CHEMICAL ENGINEERING TRANSACTIONS
VOL. 70, 2018

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

ISBN 978-88-95608-67-9; **ISSN** 2283-9216
DOI: 10.3303/CET1870226

Influence of Temperature and Vessel Volume on Explosion Characteristics of Propanol/Air Mixtures in Closed Spherical Vessels

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A comparative preliminary study on explosion characteristics of propanol/air mixtures was experimentally performed. The maximum explosion pressure, p_{max}, deflagration index, K_G, lower explosion limit, LEL, upper explosion limit, UEL are determined in two spherical vessels (volume: 1.00 m^3 and 0.020 m^3) for various 1-propanol/air mixtures (Φ = 0.57 - 1.33) at ambient initial pressure (100 kPa) and two initial temperatures (50 °C and 150 °C).

1. Introduction

Decreasing reserves of fossil fuels and current regulations for emissions from internal combustion engines that affect the environment and human health have stimulated a pronounced interest in nonconventional fuels and fuel additives. Alcohols derived from agricultural residues, feed-stocks and forestry wood wastes by means of biochemical processes have the potential to provide a path towards renewable, carbon-neutral fuels (Mitu et al., 2017). Unlike gasoline and diesel, alcohols contain oxygen. Adding alcohols to petroleum products allows the fuel to combust more completely due to the presence of oxygen, which increases the combustion efficiency and reduces air pollution. Using gasoline blended with 10 % ethanol can reduce greenhouse gas emissions (Surisetty et al., 2011). Low alcohols like ethanol with high octane number and relatively low cost have been successful in the practical use as the gasoline additives. However, low alcohols still have their disadvantages such as low energy content and high hygroscopicity. This leads to an inconvenient storage and transportation and restricts their wide applications in engines. Meanwhile, low alcohols favor to the knock resistance in the spark ignition (SI) engines but they are bad for compression ignition (CI) engines. Recent study on the higher alcohols indicated that 1-pentanol presents a negative temperature coefficient (NTC) behavior in the intermediate temperature regime, which indicates their potential of fuels for the CI engines (Li et al., 2015a). Besides the fuel interest, there are devastating accidents likely in chemical process industry as the Boiling Liquid Expanding Vapor cloud Explosion - BLEVE (Skrinska et al., 2015). It is accompained by highly devastating blast waves and missilies. All pressure liquified gases can, and often are, associated with BLEVEs (Abbasi et al., 2007). Under standard conditions, 1-propanol is a flammable liquid with a flash point temperature of 22 °C (Skrinsky et al., 2015), spontaneous ignition temperature of 385 °C (EN 14522), classified in temperature class T2 (EN 330371) and explosion class IIA-B (EN 60079-20-1). However, the assessment of 1-propanol, as an alternative fuel or fuel additive, is currently, as with methanol and ethanol, limited to standard laboratory conditions. In reality, however, this flammable liquid can occur under different conditions, such as high temperatures and pressures. These "real" conditions require a systematic investigation of its safety characteristics at non-standard temperatures and pressures. In this initial study, the explosion characteristics of the mixture of 1-propanol and air for different volume concentrations are presented, depending on two different initial temperatures of 50 °C and 150 °C. Based on the knowledge of these characteristics, it is possible to appropriately design processes in which there is a risk of fire and explosion and to propose preventive measures for its effective reduction.

Please cite this article as: Skrinsky J., 2018, Influence of temperature and vessel volume on explosion characteristics of propanol/air mixtures in closed spherical vessels , Chemical Engineering Transactions, 70, 1351-1356 DOI:10.3303/CET1870226

2. Previous studies

The test vessel used for gas testing should be spherical, with a volume of at least 0.005 m^3 and a recommended volume of 0.02 m^3 or greater. Because the only source of initial turbulence is the ignition source employed, it is important that the flame front is not unduly distorted by the ignition process (NFPA 68, 2002). Thus, the closer the volume of V = 1 m^3 to the standard explosion chamber, the smaller the deviation and the more accurate the application of the cubic law. A very interesting previous study was published by Li et al. (2015a). In this study, the explosion parameters of 5 alcohols (ethanol, 1-butanol, 1-pentanol, 2-pentanol and 3-pentanol) are mixed with air at an initial temperature of up to 200 °C and an initial pressure up to 0.75 Mpa. Parameters were measured in a cylindrical explosion chamber with diameter D = 180 mm and length L = 210 mm (V = 5.3 dm^3). Since the ratio L / D = 1.17 and L / D < 2 apply, Cubic law could be used to calculate K_G. The same group further deepened research on a comparative study of the explosion characteristics of four isomers of pentanol (n-pentanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 2-methyl-2-butanol) (Li et al., 2015b). Parameters were measured under the same conditions as in the previous study. In the same year a study of the explosion parameters of methanol / air mixture was published in (Mitu et al., 2015). Parameters were measured for initial temperatures of 50 °C and 150 °C and supplemented by a calculation for 25 °C and 110 °C (Mitu et al., 2015). The initial pressures were 50 kPa, 75 kPa and 100 kPa. Two years later, Mitu et al. (2017) studied effect of 0.005 m^3 and 0.02 m^3 to a mixture of ethanol/air for the same initial conditions. Based on data from the above literature, there are strong deviations between K_G. These can be mainly attributed to differences in the ratio of volume and shape (ratio of length to diameter) of the explosion chamber.

