The upper explosion limit of lower alkanes and alkenes in air at elevated pressures and temperatures

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Abstract

The upper explosion limit (UEL) of ethane–air, propane–air, *n*-butane–air, ethylene–air and propylene–air mixtures is determined experimentally at initial pressures up to 30 bar and temperatures up to 250 °C. The experiments are performed in a closed spherical vessel with an internal diameter of 200 mm. The mixtures are ignited by fusing a coiled tungsten wire, placed at the centre of the vessel, by electric current. Flame propagation is said to have taken place if there is a pressure rise of at least 1% of the initial pressure after ignition of the mixture. In the pressure–temperature range investigated, a linear dependence of UEL on temperature and a bilinear dependence on pressure are found except in the vicinity of the auto-ignition range. A comparison of the UEL data of the lower alkanes shows that the UEL expressed as equivalence ratio (the actual fuel/air ratio divided by the stoichiometric fuel/air ratio) increases with increasing carbon number in the homologous series of alkanes.
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1. Introduction

Many industrial processes involve the mixing of flammable gases with oxidising gases at elevated conditions of pressure and temperature. To safely operate these processes, it is necessary to know the explosion limits of these mixtures at the process temperature and pressure. Notwithstanding this, only a limited number of studies are available in the literature in which both the pressure and temperature dependence of the explosion limits are studied [1–12]. Of these, only Christner [4] studied a homologous series: he measured explosion limits for C1–C6 straight chain alcohols in air at pressures up to 5 bar and temperatures up to 400 °C. The aim of the present study is to extend the data of Vanderstraeten et al. [10], who measured the upper explosion limit of methane–air mixtures at elevated pressures and temperatures, with measurements on ethane–air, propane–air, *n*-butane–air, ethylene–air and propylene–air mixtures at initial pressures up to 30 bar and initial temperatures up to 250 °C.

2. Experimental set-up and procedure

The experimental set-up is shown in Fig. 1. It consists of two parts: equipment for preparing homogeneous mixtures of a specified concentration and an explosion vessel for testing the flammability of the mixtures.

The composition of the mixture to be tested is established by means of the flow rates of its components. The air flow rate is regulated by a thermal mass flow controller (MFC). An MFC was also used to establish the flow rate of ethane and ethylene which were fed to the installation in gaseous form. The separate flows are mixed inside a mixing chamber to ensure homogeneity of the mixture. If the vapour pressure at room temperature of the combustible is lower than 35 bar, it is fed to the installation as a liquid. A volumetric pump is used to control its flow rate and to compress the liquid to 40 bar enabling tests to be performed at initial pressures up to 30 bar. This procedure was applied in the case of propane, *n*-butane and propylene. The liquid then flows into an evaporator where it mixes with the air flow. The evaporator guarantees complete evaporation of the liquid, together with the homogenisation of the mixture. The piping between the evaporator and the explosion vessel is kept at a temperature above the saturation temperature of the mixture by means of an electric heating system in order to prevent condensation.

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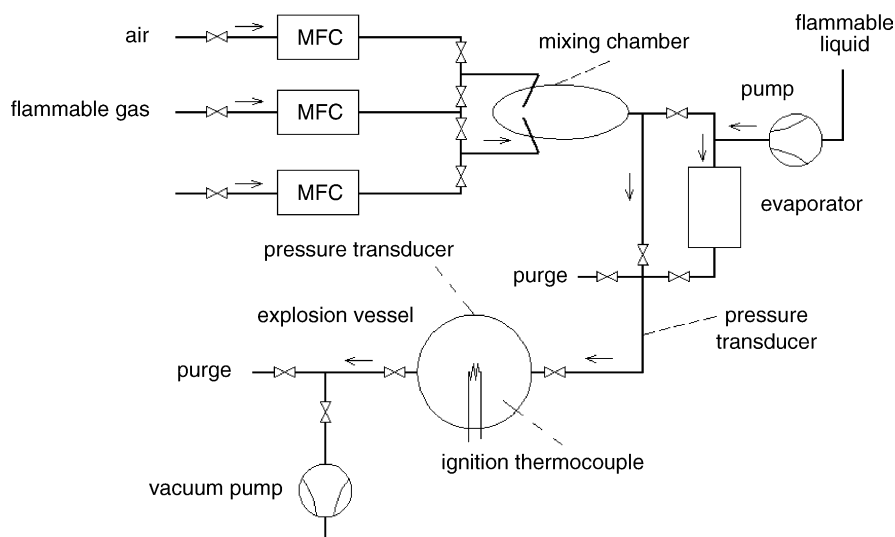(F. Van den Schoor).

Fig. 1. Experimental set-up.

Gas chromatography was used at regular intervals to verify the mixture composition.

The explosion vessel consists of a closed spherical cavity with an internal diameter of 200 mm (4.2 dm^3 internal volume). The vessel is designed to withstand explosion pressures up to 300 bar at a temperature of 250 °C. To perform experiments at elevated initial temperatures, the vessel is equipped with a thermal oil circuit. The initial gas temperature is measured with a type K thermocouple inserted a few centimetres from the vessel wall in the lower half of the explosion vessel. The initial pressure is measured with a piezoresistive pressure transducer inserted in the inlet piping to the explosion vessel.

