Journal of Hazardous Materials A120 (2005) 57–65

Journal of Hazardous Materials

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Flammability limits and explosion characteristics of toluene–nitrous oxide mixtures

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Received 20 July 2004; received in revised form 27 January 2005; accepted 27 January 2005

Abstract

Flammability limits and explosion characteristics of toluene–nitrous oxide mixtures are experimentally determined in an 8 l spherical vessel, and are compared with corresponding values of toluene–air mixtures. The experiments, performed at atmospheric pressure and at an initial temperature of 70 °C, show that the flammable range of toluene in nitrous oxide (0.25–22.5 mol%) is about three times as wide as the corresponding range of toluene in air (1.3–7.1 mol%). Maximum values of the explosion pressure ratio and the deflagration index, K_G, are clearly higher when nitrous oxide is applied as an oxidizer. This can be attributed to the increased flame temperature and burning velocity of toluene–nitrous oxide flames. Moreover, extremely high values of K_G for near-stoichiometric mixtures in combination with strong acoustic oscillations in the pressure signals of these mixtures indicate the existence of a flame accelerating mechanism. These phenomena are enhanced when an initial pressure of 6 bara is applied. Finally, when evaluating the lower flammability limit, it was found that pure nitrous oxide decomposes at pressures above 4.5 bara when applying an ignition energy of about 10 J.

Keywords: Flammability limits; Explosion pressure; Deflagration index; Toluene; Nitrous oxide

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1. Introduction

Nitrous oxide is frequently encountered in industrial processes, e.g. during the production of sulphuric acid, adipic acid and caprolactam. In order to evaluate the explosion hazards involved, it is necessary to know the flammability limits and the explosion characteristics of mixtures that may be present in these processes under normal and abnormal working conditions. Moreover, as these processes are running at elevated pressures and temperatures, the flammability limits have to be determined at the same elevated conditions. Yet, in contrast with the flammability limits of common fuels in air, flammability limits in nitrous oxide at ambient conditions are scarce [1–4], and data at elevated pressures are not available at all in the open literature.

The objectives of the present work are to determine the flammability limits and the explosion characteristics of toluene–nitrous oxide mixtures at conditions relevant to the chemical industry [5]. This was done by measuring the explosion pressure ratio and the maximum rate of pressure rise as a function of the fuel concentration. High-frequency oscillations observed in the pressure signal during a short period of time after ignition were further analysed to verify the hypothesis of acoustic ringing proposed by other researchers [9]. Finally, additional experiments were performed to get a better understanding of the exothermic decomposition of pure nitrous oxide under the applied test conditions.

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doi:10.1016/j.jhazmat.2005.01.016

2. Experimental apparatus and procedure

The experimental set-up, shown in Fig. 1, consists of a closed spherical vessel with a volume of 8 l. The vessel is large enough to neglect the influence of wall quenching [6] and is designed to withstand explosion pressures up to 3500 bar at an initial temperature of 350 °C. To produce homogeneous mixtures of a desired composition, toluene and nitrous oxide are supplied to a spiral tube evaporator at the required flow rates. The flow rates of nitrous oxide and toluene are controlled by a thermal mass flow controller and by a volumetric membrane pump, respectively. Downstream the evaporator, the piping is kept at a constant temperature of 120 °C to avoid toluene condensation. Before filling, the vessel is evacuated and subsequently purged with the gas mixture at least 10 times its volume. Ignition is achieved by fusing a spirally wound tungsten wire, placed in the centre of the vessel. The igniter releases about 10 J in 40 ms independently of pressure and temperature. The initial pressure is measured with a piezoresistive pressure transducer (Baldwin), while piezoelectric pressure transducers (Kistler 601H and 603B) are used to measure the pressure history after ignition.

Flammability is judged from the pressure rise observed during the test. A mixture is classified as flammable if ignition is followed by a relative pressure rise of at least 5%. The experimental apparatus and procedure fully comply with the European standard EN1839 method B [7], with the exception of the applied increment size for the mixture composition: the fuel concentration is varied in steps of 1.0 mol% instead of the prescribed 0.2 mol%. Strictly speaking, EN1839 only applies to the determination of the flammability limits at atmospheric pressure, but no standard procedure is available for the determination of the flammability limits at elevated pressures.

3. Experimental results

3.1. Experiments at 1 bara and 70 °C

A first set of experiments was conducted at an initial pressure of 1 bara and a temperature of 70 °C. Fig. 2 shows the original and the filtered pressure signals for various mixtures of toluene and nitrous oxide. The pressure signals are plotted on different time and pressure scales to facilitate the interpretation of the data. It is seen that the measured pressure rises for a mixture with 0.5 mol% toluene and 22 mol% toluene (Fig. 2a and f) are small, i.e. 0.63 and 0.07 bar, respectively. The small pressure rise is assumed to be associated with a limited upward propagation of the flame and is typically observed for mixtures on the edge of flammability. The pressure traces for a mixture with 1 mol% toluene and 20 mol% toluene (Fig. 2b and e) show a pressure rise of 11.7 and 11.1 bar, respectively. These values are close to the theoretical values based on chemical equilibrium calculations for adiabatic combustion in a constant volume (11.8 and 11.9 bar) [8]. This indicates that the mixture is almost completely consumed and that the flame has propagated both upwards and downwards. The pressure traces for near-stoichiometric mixtures with 5 and 10 mol% toluene (Fig. 2c and d) are peculiar as they exhibit high-frequency oscillations during a short period of time after ignition (±20 ms). Moreover, the pressure signal of Fig. 2d shows a very sharp pressure spike during the pressure build-up. Similar behaviour was observed by other researchers for other mixtures [1,9,10]. The origin and the nature of the high-frequency oscillations are discussed in more detail in Sections 4.2 and 4.3.

