

Auto-ignition and upper explosion limit of rich propane–air mixtures at elevated pressures

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Abstract

The auto-ignition limits of propane–air mixtures at elevated pressures up to 15 bar and for concentrations from 10 mol% up to 70 mol% are investigated. The experiments are performed in a closed spherical vessel with a volume of 8 dm³. The auto-ignition temperatures decrease from 300 °C to 250 °C when increasing the pressure from 1 bar to 14.5 bar. It is shown that the fuel concentration most sensitive to auto-ignition depends on initial pressure. A second series of experiments investigates the upper flammability limit of propane–air mixtures at initial temperatures up to 250 °C and pressures up to 30 bar near the auto-ignition area. Finally the propane auto-oxidation is modelled using several detailed kinetic reaction mechanisms and these numerical calculations are compared with the experimental results.

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1. Introduction

The auto-ignition temperature (AIT) of a gas mixture inside a vessel is the lowest temperature of the vessel wall at which the mixture ignites spontaneously without ignition source. The AIT values of hydrocarbon–air mixtures found in literature usually are determined according to standard test methods in small vessels and at atmospheric pressure (e.g. DIN 51795, ASTM-E 659-75 or BS 4056) [1,2]. The auto-ignition temperature is, however, not constant but dependent on, for example, the following factors: pressure, volume of the vessel and flow conditions. In industry gas mixtures are present at high pressures and large volumes. Consequently, the standardised AIT values are often not directly applicable to industrial conditions.

Experimental auto-ignition data of propane–air mixtures at high pressures are very scarce [3–5]. Kong et al. [3] investigated the auto-ignition of methane and propane–air mixtures using a 1-l explosion vessel at atmospheric pressure. The ignition criterion was the occurrence of a sudden, non-specified, pressure rise within a time period of 10 min. The AIT values for propane–air

mixtures were found to decrease monotonically from 590 °C to 500 °C with propane concentrations increasing from 0.7 vol% to 14.5 vol%. Other researchers used shock tubes [4], rapid compression machines or flow tubes to study auto-ignition phenomena at high pressures and intermediate temperatures. Their methods are characterized by ignition delay times varying from milliseconds to a few seconds. More recently the BAM and TU Delft [5] investigated the auto-ignition temperature of methane, ethylene and *n*-butane. The volumes of the test vessels were 0.1 dm³, 0.2 dm³ and 0.5 dm³ and the ignition criterion was the observation of an abrupt temperature and pressure rise of more than 5% or a visible flame within a time period of 10 min.

Over the last decades detailed numerical modelling has gained in importance in the study of the combustion of gas mixtures. Only a few analytical auto-ignition models can be found in the scientific literature [6–8]. Semenov [6] and Frank-Kamenetskii [7] developed, respectively, a zero- and a one-dimensional model with simplified chemical kinetics based upon one global reaction. The Shell auto-ignition model [8] takes into account convective flow by means of computational fluid dynamics (CFD) and a zero-dimensional model is used to solve the heat balance.

Due to increased computer capabilities, numerical computations can now be applied at an acceptable cost. Experimental

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work, on the other hand, is expensive and very time consuming. However, since numerical models need to be validated with experimental data, they can never fully replace the experimental studies.

The aim of this study is to determine the pressure and concentration dependence of the auto-ignition temperature of propane–air mixtures. In addition, the upper explosion limit of these mixtures is determined at initial temperatures up to 250 °C and pressures up to 30 bar to investigate the influence of auto-ignition on mixture flammability. Finally, experimental AIT values are compared with the results of numerical simulations using several detailed kinetic reaction mechanisms.

2. Experimental set-up and procedure

The experimental set-up, illustrated by Fig. 1, consists of four major parts: the mixture preparation equipment, the buffer vessel, the explosion vessel and the data acquisition system. To produce homogeneous mixtures of a desired composition, propane and air are supplied to a spiral tube evaporator using the constant flow method. Gas chromatography was used at regular intervals to verify the mixture composition. The spherical buffer vessel has a volume of 8 dm³ (internal diameter of 24.8 cm). It is used to maintain the premixed reactants at a high pressure (up to 50 bar) and at a temperature of 120 °C. This temperature is chosen to avoid pre-oxidation of the gas mixture. The spherical explosion vessel also has a volume of 8 dm³ and is designed to withstand pressures up to 250 bar at temperatures up to 550 °C. The pressures in both vessels are measured with Baldwin 5000 psi strain gauges, while the temperature rises during the tests are measured with two type K thermocouples, one located near the wall at mid-height and one at the top of the explosion vessel. Fig. 2 shows a typical time history of pressure and temperature inside the explosion vessel during an experiment.

