic Flame Temperatures ($T_{f,Ad}$)	36
Table 4.6 Comparison of the Experimental and Calculated Flammability Limits of Carbon Monoxide in Air as a Function of Water Vapor Concentration in the Total Mixture	39
Table 4.7 Adiabatic Flame Temperatures Calculated For the Flammability Limits of Carbon Monoxide in Air at Elevated Temperatures	41
Table 4.8 Flammability Limits of Carbon Monoxide in “Dry Air” at Different Temperatures and Residence Times	42
Table 4.9 Chemical Composition of Type 316 Steel	45
Table 4.10 Comparison of the Experimental and Calculated Flammability Limits of Carbon Monoxide in Air at Different Residence Times	55
Table 5.1 Rich Flammability Limits of Carbon Monoxide – Hydrogen Mixtures in Air at Different Temperatures	58
Table 5.2 Lean Flammability Limits of Carbon Monoxide – Hydrogen Mixtures in Air at Different Temperatures	65

Table 5.3 Calculated Adiabatic Flame Temperatures	71
--	----

Table 5.4 Comparison of the Experimental and Calculated Flammability Limits of Carbon Monoxide – Hydrogen Mixtures at Different Temperatures	72
---	----

Table 5.5 Comparison of the Experimental and Calculated Flammability Limits of Carbon Monoxide – Hydrogen Mixtures With Different Concentrations of Water Vapor	74
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Table 5.6 Adiabatic Flame Temperatures Calculated on the Basis of Flammability Limits at 150°C	76
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Table 5.7 Flammability Limits of 50%CO+50%H ₂ Mixture in Air as a Function of Residence Time at 300°C	79
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LIST OF FIGURES

Figure 3.1 Schematic Diagram of the Test Apparatus	19
Figure.3.2 Experimental Apparatus	20
Figure 4.1 Flammability Limits of Carbon Monoxide in Air	27
Figure 4.2 Flammability Limits of Carbon Monoxide in Air as a Function of Water Vapor Concentration in the Mixture at Three Different Temperatures	28
Figure 4.3 Effect of Water Vapor Addition to Carbon Monoxide – “Dry Air” Mixture on the Mean Reaction Rates	31
Figure 4.4 Determination of the Lean Flammability Limit in “Dry Air” at 18°C and Residence Time of 5 min	32
Figure 4.5 Determination of the Lean Flammability Limit in “Dry Air” at 200°C and Residence Time of 5 min	32
Figure 4.6 Flammability Limits of Carbon Monoxide in Air as a Function of the Water Vapor Concentration in the Total Mixture	34
Figure 4.7 Comparison of the Experimental and Calculated Flammability Limits of Carbon Monoxide at Different Temperatures	37
Figure 4.8 Comparison of the Experimental and Calculated Rich Flammability Limits of Carbon Monoxide as a Function of Water Vapor Volumetric Concentration in the Total Mixture	40
Figure 4.9 Comparison of the Experimental and Calculated Lean Flammability Limits of Carbon Monoxide as a Function of Water Vapor Volumetric Concentration in the Total Mixture	40

Figure 4.10 Flammability Limits of Carbon Monoxide in “Dry Air” as a Function of Residence Time at Different Temperatures	43
Figure 4.11 Variation in the Concentrations of Oxygen and Carbon Dioxide Within the Test Mixture as a Function of Residence Time	43
Figure 4.12 Carbon Dioxide Concentration in the Rich Mixture of Carbon Monoxide With “Dry Air” (60%CO) as a Function of the Residence Time at Different Temperatures	44
Figure 4.13 Carbon Monoxide and Oxygen Concentrations Within a Lean Mixture of 10%CO+90% “Wet” Air as a Function of Time	46
Figure 4.14 Carbon Monoxide and Oxygen Concentrations Within a Rich Mixture of 73.6%CO+26.4% “Wet” Air as a Function of Time	46
Figure 4.15 Effect of Experimental Procedure On the Values of Rich Flammability Limits of Carbon Monoxide in Air at 300°C	48
Figure 4.16 Pressure Variation Within Rich Carbon Monoxide – Air Mixtures With Different Water Vapor Concentrations as a Function of the Residence Time	48
Figure 4.17 Effect of the Presence of Hydrogen in the Carbon Monoxide – Air Mixtures on the Intensity of Preignition Chemical Activity	49
Figure 4.18 Variation in the Concentrations of Oxygen and Carbon Dioxide Within the Test Mixture of 60% CO + 40% “Dry Air” Initial Composition as a Function of Residence Time for Three Different Test Conditions	49
Figure 4.19 Pressure Variation in Different Carbon Monoxide - “Dry Air” Mixtures as a Function of the Residence Time	52
Figure 4.20 Pressure Drop in 30%CO+70%”Dry Air” Mixtures at 300°C With Two Different Filling Pressures	52
Figure 4.21 Comparison of the Experimental and Calculated Rich Flammability Limits of Carbon Monoxide in “Dry” and Atmospheric Air at Different Residence Times	56

Figure 4.22 Variation in the Concentrations of Oxygen and Carbon Dioxide Within the 60%CO+40% “Dry Air” Mixture as a Function of Residence Time: A) the Center of the Test Tube, B) Close to the Wall	56
Figure 5.1 Rich Flammability Limits of CO-H₂ Mixtures in Air at Different Temperatures	60
Figure 5.2 Effect of Hydrogen Addition to Carbon Monoxide – “Dry Air” Mixture on the Mean Reaction Rates	61
Figure 5.3 Effect of Hydrogen, Water Vapor or Methane Addition to Carbon Monoxide – “Dry Air” Mixture on the Mean Reaction Rates	62
Figure 5.4 Rich Flammability Limits of CO-H₂ Mixtures at Room Temperature	64
Figure 5.5 Lean Flammability Limits of CO-H₂ Mixtures in Air at Different Temperatures	66
Figure 5.6 Lean Flammability Limits of CO-H₂ Mixtures at Room Temperature	67
Figure 5.7 Rich Flammability Limits of Different Carbon Monoxide – Hydrogen Mixtures as a Function of Temperature	69
Figure 5.8 Lean Flammability Limits of Different Carbon Monoxide – Hydrogen Mixtures as a Function of Temperature	69
Figure 5.9 Comparison of the Experimental and Calculated Rich Flammability Limits of Different Carbon Monoxide-Hydrogen Mixtures	73
Figure 5.10 Comparison of the Experimental and Calculated Lean Flammability Limits of Different Carbon Monoxide-Hydrogen Mixtures	73
Figure 5.11 Comparison of the Experimental and Calculated Rich Flammability Limits of Carbon Monoxide-Hydrogen Mixtures as a Function of Water Vapor Concentration at 150°C	75
Figure 5.12 Comparison of the Experimental and Calculated Lean Flammability Limits of Carbon Monoxide-Hydrogen Mixtures as a Function of Water Vapor Concentration at 150°C	75

Figure 5.13 Rich Flammability Limits of CO-H₂ Mixtures Calculated Using Adiabatic Flame Temperatures for the Experimental Values of the Limits at 150°C	77
Figure 5.14 Lean Flammability Limits of CO-H₂ Mixtures Calculated Using Adiabatic Flame Temperatures for the Experimental Values of the Limits at 150°C	77
Figure 5.15 Flammability Limits of 50%CO+50%H₂ Mixtures as a Function of Residence Time at of 300°C	79
Figure 5.16 Results of the Detailed Chemical Kinetics Simulation of Gas Phase Reactions for Mixture of 40%CO+40%H₂+20%Air at 300°C	80
Figure 5.17 Results of the Detailed Chemical Kinetics Simulation of Gas Phase Reactions for Mixture of 1.75%CO+1.75%H₂+96.5%Air at 300°C	80

LIST OF SYMBOLS

a	concentration of carbon monoxide in the fuel mixture, mol/mol
$a_{preig.}$	carbon dioxide produced in the preignition reactions, moles %
a_1, b_1, c, d	stoichiometric coefficients
b	concentration of hydrogen in the fuel mixture, mol/mol
$H_{i,react}$	enthalpies of the reactants at initial temperature, kJ/kmol
$H_{i,prod}$	enthalpies of the products at adiabatic flame temperature, kJ/kmol
L_L	lean flammability limit, % by volume
L_R	rich flammability limit, % by volume
$T_{f, ad.}$	adiabatic flame temperature, K
T_o	initial temperature of the mixture, K
W	concentration of water vapor in the mixture, % by volume

CHAPTER 1. INTRODUCTION

1.1 Background

There is a continuous interest to the phenomenon of flammability limits. The knowledge of the values of the flammability limits is important and necessary for evaluation of the potential fire and explosion hazards as well as to increase the efficiency of internal combustion devices and to lower their emissions. Different definitions of the limits can be found in the literature (Coward, H. F. and Jones, G. W., 1952; Zabetakis, M. G., 1965; Wierzba, I. and Ale, B.B., 1998; Smedt, G. De., *et al.*, 1999), the most widely accepted is that flammability limits, the rich and the lean, are correspondingly the maximum and minimum fuel concentrations in the fuel – oxidant mixture capable of self-sustained flame propagation. The mechanism of flame propagation is exceedingly complex, involving heat transfer, mass diffusion and chemical kinetics. At the limits, flame quenching occurs as a result of failure to maintain a balance at the flame front between heat generation by chemical reactions and heat losses to the surroundings. Variation of any parameter influencing this balance such as temperature, pressure, gravity acceleration, will affect the values of the flammability limits. Over the years many investigations have been performed to examine the effects of these parameters on the flammability limits of different fuels.

1.2 Objectives of the present work

Although, over the years a lot of work has been performed to examine the effect of different parameters on the flammability limits, there are still many questions yet to be answered. In the recent years, use of some fuel mixtures (e. g. reform gas, low heating value gases) increased, but there is lack in their flammability limit data. Many industrial processes take place at elevated temperatures but the flammability limits data in such conditions are scarce also.

A number of theoretical approaches have been developed to determine the limits (Zeldovich, Ya. B., 1985; Spalding, D. B., 1957; Lovachev, L. A., 1971; Hertzberg, M., 1976; Law, C. K. and Egolfopoulos, F. N., 1992). However, they are limited to certain conditions and fuel combinations and the accuracy of the estimation of the limits is still low. Le Chatelier's Rule is used by industry to calculate the limits of fuel mixtures, but it was shown that the Rule does not apply to certain fuel combinations (Coward, H. F. and Jones, G. W., 1952; Cheng, T. K. H., 1985; Ale, B. B., 1998). Therefore, empirical methods still remain the only practical means of obtaining reliably the flammability limits of fuels.

Carbon monoxide is a fuel, which is found in many different industrial fuel mixtures. The rich flammability limit values of carbon monoxide found in the literature vary from 68 to 74% and the lean limits vary from 12 to 15.9% (Coward, H. F. *et al.*, 1919; Coward, H. F. and Jones, G. W., 1952; Boon, S. L., 1982; Cheng, T. K. H., 1985; Hustad, J. E. and Sonju,

O. K., 1988; Harris, K. P., 1990). The scatter in these values makes it difficult to develop reliable predictive procedures.

The limits of carbon monoxide reported in the literature could be obtained with different and not accurately controlled concentrations of water vapor in the test mixtures. Since, the unique feature of the combustion reactions of carbon monoxide is their dependence on the presence of hydrogenous radicals in the mixture, different concentrations of water vapor in the experiments could have contributed to a significant scatter in the reported flammability limit values.

Fuel mixtures consisting of carbon monoxide and hydrogen are encountered in various industrial processes, such as steam reforming of fossil fuels for the production of hydrogen. Also, mixtures of carbon monoxide and hydrogen with steam and air may be produced in severe nuclear reactor accidents involving molten core-concrete interactions (Kumar, R. K., 1985; Lee, J. H. S. and Berman M., 1997). However, there is very little information available in the open literature relating to the flammability limits of carbon monoxide - hydrogen mixtures, especially at elevated temperatures and for upward flame propagation in the presence of water vapor.

Hence, the objectives of the present study were to:

- establish consistent flammability limit values of carbon monoxide in air at elevated temperatures up to 300°C and atmospheric pressure for upward flame propagation.
- investigate the effects of the presence of water vapor on the flammability limits of carbon monoxide.

- **establish the flammability limits of carbon monoxide – hydrogen mixtures in air at elevated temperatures, up to 300°C.**
- **establish the flammability limits of some carbon monoxide – hydrogen – water vapor mixtures at elevated temperatures.**
- **investigate the effect of existence of preignition reactions at elevated temperatures on the values of the flammability limits of carbon monoxide and carbon monoxide – hydrogen mixtures in air, when determined in a stainless steel apparatus.**

CHAPTER 2. LITERATURE SURVEY

2.1. Experimental investigations of the flammability limits

A number of good reviews are dedicated to the subject of flammability limits (Coward, H. F. and Jones, G. W., 1952; Zabetakis, M. G., 1965; Lovachev, L. A., *et al.*, 1973; Lovachev, L. A., 1979; Jarosinski, J., 1986). Experimental work on the phenomena of the flammability limits has been far ahead of theory. The first experiments related to this topic were done in connection with mine safety by Sir Humphrey Davy at the beginning of the nineteenth century. With an increase in the number of applications of combustion and diversification of fuels used, a large number of investigations have been performed on the flammability limits. However, in the accumulated literature there is a scatter in the flammability limit values determined. This scatter resulted from the use of various apparatus for the determination of the flammability limits (different shape and volume of the test vessel, ignition sources, open or closed vessel, etc.), different procedures and different criteria for flame propagation detection.

Shape and size of the test apparatus. Different apparatus have been developed to determine flammability limits. The most common have been cylindrical tubes (Coward, H. F., *at al.*, 1919; White, A. G., 1925; Coward, H. F. and Jones, G. W., 1952; Wierzba, I., 1985; Smedt, G. De. *et al.*, 1999) and spherical vessels (Bone, W. A., 1928; Bunev, V. A., 1972; Smedt, G. De., *et al.*, 1999). Various results were obtained in different size apparatus. Coward and Jones (1952) in their review of experimental studies of the

flammability limits conducted over one and a half centuries, showed that in most cases, values of the limits were in a good agreement when determined in a tubular apparatus of 2-inch (~51mm) diameter or larger. The flammability limits determined in the test tubes of smaller diameter were narrower due to a more intensive heat loss from the flame to the tube wall. The less was the diameter the more intensive were heat losses and the narrower were the flammability limits. It has also been shown by different researchers that often the flammability limits determined in large confinements (8m^3) were wider, while certain substances ($\text{C}_2\text{H}_5\text{-Br}$, $\text{C}_2\text{H}_5\text{-Br-CO}_2$) could be ignited only in large volumes (Lovachev, L. A., 1979).

Some researchers applied various methods designed to study flames in flow situations to investigate the flammability limits. For example, special burners which form counter flow flat flames were adopted (Egerton, A. and Thabet, S. H., 1952; Sorenson, S. C. and Savage, L. D., 1975; Lovachev, L. A., 1979; Law, C. K. and Egolfopoulos, F. N., 1992; Liao, C., *et al.*, 1996). In such techniques the flame was not uniform, propagated through the moving media and was influenced by additional effects such as flame stretch and turbulence (Chen, Z. N. and Sohrab, S. H., 1995; Wang, C. H. and Wu, T. S., 1997). In addition, the limits obtained by these techniques often are narrower than those obtained in the standard apparatus (Law, C. K. and Egolfopoulos, F. N., 1990; Wierzba, I. and Ale, B. B., 1998; Wierzba, I. and Ale, B. B., 1999). They were closer to flame stability limits than to flammability limits.

Ignition sources. It was reported that the values of the experimentally found flammability limits were affected by the type of ignition source employed. Different ignition methods

have been applied: pilot flame, hot rods or wires, spark ignition, chemical igniters and plasma jet (Zabetakis, M.G., et al., 1951; Coward, H. F. and Jones, G. W., 1952; Zabetakis, M. G. and Richmond, J. K., 1953; Zabetakis, M. G., 1965; Vince, I. M., *et al.*, 1984). The spark ignition is the most preferred, as it provides good control of the supplied energy, which insures high repeatability of the experimental results. Also, it does not alter the properties of the mixture tested as for example pilot flames or chemical ignition may do (Zabetakis, M.G. and Richmond, J.K., 1953). The energy supplied by a spark may be changed by varying electrode spacing and spark duration. Decreasing the electrode spacing below a certain distance would cause flame quenching because of heat losses to the electrodes. Increasing the electrode spacing would require larger amounts of energy supplied for the ignition (Blank, M. V., *et al.*, 1949; Lewis, B. and Von Elbe, G., 1987). The flammable range of a given fuel – air mixture may be widened when very high ignition energy is supplied and narrowed when the ignition source is inadequate.

Method of detection of flame propagation. Many different methods of monitoring flame propagation through the fuel – oxidant mixtures during determination of the flammability limits have been employed. Among the most common methods were: visual observation through transparent wall or window (Coward, H. F., *at al.*; Coward, H. F. and Jones, G. W., 1952; Levy, A., 1965), gas temperature monitoring (Kumar, R. K., 1985; Hustad, J. E. and Sonju, O. K., 1988; Wierzba, I., and Ale, B. B., 1998), gas pressure monitoring (Bunev, V. A., 1972; Checkel, M. D., *et al.*, 1995; Smedt, G. De. *et al.*, 1999) and measuring changes in the mixture composition after ignition (Bone W. A., *et al.*, 1928). In each of these methods a certain level of pressure or temperature increase or amount of fuel burned were

assumed as evidence. The most convenient method providing high accuracy of flame propagation detection is monitoring gas temperature along the test tube. However, it was found by Levy (1965) that the thermocouples used for measuring gas temperature may detect a bubble of hot gas rising after the flame itself was extinguished. The bubble of hot gas may rise with the same speed as the flame up to 0.15 m. before breaking up. This problem can be avoided by using a tube of sufficient length.

Different definitions of the flammability limits adopted by different researchers also contributed to the difference (up to ~2 %, by volume) in the published flammability limit values (Smedt, G. De., *et al.*, 1999). Limits were defined as fuel concentrations at the borders of non-flammable regions (Kumar R. K., 1985; Wierzba, I. and Ale, B.B., 1999), borders of flammable region (Zabetakis, M. G., 1965), or as average mixture compositions between just flammable and just non-flammable mixture compositions (Coward, H. F. and Jones, G. W., 1952).

Material of the test vessel. The material of the test apparatus can become important when experiments are conducted at elevated temperatures. There are a number of materials, which were used for a test apparatus. The most common were Pyrex, glass and steels (White, A. G., 1925; Bone, W. A., *et al.*, 1928; Coward, H. F. and Jones, G. W., 1952; Levy, A., 1965; Bunev, V. A., 1966; Checkel, M. D., *et. al.*, 1995; Wierzba, I. and Ale, B.B., 1998). It was suggested initially by White (1925) that at elevated temperatures the composition of the mixture might change due to preignition chemical activity prior to ignition and this would affect the values of the flammability limits. However, he did not determine the nature of these changes in the mixture composition. It was later reported that

the limits of some fuels determined at certain elevated initial temperatures in the steel apparatus were affected by the duration of time of exposure of the fuel – air mixture to these temperatures before spark ignition (residence time) (Wierzba, I. and Ale, B.B., 1999). The longer time of exposure to elevated temperature prior to ignition, the bigger changes were observed in the mixture composition. The changes in the values of the flammability limits were attributed to surface reactions on the steel wall of the test tube acting as catalyst. It is well known that, steels exhibit various catalytic properties. They contain elements such as Cr, Ni, Mn. These elements along with their oxides, which could be produced at the surface, are active in promoting oxidation reactions (Sittig, M., 1977; Stancheva, M., *et al.*, 1996; Twigg, M. V., 1996). In such conditions, residence time becomes an important parameter influencing values of the limits. The difference in test apparatus materials and residence times might have resulted in different surface catalytic activities, affecting the values of the flammability limits determined at elevated initial temperatures by different researchers (White, A. G., 1925; Wierzba, I. and Ale, B.B., 1999). Therefore, when reporting the flammability limit data, the test vessel material as well as the duration of the residence time should be taken into account. It appears that at elevated temperatures, wider flammability limits were obtained for very short residence times.

It has been proven experimentally that the limits are strongly dependent on the physical parameters such as mixture initial temperature, pressure and gravity acceleration. In practice, flammable mixtures are used under a wide range of operational conditions and

therefore, a great deal of attention has been given to the examination of the influence of such parameters on the flammability limits.

Effect of temperature on the flammability limits. Since many industrial processes involving fuels take place at elevated temperatures, many investigations were performed over the years to find the effect of temperature on the flammability limits. Numerous investigations showed that in most cases, an increase in the initial temperature broadens almost linearly the flammability limits of gaseous fuels (Coward, H. F. and Jones, G. W., 1952; Zabetakis, M. G. and Richmond, J. K., 1965; Wierzba, I. and Ale, B. B., 1999). Such behavior was expected since with an increase in the initial gas temperature less heat must be released by combustion reactions (at the limit) to raise the gas temperature to the certain threshold level required for self sustained flame propagation. Heat release in chemical reactions is directly related to the amount of fuel and oxygen available for the reaction, or in other words stoichiometry of the limiting mixture.

Experiments showed that after exceeding certain temperatures, the further increase in initial temperature can narrow the flammability limits of some fuels especially, when experiments are conducted in a steel apparatus and longer residence times are employed (White, A. G., 1925; Bunev, V. A., 1972; Wierzba, I. and Ale, B.B., 1998). The behavior was explained by changes in the test mixture composition before ignition due to preignition chemical activity (White, A. G., 1925; Coward, H. F. and Jones, G. W., 1952, Zabetakis, M. G., 1965; Bunev, V. A., 1972). The changes may be the result of fuel decomposition as well as its oxidation due to the gas phase or/and surface reactions.

Effect of pressure on flammability limits. Normal variations in atmospheric pressure usually have insignificant effect on the values of the flammability limits, but comparatively large pressure variations may significantly influence their values. Experiments have shown that the limits of majority of fuels are widened with increases in pressure above atmospheric and slightly narrowed with pressure decreases below atmospheric pressure (Bone, W. A., *et al.*, 1928; Coward, H. F. and Jones, G. W., 1952; Bartkowiak, A. and Zabetakis, M. G., 1959; Zabetakis, M. G. and Richmond, J. K., 1965; Zabetakis, M. G., 1965; Lovachev, L. A., 1979). In some cases, the effect of pressure on the limits is different than this trend. For example, the flammability limits of carbon monoxide were reported to narrow with an increase in pressure (Bone, W. A., *et al.*, 1928; Coward, H. F. and Jones, G. W., 1952). Accordingly, unlike the effect of initial temperature, the effect of pressure is different for different fuels and does not have a single explanation (Coward, H. F. and Jones, G. W., 1952; Lovachev, L. A., 1979). It should be noted that the investigations of the effect of pressure on the flammability limits were conducted in relatively small closed vessels. During combustion in such closed vessels, the pressure would increase due to the heat release and would affect flame structure and speed, and consequently influence the values of the flammability limits (Coward, H. F. and Jones, G. W., 1952; Lovachev, L. A., 1979).