The explosion characteristics of toluene–nitrous oxide mixtures at atmospheric pressure are shown in Fig. 3, together with the explosion characteristics of toluene–air mixtures.

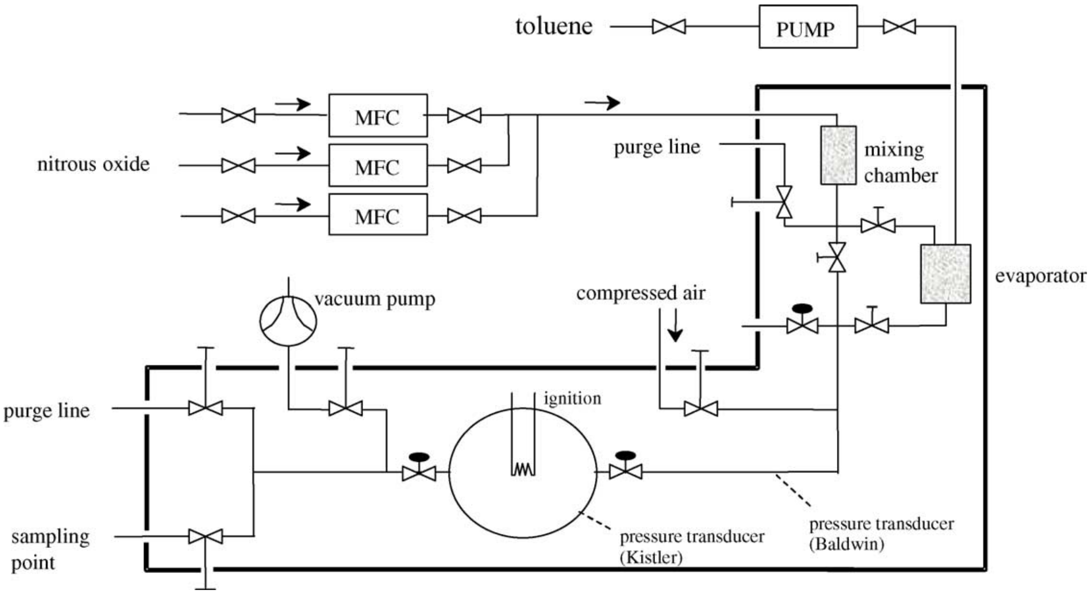

Fig. 1. Experimental set-up.

