Experimental study of the flammability limits of toluene–air mixtures at elevated pressure and temperature

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Abstract

The flammability limits of toluene–air mixtures are experimentally determined at pressures up to 500 kPa and temperatures up to 250°C in a closed spherical vessel. The results at atmospheric pressure are compared with the results obtained in a glass tube. The flammability limits depend linearly upon temperature. A twilight zone characterized by weak pressure rises is observed for toluene at all pressures, while soot is formed at elevated pressures only. The explosion characteristics of toluene are compared with those of methane. Despite their chemical differences, the explosion characteristics of toluene and methane are similar. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Combustible gases and vapours are frequently encountered in chemical processes. In order to evaluate the explosion hazards involved and to ensure safe and optimal operation of these processes, it is necessary to know their explosion characteristics under the working conditions, i.e. at process temperature and pressure. At ambient temperature

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and atmospheric pressure, these limits are well established [1–6]. At elevated pressure and temperature only limited data is available.

The present work consists of the experimental determination of the flammability limits of toluene–air mixtures at pressures up to 500 kPa and temperatures up to 250°C in a closed spherical explosion vessel. To determine the effect of the vessel geometry, additional experiments are performed using a glass tube. These experiments were performed at atmospheric pressure.

Recent research on methane–air mixtures [7] has shown that near the upper flammability limit (UFL), unusual combustion processes take place. At elevated pressures, soot and a twilight zone have been observed. Also these phenomena were investigated in the present work.

2. Experimental apparatus and procedure

A first series of experiments with toluene–air mixtures was conducted in a glass tube in accordance with the standards [8,9]. In this apparatus the mixture is ignited using an induction spark. The mixture is considered flammable when the spark creates a flame which detaches from the electrodes. Because these experiments use a standard glass tube, the resulting limits are called *glass tube flammability limits*.

In a second series of experiments a closed spherical vessel was used. This vessel allows one to perform experiments at elevated pressures. The ignition is achieved by fusing a tungsten wire. Combustion is observed through a dynamic pressure measurement. The resulting limits are called *closed vessel flammability limits*.

In the closed vessel test the mixture is considered flammable if a pressure rise of more than 2% is detected after ignition.

2.1. Glass tube apparatus

The glass tube set-up is shown in Fig. 1. This apparatus is built in accordance with DIN-51649 [8]. The test tube is a vertical glass cylinder of 300 mm length and with a diameter of 60 mm. Purging is achieved by opening a valve located at the bottom of the test tube. During testing this valve is closed. A funnel shaped glass lid is placed on top of the tube. The top of the lid is connected to a flexible tube through which purge gas and combustion products are discharged. The lid is not fixed to the tube. It covers the top of the tube by its weight. It lifts up in case overpressure occurs in the test tube and thus protects the tube from damage. The whole set-up (evaporator, mixing chamber and test tube) is placed in an oven, the temperature of which can be regulated with an accuracy of 1°C. This makes it possible to perform experiments up to 300°C.

Before each experiment the tube is purged 10 times its internal volume with the test mixture. The toluene–air mixture is produced by supplying an accurately known flow of toluene and air to an evaporator. A detailed description of the evaporator can be found in [8]. A static mixing chamber is placed after the evaporator to obtain a homogeneous mixture. The flow rate of the air is controlled by means of a mass flow controller. The toluene is supplied by a volumetric pump, the flow rate of which can be varied with an
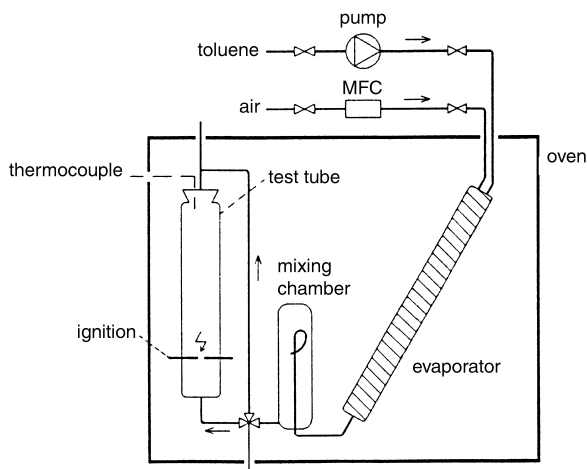
Fig. 1. Glass tube apparatus.

accuracy of 0.2%. The relative error on the mixture concentration is estimated to be less than 3%.