Effect of diluents. Many industrial low heating value gases contain diluents, such as CO₂, N₂, etc, which may affect the flammability limits. The addition of inert diluents changes the thermo-physical properties of the mixtures (specific heat, thermal conductivity, etc.). The change in the mixture properties results in the change of the necessary heat release at

the limit and as a result affects the value of the flammability limit (Zabetakis, M., *et al.*, 1948; Coward, H. F. and Jones, G. W., 1952; Glassman, I., 1987). For example, the addition of argon to methane – air mixtures lowers the lean limits mainly due to the smaller heat capacity of argon in comparison with air, which is substituted at the lean limit by a diluent (Coward, H. F. and Jones, G. W., 1952; Wierzbza, I., 1985). Also, the rich limits of some fuels (e. g. methane) are more sensitive to addition of inert diluents than lean limits. It results from a higher sensitivity of combustion reactions to the presence of third body (inert diluent) in the rich mixtures than in the lean mixtures, an inert diluent promotes chain termination reactions slowing down the overall reaction rate (Glassman, I., 1987).

It was also shown that the flammability limits could be strongly affected by the addition of chemically active substances. For example, the addition of halogenated compounds strongly affects (narrows) both flammability limits. Such substances assist in reducing hydrogen radicals concentration, which are necessary for chain branching reactions.

Effect of gravity. Flammability limits found in a standard flammability tube apparatus are always affected by the presence of the gravitational field (Ronney, P. D., *et al.*, 1980; Ronney, P. D., 1985, Strehlow, R. A., *et al.*, 1986). Heat release during combustion causes a decrease of the gas density and in a gravitational field, results in buoyant force being applied to the hot gases. Free convective currents produced due to buoyancy enhance the heat transfer from the flame zone to the unburned mixture assisting and stabilizing the upward flame propagation while hindering downward flame propagation. It results in widening of limits for upward flame propagation and narrowing the limits for downward flame propagation (Lovachev, L. A., 1971; Ronney, P. D., 1985). Values of the limits for

horizontal flame propagation usually lay between that for upward and downward flame propagation (Coward, H. F. and Jones, G. W., 1952; Kumar, R. K., 1985; Ronney, P. D. and Wachman, H. Y., 1985).

Experiments have also shown that with an increase in gravity acceleration, flammability limits narrow and this narrowing is steeper for downward flame propagation than for upward flame propagation (Lovachev, L.A., *et al.*, 1973).

2.2 Theoretical studies of the flammability limits

Many theories of flammability limits have been proposed. Initially, these theories attributed the existence of the flammability limits to the importance of only one factor such as the effects of either heat losses, chemical kinetics, flame stretch, preferential diffusion of one of the reactants, or factors bringing about flame instability (Mallard, H and LeChatelier, H. L., 1883; Zeldovich, Ya., B., 1944; Spalding, D. B., 1957; Lovachev, L. A., 1971; Hertzberg, M., 1976; Jarosinski, J., 1986; Law, C. K. and Egolfopoulos, F. N., 1990; Law, C. K. and Egolfopoulos, F. N., 1992). However, the real flame quenching mechanism is very complex and may be different in different conditions and for different mixtures. Therefore, none of the suggested theories was able to provide accurate solutions for all fuel – oxidant combinations at the variety of conditions.

Thermal theories. One of the first attempts to analyze the phenomenon of the flammability limits theoretically was made by Zeldovich (1944) over 50 years ago. Who related it to the heat transfer phenomenon. In the process of flame propagation, active chemical reactions take place in a very thin layer of gas called the flame front. The temperature in this zone is relatively high and heat losses to the surrounding may overcome heat generated by the reactions. As a result, the temperature of this zone decreases and the reaction rate, which depends logarithmically on temperature, falls causing flame quenching. According to this theory, all flammable mixtures should have limiting compositions below which flame propagation is impossible.

Lovachev (1971) in his convective theory of flammability limits related the phenomena to the effect of convection. His theory provided an explanation for the wider flammability limits for upward flame propagation. However, it failed to explain the existence of the flammability limits in zero gravity (Ronney, P. D. and Wachman, H. Y., 1985). Later, other thermal theories were offered attributing flame extinction to the conductive – radioactive heat losses and flame stretch (Andrews, G. E. and Bradley, D., 1973; Hertzberg, M., 1976; Jarosinski, J., 1986) but these theories also failed to give accurate prediction of the flammability limit values.

Chemical Kinetics Theories. The heat release in the combustion zone is related directly to reaction kinetics. The necessary heat balance can be maintained only if a certain minimum overall reaction rate is maintained. This is possible when chain-branching reactions (producing active radicals) and chain-termination reactions (consuming active radicals) are in a balance. Chain-branching reactions are, in general, more temperature sensitive than chain-termination reactions and as the limit approaches the reduction in flame temperature leads to a slowdown of the overall reaction rate (Peters, N. and Smooke, M. D., 1984; Law, C. K. and Egolfopoulos, F. N. 1990). Law and Egolfopoulos (1990) suggested that the flammability limits can be determined as the turning points where chain branching reactions cannot keep pace with chain-termination reactions causing the abrupt slowdown of the overall reaction rate. They also suggested that radiative heat losses should be considered in the flame model (Law, C. K. and Egolfopoulos, F. N. 1992). The results of their calculations showed reasonably good agreement with experimental results for some fuels and fuel mixtures (e.g. CO, H₂, CO/H₂, CH₄, C₂H₄, C₂H₆, C₃H₈).

Diffusion theories. It is well known that for some mixtures such as moist CO/O₂ and H₂/O₂ the concentrations of certain radicals (e.g. H, OH) in the flame zone are the important parameters determining flame velocity and therefore affecting the flammability limit values. These concentrations are dependent stronger on the radical diffusion process than on the heat conduction. Therefore, in some theories attempts have been made to relate the phenomenon of the flammability limits to the effect of diffusion (Kanury, M., 1975; Kuo, K. K., 1986 ; Jarosinski, J., 1986).

Other theoretical approaches for prediction of flammability limits. Some useful approaches based on different simplifying assumptions have been offered for estimation of the values of flammability limits. One of the most common methods used, for example, for estimation of flammability limits of fuel mixtures is the Le Chatelier's Rule. This method is based on the assumption that any mixture of limiting fuel mixtures is itself a limiting mixture. The results of the tests have shown that with some exceptions the rule is fairly accurate in prediction of the lean limits and to a lesser extent the rich limits of fuel mixtures (Karim, G. A., et al., 1985; Wierzba, I., et al., 1986; Wierzba, I., et al., 1992).

As early as in 1925 White (1925) and later Zabetakis (1965) reported that the calculated adiabatic flame temperatures remain almost constant at the limit when some amount of a diluent is added or initial gas temperature is changed. The so-called "constant adiabatic flame temperature" approach for estimation of the effect of diluents on flammability limits as well as the effect of temperature was proposed recently (Wierzba, I., et al., 1996). In the proposed approach it was assumed that the threshold temperature in the reaction zone (proportional to adiabatic flame temperature) remains almost constant at the limit when the

amount of a diluent or gas temperature is changed. Assuming the adiabatic flame to be constant, the values of the limits at different initial temperatures or with different concentrations of a diluent in the mixture may be estimated. This method gives very good predications for a wide range of mixture temperatures and diluent concentrations (Wierzba, I., et al., 1996).

CHAPTER 3. EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Experimental Apparatus

In this study an apparatus similar in design to the flame tube used by U.S. Bureau of Mines was employed. A schematic diagram of the apparatus is shown in Fig.3.1, while a photograph of the actual apparatus is presented in Fig.3.2.

The test apparatus consists of the following main parts:

- the test flame tube
- ignition system
- heating system
- compressed air supply system
- compressed gases supply system
- mixing chamber with agitating fan
- vacuum system

The apparatus was designed to facilitate pressure, temperature and composition measurements of the test mixture. The test flame tube consists of smooth circular stainless steel (316) tube, 50.8 mm in diameter and one metre in length. For experiments at elevated initial temperatures the tube was heated externally by an electric heater with an automatic temperature controller. To ensure uniform heating over the whole tube length two additional heaters with manual temperature controls were employed at the tube ends.

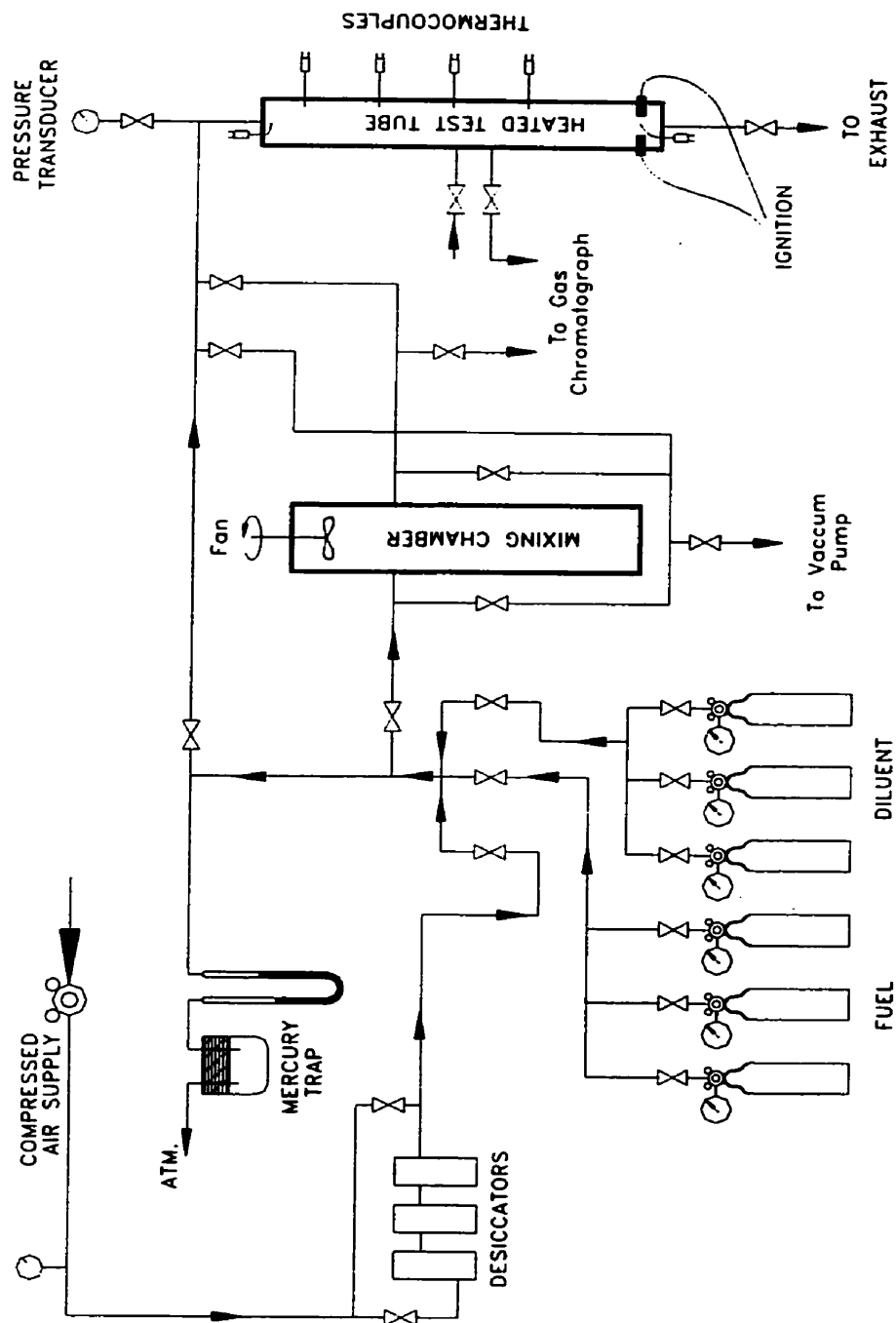


Fig. 3.1 Schematic diagram of the test apparatus.

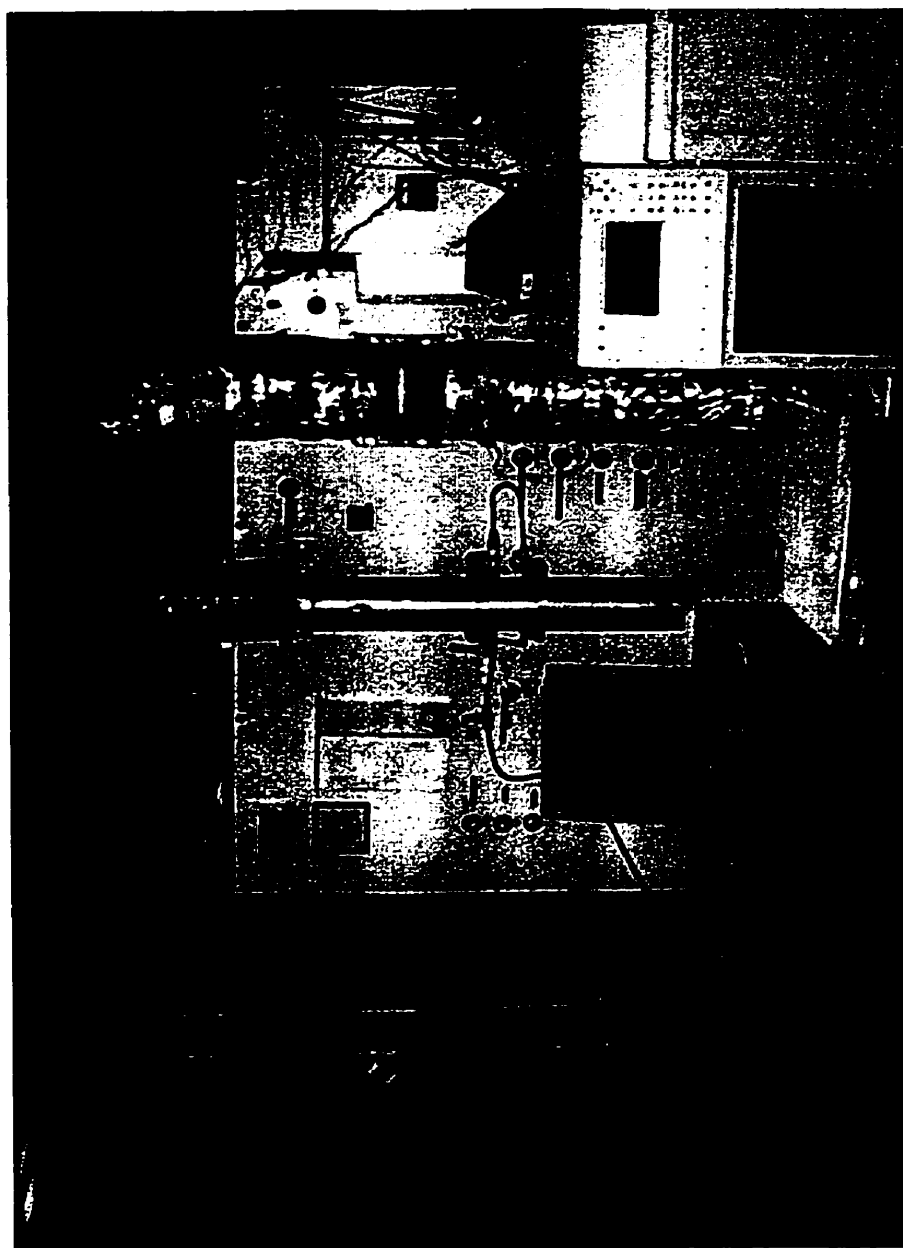


Fig.3.2 Experimental apparatus

The tube and the heaters were wrapped with a ceramic heat-insulation to decrease heat losses from the tube and to maintain uniform temperature along the tube wall. A set of chromel – alumel (K- type) thermocouples was used to monitor the gas and wall temperatures. The arrival of the flame at the top of the test tube was detected by a thermocouple installed at the centre of the test tube close to the top. An additional thermocouple at the bottom of the test tube was used to detect the flame kernel development after spark ignition. Pressure of the test mixture was measured by a strain pressure transducer (Omega, PX-425-030V), which was mounted at the top of the test tube. To avoid condensation during the experiments with higher than in the atmospheric air concentrations of water vapor in the mixture, the inlet valve and the pressure transducer were also heated.

An electrical spark discharge of 0.2 second duration between two horizontal conical tungsten electrodes placed 38 mm from the lower end of the tube was used to ignite the mixture. The electrical power for ignition was supplied by a 10 kV and 23 mA centre-tapped transformer with its primary hooked to a 110 V, 60 Hz power supply. The lower end of the tube was connected to an exhaust system to prevent contamination of the laboratory air.

Homogenous fuel – air mixtures were prepared in a separate 4.2 l stainless steel mixing chamber equipped with a mixing fan.

Ambient atmospheric air was supplied by a compressor through series of oil separating filters. For some experiments, air was dried by passing it through three desiccators installed in tandem before mixing it with a fuel. The tests were conducted with different

concentrations of water vapor ranging from the estimated concentration of about 15 ppm up to 20% by volume in the total mixture. Taking into consideration the properties of silica gel used in the desiccators (dew point of the air on the exit below -70°C) and the level of vacuum in the test tube (below $8 \cdot 10^{-3}$ torr), the minimum concentration of water vapor was estimated to be about 15ppm. In the tests conducted with the higher than in atmospheric air concentrations of water vapor, water was injected into the heated and evacuated test tube. After the desirable level of partial pressure of water vapor in the tube was reached the prepared “dry” fuel – air mixture was introduced in the test tube. Pressure and temperature in the test tube were monitored to insure no condensation after introduction of the fuel – air mixture during the residence time.

The fuels were supplied from gas cylinders. The purities of the gases used are given in Table 3.1 below.

Table 3.1 Purity of gases used

FUEL	PURITY, %
Dry carbon monoxide*	99.9
Hydrogen	99.9
Carbon dioxide	99.8

*Water vapor concentration less than 5 ppm.

A vacuum pump capable of providing vacuum less than $8 \cdot 10^{-3}$ torr was employed for evacuation of the system. The outlet of the vacuum pump was connected to the exhaust duct to prevent possible contamination of the laboratory atmosphere. Provision was made to evacuate independently the mixing chamber and the test tube.

3.2 Experimental procedure

Before conducting the experiments all fittings were checked for possible leaks.

Homogeneous fuel – air mixtures for the tests were prepared on the basis of partial pressure in the mixing chamber and then transferred to the heated and evacuated test tube. The test tube was filled with the mixture until the pressure in the tube was about 100÷105 kPa. After attaining the desired temperature, the test mixture was retained in the test tube for a certain time before spark ignition to be described as the *residence* time. For a majority of the experiments the residence time was 5 minutes. However, in some experiments related to the investigation of the effect of the preignition chemical activity at elevated temperatures on the flammability limits, the duration of the residence time was varied from 2 to 30 minutes. A mixture was considered to be *non-flammable* if a flame kernel formed in the immediate vicinity of the spark *did not propagate the whole length of the tube* in any of the three repeated identical tests using the same composition and procedure. Two trials were used to establish the value of the limit in the experiments with longer residence times. The arrival of the flame at the top of the tube was detected by a thermocouple installed at the centre of the test tube close to the top. The increase in the mixture temperature of at least 8°C (~0.3 mV) detected by the thermocouple was regarded as indication of the flame propagation. Between the experiments the test tube was purged with “dry air” for 2 – 5 minutes. The temperature and pressure within the test tube were monitored closely during the residence time, and samples of the test mixtures were taken from the test tube for gas analysis after a desired time. Relative molar concentrations (mole %) of the carbon dioxide,

oxygen and nitrogen were determined with the VARIAN gas chromatograph as well as an ORSAT apparatus.

The accuracy of the limits determined was estimated to be within $\pm 2.6\%$ for the lean mixtures (excluding “dry air” case) and $\pm 1.2\%$ for the rich mixtures. The maximum uncertainty of species concentrations (using gas chromatograph) was estimated to be within $\pm 2.5\%$.

Using the described procedure the lean and rich flammability limits of carbon monoxide and carbon monoxide – hydrogen mixtures in air with different concentrations of water vapor present in the mixtures were found at various initial temperatures up to 300°C and at different residence times up to 30 min. Repeatability of the obtained results was checked regularly.

CHAPTER 4

FLAMMABILITY LIMITS OF CARBON MONOXIDE IN AIR

The flammability limits reported in this contribution were determined experimentally for upward flame propagation at atmospheric pressure (Calgary, around 89kPa). The lean limit as quoted is the maximum concentration of fuel in the *lean* fuel – air mixture and the rich limit is the minimum concentration in the rich fuel – air mixture, at which there was no self-sustained flame propagation through the mixture.

4.1 Effect of initial temperature and water vapor concentration.

The flammability limits of carbon monoxide were established at different initial temperatures, ranging from 18°C to 300°C with mixtures containing different small concentrations of water vapor.