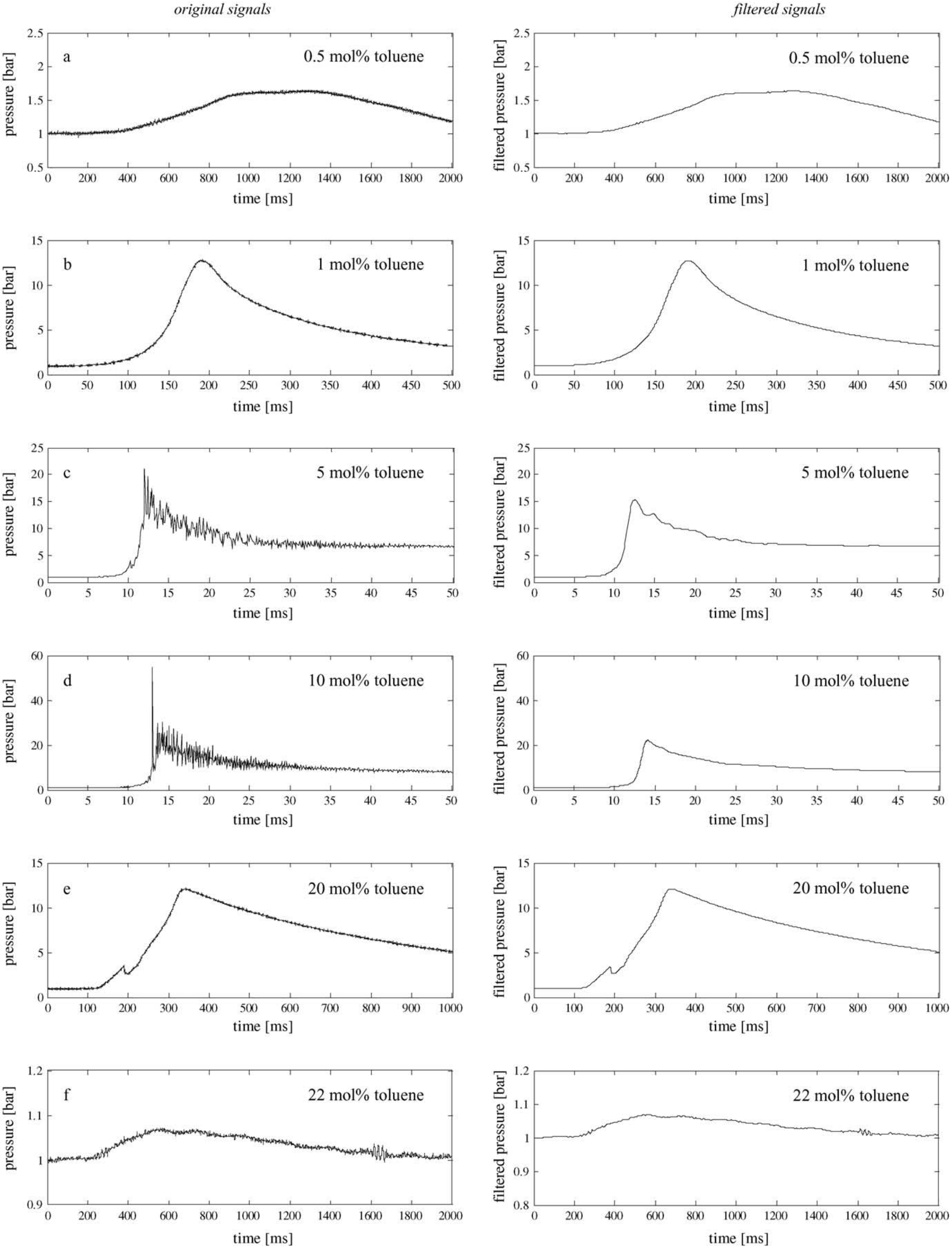

Fig. 2. Original and filtered pressure signals for various mixtures of toluene in nitrous oxide at an initial pressure of 1 bara and an initial temperature of 70 °C.

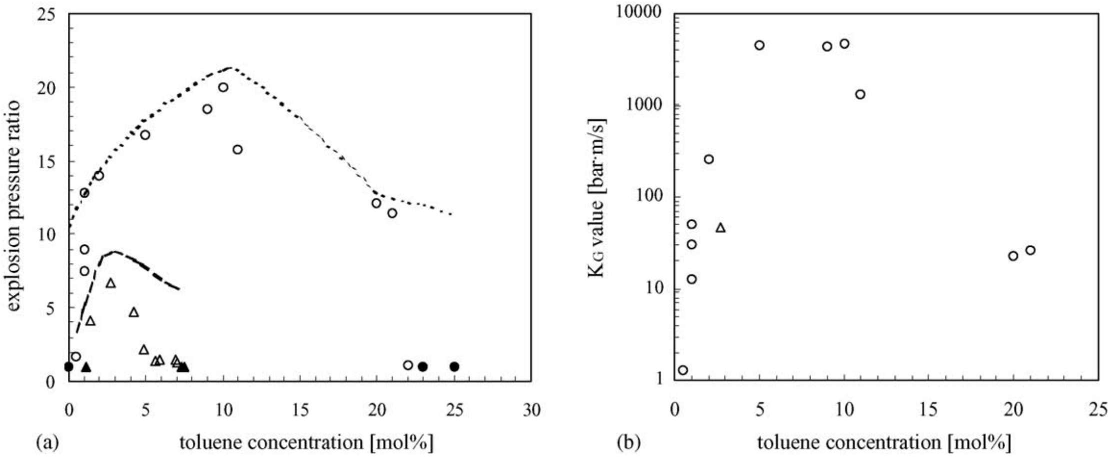

Fig. 3. Flammability data for toluene/air (△) and toluene/N_2O (○) mixtures at 1 bara and 70 °C; (a) explosion pressure ratios, and (b) K_G values.

The toluene–air experiments have been performed in the same experimental apparatus [11]. Fig. 3a and b presents the measured explosion pressure ratio and the volume normalised rate of pressure rise as a function of the toluene concentration. The volume normalised rate of pressure rise, also known as the K_G value or the deflagration index, is defined as:

$$K_G = \left(\frac{dp}{dt}\right)_{max} V^{1/3}$$

where $(dp/dt)_{max}$ is the maximum rate of pressure rise during the explosion (bar/s) and V is the volume of the vessel (m^3). The dashed lines in Fig. 3a represent calculated values of the explosion pressure ratio assuming chemical equilibrium and adiabatic combustion in a constant volume [8]. As it is difficult to determine P_{max} and K_G values from the original signals, the signals were filtered for proper interpretation. A low pass Butterworth filter was used for this purpose. Furthermore, the experimental results of the near-stoichiometric mixtures appeared to be less reproducible than the results of the other mixtures, as the onset and the amplitude of the pressure oscillations seem to have a stochastic nature (see Fig. 4). For these mixtures, P_{max} and K_G values are taken as the average of successive measurements. The flammable range of toluene in nitrous oxide at 1 bara and 70 °C is found to extend from 0.25 to 22.5 mol% and is about three times as wide as the flammable range of toluene in air (1.3–7.1 mol%). The K_G value reaches a maximum of 4700 bar m/s, which is about 100 times higher than the corresponding value of toluene in air, i.e. 46 bar m/s [11].