The ignition source is an induction spark drawn between two electrodes, located 60 mm above the bottom of the tube. This spark is generated by a high voltage transformer (15 kV) and is maintained for 0.5 s. The electrodes are 5 mm apart.

A mixture of a given concentration is considered to be non-flammable when no flame detachment is observed during at least 5 successive tests at the same concentration. The toluene concentration is gradually increased with 0.02 vol.% or decreased with 0.1 vol.% at the lower or upper flammability limit, respectively, until flame detachment is observed. The upper limit is the toluene concentration of the non-flammable mixture with the lowest concentration. The lower limit is determined in an analogous manner. This standard procedure is repeated 3 to 10 times. Finally, the limit is defined as the average of the limits found in each of the test series described above.

During the experiments it was observed that flame detachment was always accompanied by flame propagation to the top of the tube. This is rather unusual as for many gases flame detachment near the flammability limits often does not give rise to a flame travelling to the top of the test tube.

2.2. Closed explosion vessel

The closed explosion vessel is shown in Fig. 2. It consists of a spherical steel vessel of 8 dm^3 internal volume. This vessel is designed to withstand explosion pressures up to 350 MPa at an initial temperature of 350°C. To allow for experiments at elevated temperatures, the vessel is equipped with a thermostatically controlled electric heater.

To produce the toluene–air mixture toluene and air are supplied to a spiral tube evaporator at the required flow rates. The air and toluene flow rates are controlled by a mass flow controller (MFC) and a volumetric pump, respectively. The relative error on
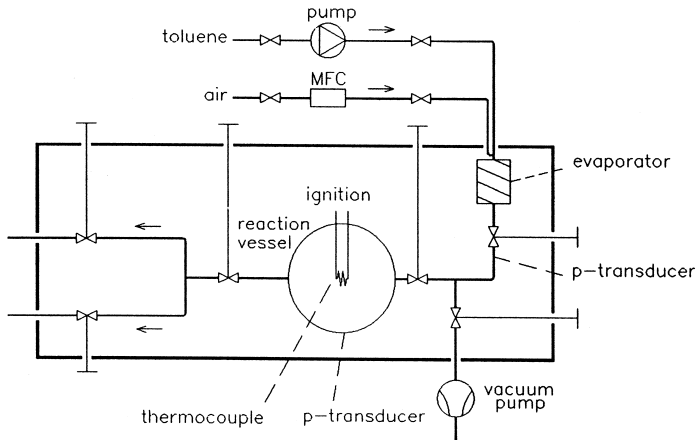
Fig. 2. Closed explosion vessel apparatus.

the concentration is estimated to be less than 3%. Before filling the vessel to the desired explosion pressure, it is purged with the gas mixture for at least 10 times its volume. The initial pressure is measured with a resistance pressure transducer. The pressure and temperature histories during explosion are measured with a piezo-electric pressure transducer and a Cr/Al thermocouple positioned at the centre of the vessel, respectively.

The ignition is achieved by fusing a tungsten wire, placed at the centre of the vessel. Such an igniter releases about 10 J in 0.040 s and operates independently of pressure or temperature [7].

The piping between the evaporator and the explosion vessel is provided with steam tracing at 150°C to prevent toluene condensation.

The occurrence of an explosion is evaluated by the pressure increase after ignition. A test showing a pressure rise of 2% or more is called an explosion. The closed vessel flammability limits are defined by the min–max criterion [7]. The min–max criterion puts the upper limit in the middle between the highest flammable toluene concentration and the lowest non-flammable toluene concentration (analogous for the lower limit). Near the limits there is a difference of 0.25 vol.% toluene between successive experiments.

When soot was generated during the explosion, the sphere was purged with pressurised air that removed all unattached soot. After a series of tests the sphere is opened and cleaned completely.