The experiments were performed with relatively short residence time (time interval between the test mixture attaining the required temperature and spark ignition) of 5 minutes to minimize the effect of possible preignition chemical activity at elevated temperatures. The results are shown in Tables 4.1 and 4.2, and Fig.4.1 and Fig.4.2. It can be seen that the flammability limits were somewhat broadened with an increase in the initial temperature. Moreover, the limits widened substantially when ambient air containing water vapor (from 0.3 to 1.5% by volume) was used in comparison with “dry air”, which contained approximately 15 ppm of water vapor. The limits were widened further when the water

Table 4.1 Rich flammability limits of carbon monoxide in air

Initial temperature	Water vapor in the mixture									
		~15ppm			Atmospheric air (~1.2%)			3.2%, by volume		
		RL _{exp}	RL _{calc}	Dev., %	RL _{exp}	RL _{calc}	Dev.,%	RL _{exp}	RL _{calc}	Dev.,%
	18°C	55.5	52.4	3.8	67.2	67.2	0	-	-	-
	100°C	54.7	54.7	0	69.3	69	0.4	73	73	0
	200°C	56.2	57	- 1.4	72.7	71.4	1.8	77.2	75.7	1.9
300°C	58.2	59.6	- 2.3	73.6	73.8	-0.3	78.9	78.1	1	

Table 4.2 Lean flammability limits of carbon monoxide in air

Initial temperature	Water vapor in the mixture									
		~15ppm			Atmospheric air (~1.2%)			3.2%, by volume		
		LL _{exp}	LL _{calc}	Dev., %	LL _{exp}	LL _{calc}	Dev., %	LL _{exp}	LL _{calc}	Dev., %
	18°C	18.3	20.7	- 13.1	13.6	13.6	0	-	-	-
	100°C	19.8	19.8	0	12.8	12.8	0	11.4	11.4	0
	200°C	17.8	18.7	- 5.1	11.3	11.7	-3.5	10.0	10.3	-3
300°C	15.8	17.6	- 11.4	10	10.6	-6	8.7	9.3	-6.5	

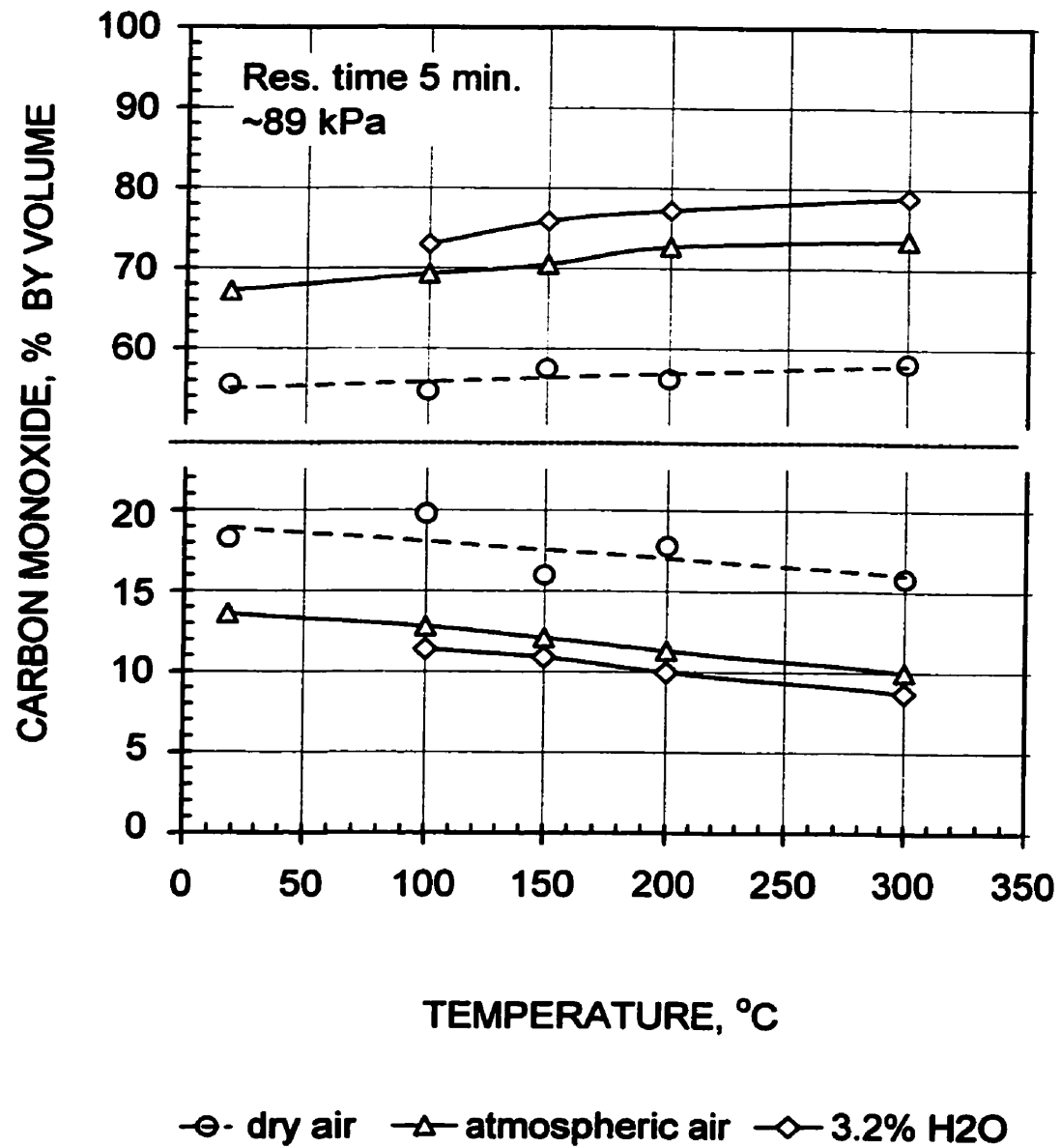


Fig. 4.1 Flammability limits of carbon monoxide in air

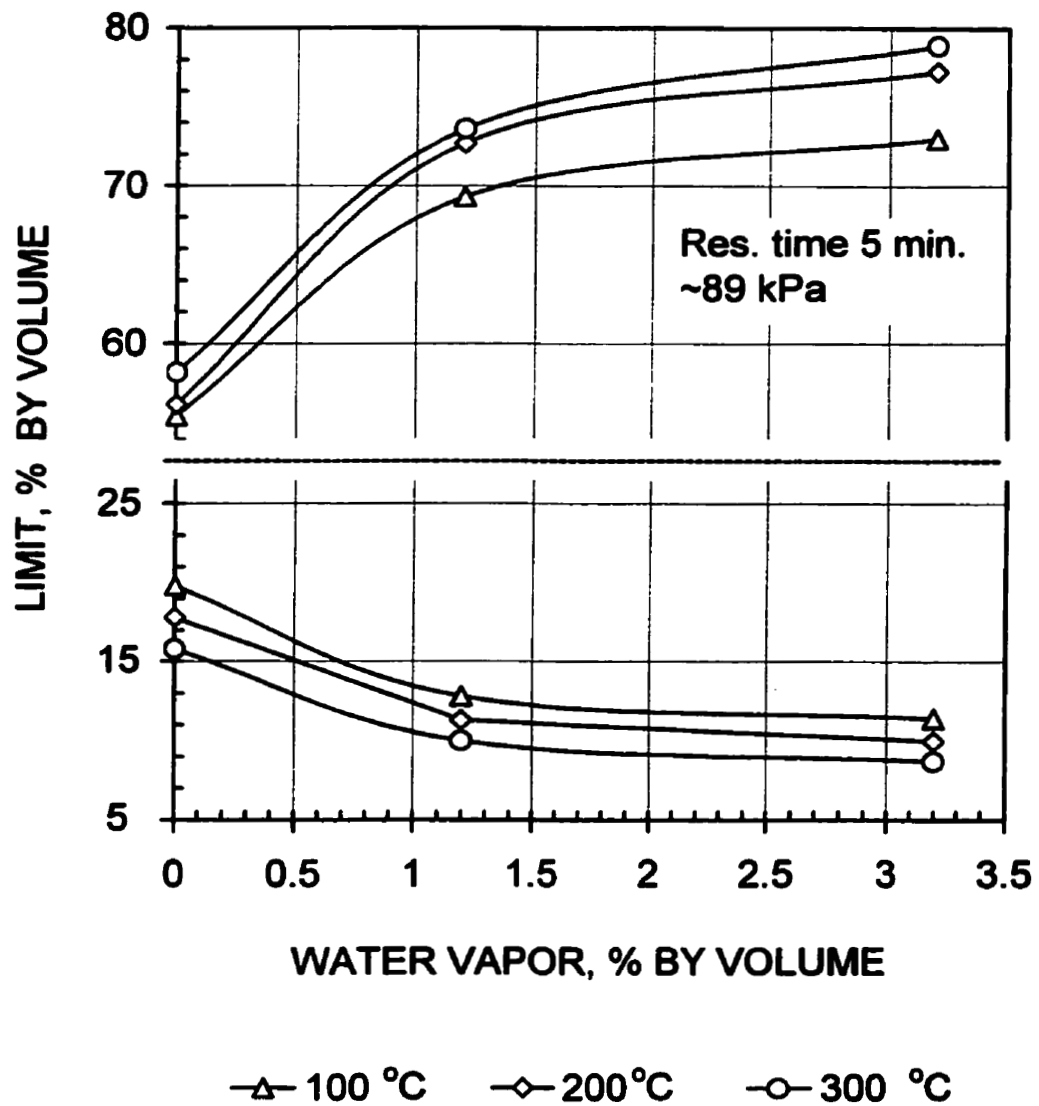


Fig. 4.2 Flammability limits of carbon monoxide in air as a function of water vapor concentration in the mixture for three different temperatures

vapor concentration was increased to ~ 3% by volume (Fig.4.1). The effect of presence of water vapor in the mixture on the limit values is stronger than that of initial temperature at the conditions considered. Coward and Jones (1952), and Harris (1990) also reported that the lean flammability limits of carbon monoxide in air at room temperature were lowered significantly when air saturated with water vapor was employed instead of “dry air”. These results were expected as small concentrations of water vapor in carbon monoxide – air mixtures have a profound effect on the chemistry of carbon monoxide oxidation through the supply of hydrogenous radicals. Due to high activation energy of the direct reaction of carbon monoxide with oxygen (Table 4.3), dry mixtures are very difficult to ignite and burn (Lewis, B. and Von Elbe G., 1987; Trujillo, J. Y. D., *et. al.*, 1997). However, if hydrogenous radicals are present in the mixture the oxidation reactions would proceed

Table 4.3 Activation energies of carbon monoxide oxidation reactions

Reaction	Activation Energy
$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	201, 600 J/mol
$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	4, 536 J/mol
$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{H}$	96,600 J/mol

Lewis, B. and Von Elbe G., 1987

through OH radicals (i. e. reactions having smaller activation energies). These hydrogenous radicals may be provided by small traces of any hydrogen-containing species such as hydrogen itself, water vapor or hydrocarbon fuels. It was also reported earlier

(Brokaw, R. S., 1967) that water vapor even in very small concentration (~20 ppm) present in the mixture controls oxidation reactions of carbon monoxide.

Also, calculations conducted by the author using a chemical kinetics code developed by Liu (1995) showed that the mean reaction rate can be increased by orders of magnitude by small increase in water vapor concentration in the mixture as shown in Fig. 4.3. Therefore, when determining the flammability limits of carbon monoxide it is very important to specify the humidity of the air used for the test mixtures.

Some difficulties were encountered while determining the lean flammability limit of carbon monoxide in “dry air” at room temperature. When a large number of the experiments have been conducted in four successive days, it was difficult to establish on the basis of three repeated tests the value of the lean limit as it can be seen in Fig. 4.4. However, this behavior diminished very significantly with an increase in the initial temperature and/or when water vapor was present in the mixture. For example, the value of the lean limit at the temperature of 200°C is clearly 17.8% as it can be seen in Fig. 4.5. The value of the lean limit in “dry air” was estimated to be 18.3%. The corresponding values reported by Harris (1990) and Coward and Jones (1952) were 14.1% and 15.9%, respectively. Migration of very small uncontrollable quantities of water vapor or vacuum oil, initially adsorbed on the walls, might cause the observed variations in the experimental results with “dry air”.

The lean limit of carbon monoxide in moist (atmospheric) air of 13.6% established in the present work is very close to the value of 13.1% reported by Coward and Jones (1952), and was higher than the value of 12.4% reported by Harris (1990).

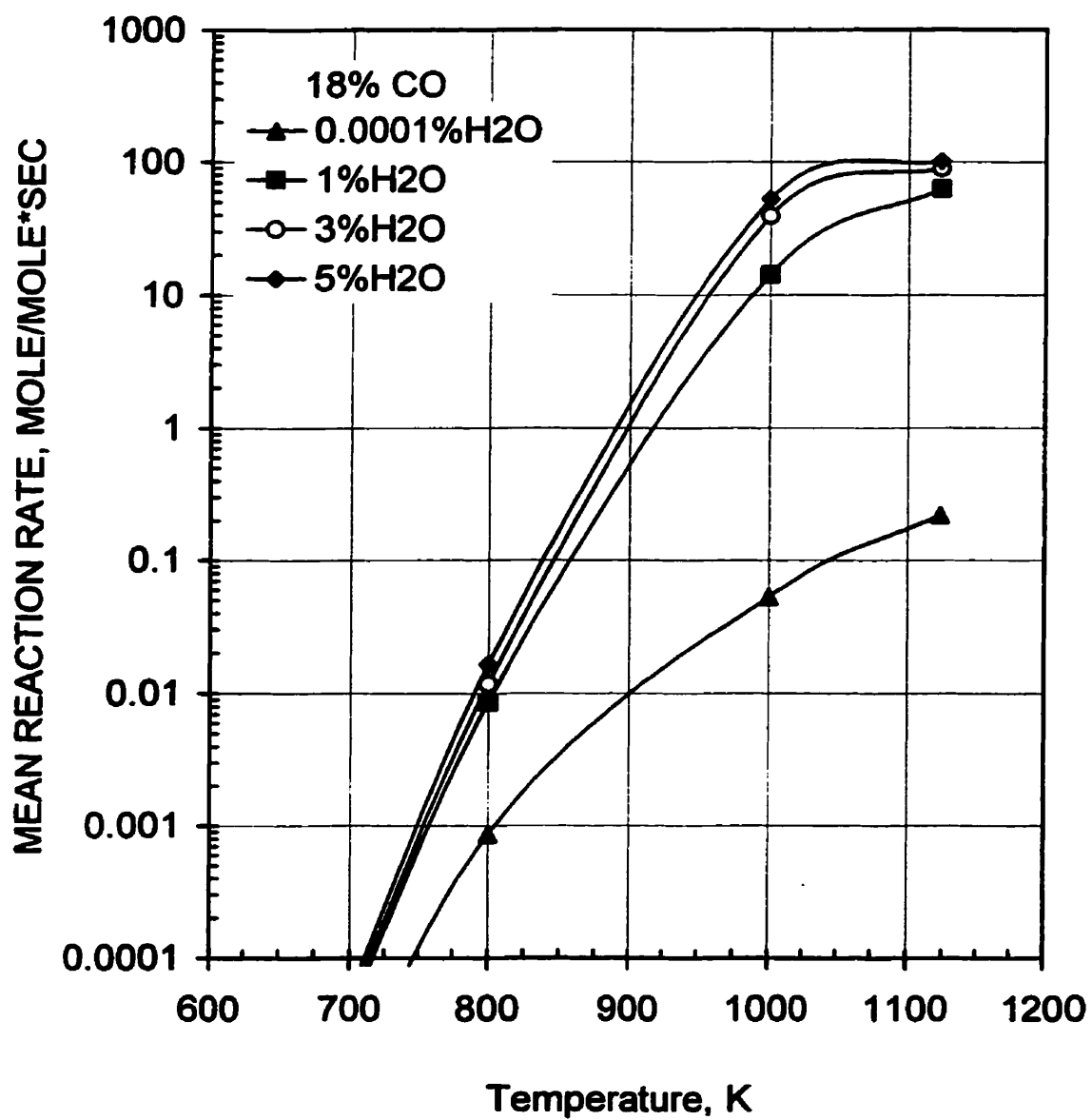


Fig.4.3 Effect of water vapor addition to carbon monoxide - dry air mixture on the mean reaction rates

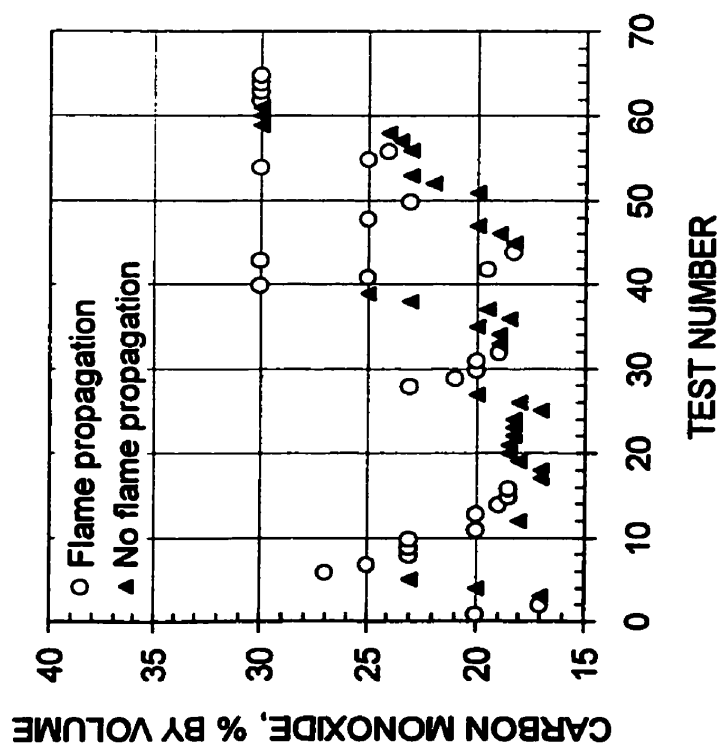


Fig. 4.4 Determination of the lean flammability limit in "dry air" at 18°C and residence time of 5 min.

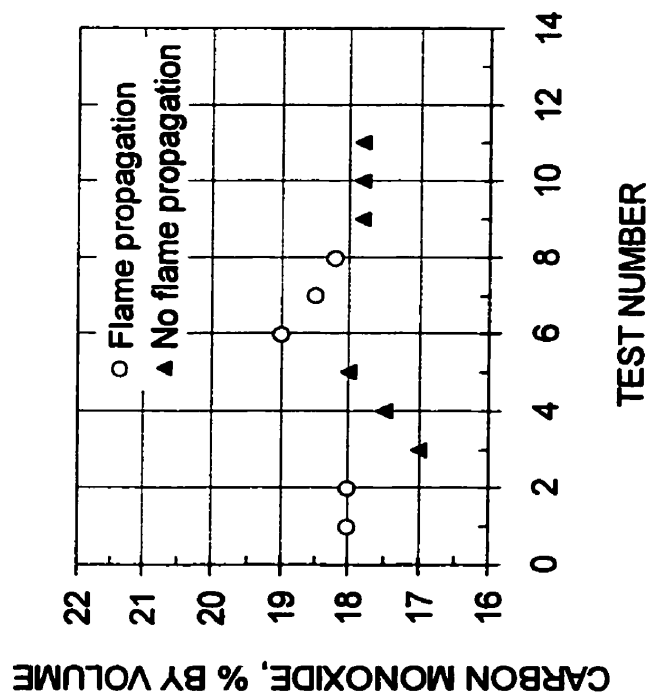


Fig.4.5 Determination of the lean flammability limit in "dry air" at 200°C and residence time of 5 min.

Table 4.4 Flammability limits of carbon monoxide in air as a function of the water vapor concentration at two different temperatures

Water vapor in the mixture	Initial temperature			
	150, °C		300, °C	
	<i>Rich limits</i>	<i>Lean limits</i>	<i>Rich limits</i>	<i>Lean limits</i>
~ 15 ppm	57.5	16	58.2	15.8
Atmospheric air (~0.3%)	70.5	12.1	73.7	10
3, % by volume	76	10.9	78.9	8.7
4, % by volume	75.1	10.9	-	-
5, % by volume	74	11.2	-	-
10, % by volume	68.6	11.7	72.5	9
20, % by volume	58.4	12	63.5	9.5

Effect of higher than 3% concentrations of water vapor was investigated at two different temperatures of 150°C and 300°C. The results are shown in Table 4.4 and Fig.4.6. It can be seen that at higher water vapor concentrations, the flammability limits narrow with an increase in the water vapor concentrations at both initial temperatures. This is because of the effect of water vapor as a diluent becomes more significant, than that of a promoter of carbon monoxide oxidation.

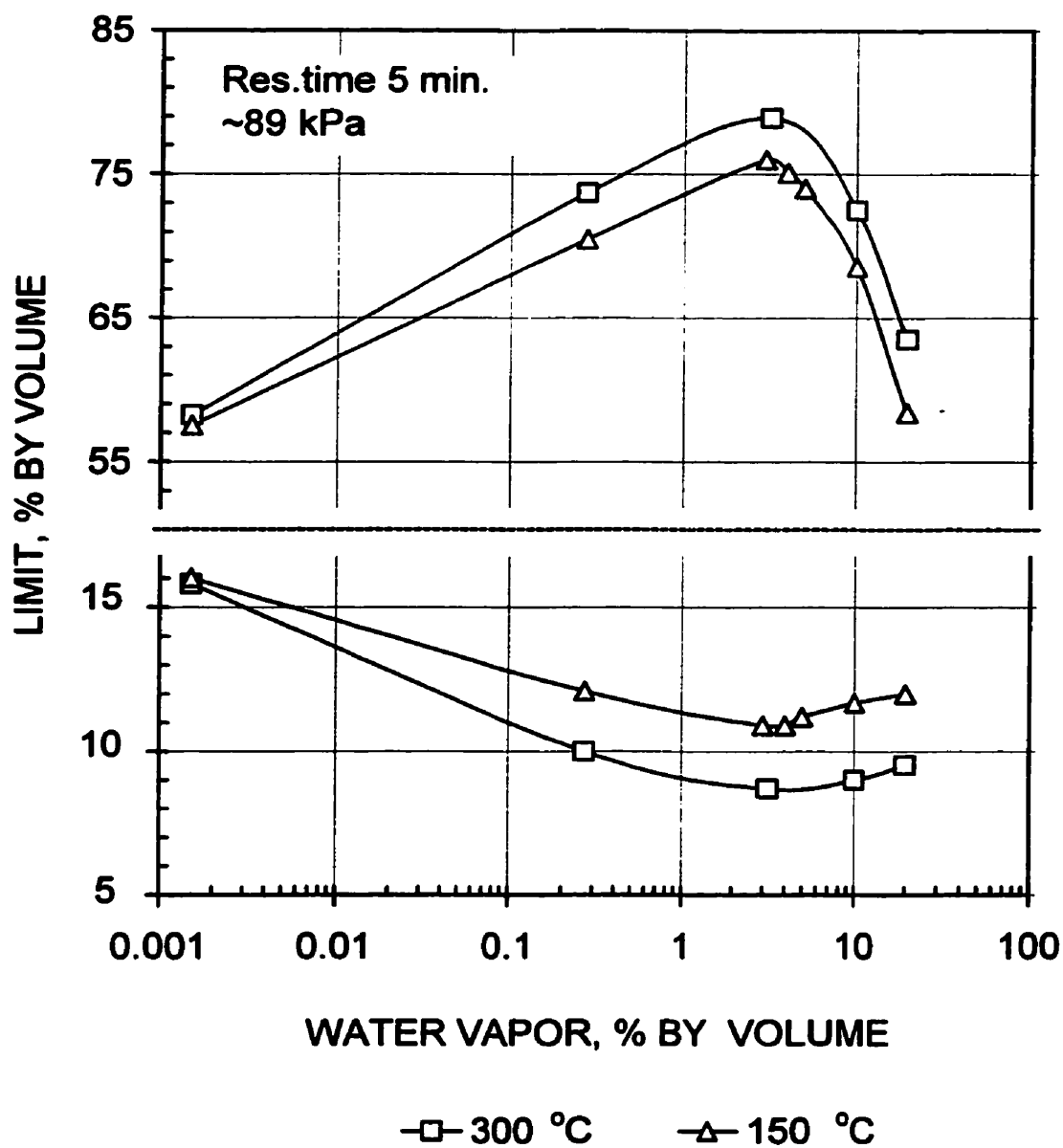


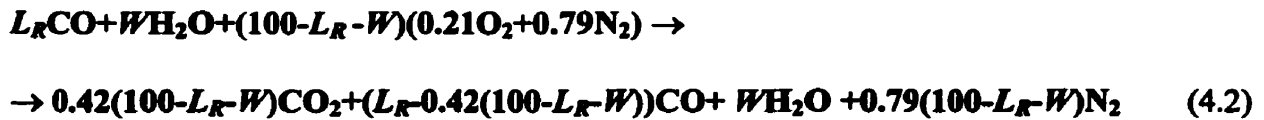
Fig. 4.6 Flammability limits of carbon monoxide as a function of water vapor concentration in the total mixture

4.2 Prediction of the flammability limits of carbon monoxide

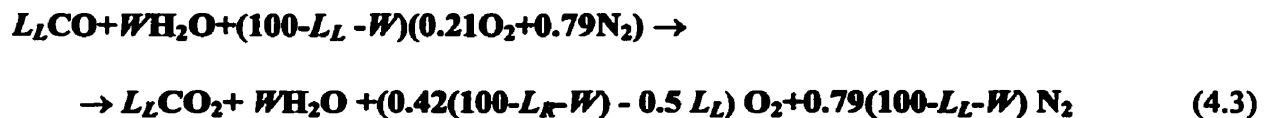
Experimentally established values of the flammability limits of carbon monoxide at elevated initial temperatures were compared with calculated values using the so-called “constant adiabatic flame temperature approach” (Bade Shrestha, S. O., *et al.*, 1995). This approach is based on the assumption that the adiabatic flame temperature remains constant at the limit regardless of the initial temperature of the mixture. The adiabatic flame temperature may be calculated on the basis of a known value of the limit at a certain temperature using the First Law of Thermodynamics (Eq. 4.1) and the corresponding overall reactions:

$$\left[\sum_i H_{i,react} \right]_{T_o} = \left[\sum_i H_{i,prod} \right]_{T_{f,ad}} \quad (4.1)$$

For rich mixtures:



For lean mixtures:



where,

T_o – initial temperature of the mixture, K

$T_{f,ad}$ – adiabatic flame temperature, K

$H_{i,react}$ – enthalpies of the reactants at initial temperature, kJ/kmol

$H_{i,prod}$ – enthalpies of the products at adiabatic flame temperature, kJ/kmol

L_R, L_L – values of the rich and lean limits respectively, % by volume

W – water vapor concentration in the mixture, % by volume

Then the value of the adiabatic flame temperature determined in this way is used to calculate the limits at different initial temperatures or for mixtures with different water vapor concentrations applying the same equations (Eq. 4.1-4.3).