The following procedure is followed to determine the auto-ignition limits and the ignition delay times. The explosion vessel is heated to the required temperature and kept at this temperature by means of three electrical wire heaters surrounding the vessel.

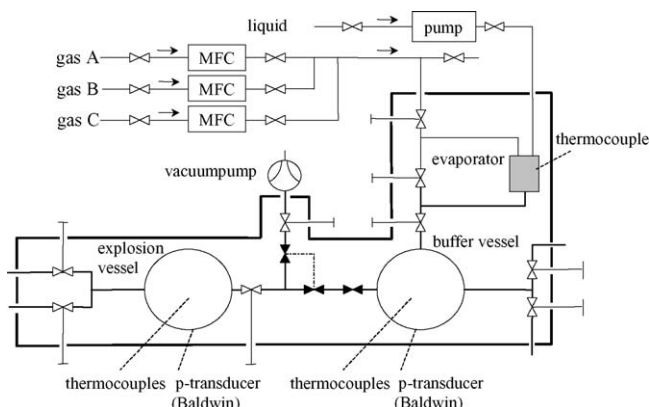


Fig. 1. Experimental apparatus.

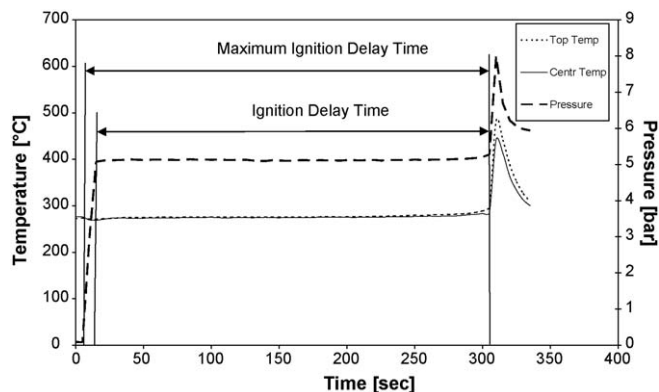


Fig. 2. Recorded pressure and temperature histories in the explosion vessel (“Top temp” represents the temperature at the top of the vessel, while “Centr Temp” represents the temperature near the wall at mid-height).

Subsequently, the vessel is brought to vacuum pressure and filled with the premixed gas mixture from the buffer vessel. The filling time varied from 5 s to 30 s, depending on the initial pressure of the test. This filling time causes an uncertainty in the ignition delay time (IDT), which is the time lag between the completed injection of the test mixture and any exothermic phenomenon (see Fig. 2). The IDT’s presented in this paper do not include the filling time. The occurrence of an auto-ignition is judged from the pressure and temperature histories (e.g. Fig. 2). When the temperature rise is smaller than 50 °C within 15 min after filling the vessel, it is concluded that auto-ignition did not take place. A temperature rise larger than 50 °C within a time period of 15 min accompanied with a pressure increase is classified as an auto-ignition. The temperature rise criterion is the same as the one used in a previous study [9] and indicates exothermic reactions that could initialise an auto-ignition. Due to experimental limitations, the maximum ignition delay time is chosen to be 15 min which is of the same order of magnitude as those used in other studies [3,5,9]. The experimental set-up and the procedure for the determination of the auto-ignition limit are described in more detail in [9].

This experimental set-up is also used to determine the upper explosion limit according to the “bomb” method of the European standard EN 1839 [10]. For these experiments the 8-l spherical buffer vessel serves as explosion vessel. Ignition of the test mixtures is achieved by fusing a tungsten wire, placed at the centre of the vessel, by applying a voltage difference of 40 V dc across the wire. This differs from the fusing of a nichrome wire by applying an ac voltage, as prescribed in the EN 1839 standard. However, during the fusion of the tungsten wire 10 J of energy is released in 40 ms. This falls in the range prescribed by the standard.

The pressure evolution after ignition is measured with a Kistler type 603B piezoelectric pressure transducer. A pressure rise criterion is used to determine the explosion limit: the mixture is flammable if ignition is followed by a pressure rise of at least 5% of the initial pressure. The procedure for the determination of the upper explosion limit is described in more detail in [10].