3. Results

3.1. Glass tube

In the glass tube, experiments were performed at atmospheric pressure and temperatures between 50°C and 250°C. 50°C was chosen as lowest temperature because at this

temperature a vapour–air mixture with a maximum toluene concentration of 12 vol.% (which is well above the upper flammability limit) has a condensation temperature below 50°C. Thus condensation of toluene would not occur in the apparatus. No experiments were performed above 250°C because toluene dissociates at higher temperatures.

At atmospheric pressure and 50°C, the limits were found to be 1.13 ± 0.02 vol.% and 7.9 ± 0.1 vol.%. Fig. 3 shows the glass tube flammability limits for toluene–air mixtures at elevated temperatures. At 250°C the lower limit is 0.83 ± 0.02 vol.%. The upper limit is 8.7 ± 0.1 vol.% at 220°C.

3.2. Closed vessel

In the closed spherical vessel, experiments were performed at pressures up to 500 kPa and temperatures between 60°C and 225°C. At elevated pressures, a minimum temperature of 120°C was chosen in connection with the vapour pressure of toluene.

As an example of the data obtained, Fig. 4 shows the ratio of the maximum explosion pressure, p_{ex}, to the initial pressure, p_1, as function of the toluene concentration. At 60°C and atmospheric pressure the highest maximum explosion pressure ratio of 7 is found around the stoichiometric concentration (2.27 vol.%). Near the UFL, a zone of toluene concentrations with pressure ratios lower than 2 is observed. This zone is called the twilight zone. At atmospheric pressure and 60°C, the twilight zone stretches from around 5 vol.% toluene to 7.1 vol.%. The closed vessel flammability limits found at atmospheric pressure and 60°C are 1.3 ± 0.1 vol.% and 7.1 ± 0.2 vol.%.

Fig. 5 shows the flammable domain of toluene–air mixtures at 100 and 500 kPa and at 120°C. The lower flammability limit and the maximum pressure ratios around the
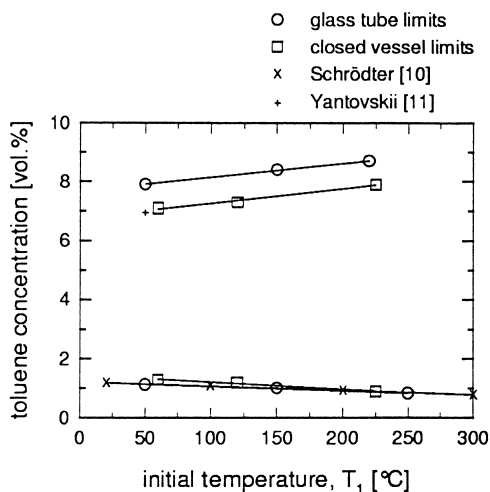

Fig. 3. The temperature dependence of the glass tube and the closed vessel flammability limits of toulene/air-mixtures at atmospheric pressure.
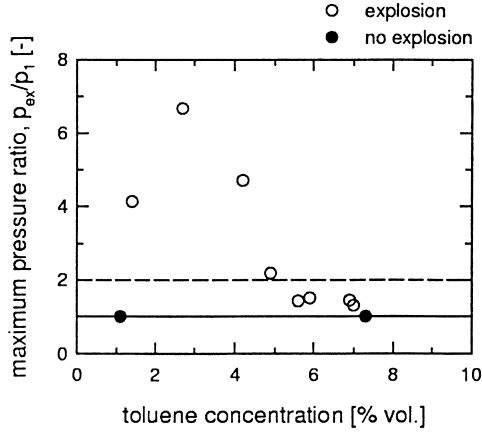
Fig. 4. Flammable region of toluene–air mixtures at atmospheric pressure and at 60°C.

