

# Explosion Parameters of Degas-Air Mixtures at Elevated Temperatures

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The maximum explosion pressure ( $p_{max}$ ), the maximum rate of pressure rise  $((dp/dt)_{max})$ , the deflagration index ( $K_G$ ), the lower explosion limit (LEL), the upper explosion limit (UEL), have been determined in spherical explosion vessel (0.02 m<sup>3</sup>) for various degas/air mixtures ratios (0.32-2.10) at ambient initial pressure (101 kPa) and four initial temperatures (25 °C, 50 °C, 100 °C, 150 °C). The outcome of this preliminary study is to quantify the dependency of explosion parameters on two variables – degas/air equivalence ratios ( $\Phi$ ) and initial temperature ( $T_0$ ). These explosion characteristics are important for design of safety devices (e.g. relief systems, vents), able to ensure active protection of pressure vessels where flammable mixtures are formed.

## 1. Introduction

Cleaner combustion devices based on the utilization of oxygenated fuels provide promising options for the development of lower carbon strategies in the transportation and energy sectors in the near future (Knoef et al., 2012). A great deal of attention has been given to determination of the explosion characteristics of combustible mixtures because explosion characteristics are of fundamental importance in regard to developing and justifying the chemical kinetics mechanism of the fuel, as well as about predicting the performance and emissions of internal and external combustion systems (Skrinsky, 2015). Other reason are devastating accidents likely in chemical process industry as the Boiling Liquid Expanding Vapor cloud Explosion - BLEVE (Skrinska et al., 2015). The explosion pressure ( $P_{max}$ ), and the maximum rate of pressure rise  $((dP/dt)_{max})$  are the most important explosion severity parameters. LEL and UEL are important explosion sensitivity parameters. The explosion time ( $t_c$ ) is the time interval between ignition and the moment when  $P_{max}$  is attained (Mittal, 2017). Explosion parameters are important in assessing the hazards of a process, for design of vessels to tolerate explosion pressure and for design of relief device against damage from gaseous explosion (Seitz and Westphal, 2016). Degas consists of flammable methane (LEL = 5.3 vol %, UEL = 14.0 vol %) and non-flammable carbon dioxide in fixed ratio 7 : 3. Once fixed the percentage of methane in the UEL of its mixture with air, the explosion parameters increase if the air content increases. On the other hand, its dilution with carbon dioxide results in substantial decrease of the flammability range. It is very interesting to investigate the ability of degas air-combustion processes with low reactivity fuels from the point of view of energetic sustainability and economy. Most scientific works deals with pure fuels, in particular with methane, whereas very few analyses have been devoted to the study of the explosion of methane in carbon dioxide-enriched air. The assessment of explosion hazard of such mixtures is important based on values of safety parameters under various conditions.

## 2. Previous studies

Methane is the main component of degas. Measured explosion parameters data ( $p_{max}$ ,  $K_G$ ,  $t_c$ ) for pure methane/air mixture at ambient initial pressure and temperature have been summarized in (Mittal, 2017). There have been presented results of 21 experimental studies published between 1965-2014. These studies have provided the values of  $p_{max}$  (680 - 870 kPa),  $K_G$  (2-11 MPa.m/s) and  $t_c$  (77.8 - 580.0 ms). The experimental data were obtained by different vessels shapes (cylindrical, spherical) and volumes (0.005 - 204 m<sup>3</sup>). The explosion severity parameters results for close to 20 dm<sup>3</sup> volumes are summarized in Table 1.

Table 1: Measured explosion severity data for 20 dm<sup>3</sup> at ambient initial pressure and temperature at  $T_0 = 1.0$  °C and  $P_0 = 1$  bar.