3.2. Experiments at 6 bara and 70 °C

A limited series of experiments were conducted at an initial pressure of 6 bara to study the influence of the initial pressure on the occurrence and the intensity of oscillations in the pressure signal. Fig. 5 shows the original and the filtered pressure signals for various mixtures of toluene and nitrous oxide at 6 bara and 70 °C. Fig. 5a refers to an

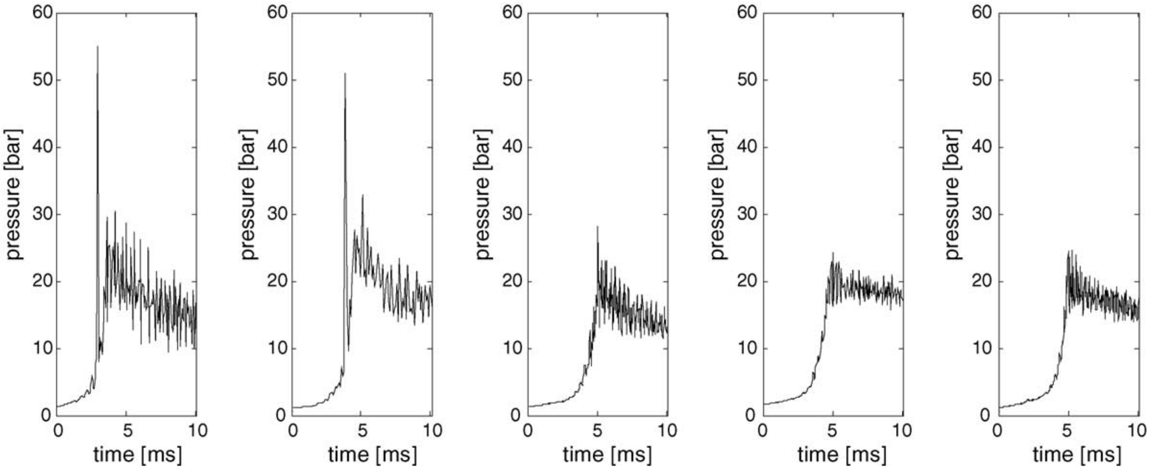

Fig. 4. Various pressure traces for a mixture of 10 mol% toluene in nitrous oxide at an initial pressure of 1 bara and an initial temperature of 70 °C.