Adiabatic flame temperatures were usually calculated on the basis of the values of the flammability limits established at room temperature. In the case of carbon monoxide – “dry air” mixtures the adiabatic flame temperature was calculated using the experimental values of the flammability limits established at 100°C, since it was less variation in the limit values at this temperature than at the room temperature. The adiabatic flame temperature used for calculations of the flammability limits are shown in Table 4.5. The flammability limits at elevated temperatures were calculated for mixtures of carbon monoxide with dry and atmospheric air as well as for mixtures containing ~3% of water vapor. The results of calculations are shown in Table 4.1 and 4.2, and Fig. 4.7. The experimental values are also shown for comparison.

Table 4.5 Calculated adiabatic flame temperatures ($T_{f,ad}$)

Water vapor	<i>Rich limit</i>	<i>Lean limit</i>
	$T_{f,ad}, K$	$T_{f,ad}, K$
~15 ppm	1961	2012
Atmospheric air	1488	1474
~3 %, by volume	1250	1361

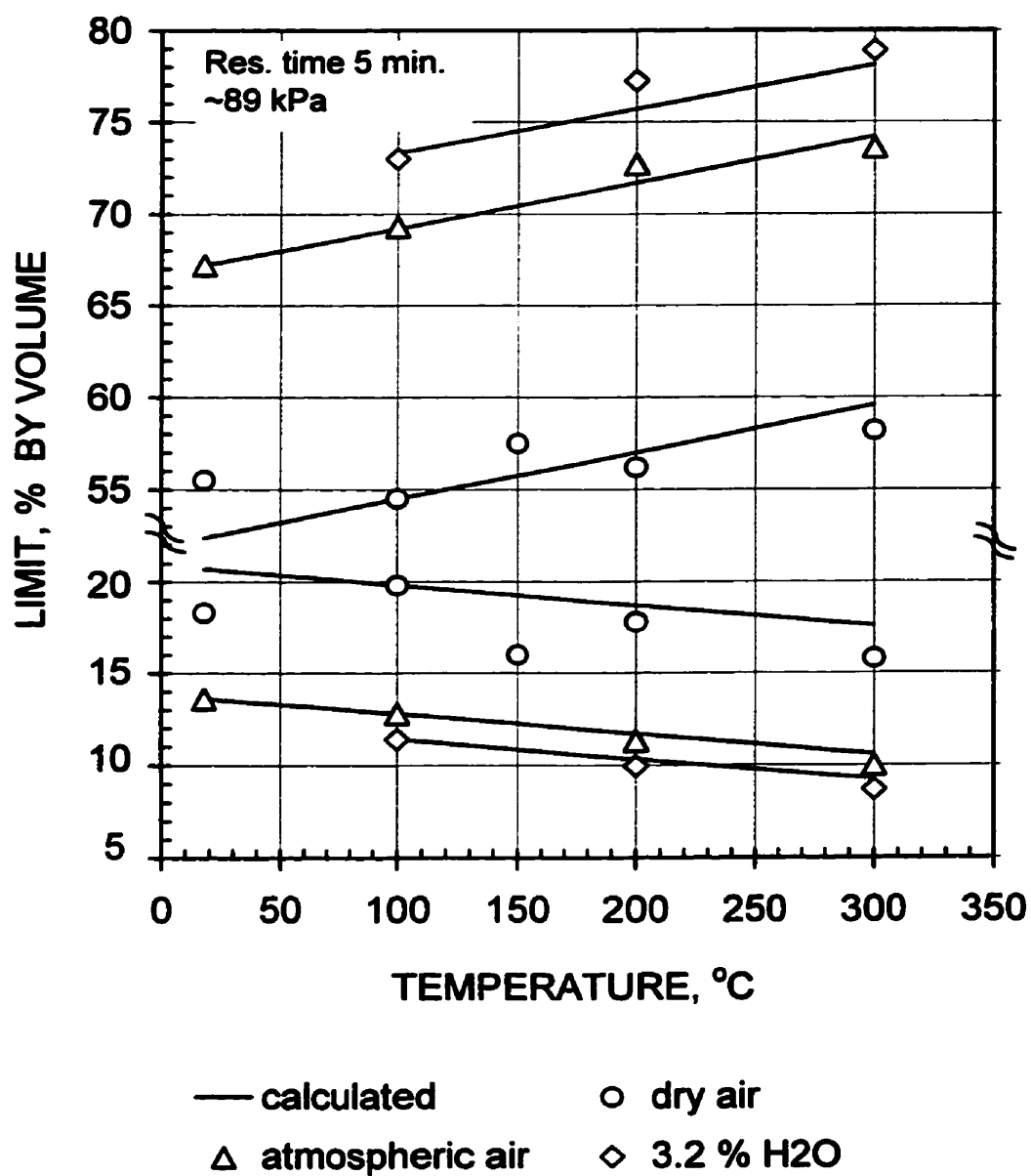


Fig. 4.7 Comparison of the experimental and calculated flammability limits of carbon monoxide at different temperatures

It can be seen that the agreement between calculated and experimentally determined values is better when moist air was employed.

The same approach can be used to estimate the effect of large concentrations of water vapor (acting as a diluent) on the flammability limits. The calculations were conducted for concentrations of water vapor higher than 3%. The adiabatic flame temperatures used in these calculations were 1250 K for the rich limit and 1361 K for the lean limit as in case of mixtures of carbon monoxide with air containing 3% of water vapor. The results of calculations are shown in Table 4.6, Fig. 4.8 and Fig.4.9. It can be seen that the deviation of the calculated values from those established experimentally did not exceed 4.7% for the rich limits and 5.8% for the lean limits.

Higher accuracy of the prediction of flammability limits of carbon monoxide with higher than 3% of water vapor concentrations could be achieved, when adiabatic flame temperatures are calculated using values of the limits obtained at the corresponding elevated temperatures. The results of the calculations are shown for comparison as broken lines in Fig.4.8 and Fig.4.9. The adiabatic flame temperatures were calculated using the experimental values of the flammability limits of carbon monoxide – air mixtures with ~3 % of water vapor at temperatures of 150° and 300°C correspondingly. These temperatures are shown in Table 4.7.

Table 4.6 Comparison of the experimental and calculated flammability limits of carbon monoxide as a function of water vapor concentration in the total mixture

Water vapor concentration % by volume	Initial temperature											
	150, °C						300, °C					
	$L_{R.exp}$	$L_{R.calc}$	Dev.,%	$L_{L.exp}$	$L_{L.calc}$	Dev.,%	$L_{R.exp}$	$L_{R.calc}$	Dev.,%	$L_{L.exp}$	$L_{L.calc}$	Dev.,%
~3	76	74.4	2.1	10.9	10.9	0	78.9	78.2	0.9	8.7	9.2	-5.7
4	75.1	73.4	2.3	10.9	10.9	0	-	77.2	-	-	9.2	-
5	74	72.3	2.3	11.2	11.0	1.8	-	76.1	-	-	9.3	-
10	68.6	67.1	2.2	11.7	11.1	5.1	72.5	70.9	2.2	9	9.4	-0.4
20	58.4	56.5	3.2	12	11.3	5.8	63.5	60.5	4.7	9.5	9.6	-1.0

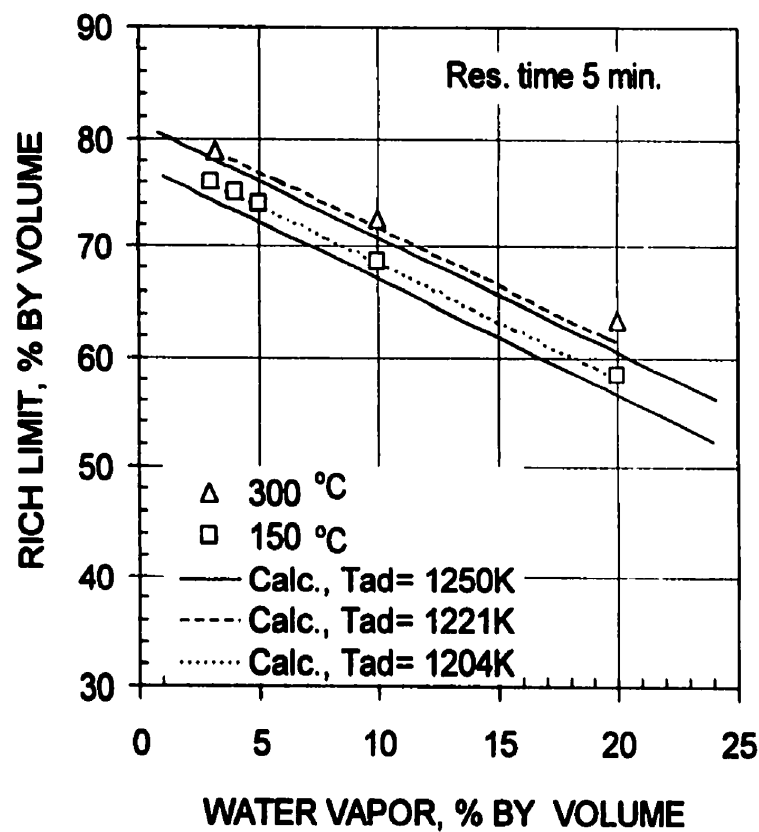


Fig.4.8 Comparison of the experimental and calculated rich flammability limits of carbon monoxide as a function of water vapor concentration in the total mixture.

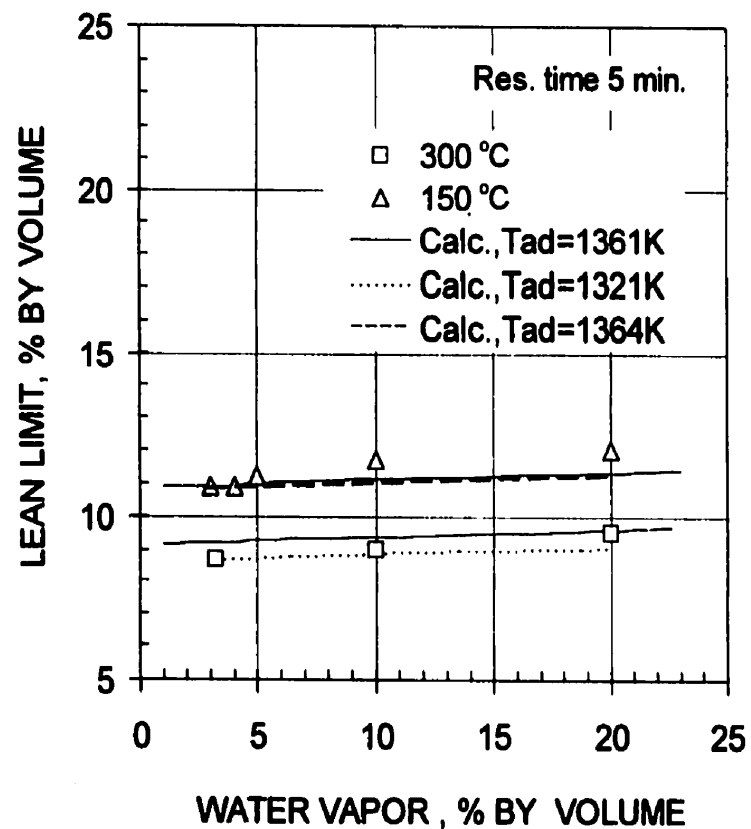


Fig.4.9 Comparison of the experimental and calculated lean flammability limits of carbon monoxide as a function of water vapor concentration in the total mixture.

Table 4.7 Adiabatic flame temperatures calculated for the flammability limits of carbon monoxide in air at elevated temperatures

Initial mixture temperature	Adiabatic flame temperature, K	
	<i>Rich limit</i>	<i>Lean limit</i>
423 K (150°C)	1204	1364
573 K (300°C)	1221	1321

4.3 Effect of the residence time/ preignition chemical activity

It was reported earlier, that there is a possibility of preignition reactions taking place at moderately elevated temperatures (Bunev, V. A., 1972; Ale, B. B., 1998), which can affect the flammability limit values. To investigate the existence of such reactions within CO-air mixtures and their effect on the flammability limits the test mixtures were kept at the desired constant temperature for different duration of time (residence time) prior to spark ignition. The experiments were conducted with “dry air”. The results of the experiments conducted are presented in Table 4.8 and Fig. 4.10. It can be seen that at relatively low temperatures of 150°C the flammability limits were unaffected by the duration of residence time. At higher temperature of 200°C the limits were narrowed with an increase in the residence time. The narrowing was much more significant at the higher temperature of 300°C.

Continuous monitoring of temperature and pressure inside the test tube during the residence time showed that the mixture temperature remained virtually constant, while the pressure was decreasing. The pressure variation at constant temperature and volume

Table 4.8 Flammability limits of carbon monoxide in “dry air” at different temperatures and residence times

Initial temperature	Residence time, min									
	Rich limits, % by volume					Lean limits, % by volume				
	5	10	20	60	120	5	10	20	60	120
150°C	57.5	57.5	57.5	57.5	57.5	16	16	16	16	16
200°C	56.2	-	-	53.5	52	17.8	-	-	18	18.5
300°C	58.2	55.5	53.5	-	-	15.8	17.5	21.8	-	-

conditions indicated a change in the number of mol s within the test tube (i.e. change in mixture composition) and is related to the preignition oxidation of carbon monoxide. Gas analysis of the mixture conducted during the residence time showed that some oxygen was consumed and some carbon dioxide was produced. For example, Fig.4.11 shows variation in the concentration of oxygen and carbon dioxide within a rich mixture of carbon monoxide with “dry air” at the temperature of 300°C at different residence times. The results of gas analysis of the same mixture (60%CO+40% “dry air”) at different temperatures are presented in Fig. 4.12. It can be seen that the intensity of the preignition reactions was strongly dependent on and increased with temperature. At the temperature of 150°C there were almost no changes in the mixture compositions with time, which indicates a very low intensity of preignition reactions at this temperature. These changes in

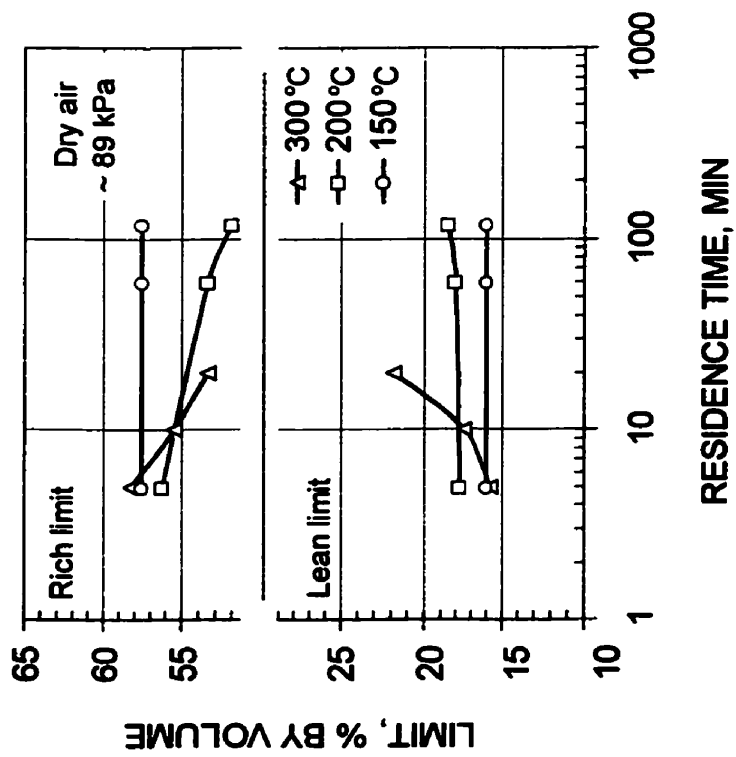


Fig. 4.10 Flammability limits of carbon monoxide in "dry air" as a function of residence time at different initial temperatures

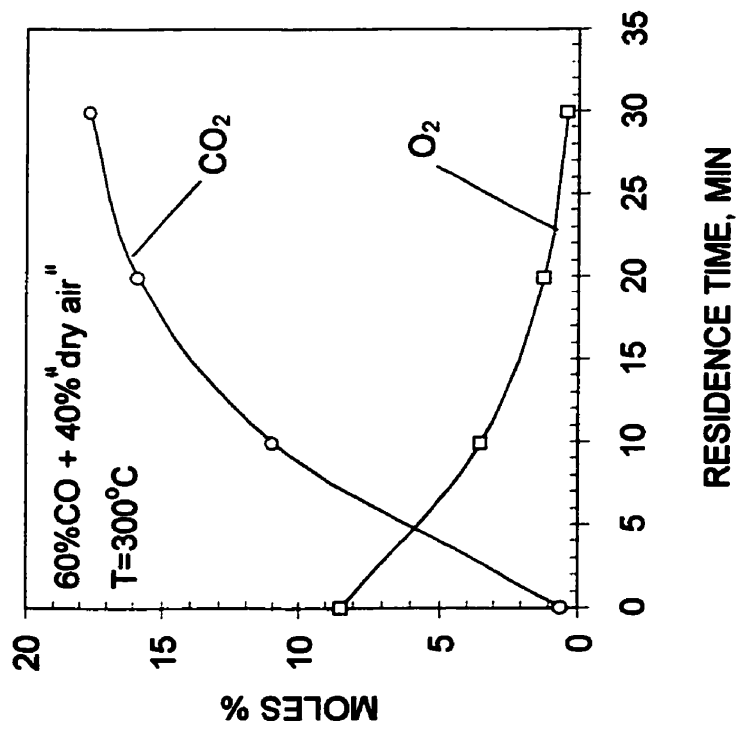


Fig. 4.11 Variation in the concentrations of oxygen and carbon dioxide within the test mixture as a function of residence time

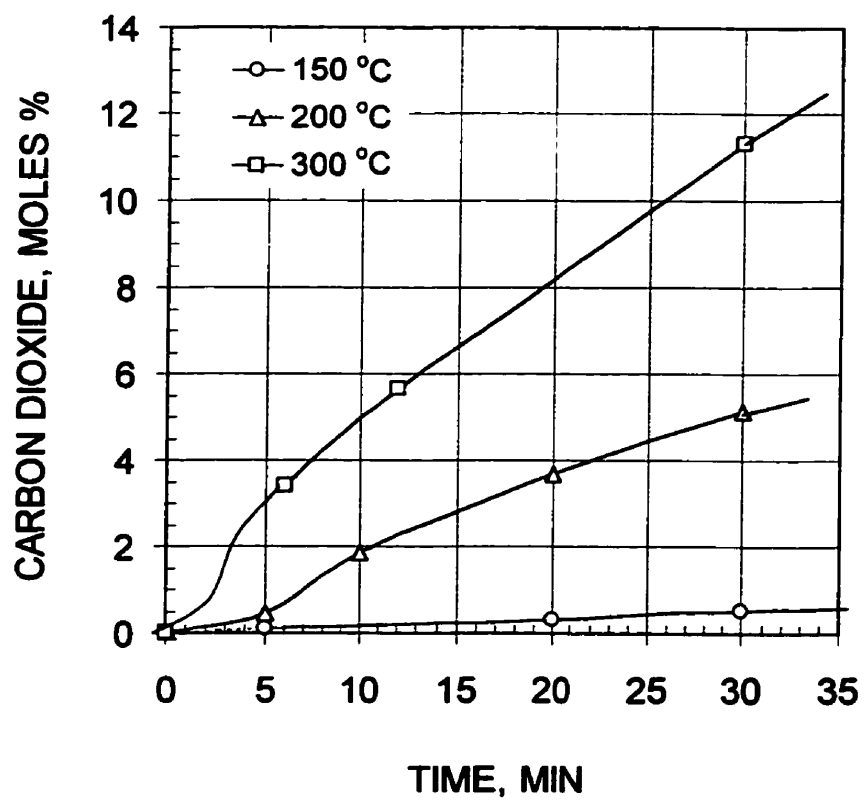


Fig.4.12 Carbon dioxide concentration in the rich mixture of carbon monoxide with "dry air" (60%CO) as a function of the residence time at different temperatures

the mixture composition could be due to gas phase reactions, surface reactions or a combination of both.