stoichiometric concentration are almost the same at 100 and 500 kPa. However, at the rich side there is an important difference in the behaviour of the maximum explosion pressure ratio at 100 kPa from the one at 500 kPa. The large twilight zone at 100 kPa disappears at 500 kPa, but a new phenomenon occurs. Between 5 and 7 vol.%, indicated by ($\blacklozenge$) in Fig. 5, a zone of toluene concentrations with almost constant maximum pressure ratios is observed. These explosions always produced soot and therefore this zone is called the soot zone. Between the soot and the twilight zone there is a sharp drop in maximum pressure ratio. Although the wide soot zone at 500 kPa extends the range of dangerous toluene concentrations (high explosion pressures), the UFL only increased half a percent with respect to the UFL at 100 kPa.
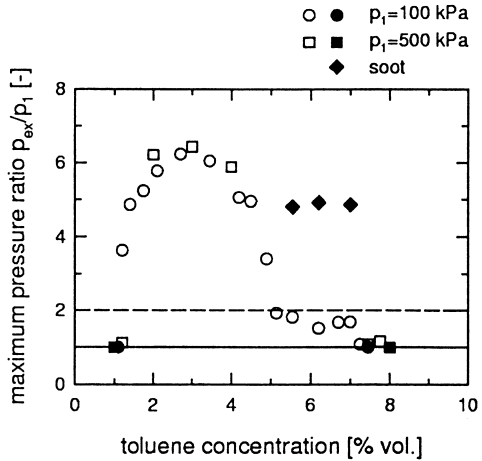

Fig. 5. Flammable region of toluene–air mixtures at 100 and 500 kPa and at 120°C.
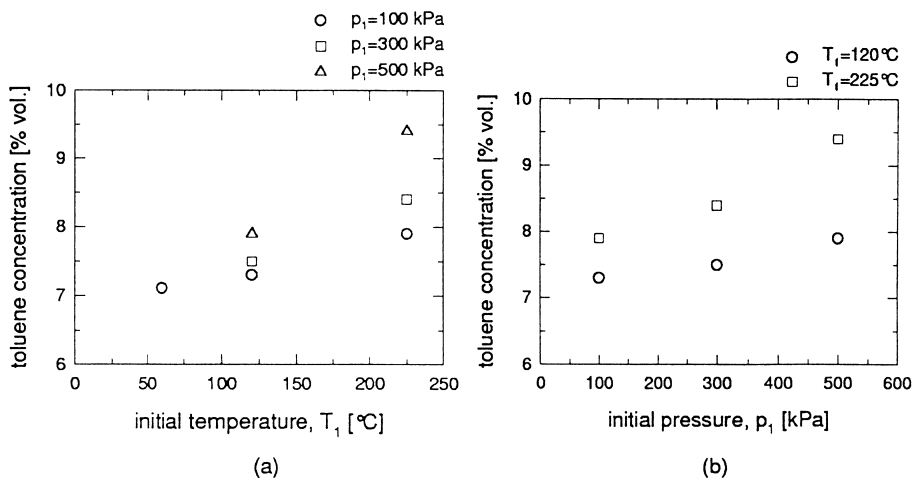
Fig. 6. (a) Temperature and (b) pressure dependence of the UFL of toluene–air mixtures at elevated pressures.

The closed vessel flammability limits at atmospheric pressure and elevated temperatures were also determined. The results are shown in Fig. 3, indicated by ($\square$).

Fig. 6(a) shows the temperature dependence of the upper flammability limit at elevated pressures. The temperature dependence of the UFL increases with higher initial pressure. In Fig. 6(b) the pressure dependence of the upper flammability limit at elevated temperatures is shown. The pressure dependence of the UFL increases with higher initial temperature.

Finally the soot zone and the twilight zone were determined for toluene. The results are shown in Figs. 8 and 9.

4. Discussion

4.1. Temperature and pressure dependence of the flammability limits of toluene–air mixtures

Fig. 3 shows the glass tube and the closed vessel flammability limits of toluene–air mixtures at atmospheric pressure and at elevated temperatures. Over the whole temperature range, the lower limits are closed to each other and close to the lower limits measured by Schrödter [10], indicated by ($\times$) in Fig. 3. The upper limits on the other hand, differ more: the glass tube upper limits are about 1 vol.% higher than the closed vessel limits. At 60°C, the closed vessel limit found here is in good agreement with the limit reported by Yantovskii [11], indicated by ($+$) in Fig. 3.