3. Experiment

3.1 Description of the 0.02 m^3 chamber set-up

It is the stainless steel (1.4435) double wall vessel of spherical shape with an internal diameter of 336 mm. The vessel is provided with an opening of an inside diameter of 148 mm made by OZM Research, s.r.o. The whole system is schematically introduced in Figure 1.

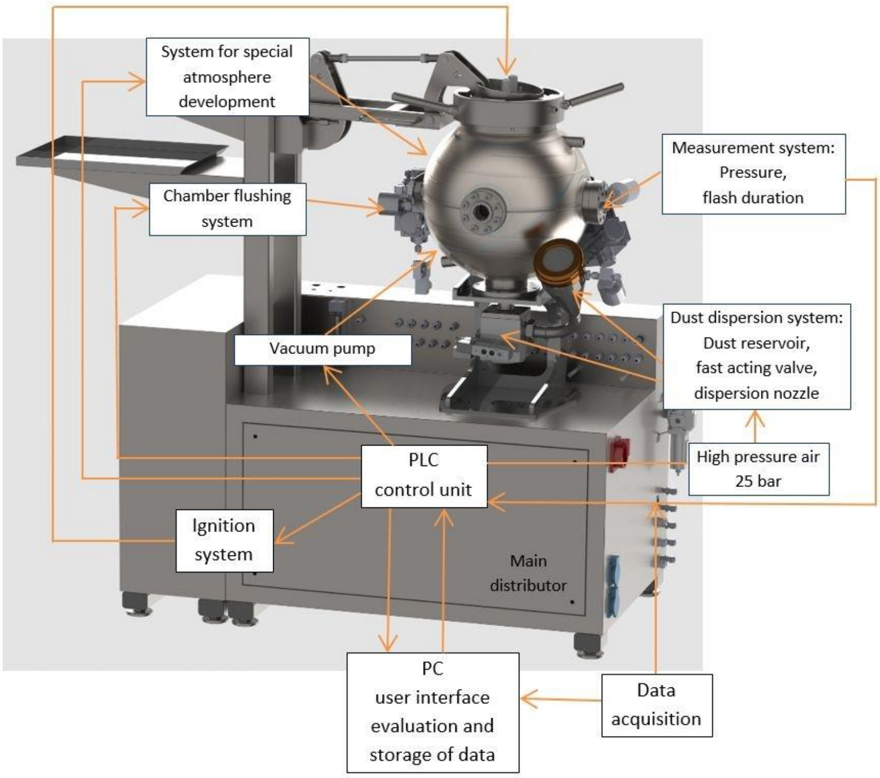

Figure 1: Schematic introduction of the 0.02 m^3 chamber set-up

Highly dynamic temperature control system Presto A30 by JULABO is used for heating of the chamber. Permanent spark generator was made in accordance of EN 15967 with Tungsten electrodes with a distance of 6 mm. A pair of piezoelectric pressure sensors by Kistler, type 701A. Pressure range set for the sensors is 2.5 MPa and natural frequency 70 kHz. Data are recorded be four-channel data card with a sampling rate 50 kS/s/channel. PLC Siemens Simatic 1215 connected to PC used as a user interface automatically control whole procedure including fast acting valve timing. The chamber is equipped by thermocouple for temperature monitoring, especially for measurement of temperature in time of ignition. Correct gas mixture composition is assured by partial pressure method. Pressure transducer measures internal pressure. Procedure for gas explosion starts with evacuation to pressure less than 40 kPa to leave a space for the gas. For example, the use of 1-propanol vapour concentrations of 2 vol.% and 8 vol.% require the partial pressures of 1-propanol to be added are 2 kPa and 8 kPa. Then the evacuation pressures should be 38 kPa and 32 kPa respectively. PLC starts the experiment where 60 ms is counted as ignition delay time, and then the gas is mixed by blowing dispersion air into the 1-propanol mixture inside the chamber. After that the mixture is ignited either by the electric discharge or by current source for pyrotechnic igniter. The explosion indices are measured and calculated.