Before filling the explosion vessel to the desired initial pressure, the vessel is evacuated and subsequently purged with a test mixture volume of at least 10 times the vessel volume. The gas mixture is allowed to come to rest by waiting at least 2 min before each test.

Ignition of the test mixtures is achieved by fusing a coiled tungsten wire, placed at the centre of the vessel, by applying a voltage of 50 V dc. The igniter releases about 10 J in 40 ms independent of pressure or temperature. The total length of the wire is approximately 60 mm and its diameter is 0.1 mm. It is attached to support leads which are approximately 6 mm apart and have a diameter of 0.5 mm. This arrangement is screwed into two electrodes which run vertically upwards through the bottom of the explosion vessel.

The pressure evolution after ignition is measured with a Kistler 701A piezoelectric pressure transducer. A pressure rise criterion is used to determine the explosion limit: flame propagation is said to have occurred if ignition is followed by a pressure rise of at least 1% of the initial pressure. The upper explosion limit is taken as the average between the highest concentration of combustible which gives a flammable mixture and the lowest concentration which does not. The concentration of the test mixtures is varied in steps of 1 mol%, while the mixtures are prepared with a maximum uncertainty of 0.5 mol%, giving a maximum uncertainty on the upper explosion limit of 1 mol%.

The experimental apparatus and procedure do not fully comply with the new European standard EN 1839 [13], which was issued after completion of the experimental campaign. However, this standard applies to gases, vapours and their mixtures at atmospheric pressure, whereas this study focuses on elevated pressures. Nevertheless, it seems necessary to elucidate the main differences between the method followed in this study and the one prescribed by the standard.

Firstly, EN 1839 states that the internal volume of the test vessel has to be at least 5 dm^3. The spherical vessel which is used in this study has an internal volume of 4.2 dm^3. Christner [4] stated that for spherical vessels, an internal diameter of 200 mm is large enough to neglect the influence of wall quenching, which is exactly the dimension of the explosion vessel in this study.

Secondly, the fusing wire used in this study is made of tungsten, while EN 1839 prescribes the use of a nichrome wire. The ignition energy, which is one of the most important parameters, however, falls in the range given by the standard, namely 10–20 J. Moreover, Takahashi et al. [14] state that ignition by fusing a nichrome wire is not very suitable for the explosion limits measurement, mainly because of the large scatter in the measured explosion pressure, which is the basis for the determination of the explosion limits. It must be added that the smallest wire diameter tested by Takahashi et al. was 0.3 mm, while according to EN 1839, wires of diameters between 0.05 and 0.2 mm must be used. In addition, the standard states that five tests must be completed to determine, if a flame cannot propagate in a mixture. This might correct for any scatter resulting from the ignition method. Takahashi et al. further conclude that the fusing of metals with a high melting point, such as molybdenum and tungsten, seems suitable for explosion limit measurement. They also mention the possibility of tungsten reacting with carbon compounds, which can affect the explosion limit determination if care is not taken to the ignition method. Fusing of tungsten wires needs a sufficiently high dc voltage to shorten the time it takes for the wire to fuse, which is also the time in which chemical interaction between the flammable mixture and the tungsten

wire might occur. They find that a dc voltage of at least 36 V is necessary, which is the case for the method used in this study.

Thirdly, the explosion criterion used in this study is 1% pressure rise, while EN 1839 uses 5% pressure rise. De Smedt et al. [15] made a comparison of two standard test methods to determine the explosion limits, namely DIN 51649 [16], which uses a visual flame detachment criterion, and ASTM E918-83 [17], which uses a pressure rise criterion of 7%. They found that the limits measured following DIN 51649 were wider than those measured following ASTM E918-83 for all the fuels tested, which led them to the conclusion that a pressure rise criterion of 7% is too high. Schröder and Daubitz [18] also compared different standard test methods. They found large deviations at the upper explosion limit of ethylene and ethanol in air between the two methods described in EN 1839, namely the tube method and the bomb (closed vessel) method. The tube method uses a visual criterion of flame detachment and propagation over a distance of 100 mm, whereas the bomb method uses a pressure rise criterion of 5%. They obtained values of 32.6 and 27.4 mol% for ethylene and 26.6 and 19.0 mol% for ethanol in the tube and bomb method, respectively. The values for methane and hydrogen, however, were the same within the experimental uncertainty of 0.2 mol%. At the lower explosion limit, the behaviour of the different fuels is totally opposite. Here, ethylene and ethanol show comparable results, while the values for methane are 4.3 and 4.9 mol% and those for hydrogen 3.6 and 4.2 mol% in the tube and bomb method, respectively. Schröder and Daubitz state that the reason for these deviations might be the pressure rise criterion, which is obviously less sensitive than the visual criterion. However, they do not conclude that the pressure rise criterion should be lowered. According to them, the use of a pressure rise criterion of 2% or lower seems to be too sensitive and difficult to interpret, because the igniter does not only cause a pressure increase itself by heating the surrounding gas, but also by triggering local burning of the mixture.