Over the whole temperature range the closed vessel flammable region lies within the glass tube flammable region. The difference between the glass tube and the closed vessel flammability limits cannot be explained in a quantitative way. A different experimental set-up and ignition source, as well as a different flammability criterion were used to

determine these limits. Medard [5] suggested that in general the limits obtained with a small pressure rise criterion in a spherical explosion vessel are in good agreement with the limits obtained for upward propagation in an open glass tube of 1.2 to 2 m length. The open glass tube apparatus used here has a length of only 300 mm.

The solid lines in Fig. 3 represent a linear relationship between the temperature and the flammability limits (FL). In general such a correlation can be written as:

$$FL(T_1) = FL(T_0)\left[1 + c\left(\frac{T_1 - T_0}{100}\right)\right]$$ (1)

where T_0 is the ambient temperature ($T_0 = 20°C$). The constant $FL(T_0)$ is the calculated flammability limit at ambient temperature. The constant c represents the relative increase or decrease of the flammability limit per 100°C temperature rise. Values for $FL(T_0)$ and c are given in Table 1, for the lower and upper limit and for the glass tube and the closed vessel experimental set-up.

The value of c for the upper closed vessel limit is in good agreement with the 8% relative increase proposed by Bodurtha [12]. The upper glass tube limit shows a smaller temperature dependence. The lower glass tube and closed vessel limits show a temperature dependence that is about twice as large as that of the corresponding upper limits. This is in contradiction with the modified Burgess–Wheeler law [6,13]:

$$\frac{LFL(T_1)}{LFL(T_0)} = 1 - \frac{c_p \cdot 10^2}{LFL(T_0)(-\Delta H_c)}(T_1 - T_0)$$ (2)

with c_p the specific heat at constant pressure of the mixture and ΔH_c the heat of combustion of the fuel. According to this law the relative temperature dependence of the LFL should be 7% instead of the 13% to 17% determined experimentally.

Gibbon et al. [14] calculated also the constant c of Eq. (1) for toluene. They used experimental data derived from different set-ups i.e. different explosion vessels and ignition sources. Their value for the constant c for the LFL is 0.13 K^{-1} which is in good agreement with our value of c.

Fig. 6(a) shows that at increased pressures the relative temperature dependence increases. Table 2 gives the coefficients of Eq. (1) for the upper closed flammability limits at increased pressures.

Although the upper flammability limit increases at elevated pressure the adiabatic flame temperature at the limit remains between 1300 and 1360 K at all researched conditions of temperature en pressure. This illustrates that the theory of constant flame temperature at the limits is valid for toluene which is in contradiction with other gases

Table 1
The constants $FL(T_0)$ and c for the temperature dependence of the flammability limits

| | Glass tube | | Closed vessel | |
	$FL(T_0)$ [vol.%]	c [1/K]	$FL(T_0)$ [vol.%]	c [1/K]
Upper	7.8	0.06	6.9	0.07
Lower	1.19	−0.13	1.42	−0.17

Table 2
Coefficients of Eq. (1)

p_1 / p_0 [–]	UFL(T_0) [vol.%]	c [1/K]
1	6.9	0.07
3	6.7	0.13
5	6.5	0.20

(e.g. methane). For most flammable gases the adiabatic flame temperature at the limit decreases when the initial pressure increases [6].

It should be pointed out that the flammability criteria applied here for the glass tube tests (flame detachment) and for the closed sphere (2% pressure rise) lead to a large flammability range. This is demonstrated by the flame temperatures at the LFL which can be derived from Eq. (1) extrapolating FL(T) to zero using the data of Table 1. This leads to 810°C for the glass tube and 608°C for the sphere. These are low temperatures indicating low LFL values.

4.2. Comparison of toluene and methane

In earlier research [7], the flammability characteristics of methane–air mixtures were determined with the same experimental apparatus that was used here to determine the closed vessel flammability limits of toluene–air mixtures. It is interesting to compare the results of this study on toluene and the results of the methane study.