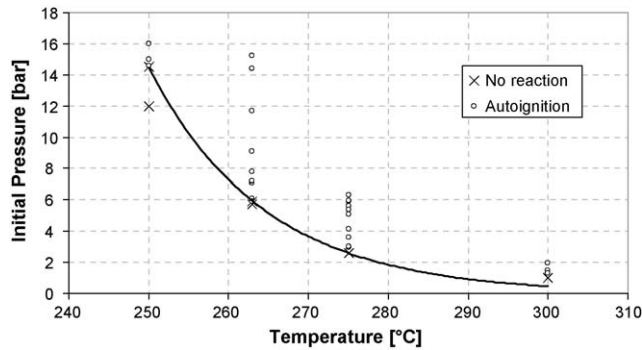


Fig. 3. The auto-ignition limit of propane–air mixtures as a function of the initial temperature, determined for 40 mol% propane in air.

3. Experimental results

3.1. Auto-ignition temperatures of propane–air mixtures

A first series of experiments was performed with a propane concentration of 40 mol% in air. Due to the thermal inertia of the explosion vessel, the auto-ignition limit was determined at a constant vessel temperature and a varying pressure. The results are summarised in Fig. 3. The auto-ignition limit is determined with a step-size of maximum 0.5 bar. The pressure limit for auto-ignition increases with decreasing initial temperatures. At atmospheric pressure the auto-ignition temperature is equal to 300 °C, while at an initial pressure of 14.5 bar the auto-ignition temperature decreases to 250 °C. An exponential correlation (Fig. 3) can be deduced for the temperature influence on the auto-ignition limit. The pressure dependency of the auto-ignition temperature can also be correlated by the “Semenov” correlation [6]:

$$\ln\left(\frac{p}{T}\right) = A \frac{1}{T} + B,$$

where p is the initial pressure [Pa], T the AIT [K] and A and B are fitting constants.

The thermal ignition theory of “Semenov” uses a single kinetic equation instead of a full reaction scheme with complex and multiple steps reactions. This approximation is acceptable for a limited temperature range as can be seen in Fig. 4.

Fig. 5 shows the pressure dependence of the ignition delay times for three different ambient temperatures with a 40 mol%

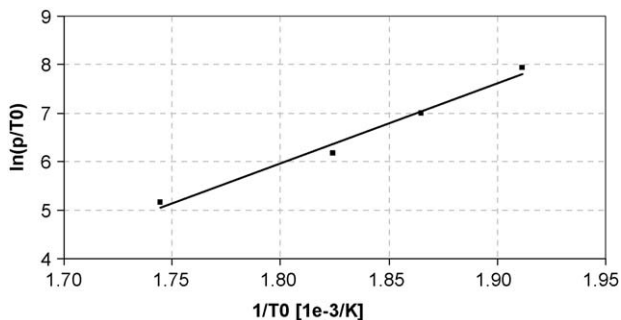


Fig. 4. Pressure dependency of the AIT for 40 mol% propane in air mixture correlated by a Semenov correlation.

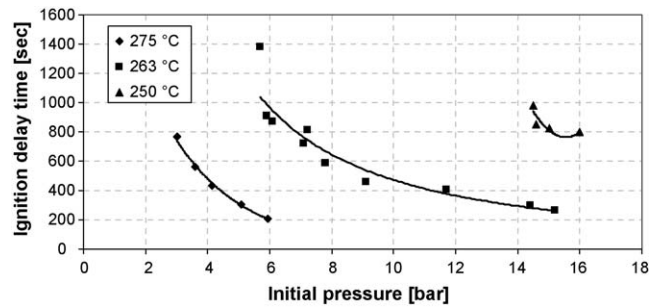


Fig. 5. Ignition delay times as function of the initial pressure determined for 40 mol% propane in air.

propane in air mixture. An increase of the ambient temperature or the initial pressure causes a decrease of the ignition delay time.