Detailed chemical kinetic simulation of the gas phase oxidation of carbon monoxide at a temperature of 300°C (the maximum initial temperature employed in the experiments) in atmospheric air containing ~1% of water vapor (carbon monoxide is more reactive in moist air than in “dry air”), was conducted using a code developed by Liu (1995). The results are shown in Fig.4.13 and 4.14 for lean and rich mixtures, respectively. No noticeable gas phase chemical activity at this temperature level was detected up to two hours. Therefore, it appears that the gas phase reactions could not be responsible for the observed changes in the mixture composition prior to spark ignition and consequently in the flammability limits. These changes were most probably a result of the surface reactions on the walls of the stainless steel tube acting as a catalyst. In Table 4.9 shown the composition of the stainless steel 316 used in the apparatus. It is well known that some elements present in the steel such as Fe, Cr, Ni, Mn (along with their oxides) are good catalysts and may promote oxidation reactions (Stancheva, M., et al., 1996; Sittig, M., 1977; Twigg, M. V., 1996).

Table 4.9 Chemical Composition of Type 316 Steel (ASM Handbook, 1991)

Alloy	Element, weight %							
	<i>C</i>	<i>Mn</i>	<i>P</i>	<i>S</i>	<i>Si</i>	<i>Cr</i>	<i>Ni</i>	<i>Mo</i>
316	0.08	2.0-3.0	0.045	0.03	1.00	16.0-18.0	10.0-14.0	2.15

Different factors might affect the intensity of surface reactions on the test tube walls resulting in the different values of the flammability limits obtained for the same initial temperature and residence time. For example, Fig. 4.15 shows values of the rich

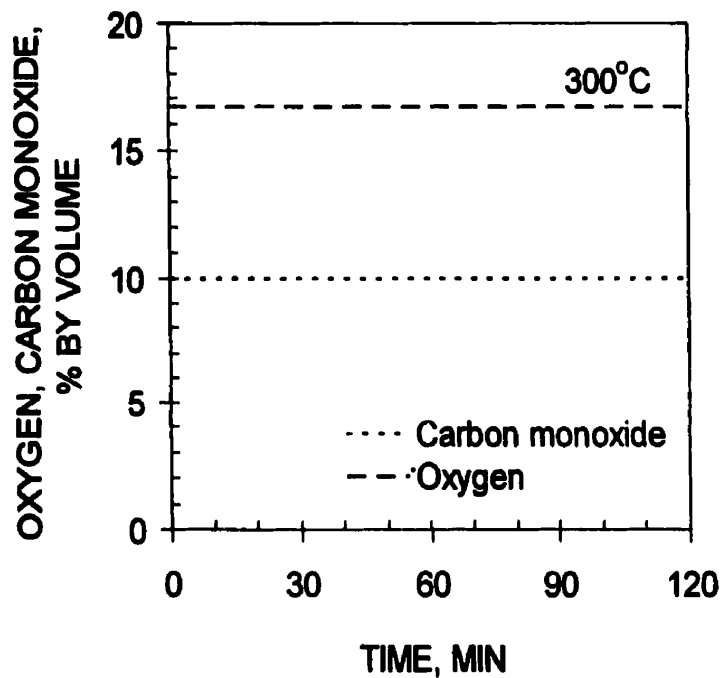


Fig. 4.13 Carbon monoxide and oxygen concentrations within a lean mixture of 10%CO+90% "wet" air as a function of time

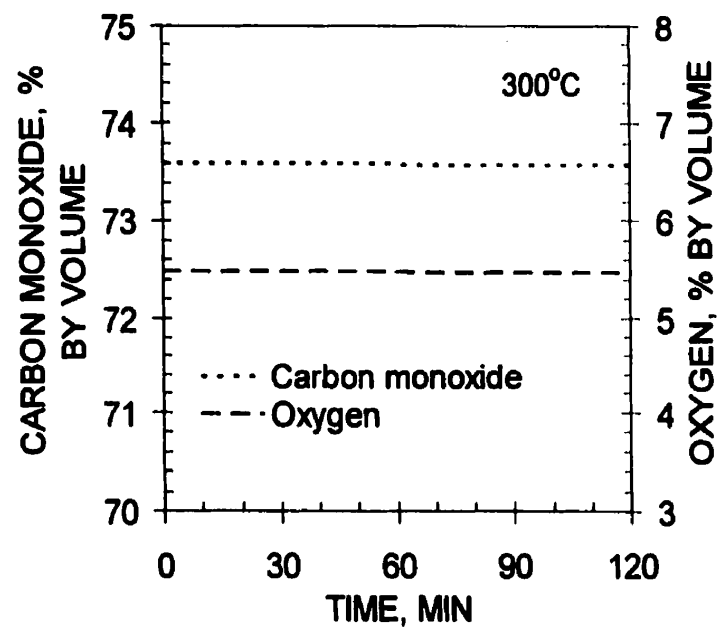


Fig. 4.14 Carbon monoxide and oxygen concentrations within a rich mixture of 73.6%CO+26.4% "wet" air as a function of time

flammability limits of carbon monoxide in dry and atmospheric air at different residence times. The tests were repeated after certain time and yielded different values of the limits. Between the two series of these tests the experiments with different concentrations of water vapor in carbon monoxide – air mixtures were performed. Variation in the values of the flammability limits was larger when “dry air” was employed than in the experiments with atmospheric air. It should be also noted that the flammability limits obtained at short residence time of 5 min were almost not affected by changes in the intensity of preignition surface reactions.

The exposure of the test tube to water vapor strongly affected the intensity of catalytic activity of the steel wall. For example, it can be seen from Fig.4.16 that an addition of 3.0 per cent of water vapor to the carbon monoxide–“dry air” mixture affected the pressure variation within the test mixture during the residence time. Pressure variations are directly related to changes in mixture composition, therefore, a smaller pressure variation indicated less preignition chemical activity. This would affect the values of the flammability limits obtained at different residence times. The variations in the pressure are consistent with the results of gas analysis. Samples taken after 2 hours of exposure of the test mixtures to the temperature of 300°C showed that the oxygen concentration in the test mixture involving “dry air” decreased from the initial concentration of 8.8% to 2.1%, while in the test mixture containing 3% of water vapor the corresponding decrease was significantly smaller from 8.2% to 4.8%. The reactions also proceeded slower (which was indicated by the rate of oxygen consumption), when a small concentration of hydrogen (1%) was present in the mixtures, as can be seen in Fig.4.17. It is possible that the water vapor produced in the

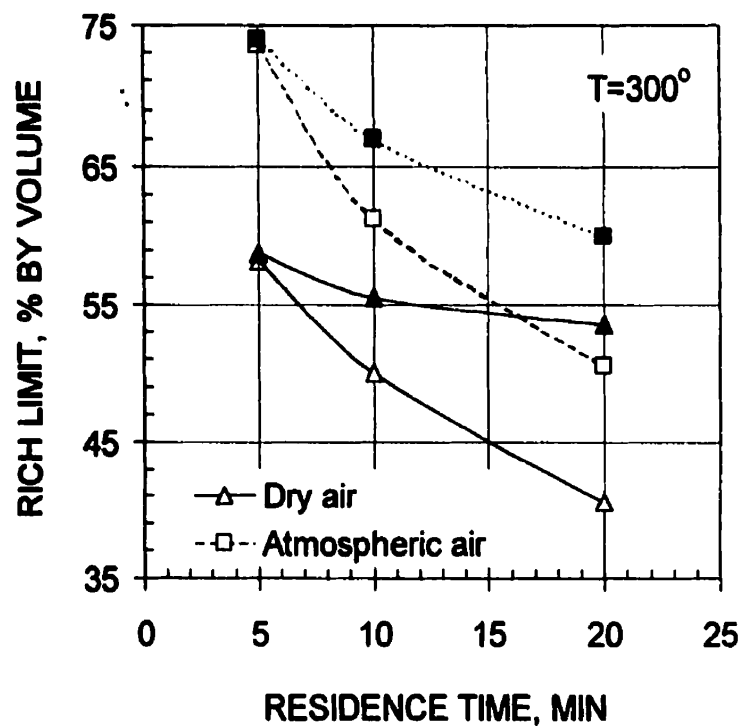


Fig. 4.15 Effect of experimental procedure on the values of rich flammability limits of carbon monoxide in air mixtures at 300°C

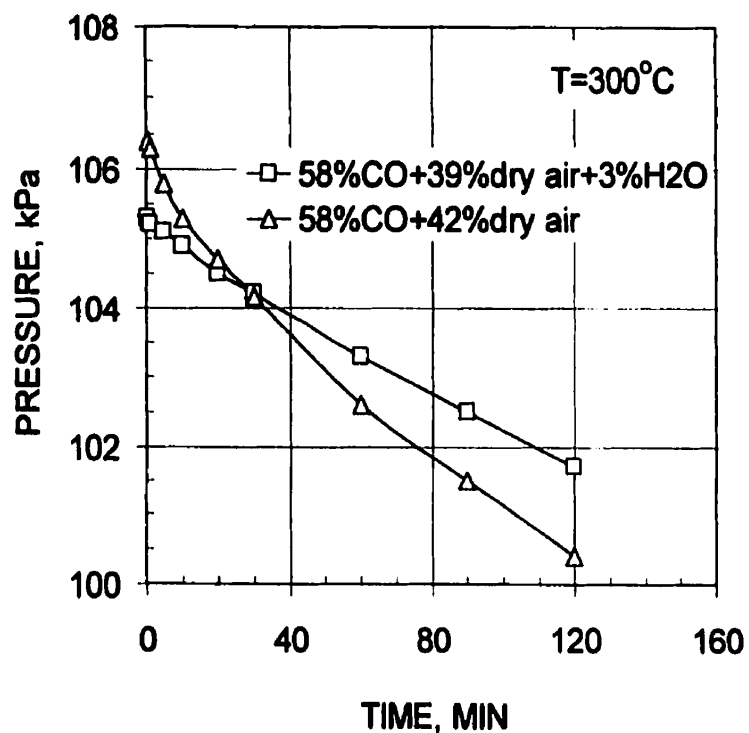


Fig. 4.16 Pressure variation within rich carbon monoxide – air mixtures with different water vapor concentrations as a function of the residence time

hydrogen oxidation reactions on the walls inhibited carbon monoxide oxidation reactions. The fact that water vapor acts as a poison for some metal catalysts such as Fe is well known (Twig, M. W., 1996). On the other side, after filling the test tube with dry carbon monoxide at the elevated temperatures, preignition chemical activity was enhanced. Fig. 4.18 shows the difference in the molar concentrations of carbon dioxide and oxygen in three mixtures of initially identical composition after the same residence time for different procedures. The exposure of the walls to carbon monoxide significantly increased the intensity of preignition chemical activity in comparison with the case when the test tube was open to the atmosphere and purged with "dry air".

The production of catalytically active carbonyls at the steel surface as a result of exposure to carbon monoxide is not plausible at the pressures and temperatures used in the experiments (Inouye, H. and DeVan, J. H., 1979). Therefore, the observed variations in the preignition chemical activity may be attributed to complex carbon monoxide and water vapor interaction with a passive thin hydrated oxide layer formed on the stainless steel surfaces at low temperatures or with metal oxide layer formed at high temperatures. Carbon monoxide is a strong reducing agent. Exposure to it at elevated temperatures may cause disruptions in the layer enhancing the surface reactions, while exposure to water vapor helps to restore the layer and diminishes surface reactions activity (Abel, L. A., 1990; Boyer, H. E. 1985).

The experiments were also performed to investigate the possible influence on the intensity of preignition chemical activity of different factors such as mixture composition and pressure. The effect of the mixture composition on the pressure variation during the

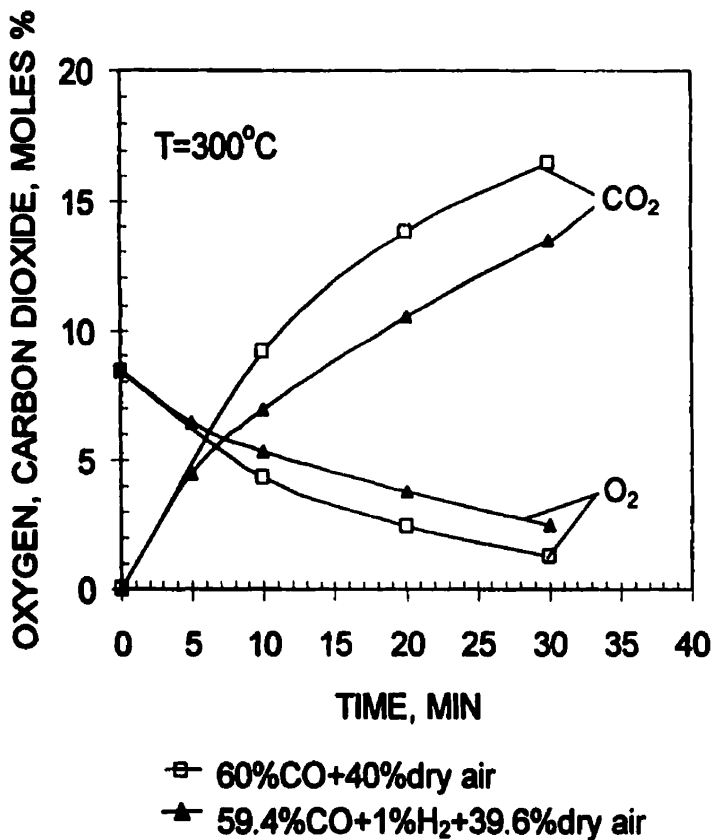


Fig.4.17 Effect of the presence of hydrogen in the carbon monoxide – air mixtures on the intensity of preignition chemical activity

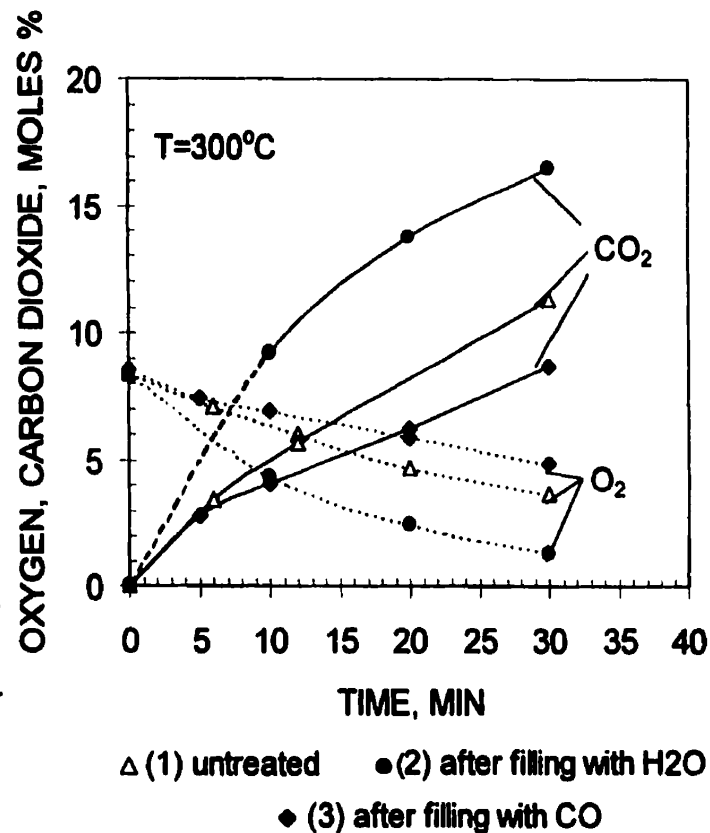


Fig. 4.18 Variation in the concentrations of oxygen and carbon dioxide within the test mixture of 60% CO + 40% "dry air" initial composition as a function of residence time for three different test conditions

residence time, which is directly related to the intensity of preignition reactions, is shown in Fig.4.19. The strongest pressure variation was in the stoichiometric mixture and the lowest in the lean mixture. The effect of the initial mixture pressure can be seen in Fig. 4.20. The pressure drop in 30%CO+70% "dry air" mixtures was much faster at higher initial pressure.

To have better repeatability in established values of the flammability limits at longer residence times the test tube was purged with "dry air" before testing for at least 30 min and left open to the atmosphere for 1- 3 days before the experiments were continued. Moreover, all tests were conducted at constant initial pressure of 105kPa.

An attempt was made to estimate the effect of residence time on the flammability limits using the described earlier constant adiabatic flame temperature approach. The preignition surface reactions may affect the uniform distribution of the mixture components, causing radial gradients of concentrations of carbon monoxide, oxygen and carbon dioxide. However, if the above effect is negligible the only considerable effect would be the change in the mixture composition. The product of the preignition reactions (CO_2) may be considered as a diluent and values of the limits may be estimated using constant adiabatic flame temperature approach if the composition is known at different residence times. An adiabatic flame temperature may be calculated using the corresponding values of the limits at low temperature, where no preignition reactions are taking place or at elevated temperature established at very short residence time. To prove this, flammability limits of rich mixtures of carbon monoxide with dry and atmospheric air were calculated for different residence times and compared with experimentally established values. The

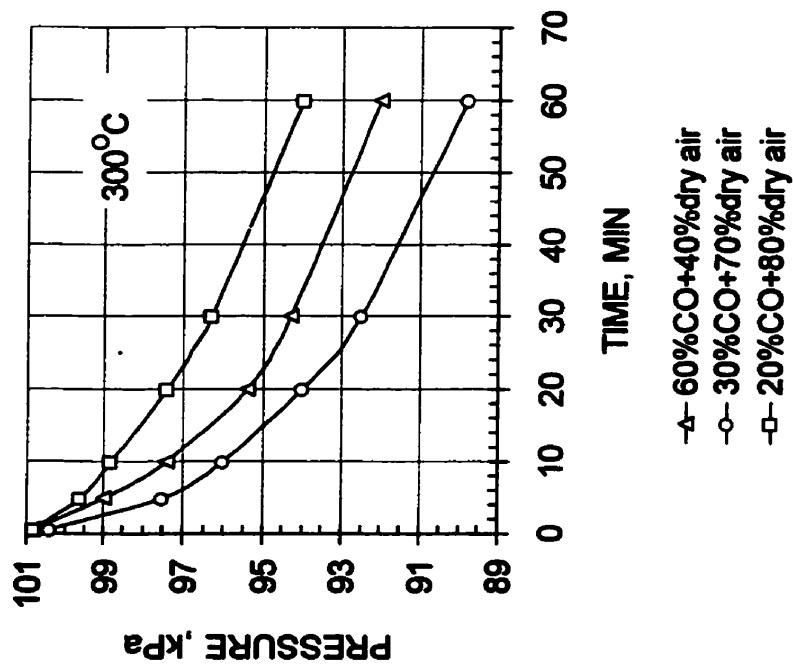


Fig.4.19 Pressure variation in different carbon monoxide - "dry air" mixtures as a function of the residence time

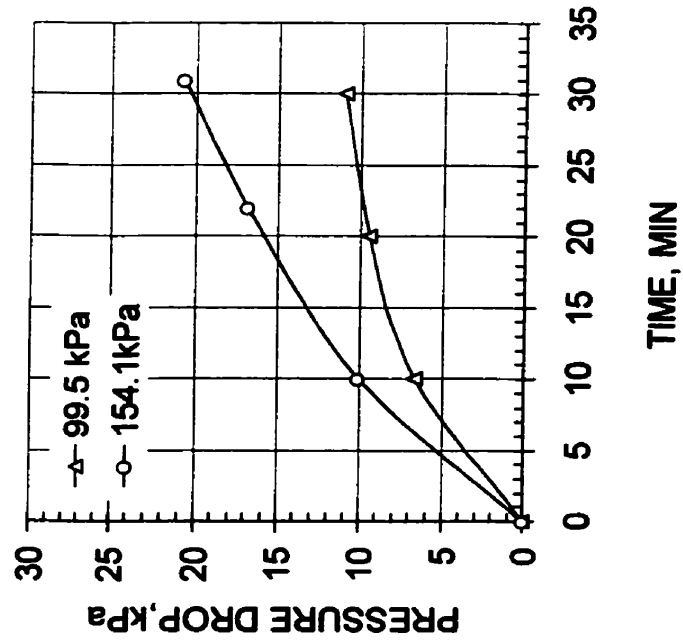


Fig.4.20 Pressure drop in 30%CO+70%dry air mixtures at 300°C with two different filling pressures

adiabatic flame temperatures used in the calculations were obtained using the experimental values of the limits for the residence time of 5 min (at 18°C for mixtures with atmospheric air, 100°C for mixtures with “dry air” and 300 °C for both mixtures with atmospheric and “dry air”).

Rich CO-“dry air” mixture:

$$\begin{aligned} (L_R - a_{\text{preig}}) \text{CO} + a_{\text{preig}} \text{CO}_2 + (21 - 0.21 \cdot L_R - 0.5 \cdot a_{\text{preig}}) \text{O}_2 + (100 - L_R) \cdot 0.79 \text{N}_2 \Big|_{T_r} = \\ = 0.42 \cdot (100 - L_R) \text{CO}_2 + (1.42 L_R - 42) \text{CO} + 0.79 \cdot (100 - L_R) \text{N}_2 \Big|_{T_{f,ad}} \end{aligned} \quad (4.4)$$

Rich CO-atmospheric air mixture (air was assumed to contain 1.2%, by volume of water vapor):

$$\begin{aligned} (L_R - a_{\text{preig}}) \text{CO} + a_{\text{preig}} \text{CO}_2 + (100 - L_R) \cdot 0.012 \text{H}_2\text{O} + \\ + [(21 - 0.21) \cdot 0.988 \cdot L_R - 0.5 \cdot a_{\text{preig}}] \text{O}_2 + [(100 - L_R) \cdot 0.988] \cdot 0.79 \text{N}_2 \Big|_{T_r} = \\ = 0.42 \cdot [(100 - L_R) \cdot 0.988] \text{CO}_2 + (1.415 L_R - 41.5) \text{CO} + \\ + (100 - L_R) \cdot 0.012 \text{H}_2\text{O} + [(100 - L_R) \cdot 0.988] \cdot 0.79 \text{N}_2 \Big|_{T_{f,ad}} \end{aligned} \quad (4.5)$$

where,

a_{preig} – carbon dioxide produced in the preignition reactions for a certain residence time, mol s

In equations (4.4) and (4.5), the values of a were taken from the experiments with the corresponding mixtures. The results of calculations are shown together with the experimental results for comparison in Table 4.10 and Fig. 4.21.

A considerable deviation of the calculated values from those established experimentally (up to ~8 %) is attributed mainly to the non-uniform gases distribution and accuracy of the gas analysis. The best accuracy could be expected in the results obtained with the gas chromatograph. However, even when a gas chromatograph was used the results were affected by the ongoing chemical reactions. The sample taken close to the test tube wall contained higher concentrations of carbon dioxide than samples taken close to the test tube center at the same conditions (the same residence time and initial mixture composition)(Fig. 4.22).