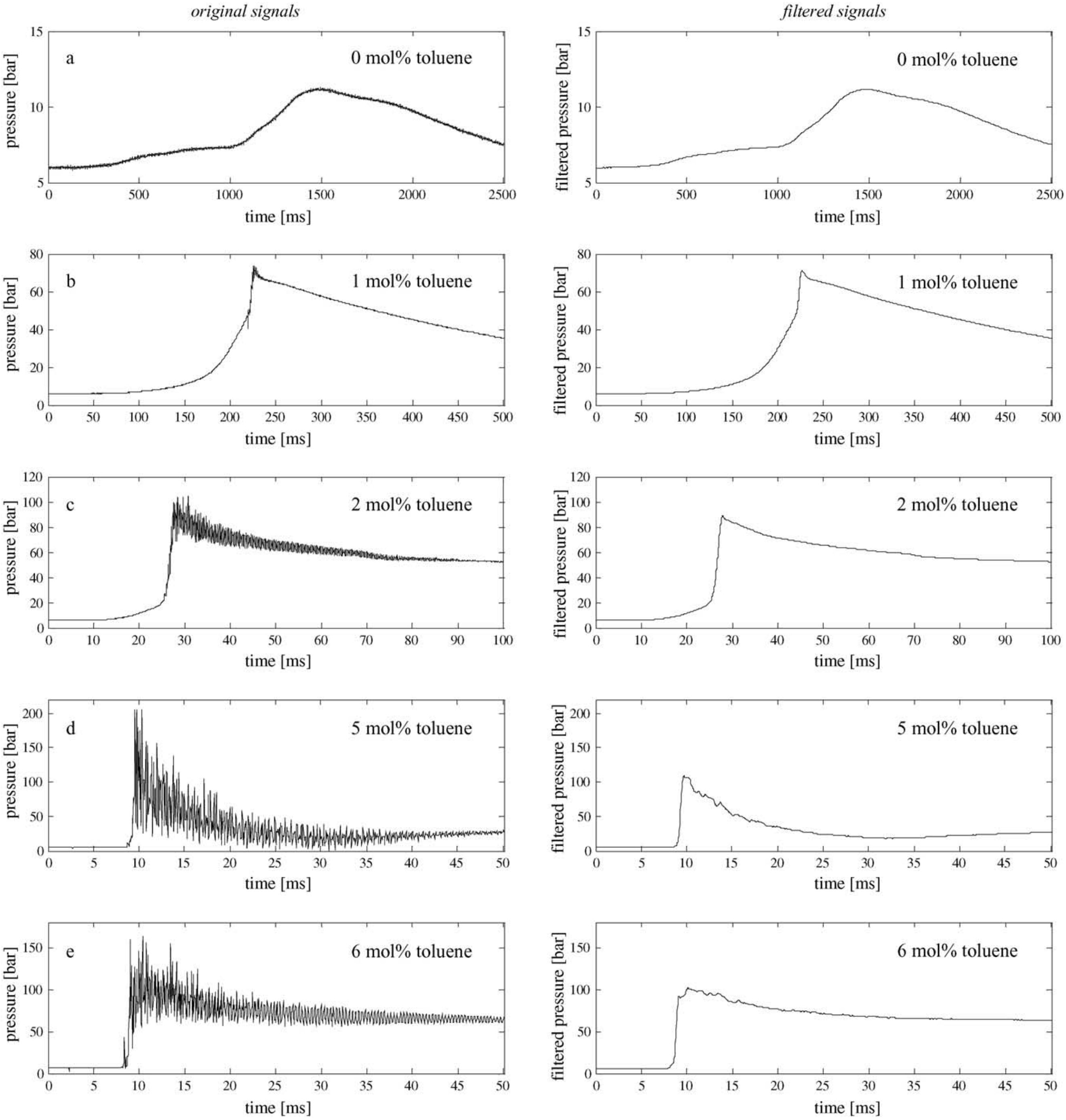

Fig. 5. Original and filtered pressure signals for various mixtures of toluene in nitrous oxide at an initial pressure of 6 bara and an initial temperature of 70 °C.

experiment with pure nitrous oxide. The observed pressure rise indicates that nitrous oxide decomposes exothermally at 6 bara in the case of an ignition energy of about 10 J (see also Section 3.3). The other pressure signals of Fig. 5 correspond to mixtures with a toluene concentration between 1 and 6 mol%. Moreover, the pressure signals of Fig. 5d and e refer to saturated mixtures as the chosen toluene concentration is higher than the saturation concentration of toluene in the vapour phase, i.e. 4.5 mol% toluene. The pressure traces of Fig. 5b–e all exhibit high-frequency oscillations which become more intense as the toluene concentration increases. Compared to the 1 bara experiments, it is found that the occurrence of these high-frequency oscillations shifts towards lower toluene concentrations and that the amplitude of the oscillations significantly increases with increasing initial pressures.

The explosion characteristics of toluene–nitrous oxide mixtures at 6 bara are summarised in Fig. 6. The lower

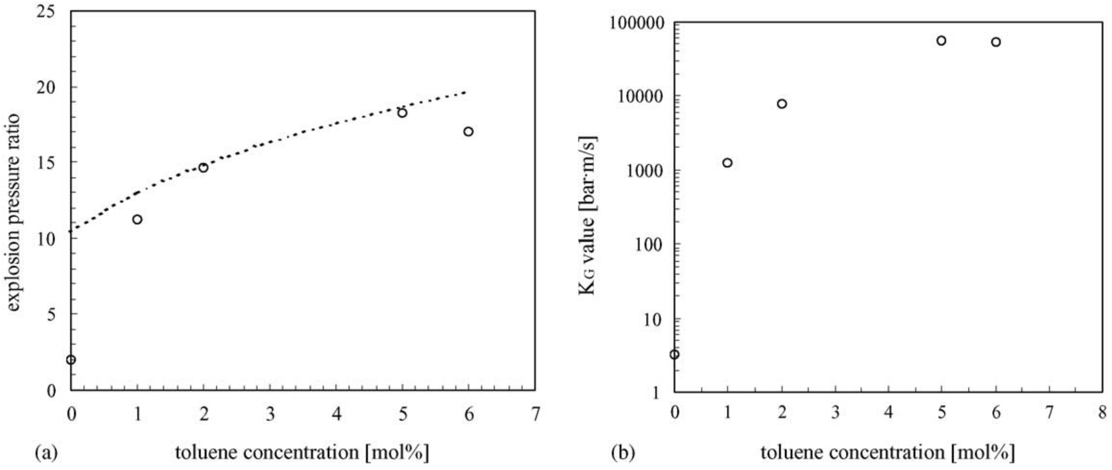

Fig. 6. Flammability data for the toluene/N_2O mixtures at 6 bara and 70 °C; (a) explosion pressure ratios, and (b) K_G values.

flammability limit is found to be 0 mol% toluene since the applied ignition energy was large enough to initiate the decomposition of nitrous oxide. The upper flammability limit at 6 bara and 70 °C could not be established as the saturated mixture composition was still flammable. The K_G value reaches a maximum of about 60,000 bar m/s for a saturated mixture of toluene in nitrous oxide.