Because the propane concentration which is most sensitive to auto-ignition can be dependent on the initial pressure, in this study different concentrations from 10 mol% up to 70 mol% are tested at different auto-ignition pressures. The results are summarised in Fig. 6. The concentrations most sensitive to auto-ignition, which are 30–40 mol% propane in air at a temperature of 300 °C, increase for increasing pressure and decreasing temperature. At a temperature of 250 °C the minimum auto-ignition limit lies at concentrations higher than 70 mol% propane. Due to the saturation pressure of propane it was impossible to perform tests at lower temperatures than 250 °C with higher concentrations. At temperatures of 250 °C and 275 °C and for 30–60 mol% propane–air mixtures two series of tests spaced one year apart were performed to investigate the reproducibility of the auto-ignition limit. At a temperature of 275 °C the reproducibility is quite good, while at a temperature of 250 °C the reproducibility is rather poor. At high pressures other factors in addition to the initial temperature, pressure and fuel concentrations, such as the inflow conditions and the previous history of the vessel, have a major influence on the ignition delay time and consequently on the auto-ignition limit. At present, further research is performed to clarify this matter.

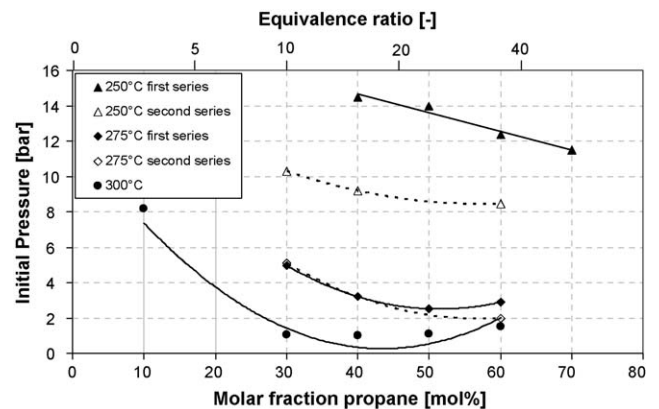


Fig. 6. Influence of fuel concentration on the auto-ignition limit of propane–air mixtures with equivalence ratio (the actual fuel/air ratio divided by the stoichiometric fuel/air ratio).

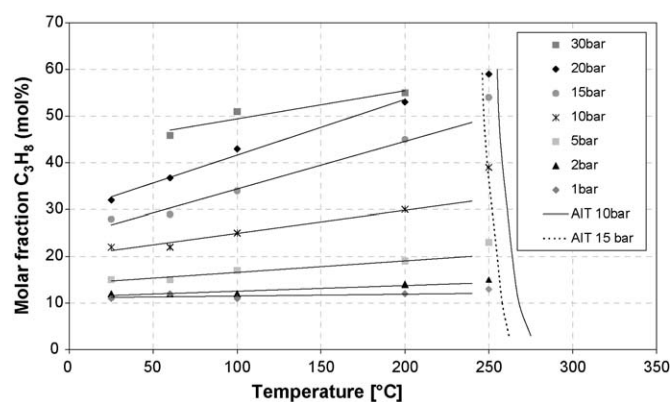


Fig. 7. Upper explosion limit and auto-ignition limit of propane–air mixtures at elevated conditions.

3.2. Upper explosion limits of propane–air mixtures

Fig. 7 shows the experimentally determined upper explosion limits of propane–air mixtures at initial pressures up to 30 bar and temperatures up to 250 °C. The auto-ignition area for different pressures is also shown in Fig. 7. These curves are interpolated from the auto-ignition data described in the previous section. It can be seen that the upper explosion limit increases linearly with increasing temperature. However, near the auto-ignition area a deviation from the linear temperature dependence is observed. This was also observed in a previous study by Van den Schoor and Verplaetsen [11], who attributed this deviation to the proximity of the auto-ignition area. The results of this study corroborate this idea. At an initial pressure of 15 bar it can be seen that a mixture which is outside the upper explosion limit reacts spontaneously. Thus, this mixture does not support flame propagation after ignition, but auto-ignites after a time period of more than 2 min, which is the typical duration of a test for the determination of explosion limits. This might seem contradictive, but can be explained by the underlying phenomena. Propagation of a flame requires not only a fast chemical conversion, but also a high heat and mass transfer rate, whereas auto-ignition is initially primarily governed by chemistry alone. Therefore, it is possible for a mixture, which is too lean or too rich to sustain flame propagation, to have auto-ignition.