Since the majority of the experiments for the determination of the flammability limits at elevated temperature and pressures are performed in apparatus made of stainless steel, the flammability limits determined in such apparatuses may be affected by the preignition reactions, usually narrowing the limits (Ale, B. B., 1998; Bunev, V. A., 1972). For safety guidelines it is important to obtain the widest flammable range at any specified conditions. Using an approach similar to this, it is possible to estimate the flammability limits of highly reactive chemical compounds when their experimentally determined flammability limits are always affected by the preignition chemical activity. For example, in Fig. 4.21 the values of the flammability limits not affected by the preignition chemical reactions are shown as flammability limits at zero residence time. These values of the limits were calculated using adiabatic flame temperatures calculated for flammability limits at 300°C and 5 min residence time (with $a \neq 0$). Then values of the flammability limits not affected by the preignition chemical activity were calculated using $a = 0$ in Eq. 4.4 and 4.5.

Table 4.10 Comparison of the experimental and calculated flammability limits of carbon monoxide in air at different residence times

Residence time, min.		0	5	10	20
Calculated adiabatic flame temp.					
Using values of the rich limits at room temperature	<i>Dry air, Experimental</i>		58.2	50	40.5
	<i>Dry air, Calculated</i>	61.6	56.8	46.6	38.5
	<i>Accuracy, %</i>		2.5	7.3	5.2
	<i>Atmospheric air, experimental</i>		74.4*	61.3	50.5
	<i>Atmospheric air, calculated</i>	74.3	73	62.9	53.7
	<i>Accuracy, %</i>		1.9	2.5	-5.9
Using values of the rich limits at temperature of 300 °C	<i>Dry air, experimental</i>		58.2	50	40.5
	<i>Dry air, calculated</i>	63	58.2	48	40
	<i>Accuracy,%</i>		0	4.2	1.2
	<i>Atmospheric air, experimental</i>		74.4*	61.3	50.5
	<i>Atmospheric air, calculated</i>	75.8	74.5	64.3	55.1
	<i>Accuracy, %</i>		-0.1	-4.7	- 8.3

* Limits are quoted as initial concentration of carbon monoxide in the mixture.

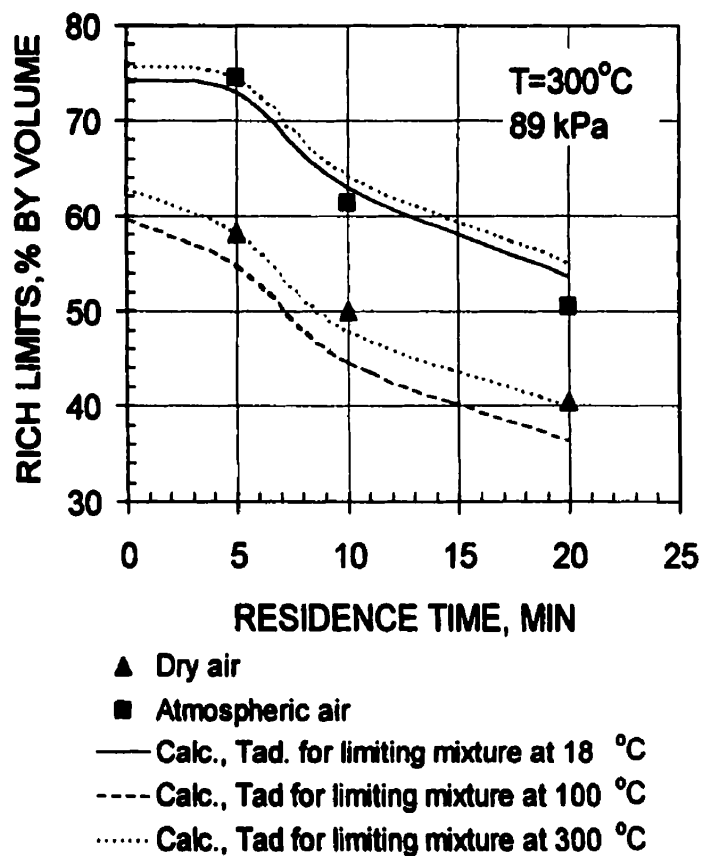


Fig.4.21 Experimental and calculated rich flammability limits of carbon monoxide in "dry" and in atmospheric air at different residence times

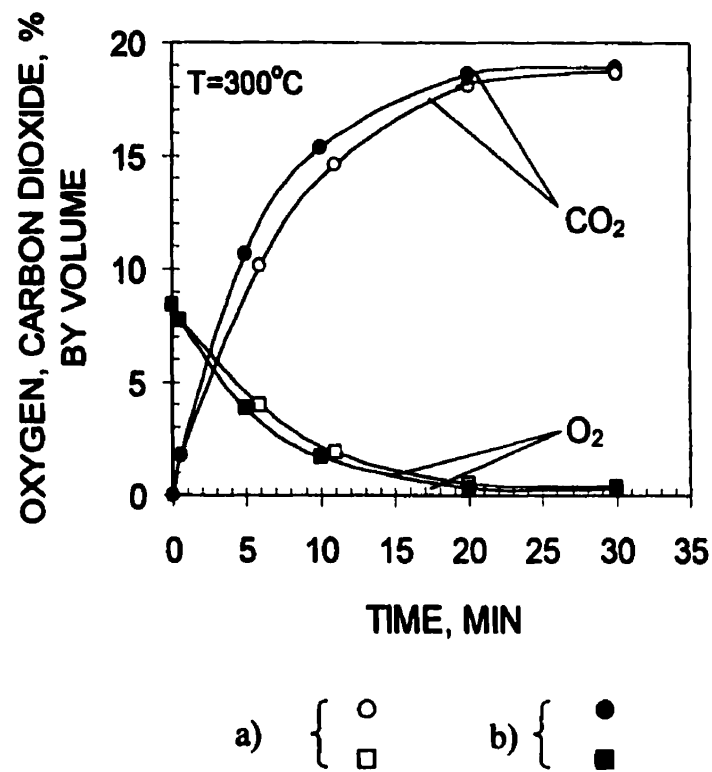


Fig.4.22 Variation in the concentrations of oxygen and carbon dioxide within the 60%CO+40% "dry air" mixture as a function of residence time: a) the center of the test tube, b) close to the wall

CHAPTER 5

FLAMMABILITY LIMITS OF CARBON MONOXIDE - HYDROGEN MIXTURES IN AIR

5.1 Effect of mixture composition

Rich flammability limits of various carbon monoxide - hydrogen mixtures in air were determined experimentally for three different initial temperatures at five minutes residence time. The results are shown in Table 5.1 and Fig. 5.1. It can be seen that at the low initial temperature of 18 °C, a very small addition of hydrogen (less than 4 % by volume) to the carbon monoxide produced a significant increase in the value of the rich limit. This increase was expected taking into consideration the importance of hydrogenous radicals in the oxidation chemistry of carbon monoxide. However, it was not anticipated that the value of the limit of a fuel mixture containing only 2.6% of hydrogen actually exceeded the corresponding values of the rich limits of both hydrogen and carbon monoxide on their own in air. The value of the limit decreased slightly when the hydrogen concentration in the mixture with carbon monoxide further increased from ~ 4% to 75%. Similarly at elevated temperatures of 150°C and 300°C a small addition of hydrogen produced a significant increase in the value of the rich flammability limit. However, at elevated temperatures the variations in the value of the rich limit of a wide range of fuel mixtures were much smaller; at temperature of 300°C, the rich limit of carbon monoxide – hydrogen mixtures containing more than 20% hydrogen was constant and approximately equal to the limit of hydrogen.

Table 5.1 Rich flammability limits of carbon monoxide – hydrogen mixtures in air at different temperatures

	Amount of carbon monoxide in fuel mixture		Initial temperature		
			~ 18°C	150°C	300°C
Rich limits, % by volume	100%CO	Experimental	67.7	71.2	73.7
	99.7%CO	Experimental	72.3	76.3	76.2
		Calculated	67.7	71.2	73.7
		Deviation, %	6.4	6.7	3.3
	97.4 %CO	Experimental	75.2	78.9	80.6
		Calculated	67.9	71.4	73.9
		Deviation, %	9.7	9.5	8.3
	93.7%CO	Experimental	75	78.9	80.5
		Calculated	68.1	71.7	74.1
		Deviation, %	9.2	9.1	8.0
	74.4%CO	Experimental	74.2	78.3	80.4
		Calculated	69.3	73.2	75.3
		Deviation, %	6.6	6.5	6.3
	50%CO	Experimental	73.6	78.3	80.4
		Calculated	70.9	75.1	79
		Deviation, %	3.7	4.1	1.7
	25%CO	Experimental	73.4	78.3	80.4
		Calculated	72.6	77.2	78.8
		Deviation, %	1.1	1.4	2
	0%CO	Experimental	74.4	79.4	80.6

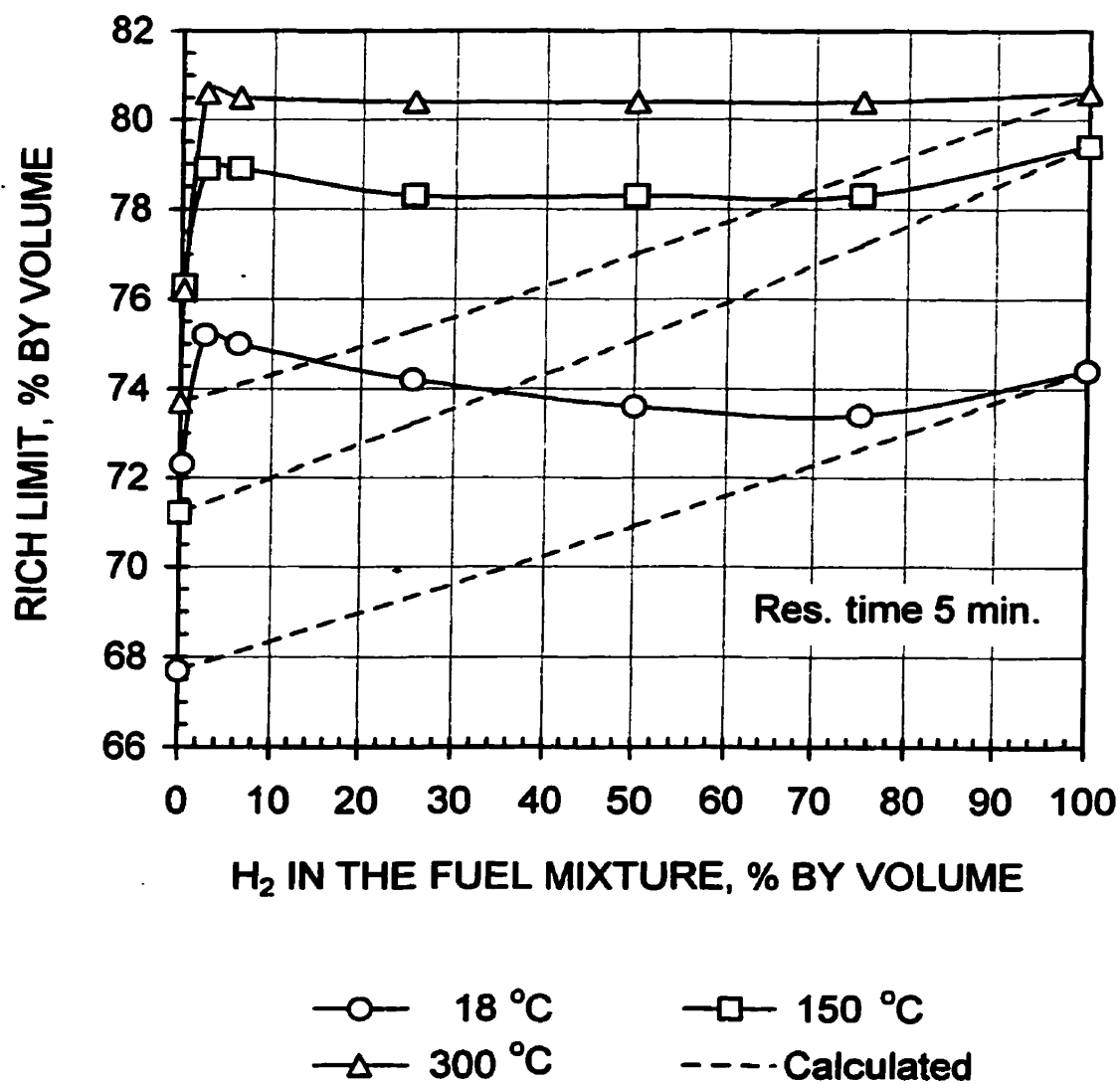


Fig.5.1 Rich flammability limits of CO-H₂ mixtures in air at different temperatures

The sharp increase in the values of the rich flammability limits of carbon monoxide with a small addition of hydrogen was expected, since radicals, mainly OH, contribute significantly towards the carbon monoxide oxidation rates (Miller, J. A., 1996). The addition of hydrogen to carbon monoxide – air mixtures influences mixture autoignition temperature and flame parameters such as the laminar flame speed (Kanury, A., M., 1975; Trujillo, J. Y. D., et al., 1997).

The effect of hydrogen addition on the mean reaction rates in lean carbon monoxide “dry air” mixtures was investigated using detailed chemical kinetics modelling optimized for preignition and auto-ignition conditions (Liu, Z., 1995). All mixtures shown on the graph (Fig.5.2) contained an equal initial amount of carbon monoxide (18%) and different amounts of hydrogen. The results of chemical kinetics simulation showed that a very small increase in the hydrogen concentration has the strongest effect on mean reaction rates. The effect of hydrogen addition was compared with the effect of water vapor and methane addition. The results of the calculations are shown in Fig. 5.3. The effect of hydrogen addition is very close to that of methane addition and much stronger than that of water vapor.

The flammability limits of fuel mixtures are usually calculated using the well-known Le Chatelier's Rule based on the mixture composition and individual flammability limits. The limits of rich carbon monoxide – hydrogen mixtures calculated using this Rule are also shown as broken lines in Fig.5.1. It is evident that the experimentally determined values of the rich limit do not follow those predicted by Le Chatelier's Rule for a very wide range of mixtures at all initial temperatures tested. Therefore, reliance on limit values generated

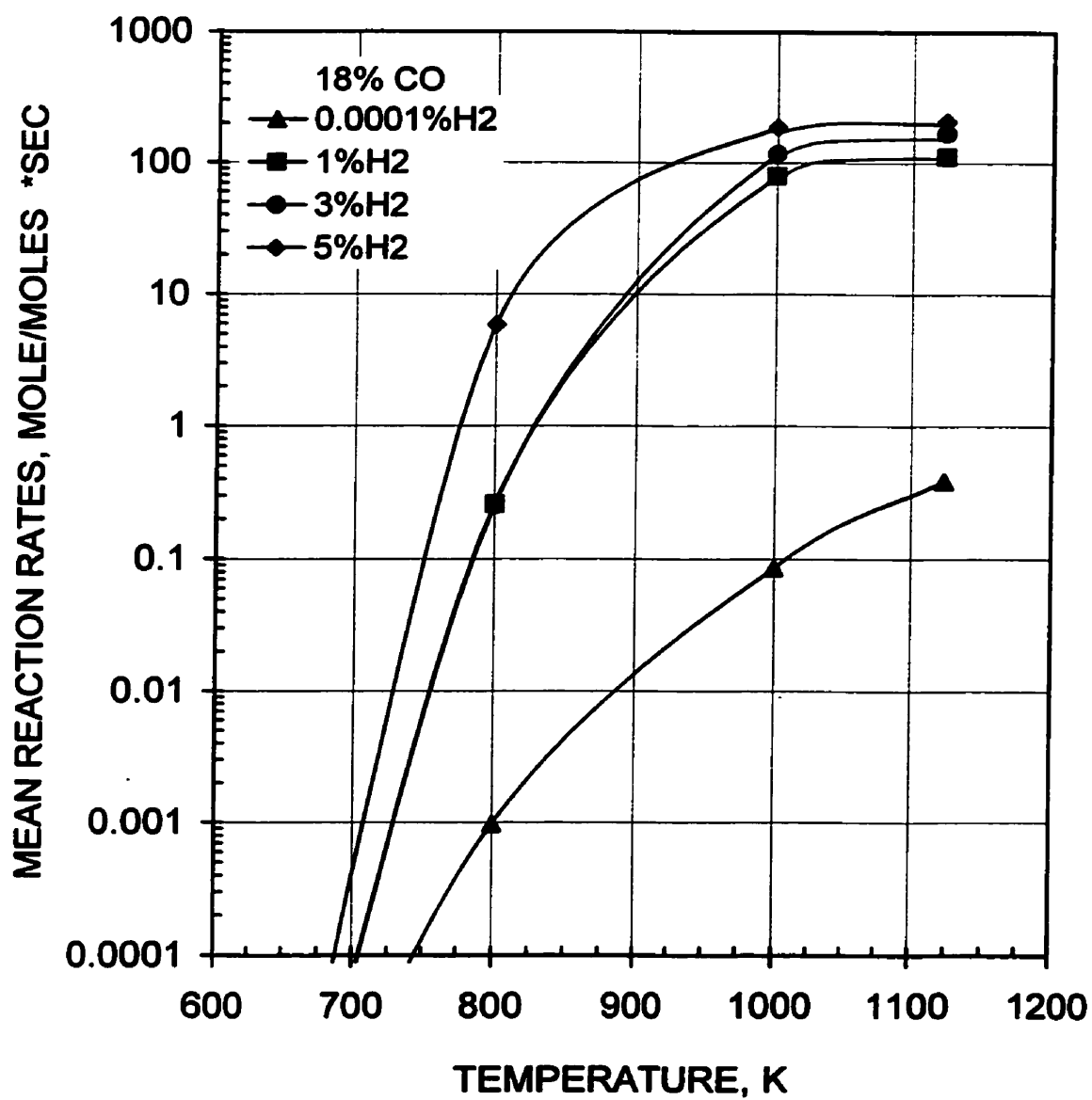


Fig.5.2 Effect of hydrogen addition to carbon monoxide - "dry air" mixture on the mean reaction rates

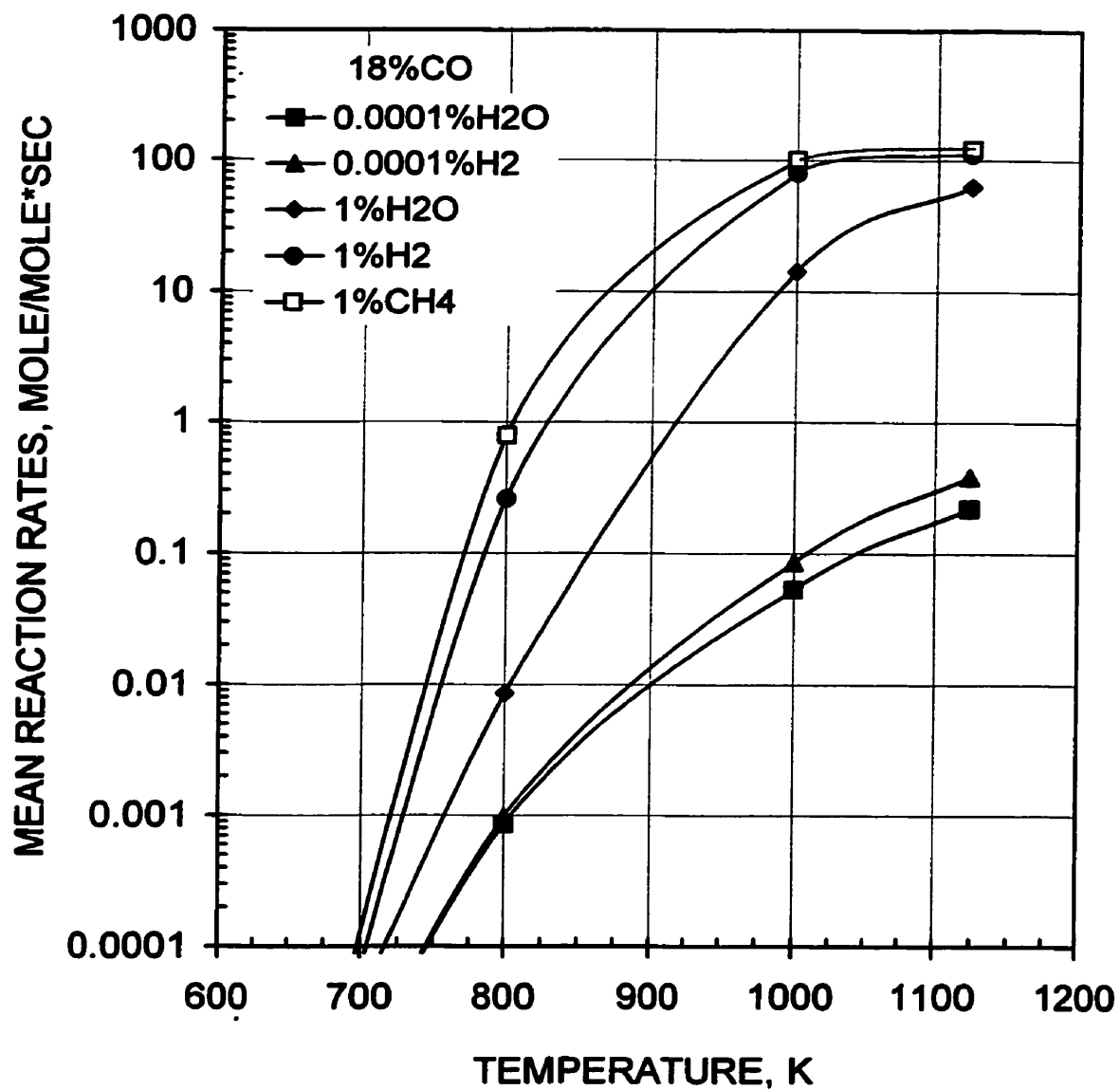


Fig.5.3 Effect of hydrogen, water vapor or methane addition to carbon monoxide - "dry air" mixture on the mean reaction rates

according to the Rule would underestimate the potential hazards when dealing with such fuel mixtures.

There is no data available for comparison of the results obtained at elevated temperatures. Rich flammability limits of carbon monoxide – hydrogen mixtures were obtained at room temperature by Cheng (1985) using similar apparatus as used in the present work. His results are shown for comparison in the Fig. 5.4. The deviation between the limits for similar mixtures does not exceed 3.5%.

Lean flammability limits of different carbon monoxide – hydrogen mixtures were established experimentally at different initial temperatures and residence time of 5 minutes. The results are shown in Table 5.2 and Fig.5.5. The limits expectedly decrease with an increase in the hydrogen concentration for all the initial temperatures considered. Generally, the lean limits can be predicted reasonably well when using Le Chatelier's Rule especially for the fuel mixtures containing more than 20 % of hydrogen. The calculated limits are shown in Fig.5.5 as solid lines. The Rule tends to overestimate slightly the values of the lean limits of the fuel mixtures containing small amount of hydrogen. There is no data available for comparison of the lean flammability limits of carbon monoxide – hydrogen mixtures at elevated temperatures. However, at room temperature the lean limits were found by Boon (1982). The results obtained by Boon are shown for comparison in Fig. 5.6. His results are consistently somewhat higher than obtained in the present work with the maximum deviation ~14%. The tests were performed by Boon on an apparatus designed for determination of the flammability limits at low temperatures.