3.2 Description of the 1 m^3 chamber set-up

The chamber is a vessel of a spherical shape with an inside diameter of 1240 mm and a capacity of 1 m^3 made by OZM Research, s.r.o. The vessel is provided with an opening of an inside diameter of 800 mm, which is provided with a flange and a lock for locking the door. Schematic representation of the whole system is shown in Figure 2. The material and components comply with the use of equipment for experiments at atmospheric initial pressure and initial laboratory temperature (15 °C - 200 °C).

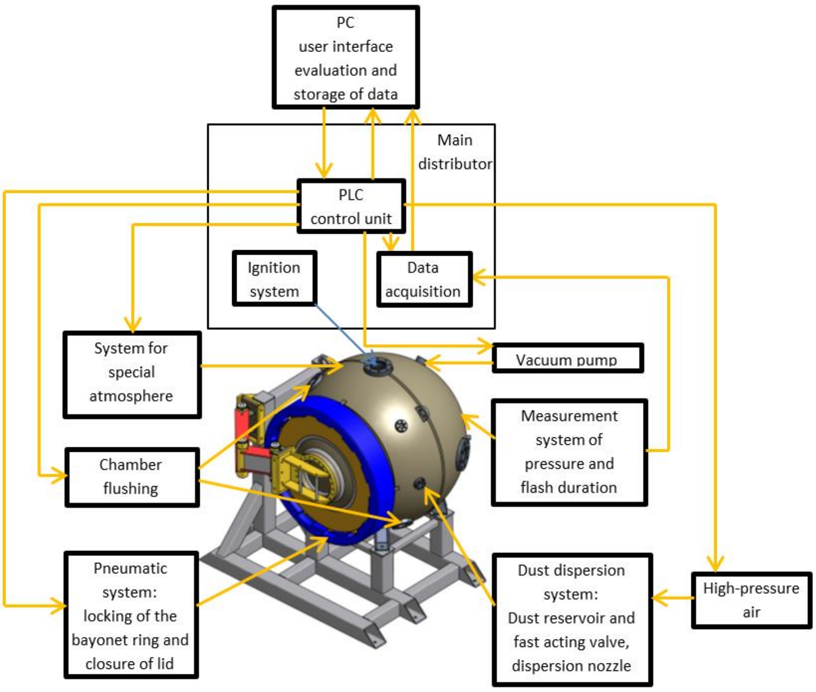

Figure 2: Schematic introduction of the 1 m^3 chamber set-up.

The explosion chamber is equipped with measurement of time depended dynamic pressure using two pressure sensors by Kistler type 701A calibrated for the range up to 2.5 MPa. Natural frequency of the sensor is 70 kHz. Optical probe is installed for the measurement of the flash duration. For this purpose, it is fitted with a flange having an inner diameter DN 100 and holes for mounting the sensors. Data are recorded be four-channel data card with a sampling rate 50 kS/s/channel. PLC Siemens Simatic 1215 connected to PC used as a user interface automatically control whole procedure including fast acting valve timing. The chamber is equipped by thermocouple for temperature monitoring, especially for measurement of temperature in time of ignition. Correct gas mixture composition is assured by partial pressure method. Pressure transducer measures internal pressure. Procedure for gas explosion starts with evacuation to pressure less than 89 kPa to leave a space for the gas. For example, the use of 1-propanol vapour concentrations of 2 vol.% and 8 vol.% require the partial pressures of 1-propanol vapour to be added are 2 kPa and 8 kPa respectively. Then the evacuation pressures should be 87 kPa and 81 kPa respectively. PLC starts the experiment where 600 ms is counted as ignition delay time, and then the gas is mixed by blowing dispersion air into the 1-propanol/air mixture inside the chamber. After that the mixture is ignited by the electric discharge. In both experiments, 1-Propanol (99.9 %) was used without further purification.

4. Calculation procedure

The calculation procedure is described in (Skřínský and Skřínská, 2014). To quantify adiabatic explosion pressures and constant volume temperatures at 11 different concentrations of the mixture, a calculation method of minimizing free Gibbs energy was used. As input parameters, the kinetic mechanisms and thermodynamic data sets (C_p, S_0, H_0, G_0) were used primarily in the default THERMO.dat databases of Explosion Pressure (Wolanski et al., 2004) and Thermdat.tdd for GASEQ (Morley, 2004) in CHEMKIN standard polynomial format. Calculations of LEL and UEL values were made using modified Le Chatelier equations with temperature correction (Skrinsky and Skrinska, 2014). The results of adiabatic explosion pressure calculations, P_{admax}, were used to predict the initial values for experimental 1-propanol- air measurement and are in Figure 1.