3.3. Numerical results for the auto-ignition of propane–air mixtures

In order to simulate the auto-ignition process, a mathematical model, a numerical code and a kinetic reaction mecha-

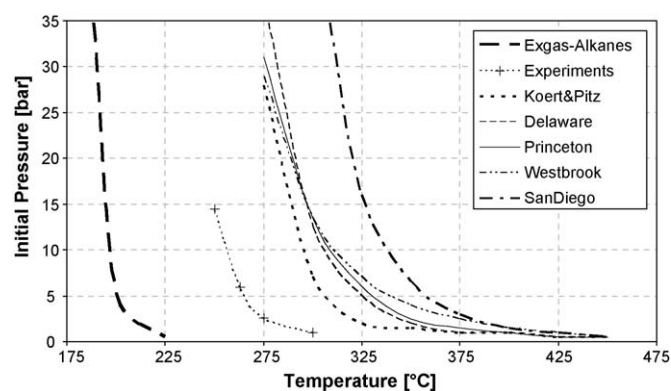


Fig. 8. Numerical modelling of auto-ignition limit of a 40 mol% propane–air mixture, compared with experimental data.

nism describing the oxidation of the fuel are needed. As a first approach, it is chosen to focus on the chemistry of the auto-ignition process using a physical model which includes chemical reaction but neglects diffusion and free and forced convection of heat and mass. This model is implemented in CHEMKIN 4.0.2 [12]. A homogeneous zero-dimensional model is selected with a convective heat loss at the wall:

$$Q_{\text{loss}} = h \cdot A \cdot (T - T_{\text{wall}})$$

Here the convective heat transfer coefficient h is taken equal to 5 W/m² K and the total internal surface area A is 1932 cm². The problem is solved for a constant volume case. The governing equations consist of the species mass and energy conservation equations. This system of ordinary differential equations is generally stiff and is most efficiently solved by implicit techniques for time integration. For this purpose CHEMKIN uses the software package DASPK [13].

Hydrocarbons are a family of compounds for which reliable and detailed chemical kinetic models exist [14]. However, most of these mechanisms are only valid for high temperature combustion (>1000 K), while kinetic data and mechanisms for the low temperature region are still scarce [15]. The lack of quantitative experimental data for the rate constants of elementary reactions in the low temperature region is the main difficulty. So far, we have tested six kinetic reaction mechanisms against auto-ignition data of propane–air mixtures between 450 K and 700 K. Table 1 summarises these reaction mechanisms.

The first five reaction mechanisms are published reaction mechanisms [16–20], while the last one is composed by the software package EXGAS-ALKANES [21]. Fig. 8 compares the auto-ignition limits predicted by the different reaction schemes.

Table 1
Summary of reaction mechanisms for propane oxidation

Reaction mechanism	Number of species	Number of reactions	Based on experimental data of	Concentration range
San Diego [16]	39	173	Rapid compression shock tube (1–30 bar)	2.05–7.73 vol% ($\Phi = 0.5$ –2)
Westbrook [17]	36	168	Propane and propene oxidation and pyrolysis	Unknown
Princeton [18]	92	621	Counterflow diffusion flames (1–15 bar)	Rich mixtures till 16 vol%
Delaware [19]	70	463	Rapid compression	2.05–7.73 vol% ($\Phi = 0.5$ –2)
Koert and Pitz [20]	155	689	High pressure flow reactor (650–800 K, 10–15 bar)	1.65 vol% ($\Phi = 0.4$)
EXGAS-ALKANES [21]	118	713	Low temperature oxidation	–

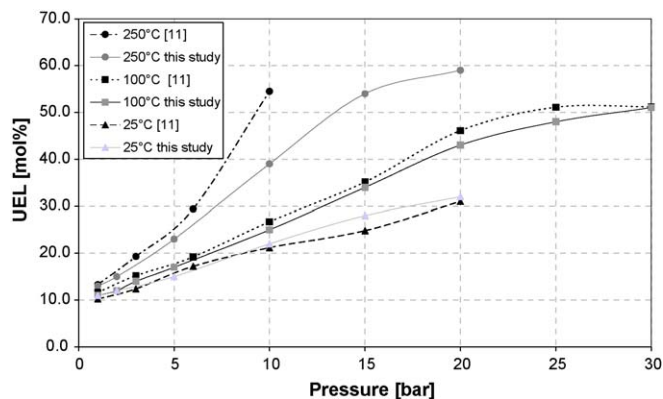


Fig. 9. Comparison of UEL data of propane–air mixtures obtained in this study and from Van den Schoor and Verplaetsen [11].

The reaction mechanisms can be divided into two groups. The first five overestimate the auto-ignition temperature. For these reaction mechanisms the explosion criterion applied was a temperature rise of 50 °C. At the auto-ignition temperature of 300 °C their respective ignition delay times were 18,000 s, 10,000 s, 5000 s, 13,500 s and 23,000 s. The explosion criterion with the experiments was a combined temperature rise (>50 °C) and ignition delay time criterion (<900 s). The model with the EXGAS-ALKANES kinetics also uses this criterion. Nevertheless, this mechanism overrates the auto-ignition risk compared with the experimental data.