Volume dm <sup>3</sup>	Shape	Conc. vol. %	$P_{max}$ bar	Conc. vol. %	$K_G$ bar.m/s	$t_c$ ms
20	semi sphere	10.00	$8.3 \pm 0.1$	10.00	$66 \pm 2$	-
20	sphere	9.51	8.7	9.51	80	90
20	sphere	11.00	8.3	10.00	75	-
20	sphere	10.50	8.5	10.50	45	-
20	sphere	11.00	8.4	10.00	68	-
20	sphere	10.00	8.2	10.00	80	-
20	sphere	10.90	8.5	-	-	-
20	sphere	9.80	7.1	9.80	60	-
22	cylinder	9.51	7.7	9.51	46	-

There are substantial discrepancies in the explosion severity characteristics measured by different researchers for the same methane-air mixture (9.51-11.00 vol. %). Di Benedetto have studied the explosion behaviour of CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub> in a closed 5 dm<sup>3</sup> cylindrical vessel for various gas mixture compositions ( $\Phi = 0.21 - 0.8$ ) at atmospheric initial conditions (Di Benedetto et al., 2009). Wang et al. (2014) have also investigated the effects of inert gas (CO<sub>2</sub>) on methane explosion characteristics in a closed 22 dm<sup>3</sup> vessel at atmospheric initial conditions. They have found  $P_{max} = 7.0$  bar for CH<sub>4</sub>/CO<sub>2</sub> gas mixture compositions (1:1). The present research obtain information on explosion pressure, explosion time, deflagration index and explosion limits of degas/air mixture in closed spherical 20 dm<sup>3</sup> chamber at different initial temperatures.

### 3. Experimental methods

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

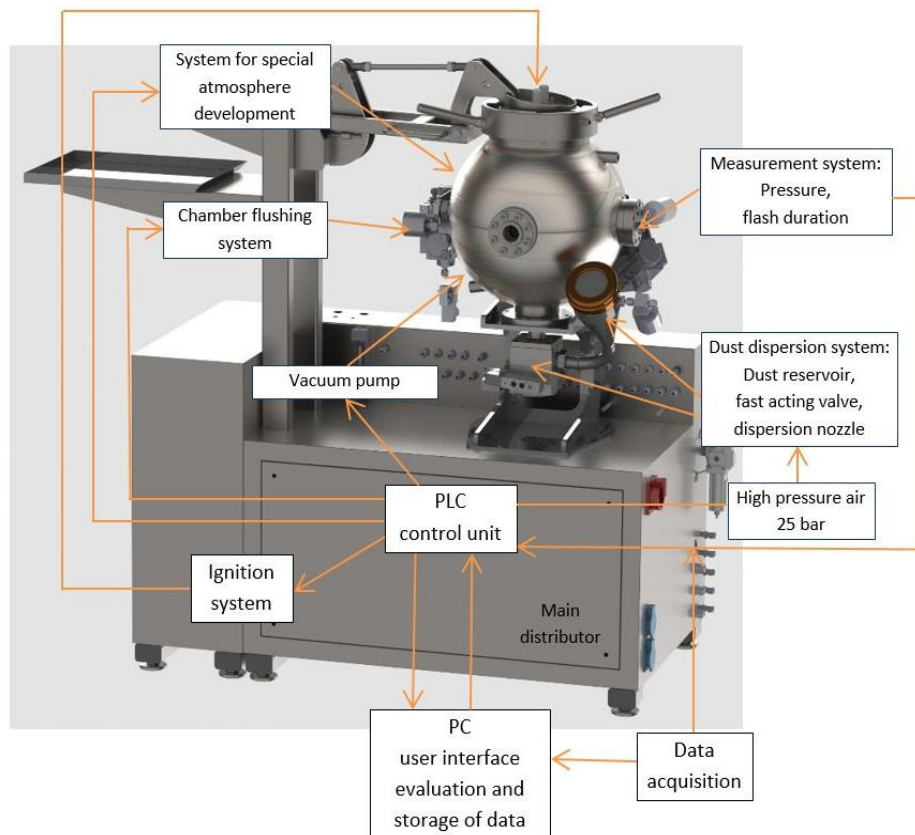


Figure 1: Schematic of the 0.02 m<sup>3</sup> vessel set-up

Highly dynamic temperature control system Presto A30 by JULABO is used for heating of the vessel. Permanent spark generator was made in accordance of EN 15967 with Tungsten electrodes with a distance up to 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 by 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 with 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 degas concentrations of 8 vol. % require the partial pressure of degas to be added is 8 kPa. Then the evacuation pressure should be 32 kPa. 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 degas mixture inside the chamber. The mixture is ignited by the electric discharge. The explosion indices are measured and calculated.