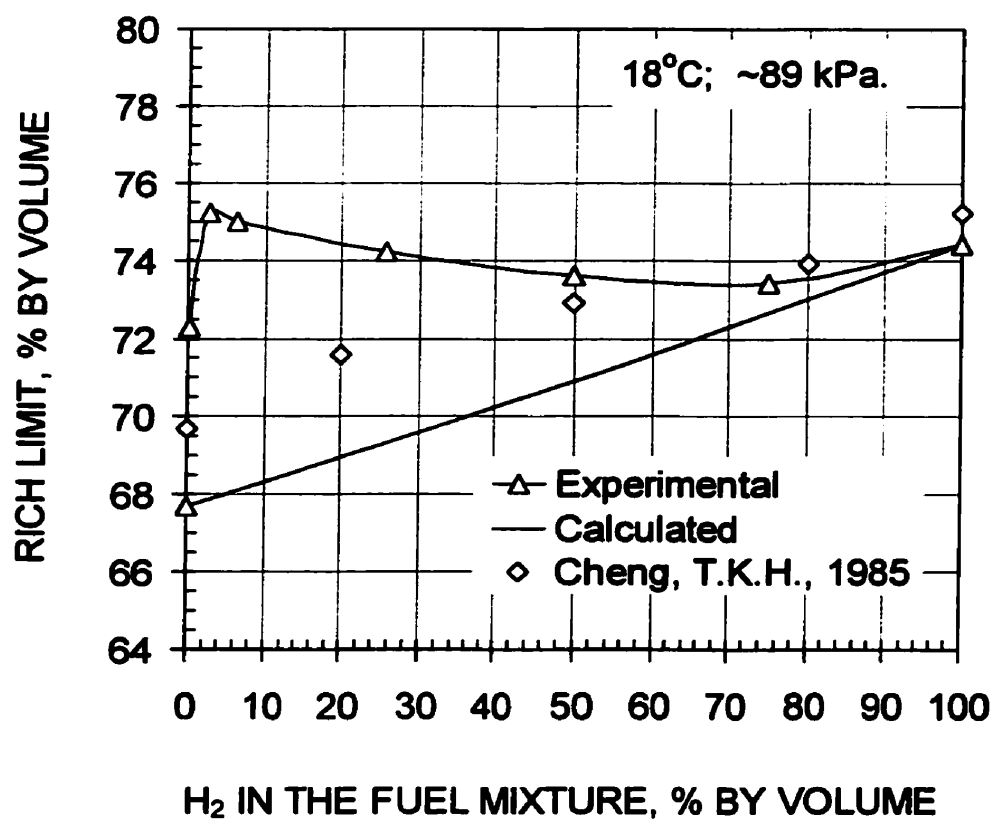


Fig.5.4 Rich flammability limits of CO-H₂ mixtures at room temperature

Table 5.2 Lean flammability limits of carbon monoxide – hydrogen mixtures in air at different temperatures

	Amount of carbon monoxide in fuel mixture		Initial temperature		
			~ 18°C	150°C	300°C
Lean limits, % by volume	100%CO	Experimental	13.6	12.2	10
	98.4%CO	Experimental	12.5	-	-
		Calculated	13.0	11.6	9.5
		Deviation, %	- 4	-	-
	93.7%CO	Experimental	11.5	-	-
		Calculated	11.6	10.2	8.2
		Deviation, %	- 0.1	-	-
	74.4%CO	Experimental	7.8	6.8	5
		Calculated	8.1	6.8	5.2
		Deviation, %	- 3.8	0	- 0.4
	50%CO	Experimental	5.6	5	3.5
		Calculated	5.8	4.8	3.6
		Deviation, %	- 3.6	0.4	- 2.8
	25%CO	Experimental	4.3	3.7	2.8
		Calculated	4.5	3.7	2.7
		Deviation, %	4.7	0	3.5
	0%CO	Experimental	3.7	3	2.2

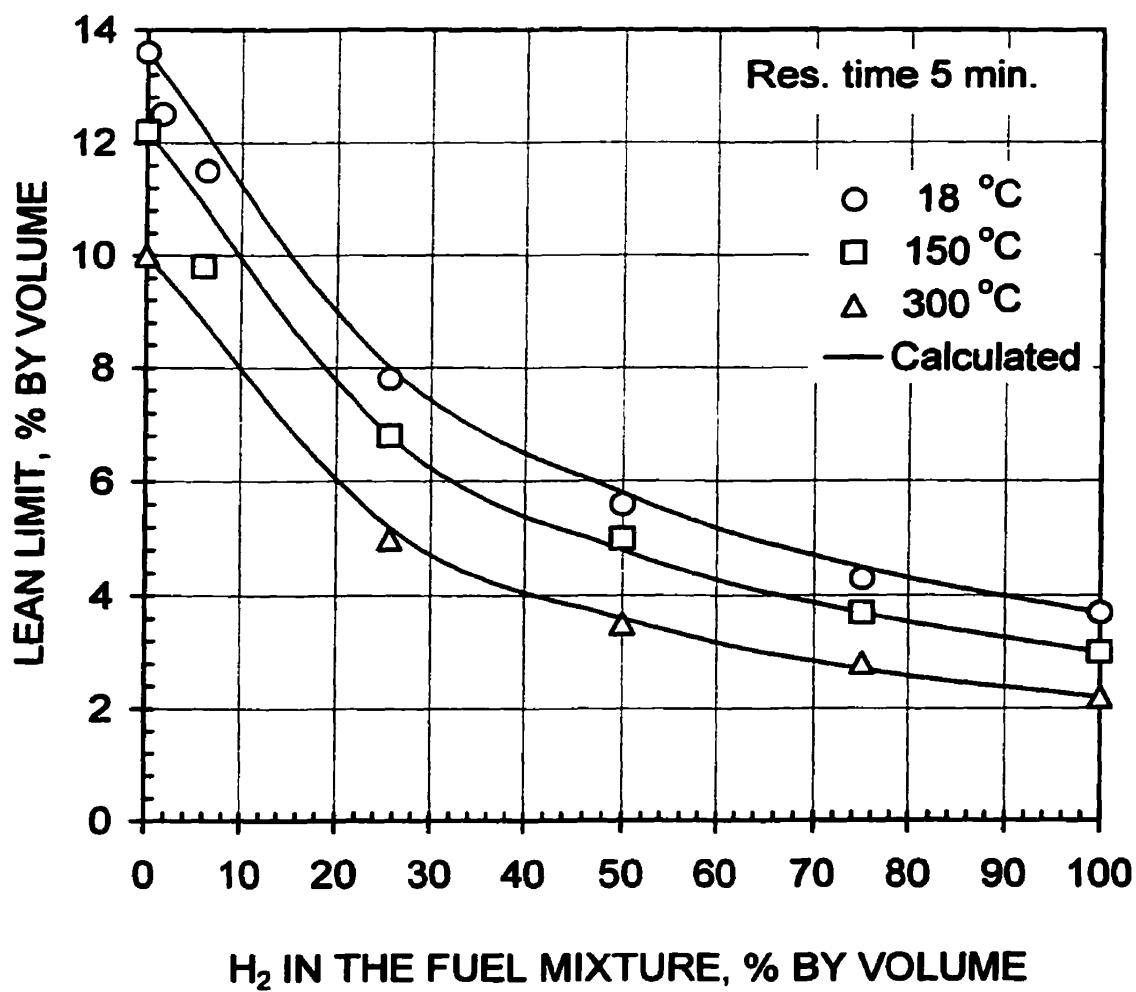


Fig.5.5 Lean flammability limits of CO-H₂ mixtures in air at different temperatures

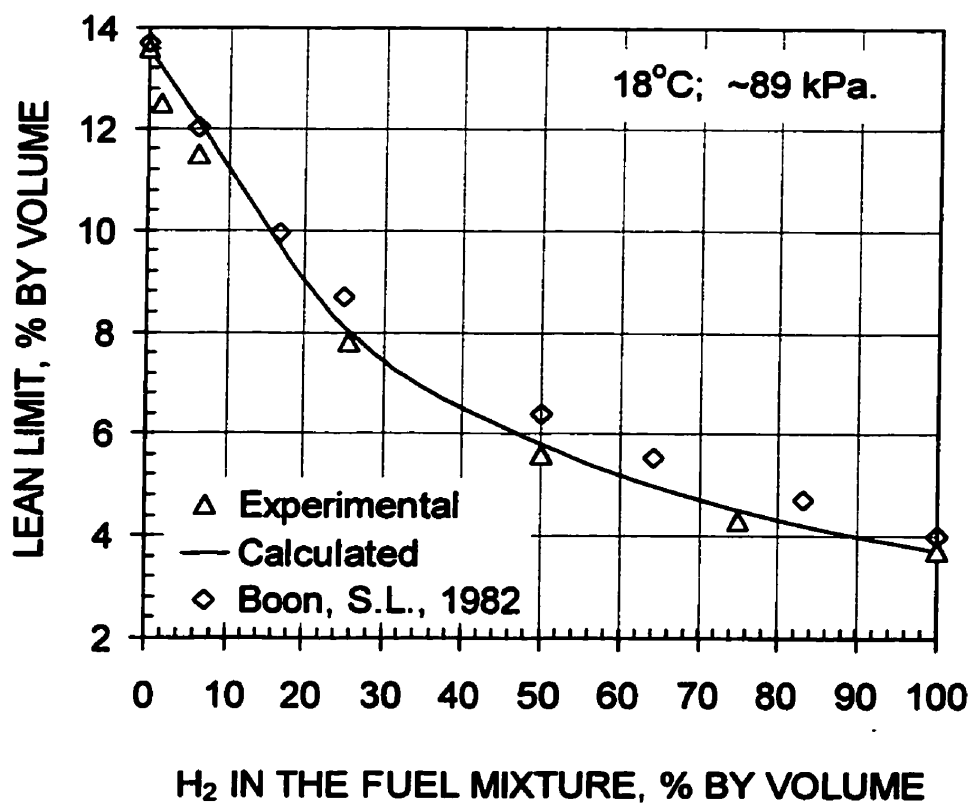


Fig.5.6 Lean flammability limits of CO-H₂ mixtures at room temperature

Therefore, the difference in established values may be attributed to the different experimental apparatus and procedure.

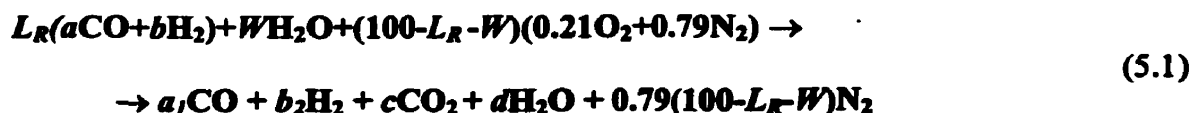
5.2 Effect of initial temperature

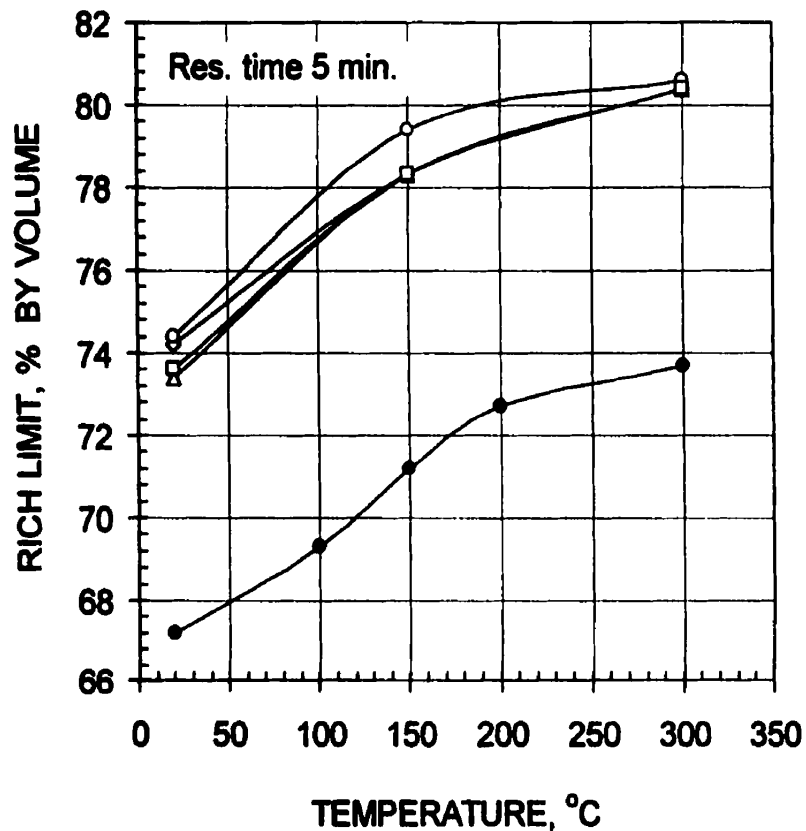
The effect of changes in the initial temperature on the values of the rich and lean flammability limits of carbon monoxide – hydrogen mixtures can also be seen more clearly in Fig. 5.7 and 5.8, respectively. The rich limits widened with temperature, but the increase tended to level off at temperatures exceeding 150 °C. This could be expected since the limits of hydrogen as well as of carbon monoxide on their own in air exhibited similar behaviour, however, to a different extent at this temperature due to the onset of preignition chemical activity even at short residence times.

The preignition reactions are more intensive in rich mixtures. The lean limits decreased almost linearly with an increase in the initial temperature over the temperature range employed for all fuel mixtures tested.

Flammability limits of carbon monoxide – hydrogen mixtures at different initial temperatures also were calculated using constant adiabatic flame temperature approach described in Chapter 4 using known flammability limit values at room temperature and assuming no preignition reactions were taking place for the following overall equations:

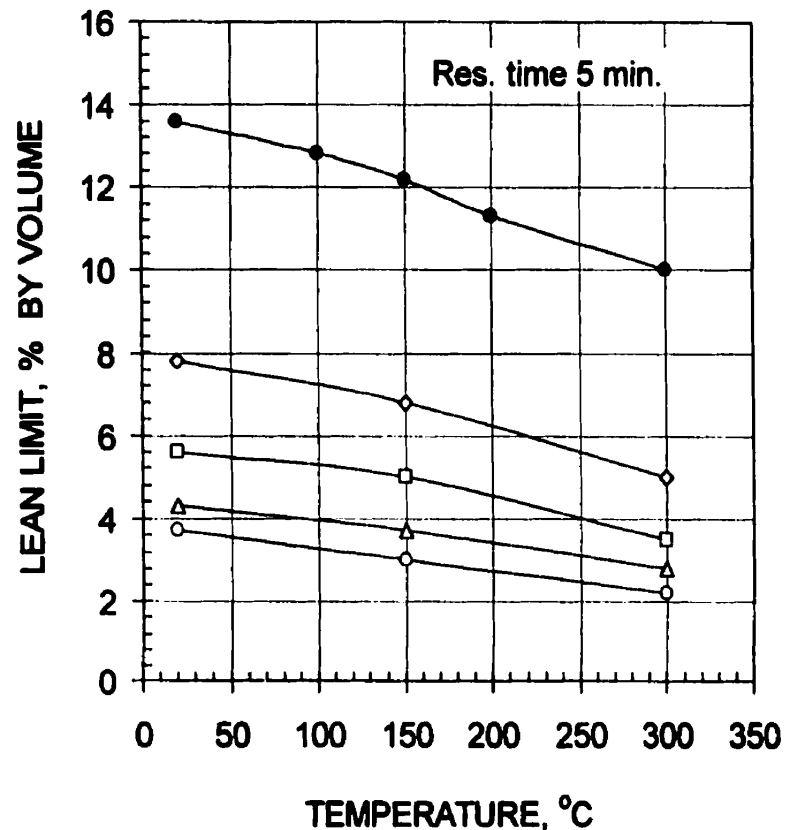
For rich mixtures:





● 100%CO △ 25%CO+75%H2
 ◊ 74.4%CO+25.6%H2 ○ 100%H2
 ◻ 50%CO+50%H2

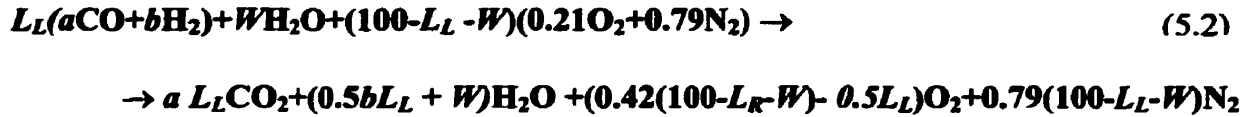
Fig.5.7 Rich flammability limits of different carbon monoxide - hydrogen mixtures as a function of temperature



● 100%CO △ 25%CO+75%H2
 ◊ 74.4%CO+25.6%H2 ○ 100%H2
 ◻ 50%CO+50%H2

Fig.5.8 Lean flammability limits of different carbon monoxide - hydrogen mixtures as a function of temperature

For lean mixtures:



where:

a – amount of carbon monoxide in the fuel mixture, mole/mole

b – amount of hydrogen in the fuel mixture, mole/mole

a_1, b_2, c, d – stoichiometric coefficients, determined from the conservation equations of species

In accordance with the finding of Wierzbza (Wierzbza, I., et al., 1996), it was assumed that the available oxygen in the rich fuel – air mixture was consumed on priority basis: firstly to oxidize the fuel hydrogen to water vapor, secondly if there still was some unconsumed oxygen in the mixture, to oxidize fuel carbon monoxide to carbon dioxide.

As an example, the rich and the lean limits of two mixtures (50%CO+50%H₂ and 93.7%CO+6.3%H₂) were calculated. Calculated adiabatic flame temperatures determined for the experimentally obtained rich and lean flammability limit values at room temperature are shown in Table 5.3. Calculated values of flammability limits are shown on Fig.5.9 and 5.10. The deviation of the calculated values from experimental is relatively small at the rich limits (up to 1.6%) and larger at the lean limits (up to 28%) (Table 5.4). At elevated temperatures it is to be expected because the calculation method does not take into consideration the possible changes in the mixture composition during the residence

Table 5.3 Calculated adiabatic flame temperatures

Composition	L_R, K	T_f, K	L_L, %	T_f, K
50%CO+50%H ₂	73.6	1189	5.6	783
74.4%CO+25.6%H ₂	74.2	1188	7.8	979
93.7%CO+6.3%H ₂	75	1187	11.5	1299

time (5 min) due to the onset of surface reactions. The deviation is more pronounced on the lean side because of relatively small absolute values of the lean limits.

5.3 Effect of water vapor

The effect of the presence of water vapor on the flammability limits of carbon monoxide – hydrogen mixtures was investigated at the temperature of 150 °C for two different mixtures. This temperature was chosen because of the importance of knowledge of the flammability limits of CO-H₂-H₂O mixtures, which may be formed as a result of nuclear reactor accident with temperatures close to 150°C (Kumar, R. K., 1985; Lee, J. H. S. and Berman M., 1997). Such data is not available in the literature.

The residence time in the experiments was 5 minutes. The results are shown in Table 5.5, Fig 5.11 and 5.12 for the rich and lean limits, respectively. It can be seen that water vapor acts as a diluent lowering the rich limit while increasing the lean limit. The flammability limits of these mixtures were calculated using the constant adiabatic flame temperature concept as discussed above using the same overall equations (Eq.5.1 and 5.2) and adiabatic

Table 5.4 Comparison of the experimental and calculated flammability limits of carbon monoxide – hydrogen mixtures at different temperatures

Mixture	Flammability limits			
	Temperature	18°C	150°C	300°C
93.7%CO+6.3%H ₂	<i>R.L. exp., % by volume</i>	75	78.9	80.5
	<i>R.L. calc., % by volume</i>	75	78.1	81.8
	<i>Deviation, %</i>	0	1.0	-1.6
74.4%CO+25.6%H ₂	<i>L.L. exp., % by volume</i>	7.8	6.8	5
	<i>L.L. calc., % by volume</i>	7.8	6.4	4.8
	<i>Deviation, %</i>	0	5.9	4
50%CO+50%H ₂	<i>R.L. exp., % by volume</i>	73.6	78.3	80.4
	<i>R.L. calc., % by volume</i>	73.6	77.2	81.5
	<i>Deviation, %</i>	0	1.4	-1.4
	<i>L.L. exp., % by volume</i>	5.6	5	3.5
	<i>L.L. calc., % by volume</i>	5.6	4.2	2.5
	<i>Deviation, %</i>	0	16	28

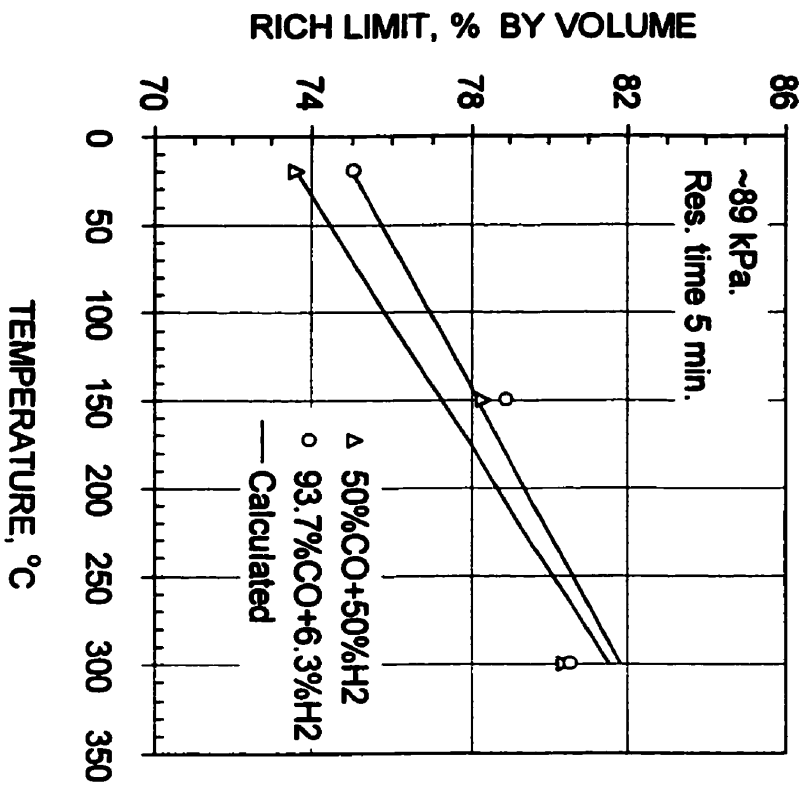


Fig.5.9 Comparison of the experimental and calculated rich flammability limits of different carbon monoxide-hydrogen mixtures