5. Results

Figure 3 plots the peak explosion pressure (P_{max}/P_0) and normalized maximum equilibrium pressure (P_e/P_0) versus equivalence ratio for the stoichiometric 1-propanol/air mixture at various fuel fractions and two initial temperatures (50 °C and 150 °C).

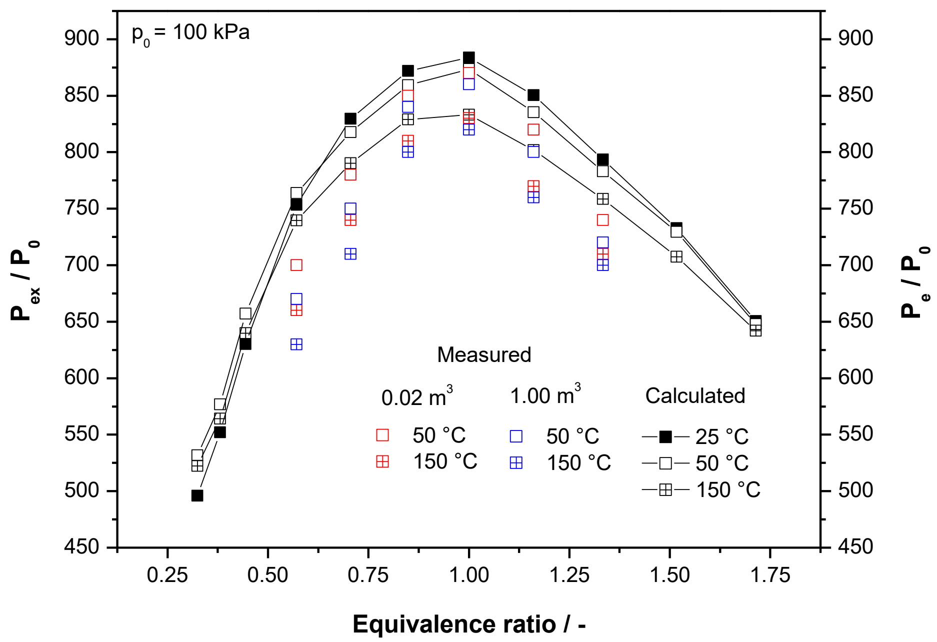

Figure 3: P_{ex}/P_0 and P_e/P_0 versus Φ=0.57-1.33 for 1-propanol-air mixtures various initial temperatures and mixture compositions, P_0 = 100 kPa.

The experimental and calculated values of explosion pressures are determined in a spherical vessel for both temperatures. The shape of the explosion pressure curves with varying 1-propanol concentration is similar at all investigated initial temperatures. The maximum explosion pressure, p_{max}, was determined as the highest p_{ex} found for the mixture compositions investigated. The maximum value of the explosion pressure is found at Φ=1.06 of 1-propanol for all temperatures. As expected the increase in the initial temperature lowers the explosion pressure and increases the flammability range. The upper explosion limit increases and the lower explosion limit decreases. When the mixture composition approaches the flammability limits the explosion pressure drops sharply to zero in all investigated cases. The calculated results show a reasonable agreement at the near stoichiometric concentrations with the previous studies. Diferencies are presented between P_{ex}/P_0

and P_e/P_0, Real combustion is not under the absolute adiabatic condition. It accompanies both radiant and convective heat losses to the wall, leading to the lower P_{max}/P_0 than P_e/P_0. It is noted that the difference between P_e/P_0 and P_{max}/P_0 is remarkably increased at highly rich mixtures and show the reasonable agreement with (Li et al., 2015a).