Figs. 6(a) and 7(a) show the temperature dependence of the UFL of toluene– and methane–air mixtures at elevated temperature. A linear temperature dependence is
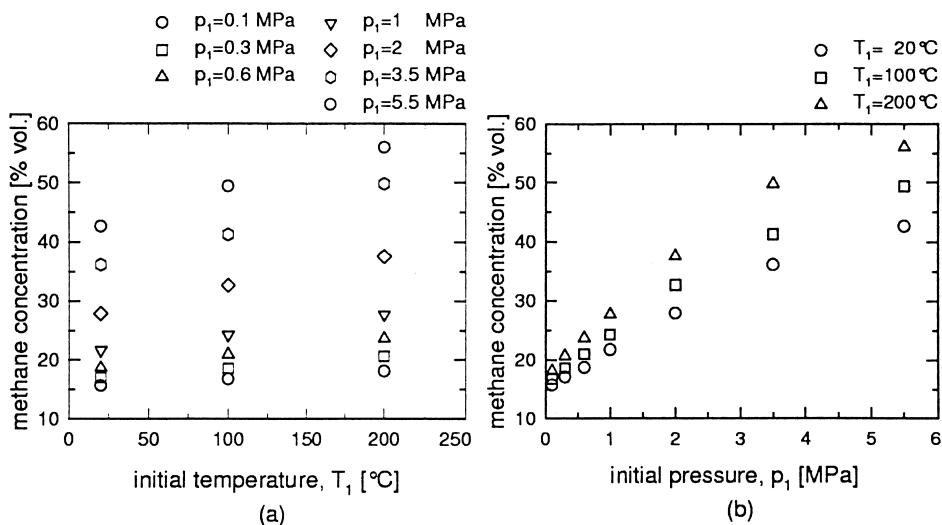

Fig. 7. (a) Temperature and (b) pressure dependence of the UFL of methane–air mixtures at elevated temperatures.

observed for toluene as well as for methane. In both cases, the temperature dependence increases with higher initial pressure.

The pressure dependence, at elevated temperature of the UFL of toluene– and methane–air mixtures are shown in Figs. 6(b) and 7(b). Both toluene and methane have an increased pressure dependence at higher initial temperature. The second order pressure dependence found for methane by Vanderstraeten et al. [7] does not seem to fit for toluene, but additional experiments should be performed in order to develop a reliable correlation for toluene.

The results of this study on toluene and the earlier study on methane indicate that both temperature and pressure intensify each others influence on the UFL.

At the UFL two concentration zones with different characteristics occur: the soot zone and the twilight zone. The soot zone is characterised by an almost constant maximum pressure ratio situated at the rich side of the flammable region. The twilight zone is a zone of weak pressure rises, with a pressure ratio smaller than 2, situated between the soot zone and the UFL. According to Coffee [15] the reaction mechanisms in the twilight zone resemble those of cool flames. Between the soot zone and the twilight zone there is a sharp transition from high to low pressure ratios.

Fig. 8 shows the pressures and temperatures at which soot is formed for toluene and methane. The occurrence of soot is principally dependent on the initial pressure. A higher initial temperature lowers the pressure at which soot formation starts. At around 100°C the occurrence of soot starts at 3 kPa for toluene and at 5 kPa for methane. Due to the lower hydrogen–carbon ratio of toluene compared to methane it can be expected that toluene will give rise to soot formation sooner (lower pressures and temperatures) than methane. This is demonstrated by the experimental data of Fig. 8. A detailed quantitative analyses of the aspects requires reaction kinetics modeling which is out of the scope of this work.
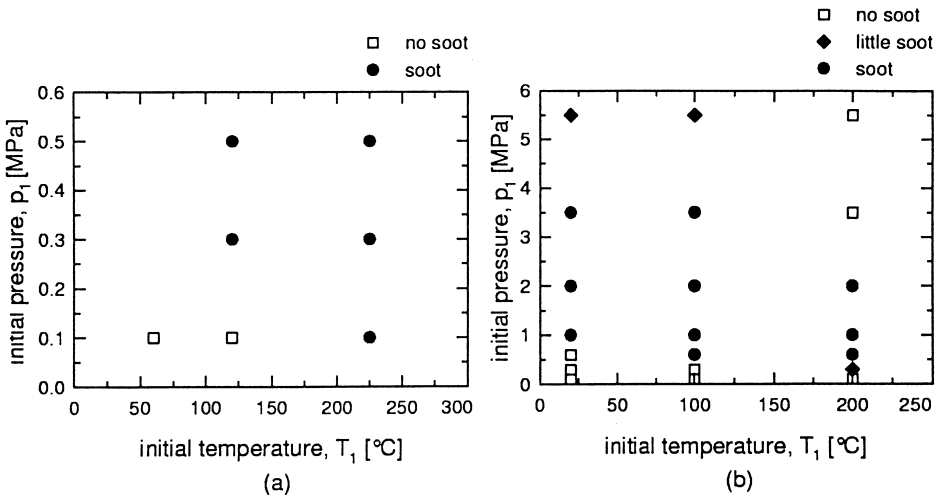