#### 4. Calculation procedure

To quantify adiabatic explosion pressures and constant volume temperatures at 13 different concentrations of the mixture, a calculation method of minimizing free Gibbs energy was used (Skřínský and Skřínská, 2014). 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 (GASEQ, 2005) and Thermdat.tdd for GASEQ (Explosion Pressure, 2004) in CHEMKIN standard polynomial format. Calculations of LEL and UEL values were made using modified Le Chatelier equations with temperature correction (Skřínský and Skřínská, 2014). The results of adiabatic explosion pressure calculations,  $P_{admax}$ , were used to predict the initial values for experimental degas/air measurement and are in Figure 2.

### 5. Results

#### 5.1 Influence of the concentration

Figure 2 plots the  $P_{ex}/P_0$  time curves at 5 various fuel/air fractions (0.50-1.50) for degas/air mixtures at  $P_0 = 1$  bar in  $T_0 = 25$  °C in 20 dm<sup>3</sup> spherical vessel.

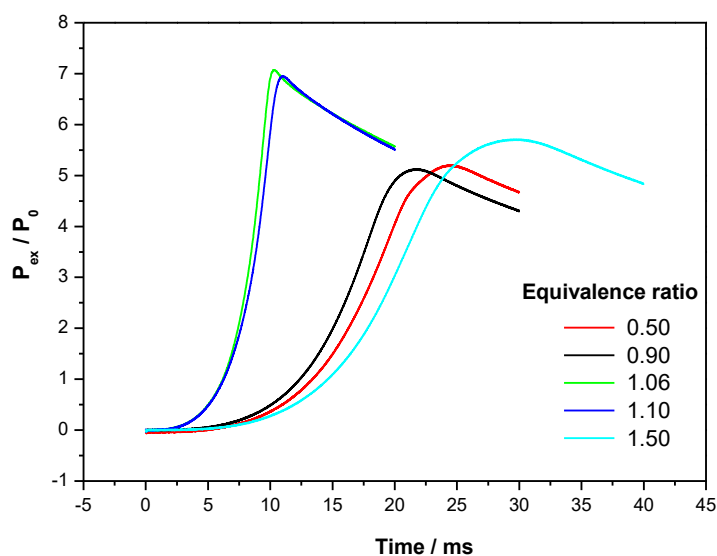


Figure 2:  $P_{ex}/P_0$  time curves during the explosion of a 0.50-1.50 degas/air mixtures at  $P_0 = 1$  bar in  $T_0 = 25$  °C in 20 dm<sup>3</sup> spherical vessel

Figure 2 shows that under  $P_{max}/P_0$  ( $7.2 \pm 0.4$ ) pressure reached its maximum most rapidly at equivalence ratio of 1.06, while the  $t_c$  gradually increase and the  $P_{ex}/P_0$  decrease with the mixture getting richer. Figure 3 plots  $K_G$  time curves during the explosion of a 0.50-1.50 degas/air mixtures at  $P_0 = 1$  bar in  $T_0 = 50$  °C in 20 dm<sup>3</sup> spherical vessel. The explosion pressures hit top and the explosion durations hit bottom rapidly at equivalence ratio of

1.06. The maximum  $K_G$  hits its top here. When it comes to lean burn limit or rich limit of mixture, things go to the reverse side, as shown in Figure 2.