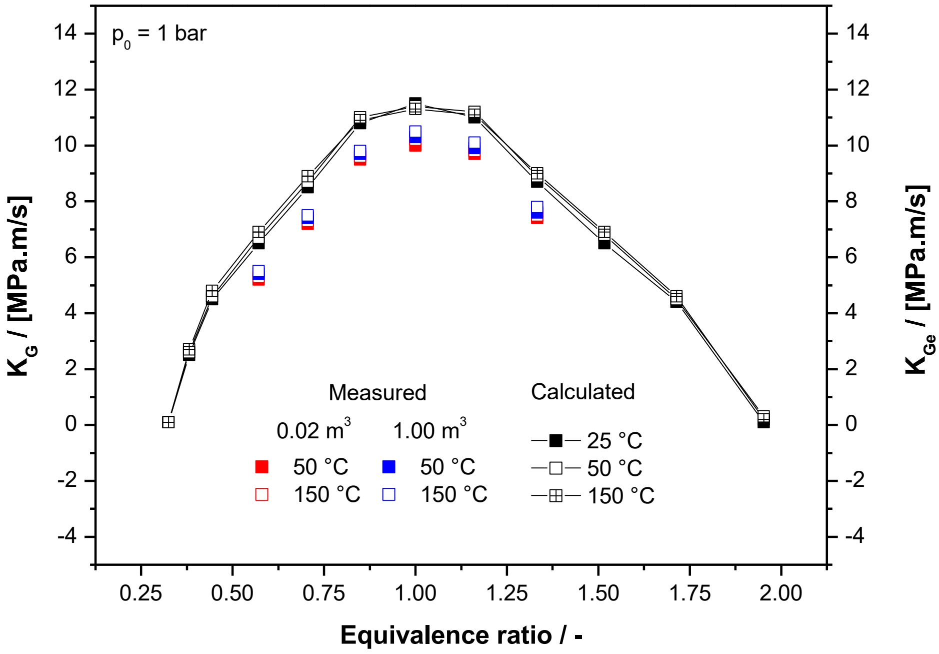

Figure 4: K_G and K_{Ge} versus Φ=0.57-1.33 at elevated temperatures for 1-propanol-air mixtures various initial temperatures and mixture compositions, p = 100 kPa.

Figure 4 shows the variation of K_G with vessel volume for 1-propanol as measured in 0.02 m^3 and 1.00 m^3 spherical test vessels. The K_G value was calculated from the experimentally determined $(dp/dt)_{max}$ values. The increase in K_G is related to various flame acceleration effects, as described in (NFPA 68, 2002). The experimental and calculated values of K_G are determined in a spherical vessel for both temperatures. At both initial temperatures, the K_G is observed at the same concentration range where P_{max} is found. Deflagration indexes reach their peaks at Φ=1.06, and they decrease at both lean and rich mixtures. K_G give an approximate value at varied initial temperatures, indicating that K_G are insensitive to the variation of temperature and support Mitu et al. (2015) and Li et al. (2015a).
The resulting values are summarized in Table 1, where the measurement uncertainties are determined by the test method.

Table 1: Values of explosion characteristics for the most reactive 1-propanol/air mixtures at p0 = 100 kPa.

		0.02 m^3 (current data)		1.00 m^3 (current data)	
		50 °C	150 °C	50 °C	150 °C
p_{max}	(kPa)	870±30	830±30	860±30	820±80
K_G	(MPa.m/s)	10±0.5	10.2±0.5	10.3±0.5	10.4±0.6
LEL	(%)	3.5-0.2	3.0-0.2	2.1-0.2	2.1-0.2
UEL	(%)	14.0+0.2	14.5+0.2	13.0+0.2	13.5+0.2

6. Conclusions

The experimental study of the explosion characteristics of a mixture of 1-propanol and air in an enclosed spherical vessel with a central initiation of 0.02 m^3 and 1 m^3 was performed for different 1-propnanol/ air mixtures at two different initial temperatures and atmospheric pressure.

- P_{max} of 1-propanol and air mixtures decrease with increasing initial temperature. Quantitative decrease is from 870 kPa to 830 kPa for 0.02 m^3 and from 860 kPa to 820 kPa for 1 m^3.
- K_G are insensitive to the variation of the initial temperature (in both explosion vessels volumes).
- LEL values slightly decrease with increasing temperature from 3.5 % to 3.0 % for 0.02 m^3 and do not change for 1 m^3.
- UEL values slightly increase with increasing temperature from 13.0 % to 13.5 % for 0.02 m^3 and do not change for 1 m^3.

The results support comparative studies on the explosion characteristics of alcohols (methanol, ethanol, 1-butanol, 1-pentanol, 2-pentanol, and 3-pentanol)/air mixtures at elevated temperatures. Present values of explosion characteristics can be practically used in designing explosion protection techniques, such as explosion-proof design and explosion-proof design, explosion relief, and explosion suppression. They can also be used to eliminate the risk of explosion by preventing the formation of an explosive gas mixture and as a basis for explosion protection by "inertisation".

Acknowledgments

This work was prepared within the project „Innovation for Efficiency and Environment - Growth“, identification code LO1403 with the financial support from the Ministry of Education, Youth and Sports in the framework of the National Sustainability Programme I.

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