The effect of the ignition energy on the pressure evolution after ignition was investigated in the present study. An energy input of 10 J could in theory raise the pressure of 4.2 dm^3 of air at 1 bar and 20 °C by 0.01 bar, giving a pressure increase of 1%. At an initial pressure of 3 bar, the theoretical pressure increase is 0.3%. However, experiments in which wires were fused in air at pressures up to 30 bar showed a maximum pressure increase of 0.3% at 1 bar, 0.2% at 3 and 6 bar and no measurable pressure increase for pressures of 10 bar and above. It can be concluded that the pressure increase caused by the igniter is important only at low pressures.

3. Experimental results

3.1. Temperature dependence

It is found that for all initial pressures, the upper explosion limit (UEL) of ethane–air (Fig. 2a) and ethylene–air (Fig. 5a) mixtures increases linearly with initial temperature. A straight line can be fitted through the data points representing the equality:

$$\text{UEL}(T) = \text{UEL}(T_0) \cdot \left[1 + c \cdot \left(\frac{T - T_0}{100}\right)\right], \tag{1}$$

in which T is the initial temperature, T_0 the reference temperature (20 °C) and $\text{UEL}(T_0)$ and c are constants to be determined from the least squares fit.

This equation is a slight modification of an often used correlation for the prediction of explosion limits at temperatures above ambient, namely the modified law of Burgess and Wheeler [19]. Burgess and Wheeler [20] found empirically that the heat liberated by a mole of flammable substance at the lean limit is nearly constant for a number of combustible-air mixtures at ambient temperature. Based upon the observation of White [21] that the adiabatic flame temperature of limit mixtures is nearly constant, independent of the initial temperature, Zabetakis et al. [19] extended the law of Burgess and Wheeler to include the effect of initial temperature on the explosion limits. The resulting expression is a linear relationship between the lower explosion limit and the initial mixture temperature:

$$\frac{\text{LEL}(T)}{\text{LEL}(T_0)} = 1 - c \cdot (T - T_0).$$

Zabetakis [22] suggested the use of an equivalent expression for the temperature dependence of the upper explosion limit,
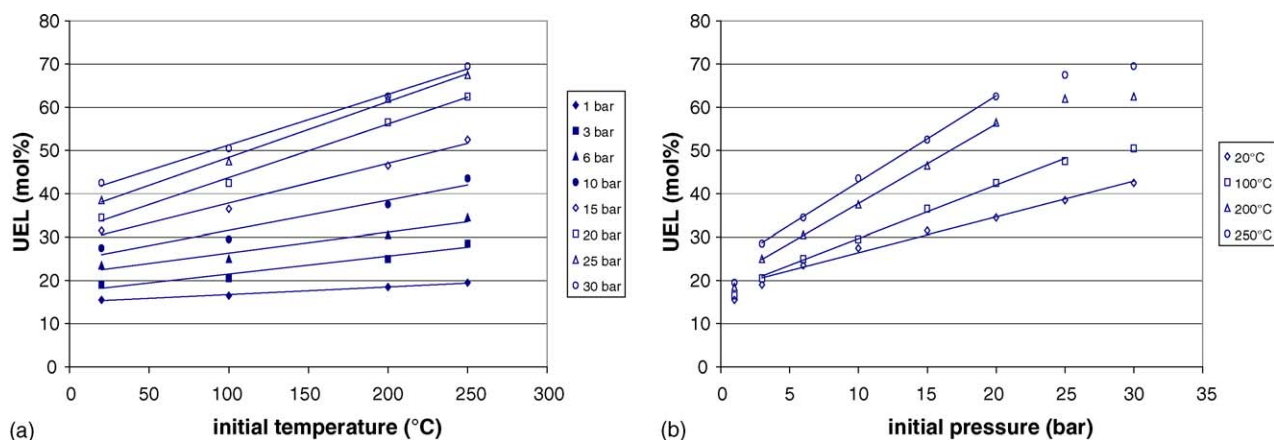

Fig. 2. (a and b) Upper explosion limit of ethane–air mixtures at elevated temperatures and pressures.

Table 1
Parameters and coefficient of determination R^2 of the straight line fit of the temperature dependence of the UEL of ethane–air mixtures at initial pressures up to 30 bar

Initial pressure (bar)	UEL(T_0) (mol%)	c (°C^{-1})	R^2
1	15.3	0.115	0.990
3	18.2	0.226	0.952
6	22.5	0.214	0.949
10	26.0	0.269	0.940
15	30.5	0.301	0.986
20	33.8	0.368	0.996
25	38.1	0.339	0.997
30	41.9	0.280	0.996

Table 2
Parameters and coefficient of determination R^2 of the straight line fit of the temperature dependence of the UEL of propane–air mixtures at initial pressures up to 10 bar

Initial pressure (bar)	UEL(T_0) (mol%)	c (°C^{-1})	R^2
1	10.4	0.138	0.957
3	12.6	0.234	0.996
6	16.3	0.344	0.966
10	20.7	0.416	0.990

which would hold in the absence of cool flames:

$$\frac{\text{UEL}(T)}{\text{UEL}(T_0)} = 1 + c \cdot (T - T_0).$$

Table 1 gives the values for the parameters UEL(T_0) and c of the straight line fits using Eq. (1) for ethane.

The data show that for low initial pressures, the slope of the lines increases with increasing initial pressure. At an initial pressure of 20 bar, a maximum slope is found and at still higher pressures, the slope starts to decrease. The temperature dependence of the UEL thus depends on the initial pressure. For methane–air mixtures, the same conclusion was arrived at by Vanderstraeten et al. [10].