3.3. Decomposition of nitrous oxide

As mentioned above, pure nitrous oxide decomposes at an initial pressure of 6 bara and an ignition energy of about 10 J. Experiments were conducted to determine the decomposition pressure ratio as a function of the initial pressure and to assess the minimum initiation energy for the decomposition of nitrous oxide at 30 bara. The results presented in Fig. 7 show that an ignition energy of 10 J initiates the decomposition of nitrous oxide for pressures above 4.5 bara. The initiation energy was altered by modifying the voltage level and the time during which voltage is applied to the tungsten wire. Voltage and current histories were recorded during the test and the energy released was calculated as the cumulative sum of voltage times current, as illustrated in Fig. 8. Table 1 shows that the minimum initiation energy at a pressure of 30 bara is between 2 and 3.5 J. For comparison, the minimum value of ignition energy for hydrocarbon fuels in air is typically on the order of 0.2–0.25 mJ [2].

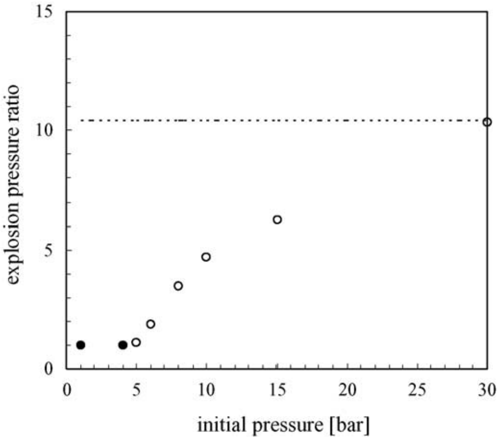

Fig. 7. Explosion pressure ratio as a function of the initial pressure for the decomposition of nitrous oxide.

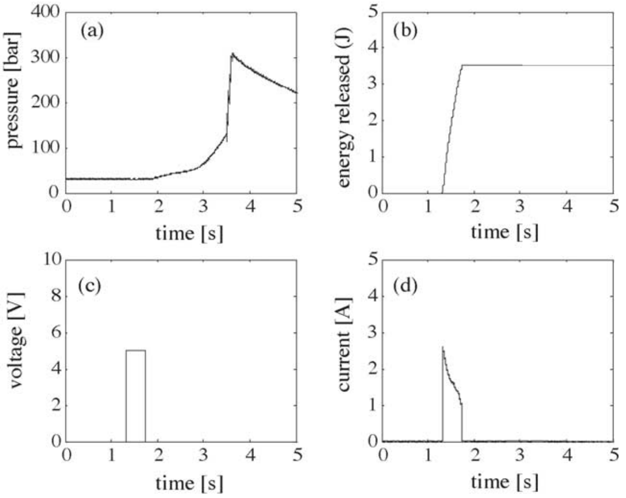

Fig. 8. (a) Recorded pressure history, (b) calculated energy released by ignition source, (c) recorded voltage history, and (d) recorded current history during an experiment with pure nitrous oxide at 30 bara.

Table 1
Influence of the initiation energy on the exothermic decomposition of nitrous oxide at 30 bara

Initiation energy (J)	Decomposition pressure ratio
10.0	10.5
5.0	11.4
3.5	10.2
2.0	1.0

4. Discussion

4.1. Extended flammable range

The flammable range of toluene in nitrous oxide at atmospheric pressure is found to extend from 0.25 to 22.5 mol% and is about three times as wide as the flammable range of toluene in air. Comparison of the equivalence ratios ϕ of the limit mixtures in air and nitrous oxide shows that the extension is most pronounced at the lower flammability limit (LFL), where it decreases from 0.57 in air to 0.05 in nitrous oxide, whereas at the upper flammability limit (UFL) the equivalence ratio increases from 3.3 in air to 5.2 in nitrous oxide. Experiments at elevated initial pressures show that pure nitrous oxide decomposes for pressures above 4.5 bara and an ignition energy of 10 J. At 1 bara, an ignition energy of 10 J is insufficient to obtain a decomposition pressure ratio of 1.05, which would term the mixture flammable. However, addition of a small amount of fuel would increase the available energy for decomposition. Fusing of the tungsten wire causes local reaction in a small volume near the ignition source. The additional heat liberated in this reaction seems to be enough to decompose some of the nitrous oxide outside this flame kernel in order to raise the pressure ratio above 1.05, which would explain the exceptionally low LFL. At the UFL the extension of the flammable range is approximately the same as that for methane with a value of 16.8 mol% ($\phi = 1.93$) in air [7] and 43 mol% ($\phi = 3.0$) in nitrous oxide [2]. A qualitative explanation of this extension is found in the higher flame temperature and hence burning velocity of toluene–nitrous oxide flames, which makes the mixture less sensitive to loss phenomena such as radiative heat loss and flame stretch.

4.2. High values of K_G

Using a thin flame model and assuming adiabatic spherically symmetric flame propagation and ideal gas behaviour for the reactants and products, Dahoe et al. [12] have derived an analytical expression for the maximum value of K_G:

$$K_G = (36\pi)^{1/3}(P_{max} - 1)\left(\frac{P_{max}}{P_0}\right)^{1/\bar{\gamma}_u} S_f$$

where P_0 and P_{max} are the initial and maximum pressure within the combustion vessel, S_f is the burning velocity and $\bar{\gamma}_u$ is the average specific heat ratio of the unburned reactants. The equation can be used to estimate burning velocities based upon measured values of K_G and P_{max}. For the experiments at 1 bara this results in a burning velocity of 0.35 m/s for toluene–air flames and 5.8 m/s for toluene–nitrous oxide flames. The implausibly high value of 5.8 m/s for toluene–nitrous flames suggests that the thin flame model is no longer applicable for the investigated mixtures under the imposed conditions.