4. Discussion

The auto-ignition temperatures measured in the experimental set-up are significantly lower than the auto-ignition temperature found in literature. For example, the auto-ignition temperature provided by the gas supplier is 470 °C [22] and Kong et al. [3] measured values from 590 °C to 500 °C depending on the fuel concentration. The difference in auto-ignition temperatures can be described qualitatively by the difference in experimental set-up and the fuel concentrations. The British standard [2] describes an open cup set-up, which gives rise to higher auto-ignition temperatures. Kong et al. [3] measured their auto-ignition temperatures in a closed bomb 1-l apparatus. The effect of the vessel volume on the auto-ignition temperature can be predicted by the Beerbower correlation [23]:

$$T_2 = \frac{T_1 - 75}{\log V_1 - 12} \cdot \log V_2 + \left[75 - \frac{T_1 - 75}{\log V_1 - 12} \cdot 12 \right]$$

where T_i is the AIT (°C) and V_i is the vessel volume (dm³).

The calculated auto-ignition temperature is consequently 468 °C for an 8-l vessel derived from 500 °C for a 1-l vessel. The remaining difference in auto-ignition temperature is due to the lower fuel concentrations and the “semi-closed” 1-l vessel [3].

Fig. 9 compares the measured upper explosion limits of this study with previous flammability experiments performed by Van den Schoor and Verplaetsen [11]. There is a good agreement between both UEL data. The differences in set-up of both series of experiments are firstly the volume of the vessel: 8 l instead of

4.2 l, and secondly the pressure rise criterion: a relative pressure rise of 5% instead of 1% for the data of [11]. It can be seen that for high temperatures the upper explosion limit determined with the 5% pressure rise criterion is lower than with the more conservative 1% pressure rise criterion as was expected. At ambient temperature both limits overlap and at a pressure from 10 bar to 20 bar the difference is in the other direction. This could be due to the smaller size of the explosion vessel.

Most of the reaction mechanisms overestimate the auto-ignition temperature of the 40 mol% propane–air mixture. These mechanisms were validated for low concentrations and rather rapid ignitions. The accompanying ignition delay times are consequently too large. Reaction mechanisms that work at low temperature and high pressure are very scarce. The reaction mechanism produced by EXGAS-ALKANES for low temperature oxidation of propane produces realistic ignition delay times compared with the experiments, but overrates the auto-ignition risk. Further research has to be performed to improve the reaction mechanisms for these specific conditions.

5. Conclusions

The auto-ignition limit of propane–air mixtures is determined at high pressure and high concentrations in a closed vessel apparatus. The auto-ignition temperature of a 40 mol% propane–air mixture is 300 °C for atmospheric pressure and decreases to 250 °C at a pressure of 14.5 bar. It is also found that the propane concentration most sensitive to auto-ignition depends on the initial pressure.

The upper explosion limit of propane–air mixtures is determined at elevated pressure and temperature according to the European standard EN 1839. There is a good agreement with previous flammability experiments. It is also shown that a propane–air mixture can react spontaneously for propane concentrations outside the flammability limits.

Finally the numerical auto-ignition calculations in which various reaction mechanisms are used show a qualitative agreement with the experimental results. Further research has to be performed to improve the prediction of the ignition delay times.

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References

- [1] B.P. Mullins, Spontaneous Ignition of Liquid Fuels, Butterworths, London, 1955.
- [2] BS 4056: Method of Test for Ignition Temperature of Gases and Vapours, British Standard Institution, 1966.
- [3] D. Kong, F. Alfert, R.K. Eckhoff, Autoignition of CH₄/air, C₃H₈/air, CH₄/C₃H₈/air and CH₄/CO₂/air using 1 l ignition bomb, J. Hazard. Mater. 40 (1995) 69–84.
- [4] P. Cadman, G.O. Thomas, P. Butler, The auto-ignition of propane at intermediate temperatures and high pressures, Phys. Chem. Chem. Phys. 2 (2000) 5411–5419.