Tables 2–5 give the values for the parameters UEL(T_0) and c of the straight line fits using Eq. (1) for propane, *n*-butane, ethylene and propylene, respectively. A similar increase of the slope c with increasing initial pressure is found for all the combustibles tested. The subsequent decrease of the slope at high pressures is found for ethylene and propylene.

It is seen (Fig. 3a) that, whereas the experimental results for ethane–air mixtures do not show a deviation from a linear dependence of the upper explosion limit on initial temperature, the data for propane–air mixtures at initial pressures of 10 and

Table 3
Parameters and coefficient of determination R^2 of the straight line fit of the temperature dependence of the UEL of *n*-butane–air mixtures at initial pressures up to 3 bar

Initial pressure (bar)	UEL(T_0) (mol%)	c (°C^{-1})	R^2
1	9.6	0.113	0.997
3	11.5	0.202	0.996

Table 4
Parameters and coefficient of determination R^2 of the straight line fit of the temperature dependence of the UEL of ethylene–air mixtures at initial pressures up to 30 bar

Initial pressure (bar)	UEL(T_0) (mol%)	c (°C^{-1})	R^2
1	34.7	0.156	0.995
3	43.5	0.138	0.997
6	47.7	0.172	0.966
10	52.7	0.186	0.979
15	58.9	0.163	0.999
20	64.1	0.128	0.998
25	66.3	0.132	0.993
30	68.2	0.118	0.996

15 bar clearly show a more than linear increase at higher temperatures. The UEL at 10 bar and 250 °C is found to be 54.5 mol%, whereas extrapolation from the data at lower temperatures would only give 40.5 mol%. This deviation is most likely caused by the proximity of the auto-ignition range, which renders the mixtures more flammable. At 12 bar and 250 °C, a mixture containing 64 mol% of propane was found to be within the auto-ignition range. It might be that the extra increase of the upper explosion limit is the result of partial oxidation, but this was not ascertained since it was outside the scope of the present study. This idea, however, is not new: Grewer and Lamprecht [3] observed similar deviations from linearity for ethylene–oxygen mixtures in the temperature range 130–200 °C. They mention the possibility that at 200 °C, cool flames occurred, since the pressure rise was small (10–30%, whereas the explosion criterion they used was 20% pressure rise) and an aldehyde-like smell was observed from the reaction products.

For *n*-butane (Fig. 4a), the temperature dependence exhibits a similar deviation from a linear dependence at an initial pressure of 6 bar. *n*-Butane–air mixtures at 250 °C and 6 bar were found to auto-ignite for concentrations above 40 mol% *n*-butane. For propylene (Fig. 6a), a deviation is found at an initial pressure of 15 bar.

3.2. Pressure dependence

As can be seen in Fig. 3b, the UEL for propane–air mixtures increases linearly with increasing initial pressure up to a certain point, where a sharp decrease of the slope is observed. This gives rise to a bilinear dependence of the UEL. Similar results are found for ethane–air and *n*-butane–air mixtures (see Figs. 2b and 4b). Vanderstraeten et al. [10] found a second-order dependence for methane–air mixtures, while Claessen et al. [7]

Table 5
Parameters and coefficient of determination R^2 of the straight line fit of the temperature dependence of the UEL of propylene–air mixtures at initial pressures up to 10 bar

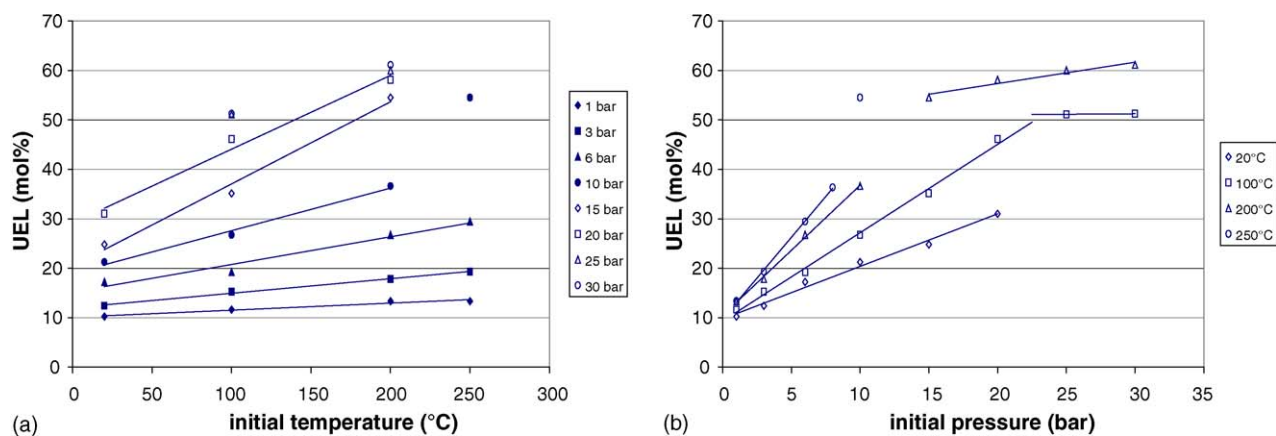| Initial pressure (bar)	UEL(T_0) (mol%)	c (°C^{-1})	R^2
1	12.7	0.128	0.966
3	13.7	0.191	0.994
6	16.5	0.336	0.944
10	22.3	0.263	0.995

Fig. 3. (a and b) Upper explosion limit of propane–air mixtures at elevated temperatures and pressures.

used a higher order polynomial to fit their data for methane–air and ethane–air mixtures. The data of these researchers, however, can also be fitted with two straight lines, while higher order polynomials cannot be used to fit the data obtained in the present work for propane–air and *n*-butane–air mixtures.