The high values of K_G and the strong pressure oscillations are most likely due to a sudden flame accelerating mechanism. The origin of the flame accelerating mechanism cannot be revealed with certainty based upon the present measurements, yet flame instabilities and the formation of cellular flame structures due to hydrodynamic effects give the most plausible explanation [13,14]. An alternative mechanism that can account for the sharp pressure rise and the high-frequency oscillations in the pressure signal is an induced local explosion in the pre-compressed unburned mixture, which forms the onset of a transition-to-detonation [9,10]. The extremely high values of K_G and the intensified pressure oscillations at elevated pressure confirm the hypothesis of a flame accelerating mechanism.

4.3. High-frequency oscillations in pressure signals

High-frequency oscillations are observed in the pressure signals of various mixture compositions at 1 and 6 bara. Both the above-mentioned mechanisms result in an enhanced energy release that seems to be sufficiently fast to excite acoustic resonances in the explosion vessel [9]. In order to support this theory of acoustic ringing, results of frequency analyses performed on the relevant pressure signals are compared with the natural frequencies of spherically symmetrical acoustic modes in our vessel. The natural frequencies in a spherical cavity are given by [15]:

$$f_i = \frac{\lambda_i c}{2\pi R}, \quad \lambda_i = 4.4934, 7.7253, 10.9041, 14.0662, \ldots$$

where c is the speed of sound (m/s) and R is the radius of the spherical cavity (m). The speed of sound can be calculated as:

$$c = \sqrt{\gamma \frac{p}{\rho}}$$

where γ is the ratio of specific heats, ρ is the density (kg/m^3) and p is the absolute pressure (Pa) of the gas mixture. The thermodynamic properties, γ and ρ, have to be calculated for the burned mixture, since the pressure oscillations appear during the cooling down of the gas mixture after combustion. They were calculated from the initial conditions and the initial mixture composition assuming chemical equilibrium at specified pressure and volume. Calculated values for the first and second natural frequency are presented in Table 2 as a function of the pressure, the initial toluene concentration and the initial pressure.

The frequency spectra of the pressure oscillations in the recorded traces were calculated using the fast-Fourier transformation (FFT) algorithm. Fig. 9 shows the frequency spectrum of the pressure oscillations observed for a mixture with 2 mol% toluene at an initial pressure of 6 bara (pressure trace of Fig. 5c). The oscillations are observed in the 55–85 bara pressure interval. The spectrum of Fig. 9, which was calculated for the entire pressure interval showing high-frequency oscillations, exhibits a clear peak at a frequency of about 2.7 kHz. This frequency corresponds well to the first natural frequency of acoustic resonances in the reaction vessel (see

Table 2
The calculated first and second natural frequency of acoustic resonances in the spherical vessel as a function of the initial conditions, the toluene concentration and the pressure

Initial conditions	Toluene concentration (mol%)	Pressure (bara)	f_1 (kHz)	f_2 (kHz)
70 °C and 1 bara	5	7	2.08	3.58
		10	2.47	4.25
		13	2.82	4.85
	10	12	2.96	4.63
		16	3.10	5.33
		20	3.46	5.96
70 °C and 6 bara	2	60	2.54	4.37
		70	2.74	4.72
		80	2.93	5.04
	5	70	2.67	4.59
		80	2.85	4.90
		90	3.02	5.20

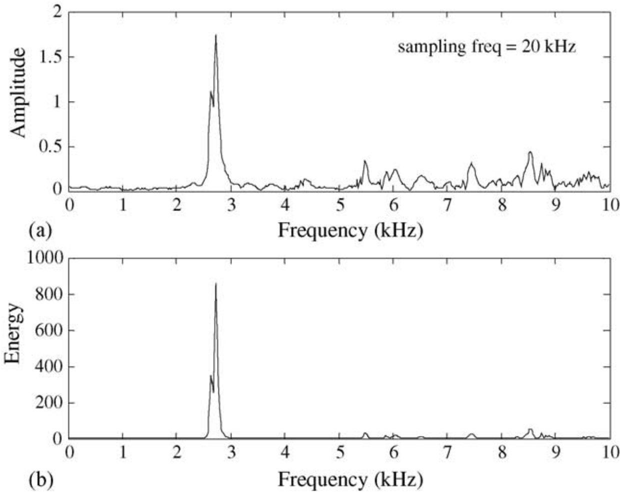

Fig. 9. Frequency analysis of the observed oscillations in the pressure signal for a mixture with 2% toluene in nitrous oxide at 6 bara: (a) magnitude spectrum, and (b) power spectrum.