- [5] SAFEKINEX, Deliverable No. 5 (BAM, TUD), Report on Experimentally Determined Self-Ignition Temperature and the Ignition Delay Time, 2005.
- [6] N.N. Semenov, *Chemical Kinetics and Chain Reactions*, Oxford University Press, London, 1935.
- [7] D.A. Frank-Kamenetskii, *Diffusion and Heat Exchange in Chemical Kinetics*, Princeton University Press, Princeton, NJ, 1955.
- [8] Shell Global Solutions (UK) for the Health and Safety Executive, CFD Simulation and Detailed Chemical Modelling of Alkane Auto-Ignition near a Heated Metal Surface, Contract Research Report 352/2001, 2001.
- [9] L. Vandebroek, F. Verplaetsen, J. Berghmans, A. van den Aarssen, H. Winter, G. Vliegen, E. van't Oost, Auto-ignition hazard of mixtures of ammonia, hydrogen, methane and air in a urea plant, *J. Hazard. Mater.* 93 (2002) 123–136.
- [10] EN 1839, Determination of Explosion Limits of Gases and Vapours, European Committee for Standardisation, Brussels, 2003.
- [11] F. Van den Schoor, F. Verplaetsen, The upper explosion limit of lower alkanes and alkenes in air at elevated pressures and temperatures, *J. Hazard. Mater.* 128 (2006) 1–9.
- [12] R.J. Kee, F.M. Rupley, J.A. Miller, M.E. Coltrin, J.F. Grcar, E. Meeks, H.K. Moffat, A.E. Lutz, G. Dixon-Lewis, M.D. Smooke, J. Warnatz, G.H. Evans, R.S. Larson, R.E. Mitchell, L.R. Petzold, W.C. Reynolds, M. Caracotsios, W.E. Stewart, P. Glarborg, C. Wang, C.L. McLellan, O. Adigun, W.G. Houf, C.P. Chou, S.F. Miller, P. Ho, P.D. Young, D.J. Young, CHEMKIN Release 4.0.2, Reaction Design, San Diego, CA, 2005.
- [13] S. Li, L.R. Petzold, Software and algorithms for sensitivity analysis of large-scale differential algebraic systems, *J. Comput. Appl. Math.* 125 (1/2) (2000) 131–145.
- [14] J.M. Simmie, Detailed chemical kinetic models for the combustion of hydrocarbon fuels, *Prog. Energy Combust. Sci.* 29 (6) (2003) 599–634.
- [15] M.J. Pilling, *Low-Temperature Combustion and Autoignition*, *Comprehensive Chemical Kinetics*, vol. 35, Elsevier Science B.V., Amsterdam, 1997.
- [16] *Chemical-Kinetic Mechanisms for Combustion Applications*, San Diego Mechanism Web Page, Center for Energy Research (Combustion Division), University of California at San Diego, 2005, <http://maeweb.ucsd.edu/combustion>.
- [17] C.K. Westbrook, W.J. Pitz, A comprehensive chemical kinetic mechanism for oxidation and pyrolysis of propane and propene, *Combust. Sci. Technol.* 37 (1984) 117–152.
- [18] C.J. Sung, B. Li, C.K. Law, Structure and sooting limits in counterflow methane/air and propane/air diffusion flames from 1 to 5 atmospheres, in: 27th International Symposium on Combustion, 1998, pp. 1523–1530.
- [19] Q. Zhiwei, V.L. Vitali, Y. Huixing, C.G. William, G.D. Scott, W. Hai, Combustion chemistry of propane: a case study of detailed reaction mechanism optimization, in: *Proceedings of the Combustion Institute*, vol. 28, 2000, pp. 1663–1669.
- [20] D. Koert, W.J. Pitz, J.W. Borelli, N.P. Ceransky, Chemical kinetic modeling of high pressure propane oxidation and comparison to experimental results, *Symp. (Int.) Combust. Proc.* 26 (1996) 633–640.
- [21] F. Battin-Leclerc, R. Bounaceur, G.M. Côme, R. Fournet, P.A. Glaude, G. Scacchi, V. Conraud, EXGAS-ALKANES, A Software for the Automatic Generation of Mechanisms for the Oxidation of Alkanes, CNRS-DCPR, 2004.
- [22] Material Safety Data Sheet (MSDS) of Propane provided by Air Liquide, <http://www.airliquide.com/safety/msds/en/104.AL.EN.pdf>.
- [23] R.D. Coffee, Cool flames and autoignitions: two oxidation processes, *Chem. Eng. Prog. Loss Prev.* 13 (1980) 74–82.