The pressure at which the slope of the linear increase of the UEL with initial pressure changes abruptly (transition pressure) for *n*-butane at 100 °C lies at approximately 10 bar, while for propane it lies between 20 and 25 bar, for ethane between 25 and 30 bar and for methane [10] it is higher than 35 bar. There appears to be a tendency for this pressure to shift to lower values with increasing carbon number in the homologous series of alkanes. Hsieh and Townend [23] made the same observation based on experiments performed with some higher alkanes in a 2 in. diameter cylindrical explosion tube. They state: "The widening of the upper limit with increase of pressure was not only progressively greater as the series was ascended, but in each case on the attainment of an adequate pressure which decreased in the same order, it became accentuated abruptly." They, however, do not give any experimental data as the explosion criterion which was used in the study could not determine the explosion limits with precision.

The alkenes tested do also show this (bi)linear dependence (Figs. 5b and 6b). However, since the data for propylene do not show any decline in slope, it could not be ascertained whether

the transition pressure shows a comparable behaviour for the homologous series of alkenes.

3.3. Comparison of the data for methane, ethane, propane and n-butane

Fig. 7 gives a comparison of the UEL data at an initial temperature of 200 °C of the alkanes tested in this study with data for methane from Vanderstraeten et al. [10]. It can be seen that the UEL expressed as equivalence ratio (the actual fuel/air ratio divided by the stoichiometric fuel/air ratio) increases with increasing carbon number in the homologous series of alkanes. The same observation was made by Hsieh and Townend [23].

This increase is probably caused by chemical kinetics and preferential diffusion. The oxidation kinetics for methane differs substantially from that of the other hydrocarbons [24]. It is known that methane is more difficult to ignite than other alkanes, because of the higher bond energy for the first broken C–H bond. This results in a higher auto-ignition temperature and might also lead to smaller flammable regions.

The effect of preferential diffusion occurs when the mass diffusivities of the reactants differ. For flammable gases having a lower diffusivity than oxygen, preferential diffusion causes the mixture at the flame front to behave as though it were actually leaner than the bulk composition of the unburnt mixture
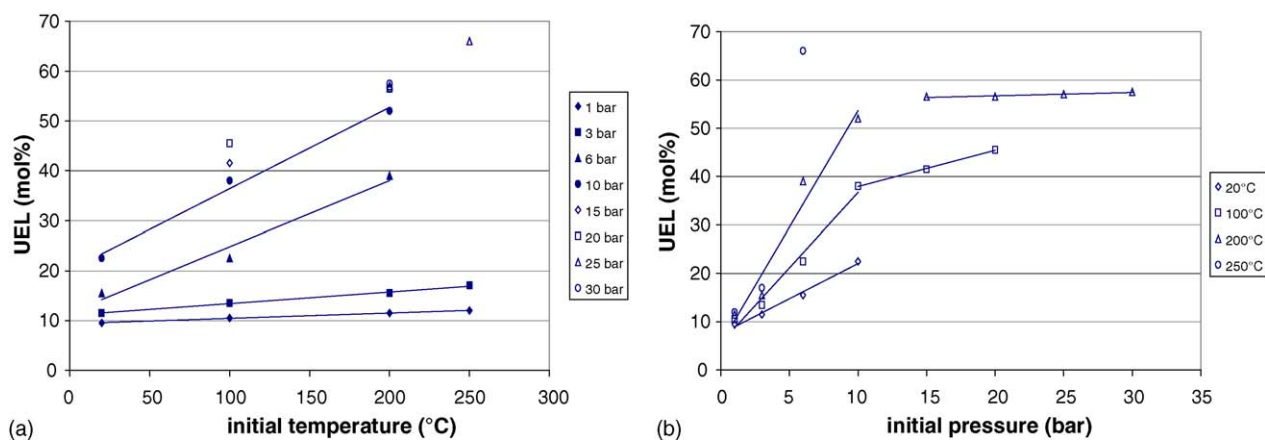