Fig. 8. Indication of the soot formation at elevated pressures and temperatures for (a) toluene– and (b) methane–air mixtures.
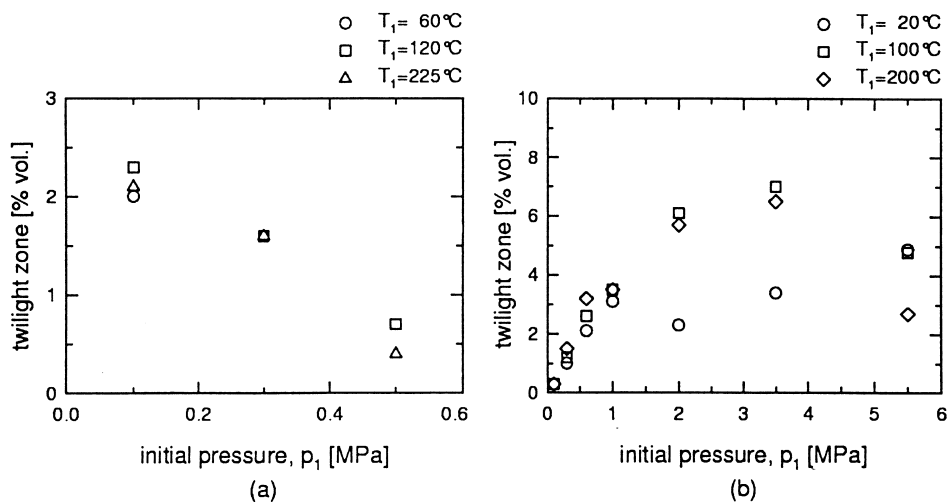
Fig. 9. Width of the twilight zone for (a) toluene– and (b) methane–air mixtures at elevated pressures and temperatures.

Fig. 9 shows the width of the twilight zone of toluene and methane at elevated pressures and temperatures. The width of this zone is primarily dependent on the initial pressure, as is the case with the occurrence of the soot zone. Increasing the temperature has only limited influence on the twilight zone of toluene. Up to 100 kPa this is also the case for methane, but at higher initial pressures a larger temperature dependence is observed. Toluene has a broad twilight zone at atmospheric pressure (Fig. 4), but increasing the initial pressure rapidly decreases its twilight zone width. For methane on the other hand, increasing the initial pressure increases the twilight zone width.

The soot and twilight zone occur at different pressures and temperatures for toluene and methane and have different pressure dependencies. For methane the soot and twilight zone only develop at elevated pressures.

The occurrence of a soot and twilight zone for both toluene and methane, two different hydrocarbons, indicates that one may expect soot and twilight zones to exist for most hydrocarbons.

5. Conclusions

The glass tube flammability limits at ambient conditions, found by using the DIN 51649 standard test, led to broader limits than those reported in the literature. The closed vessel flammability limits at ambient conditions are in agreement with the values reported in the literature and are situated within the glass tube flammability limits.

The glass tube and closed vessel flammability limits have a similar linear temperature dependence at atmospheric pressure. The closed vessel experiments show that increasing the initial pressure widens the flammable range.

Toluene as well as methane, mixed with air, show soot and twilight phenomena at elevated pressures, but the starting pressure for their occurrence differs. Also the width of the soot and twilight zone differs for both hydrocarbons. The similarity of the explosion characteristics of toluene and methane, despite their chemical differences, leads one to expect a soot and twilight zone to exist for most hydrocarbons.

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