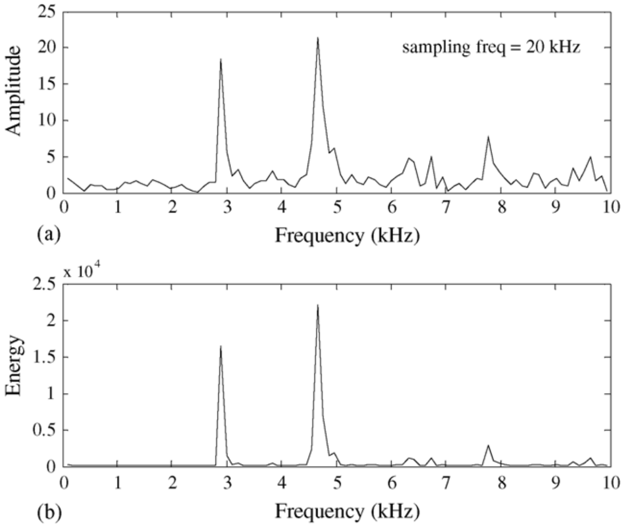

Fig. 11. Frequency analysis of the observed oscillations in the pressure signal for a mixture with 5 mol% toluene in nitrous oxide at 6 bara: (a) magnitude spectrum, and (b) power spectrum.

Table 2). If only part of the high-frequency data is analysed, the peak in the frequency spectrum becomes sharper, as the natural frequency is better defined in a more narrow pressure interval. Moreover, upon analysing various parts of the data at different pressure intervals the peak in the spectrum shifts to lower frequencies as the pressure decreases. This behaviour, shown in Fig. 10, was expected since in the present case the specific density is constant (constant test volume) and the natural frequency is directly proportional to the square root of the pressure. Fig. 11 shows the frequency spectrum of the pressure oscillations observed for a mixture with 5 mol% toluene at an initial pressure of 6 bara (pressure trace of Fig. 5d). The corresponding pressure interval is 50–100 bara. From the spectrum two peaks can clearly be identified, matching with the first and second natural frequency, shown in Table 2. The appearance of the second peak in the spectrum indicates

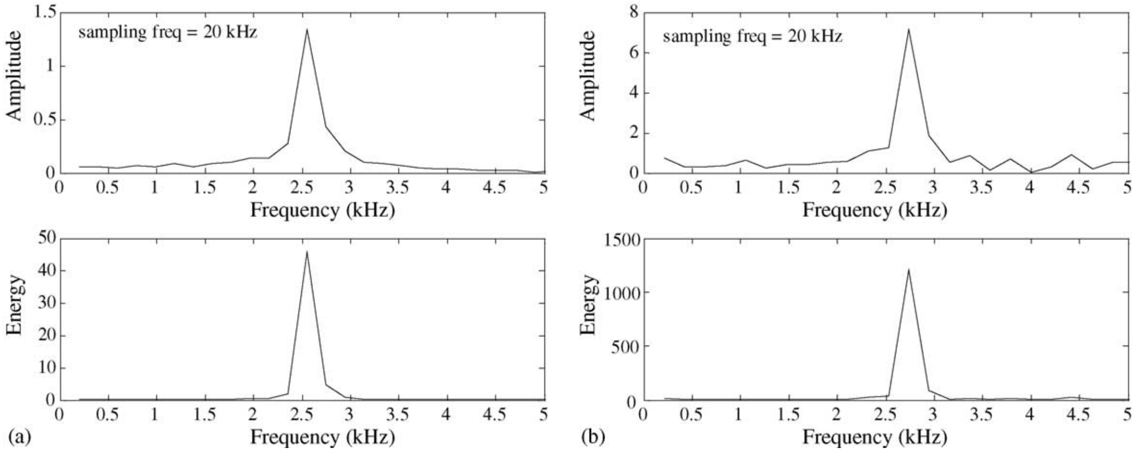

Fig. 10. Frequency analysis of selected parts of the data for a mixture with 2% toluene in nitrous oxide at 6 bara: (a) 55–60 bara interval, and (b) 80–85 bara interval.

that the energy release for this mixture (5 mol% toluene) is even faster than for the above mentioned mixture (2 mol% toluene), since higher natural frequencies are only excited by very rapid initiation phenomena. Similar observations can be made for all pressure signals that show high-frequency oscillations. Most of the calculated spectra show two peaks, corresponding to the first and second natural frequency of acoustic resonances in the closed vessel.

5. Conclusion

Flammability limits and explosion characteristics of toluene–nitrous oxide mixtures have been measured at 1 and 6 bara at an initial temperature of 70 °C using an 8 l spherical explosion vessel. The experiments show that the flammable range of toluene in nitrous oxide is about three times as wide as the flammable range of toluene in air at atmospheric pressure. Measured explosion pressure ratios and K_G values are higher than the corresponding values of toluene in air, which can be attributed to an increased flame temperature and burning velocity of toluene–nitrous oxide flames. High-frequency pressure oscillations over a broad concentration range and extremely high values of the deflagration index indicate the existence of a flame accelerating mechanism which is more pronounced at elevated pressures. Finally, the experiments show that nitrous oxide decomposes at pressures above 4.5 bara when applying an ignition energy of about 10 J.

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