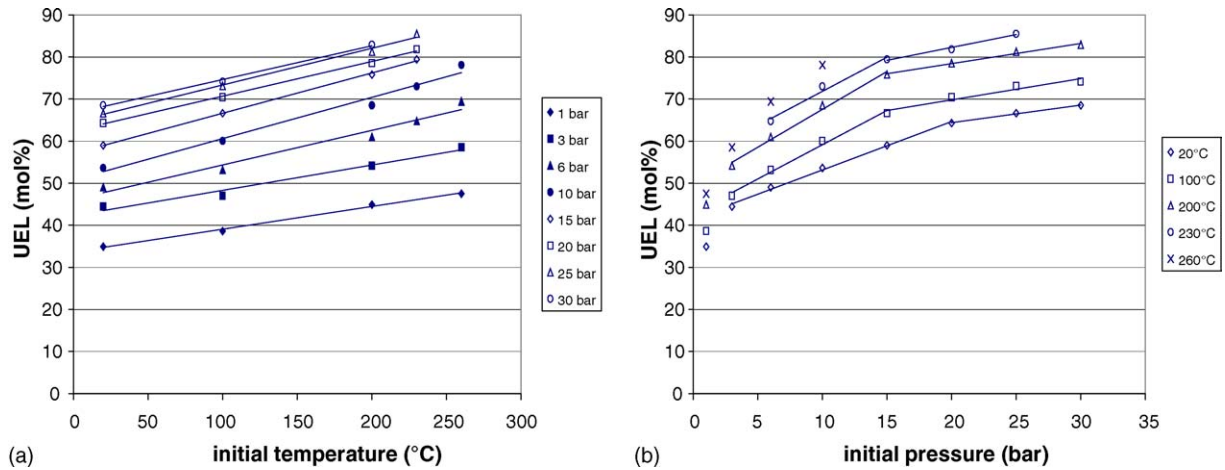Fig. 4. (a and b) Upper explosion limit of *n*-butane–air mixtures at elevated temperatures and pressures.

Fig. 5. (a and b) Upper explosion limit of ethylene–air mixtures at elevated temperatures and pressures.
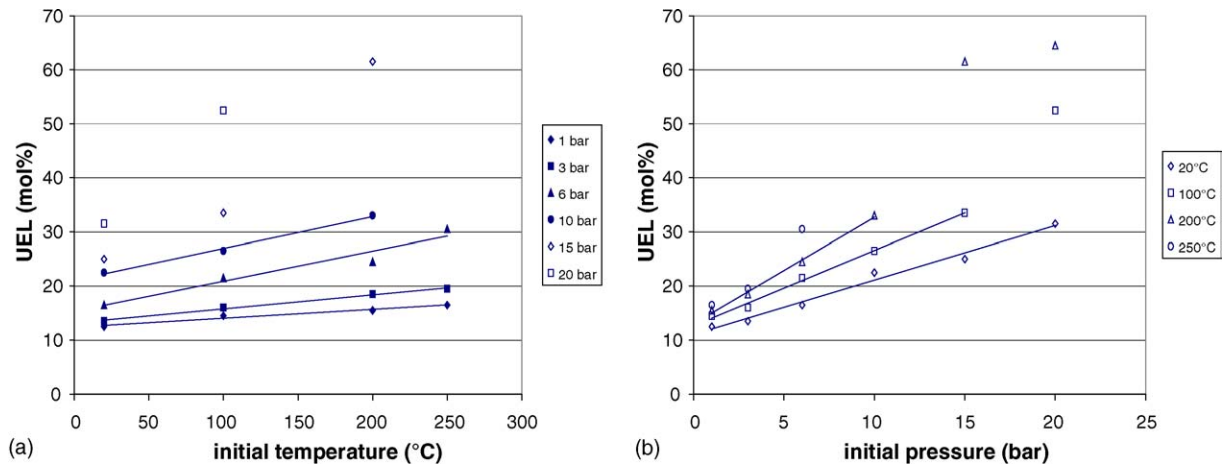

Fig. 6. (a and b) Upper explosion limit of propylene–air mixtures at elevated temperatures and pressures.

[25]. Rich mixtures are thus rendered more flammable. This is the case for ethane, propane and *n*-butane. Moreover, the effect increases as the difference in diffusivity between the fuel and oxygen increases. For methane, on the other hand, the fuel is the fastest diffusing component and rich mixtures of methane and air appear to be even richer.

3.4. Comparison of the data for ethylene and propylene

Comparison of the UEL data for ethylene and propylene as shown in Fig. 8 leads to the conclusion that any effect that preferential diffusion might have, is completely overshadowed by the fact that the reactivity of ethylene is greater than the reactivity
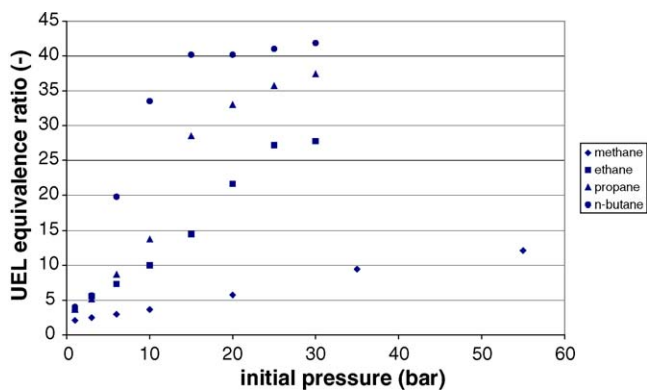