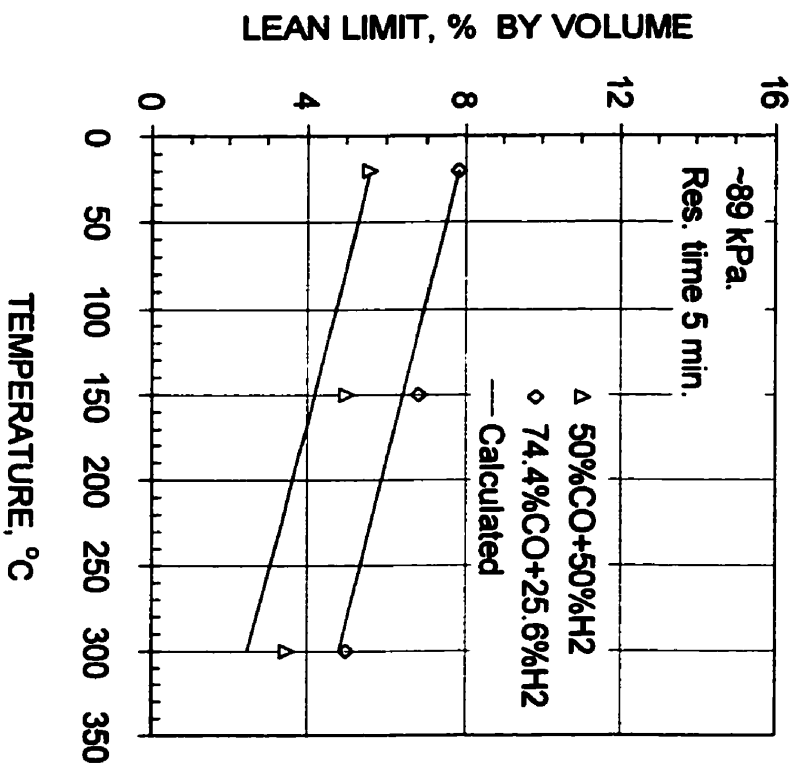


Fig.5.10. Comparison of the experimental and calculated lean flammability limits of different carbon monoxide-hydrogen mixtures

Table 5.5 Comparison of the experimental and calculated flammability limits of carbon monoxide – hydrogen mixtures with different concentrations of water vapor

Mixture	Flammability limits, % by volume					
	Water vapor, % by volume	~1.2 (atm. air)	5	10	20	
94%CO+6%H ₂	R.L. exp.	78.6	74.5	68.8	57.6	
	R.L. cal.	77.9	73.0	67.9	57.6	
	Deviation, %	0.9	2	1.3	0	
	L.L. exp.	9.8	10.0	11.0	11.5	
	L.L. cal.	10	10.1	10.3	10.6	
	Deviation, %	-2	-1	6.8	7.8	
50%CO+50%H ₂	R.L. exp.	78	72.5	66.4	55.4	
	R.L. cal.	77	72.0	66.7	56.1	
	Deviation, %	1.3	0.7	-0.5	-1.3	
	L.L. exp.	4.9	5.5	5.9	6.2	
	L.L. cal.	4.2	4.2	4.3	4.3	
	Deviation, %	14.3	23.6	27.1	30.6	

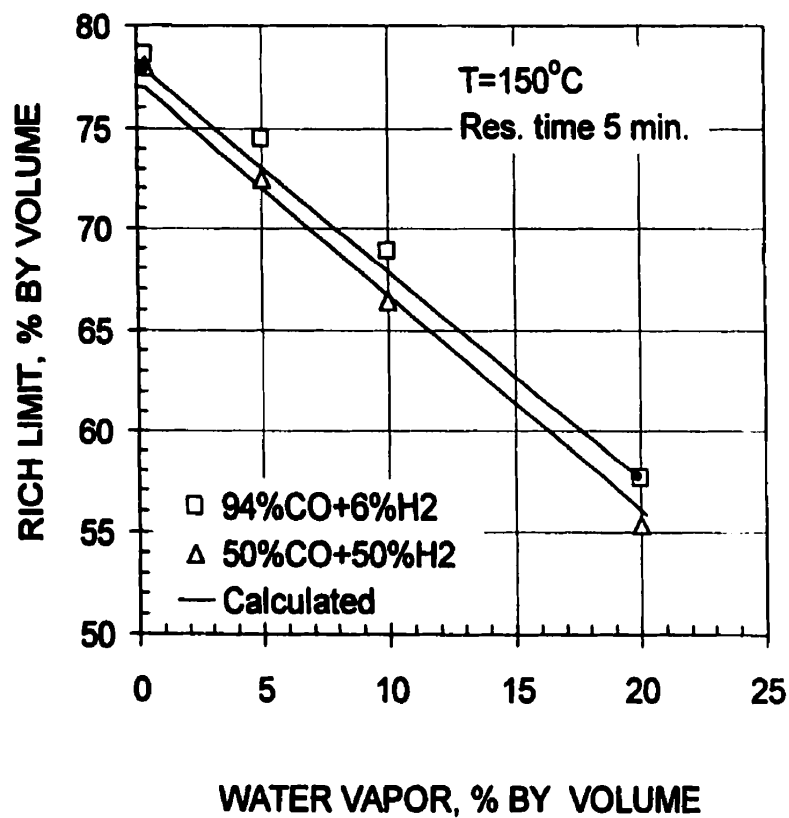


Fig. 5.11 Comparison of the experimental and calculated rich flammability limits of carbon monoxide-hydrogen mixtures as a function of water vapor concentration at 150°C

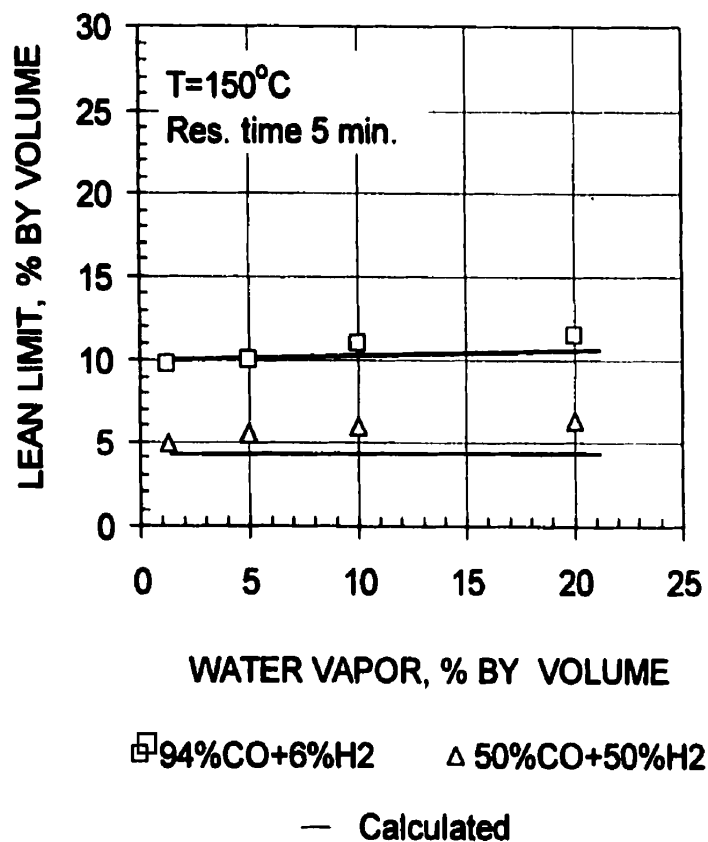


Fig. 5.12 Comparison of the experimental and calculated lean flammability limits of carbon monoxide-hydrogen mixtures as a function of water vapor concentration at 150°C

flame temperatures determined for the experimental rich and lean flammability limit values at room temperature (Table 5.3).

The agreement of the calculated rich limits with the corresponding values determined experimentally is good, as it can be seen in Fig. 11 and Table 5.5. However, there is less agreement between the lean limits (Fig. 5.12). Employing adiabatic flame temperatures calculated on the basis of the values of the flammability limits established at 150°C temperature (as opposed to room temperature) did not increase the accuracy of the prediction. The results are shown for comparison in Fig.13 and 14, and Table 5.6.

Table 5.6 Adiabatic flame temperatures calculated on the basis of the flammability limits at 150°C

Mixture	Adiabatic flame temperature, K	
	<i>Rich limit</i>	<i>Lean limit</i>
50%CO+50%H ₂	1160	857
94%CO+6%H ₂	1238	1274

5.4 Effect of residence time

As it was described in Chapter 4, the values of the limits of carbon monoxide in air were dependent on the duration of the residence time. The same effect took place in hydrogen – air mixtures at elevated temperatures (Ale, B. B., 1998). Therefore, a similar dependence would be expected for carbon monoxide-hydrogen mixtures. For example, the flammability limits of a mixture containing 50 % hydrogen and 50 % carbon monoxide

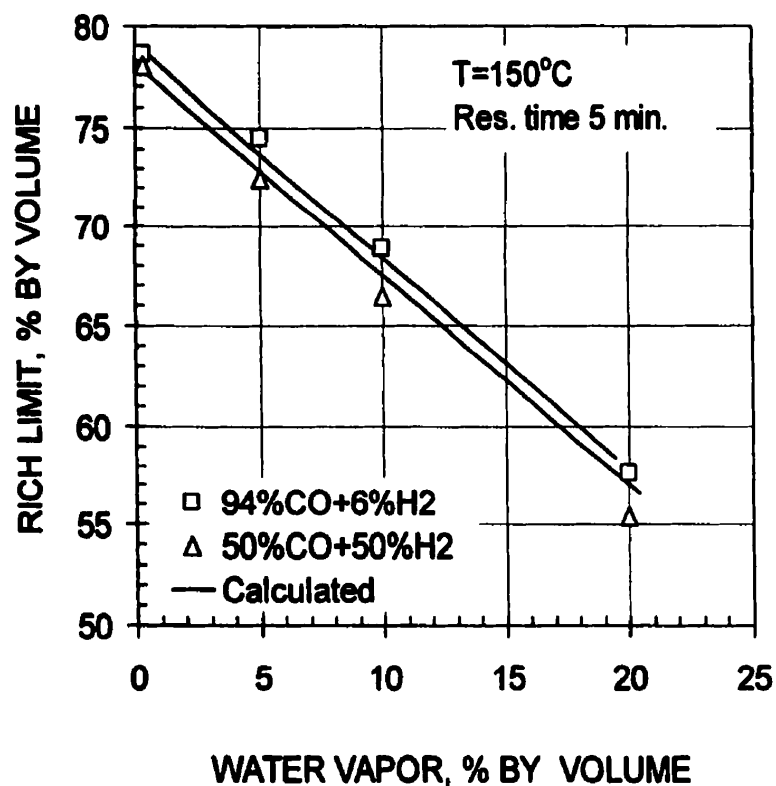


Fig. 5.13 Rich flammability limits of CO-H₂ mixtures calculated using adiabatic flame temperatures for the experimental values of the limits at 150°C

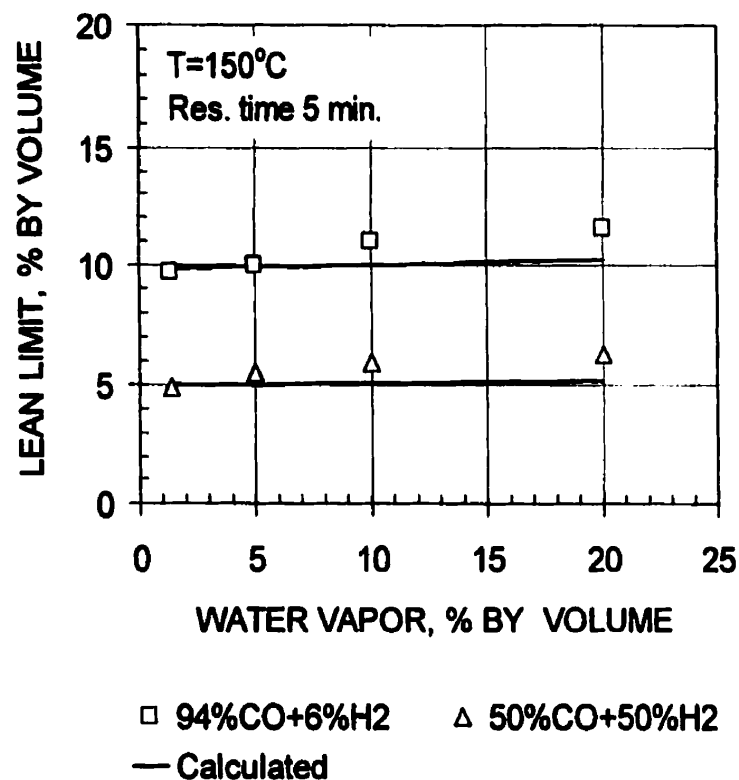


Figure 5.14 Lean flammability limits of CO-H₂ mixtures calculated using adiabatic flame temperatures for the experimental values of the limits at 150°C

show a significant variation in the values of the limits with residence time as shown in Fig.5.15 for the initial temperature of 300°C. The changes were larger at small residence times, while they were relatively smaller for residence times larger than ~15 minutes. As in the case of pure fuels, this behaviour of the limits indicated the existence of some preignition chemical activity within the fuel – air mixture that effectively changes the mixture composition before ignition. The existence of the chemical activity during the residence time was confirmed by gas analysis, which showed the consumption of some of the oxygen present and the production of carbon dioxide. This was also consistent with the mixture temperature and pressure measurements, which indicated that the bulk mixture temperature remained effectively unchanged while the pressure was decreasing throughout the period of the residence time.

Detailed chemical kinetics modelling as in the case of carbon monoxide on its own in air, was conducted for rich and lean carbon monoxide - hydrogen mixtures. The results of the calculations show that changes in mixture composition resulting from gas-phase activity within such mixtures (rich 5.16 and lean 5.17) were very small and could not be responsible for the trends observed. It can be seen in Fig. 5.2 that at temperatures below 600 K, the mean reaction rates become extremely small. Experiments with carbon monoxide – hydrogen mixtures were conducted at initial temperatures not exceeding 573 K (300°C) and 5 minutes residence time. Therefore, there should be no significant preignition chemical activity within mixtures tested at the experimental conditions due to gas phase reactions. It was concluded that surface reactions on the stainless steel wall of the test tube must have been responsible for the trends observed.

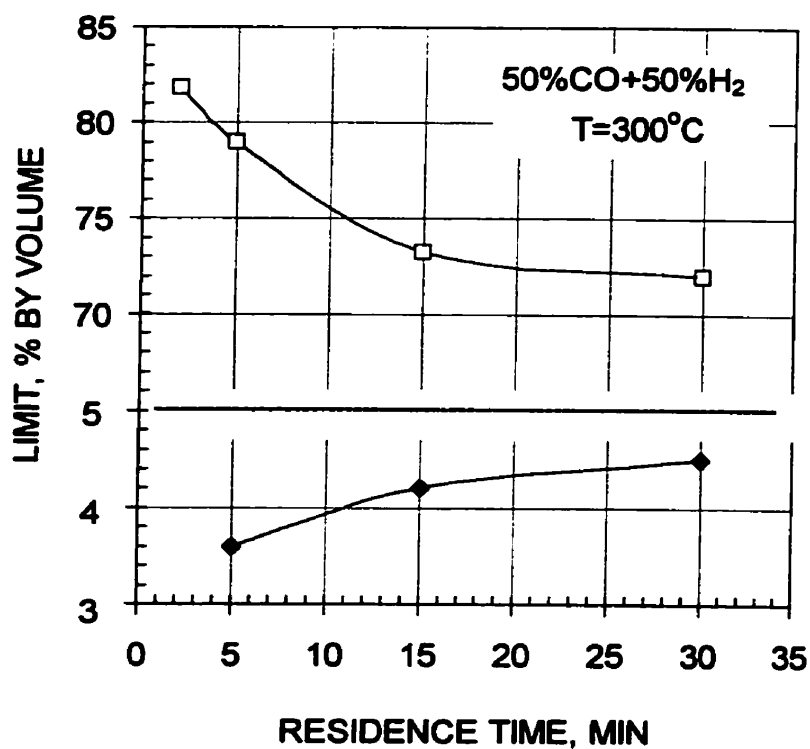


Fig. 5.15 Flammability limits of 50%CO+50%H₂ mixture in air as a function of residence time at temperature of 300°C

Table 5.7 Flammability limits of 50%CO+50%H₂ mixture in air as a function of residence time at 300°C

<i>Residence time, min.</i>	<i>2</i>	<i>5</i>	<i>15</i>	<i>30</i>
Flammability limit				
Rich limit, % by volume	81.8	79	73.2	72
Lean limit, % by volume	-	3.6	4.2	4.5

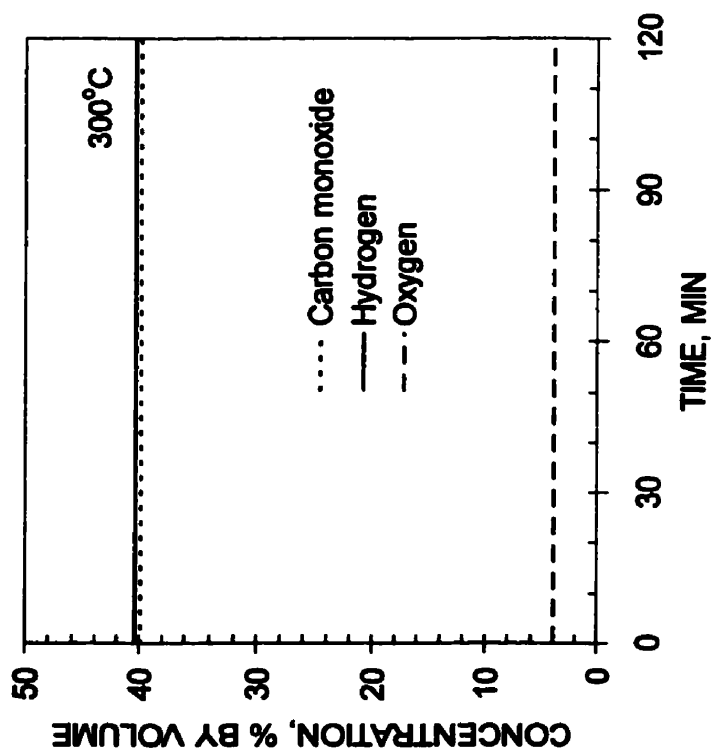


Fig.5.16 Results of the detailed chemical kinetics simulation of gas phase reactions for mixture of 40%CO+40%H₂+20%air at 300°C

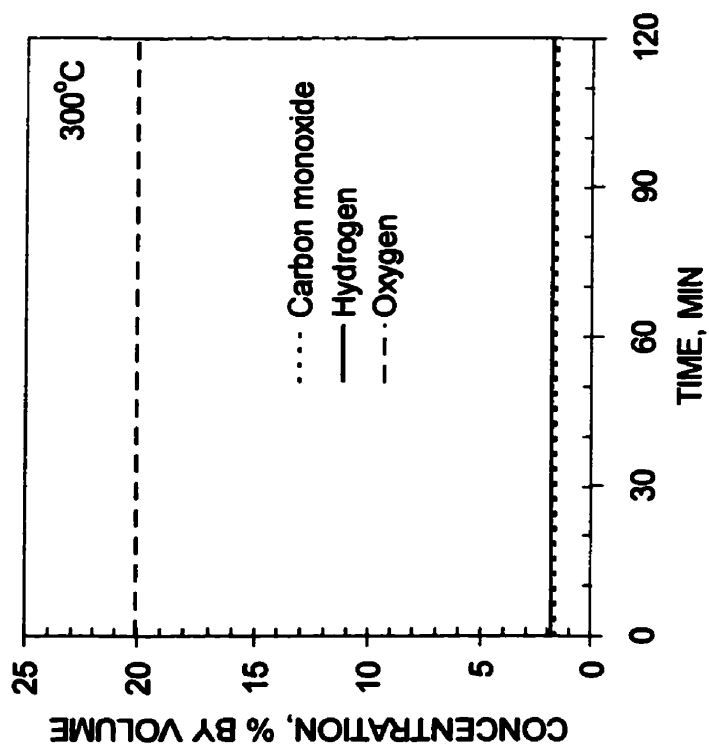


Fig.5.17 Results of the detailed chemical kinetics simulation of gas phase reaction for mixture of 1.75%CO+1.75%H₂+96.5%air at 300°C

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusion

- The flammability limits of carbon monoxide in air are strongly affected by water vapor concentration in the fuel – air mixture. The flammability limits widen significantly with a small increase in concentration of water vapor up to ~3%. However, the limits narrowed with a further increase in the concentration of water vapor in the mixture.
- The flammability limits of carbon monoxide in air established for a 5 minutes residence time widened almost linearly with an increase in temperature up to 300°C.
- The effect of temperature on the limits is weaker than that of water vapor concentration.
- Preignition chemical activity was observed during the residence time at temperatures $\geq 200^{\circ}\text{C}$, which changed the mixture composition and affected the values of the flammability limits. The longer was the residence time and higher was the temperature the narrower were the flammability limits. It was suggested that the change in the mixture composition resulted from catalytic reactions on the surface of stainless steel test tube. Therefore, when the effect of temperature on the flammability limits of carbon monoxide is investigated in stainless steel apparatus, the residence time becomes an important influencing parameter, which ought to be controlled and specified.

- The observed preignition chemical activity was more intense in dry carbon monoxide - air mixtures than in corresponding mixtures, containing small amounts of water vapor.
- A very small addition of hydrogen (less than 4 % by volume) to the carbon monoxide – “wet” air mixture produced a significant increase in the values of the rich limits. The value of the limit at room temperature of a fuel mixture containing only 2.6 percent of hydrogen actually exceeds the corresponding values of the rich limits of both hydrogen and carbon monoxide on their own in atmospheric air.
- The experimental values of the rich limits of carbon monoxide - hydrogen mixtures are significantly higher than those calculated by Le Chatelier’s Rule. The lean limits obey the Rule reasonably well.
- An increase in the initial mixture temperature widens somewhat the experimental flammability limits of various carbon monoxide – hydrogen mixtures over the temperature range employed (from room temperature up to 300°C) at the residence time of 5 min. However, at the rich limits, the increase tended to level off at temperatures exceeding 150 °C.
- The values of the flammability limits of carbon monoxide – hydrogen mixtures at elevated temperatures when determined in a stainless steel apparatus were also affected by preignition chemical activity during the residence time. The longer was the residence time, the narrower were the limits.
- The flammability limits of carbon monoxide – hydrogen mixtures narrowed with an addition of water vapor.

6.2 Recommendations for future work

There is a need for research work in the following areas:

- 1. To obtain flammability limits data of other important industrial fuel mixtures containing carbon monoxide (e.g. carbon monoxide – methane, carbon monoxide – propane etc.)**
- 2. To examine the effect of different test tube materials on the intensity of surface reactions.**
- 3. To develop a model of the low temperature catalytic oxidation and to estimate the possibility of catalytic autoignition at different surfaces, that may be important in estimation of fire and explosion hazards.**
- 4. To investigate further the flammability limits of carbon monoxide in dry air and to determine the reason for the scatter in the obtained values.**

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