Fig. 7. Comparison of the dependence of the UEL of methane–air, ethane–air, propane–air and *n*-butane–air mixtures on initial pressure for an initial temperature of 200 °C.
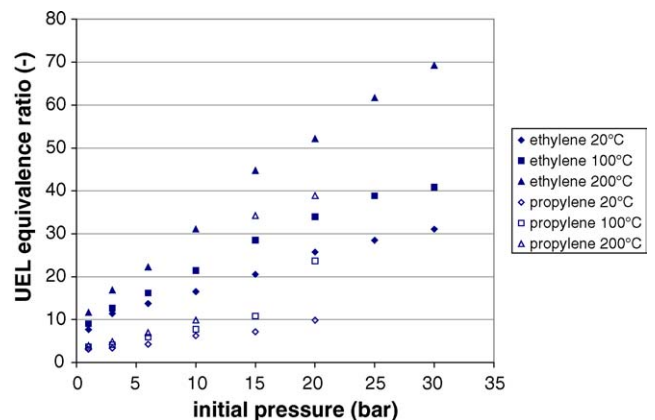

Fig. 8. Comparison of the dependence of the UEL of ethylene–air and propylene–air mixtures on initial pressure.

of propylene. It is well known that ethylene is highly reactive, as is evidenced by the high burning velocity in comparison with the other alkenes [24].

3.5. Comparison with previous studies

Hashiguchi et al. [2] have measured the explosion limits of ethylene–air mixtures for pressures up to 50 bar in a small cylindrical tube, with a diameter of 100 mm and a height of 150 mm. Ignition occurred by fusing a platinum wire of 20 mm length and 0.3 mm diameter, placed at the bottom of the vessel, by applying a voltage of 12 V dc. The igniter released approximately 20 J in 70 ms. It is not clear which explosion criterion was used. Craven and Foster [1] have determined the explosion limits of ethylene–air mixtures for pressures up to 9 bar in a 3 dm^3 spherical bomb. They used a 60/40 nichrome hot wire as ignition source with an unknown ignition energy. Any detectable pressure – this was not stated more precisely – was taken as an indication of flammability. Holtappels et al. [26] have measured the explosion limits of ethylene–air mixtures for pressures of 1, 10 and 100 bar in a 2.65 dm^3 explosion bomb. Ignition occurred by fusing a nichrome wire of 5 mm length and 0.12 mm diameter by applying 230 V ac. The ignition energy was limited to give a pressure rise of less than 1% in air so as to not interfere with the explosion criterion of 10% pressure rise. This was done by a chopping technique that allowed only part of the ac current to pass through the wire. Fig. 9 shows a comparison of the results of these surveys with those obtained in this study. There is good agreement between the results of this study and those of Hashiguchi et al. at pressures above 10 bar. The discrepancy between the data at pressures below 10 bar might be caused by the smaller size of the explosion vessel in combination with the explosion criterion. The data of Hashiguchi et al. at high pressures seem to indicate that there is a limit pressure above which the UEL barely increases. This idea is further corroborated by Berl and Werner [27] who give a UEL of 68 mol% at 91 atm and of 71 mol% at 381 atm. Holtappels et al. [26], however, have found a value of 80.8 mol% at 100 bar, which is about 10 mol% higher than the asymptotic value which would be found when extrapolating the data of Hashiguchi et al. to an initial pressure of 100 bar. As the results of Holtappels et al. correspond well with
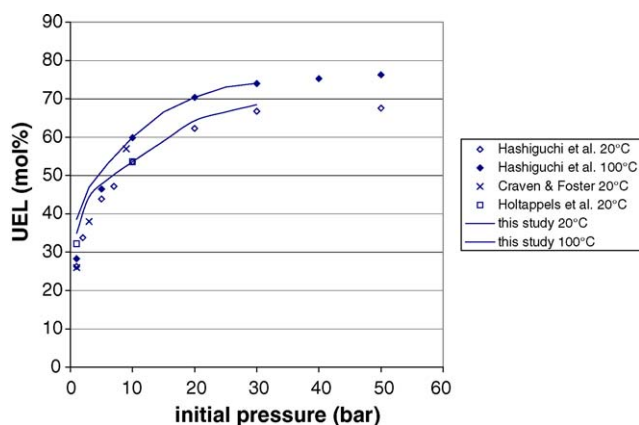
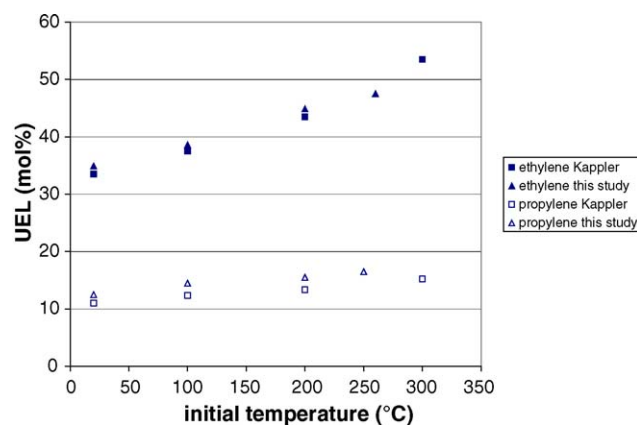Fig. 9. Comparison of UEL data for ethylene–air mixtures.

Fig. 10. Comparison of UEL data for ethylene–air and propylene–air mixtures.

the data of this study for initial pressures of 1 and 10 bar, this would indicate a substantial increase of the UEL of ethylene–air mixtures at pressures above 50 bar. A possible explanation is the instability of ethylene which is prone to decomposition at high pressures [26].

Kappler [28] has measured the explosion limits of ethylene–air and propylene–air mixtures at temperatures up to 300 °C in a cylindrical explosion tube of 64 mm diameter and 1 m length. An electric spark was used to ignite the mixtures. The electrodes were placed at the bottom of the tube and the stored capacitor energy was 20 J. He used three thermocouples, placed at 0.2, 0.4 and 0.8 m along the inside of the tube, to establish whether there was flame propagation inside the tube. Although the results of this study are 1–2 mol% higher than those of Kappler, the agreement in temperature dependence is very good as can be seen in Fig. 10. The data of Kappler show a more than linear increase at 300 °C for ethylene–air mixtures, similar to the deviations found in the present study as mentioned in Section 3.1.

Wierzba and Ale [29] have studied the effect of residence time at high temperature on the explosion limits. The tests were performed in a cylindrical explosion tube of 50.8 mm diameter and 1 m length, with electrodes placed at the bottom as a means of igniting the mixture by electric spark discharge. A visual criterion of flame propagation throughout the whole length of the tube was used. Fig. 11 shows a comparison between their data for a residence time of 10 min prior to ignition and those obtained in this study (with a residence time of less than 2 min as mentioned in Section 2). Again, there is good agreement between the observed dependence on initial temperature in both studies. At temperatures above 300 °C, Wierzba and Ale have observed a decrease in UEL with increasing initial temperature. This narrowing of the limits was attributed to pre-ignition reactions, catalysed by the stainless steel surface of the explosion tube. Since these pre-ignition reactions seem to occur at temperatures above 300 °C for ethylene and propane at atmospheric pressure and since the present study focuses on the UEL at temperatures up to 250 °C in combination with pressures up to 30 bar, it was necessary to verify whether these pre-ignition reactions had an influence on the explosion limits measured. Gas chromatography measurements of mixtures kept inside the explosion vessel
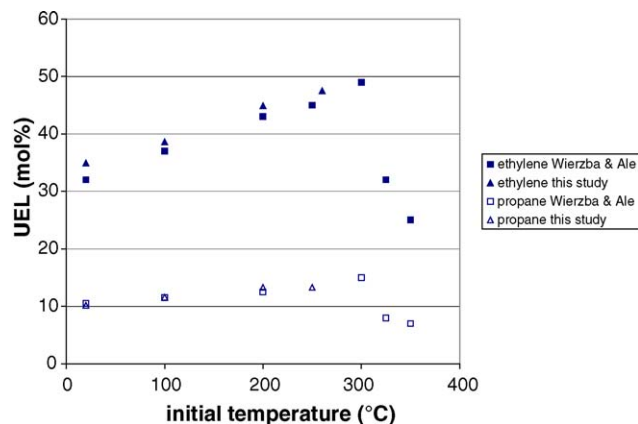
Fig. 11. Comparison of UEL data for ethylene–air and propane–air mixtures.

for an extended period of 15 min show only a negligible decrease of the oxygen concentration, indicating that pre-ignition reactions do not play any important role at a residence time less than 2 min for the conditions tested.

4. Discussion

Flame propagation is a complex phenomenon. At atmospheric pressure and ambient temperature, the results of numerous experimental studies on the determination of the explosion limits are available [22,30]. Close examination of these data, however, shows large discrepancies between the results of different researchers. In the past, attempts have been made to determine explosion limits as physico-chemical constants of a reacting mixture by simulating planar one-dimensional flames with a detailed chemical kinetics scheme, all the transport properties and radiation heat loss [31,32]. Although these numerical simulations represent an important milestone in the calculation of explosion limits, their limitations should be kept in mind. In real life situations, flames cease to propagate not merely as the result of a competition between chain branching and chain termination reactions or radiation heat loss. These phenomena are only part of a more complex process in which flame front instabilities (cellular flames, preferential diffusion, . . .) and interactions between the flame front and the flow induced by the buoyant rise of the burnt gases play an equally important role.

In the present study, the fuels investigated were chosen not only because of their practical relevance, but also because of the fact that the investigation of a homologous series can shed light on the importance of factors not related to chemical kinetics. The large differences observed between the various members of the series of alkanes cannot be attributed to differences in chemical kinetics alone, since especially propane and *n*-butane have a similar flame chemistry [24]. It is therefore concluded that preferential diffusion is an important factor in near-upper explosion limit flames. The experimental results further show that care should be taken when applying at elevated pressures correlations, which are based upon observations at atmospheric pressure, such as the modified law of Burgess and Wheeler. Care should also be taken when extrapolating experimental data to higher temperatures, in particular near the auto-ignition range, as this could lead to underestimating the UEL.

5. Conclusions

The upper explosion limits for ethane, propane, *n*-butane, ethylene and propylene in air are determined at initial pressures up to 30 bar and temperatures up to 250 °C. It is found that:

1. The UEL increases linearly with initial temperature; however, the slope of the straight line is not a constant but depends on the initial pressure.
2. A strong deviation from the linear dependence of the UEL on initial temperature occurs in the proximity of the auto-ignition range for propane–air, *n*-butane–air and propylene–air mixtures.
3. A (bi)linear dependence of UEL on initial pressure is found, where a strong decrease in the slope might indicate a limit pressure above which the UEL does not increase.
4. A comparison of the data for the alkanes indicates that the effect of preferential diffusion plays an important role in near-upper explosion limit combustion.

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