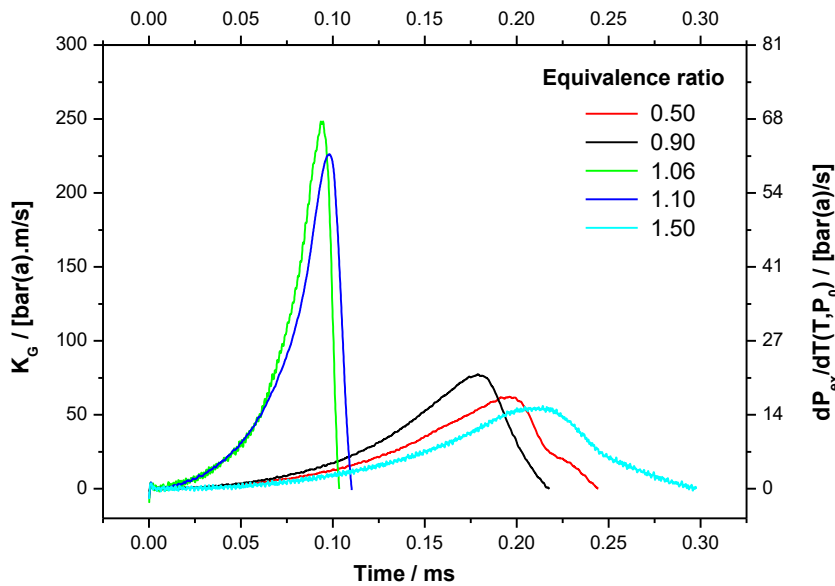


Figure 3:  $K_G$  time curves during the explosion of a 0.50-1.50 degas/air mixtures at  $P_0 = 1\text{ bar}$  in  $T_0 = 50\text{ }^\circ\text{C}$  in  $20\text{ dm}^3$  spherical vessel

### 5.2 Influence of the temperature

Figure 3 plots the normalized peak explosion pressure ( $P_{ex}/P_0$ ) versus equivalence ratio for degas/air mixture at four initial temperatures ( $25\text{ }^\circ\text{C}$ ,  $50\text{ }^\circ\text{C}$ ,  $100\text{ }^\circ\text{C}$ ,  $150\text{ }^\circ\text{C}$ ).

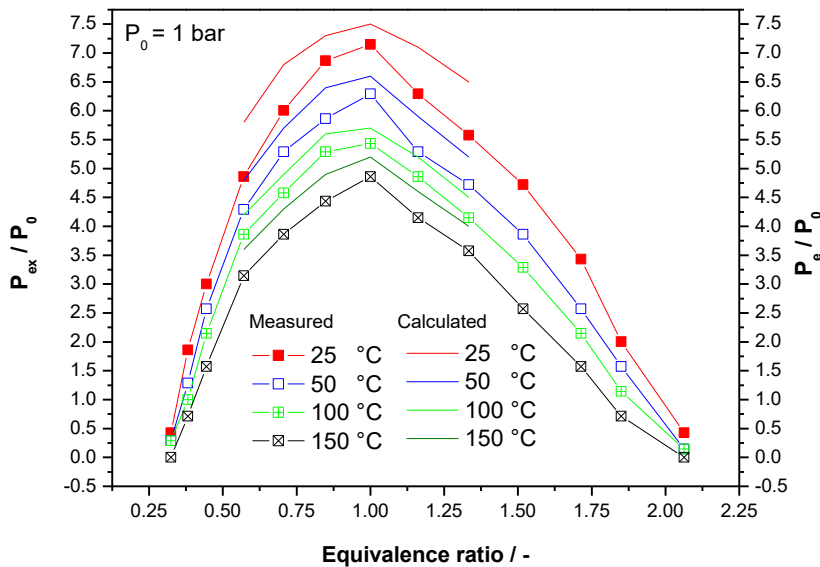


Figure 3:  $P_{ex}/P_0$  at various degas/air equivalence ratios ( $\Phi$ ) and initial temperatures ( $T_0$ ) for ambient initial pressure ( $P_0 = 100\text{ kPa}$ ).

Differences 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  $P_e/P_0$ . The experimental ( $P_{ex}/P_0$ ) values of explosion pressures are determined in a spherical vessel for four

initial temperatures. The shape of the explosion pressure curves with varying degas concentration is similar at all investigated initial temperatures. The maximum explosion pressure,  $P_{\max}$ , was determined as the highest  $P_{\text{ex}}$  found for the mixture compositions investigated. The maximum value of the explosion pressure is found at  $\Phi=1.06$  of degas for all temperatures. This observation indicates that the worst-case accident for a degas-air mixture is close to the stoichiometric concentration of degas. When the mixture composition approaches the flammability limits the explosion pressure drops sharply to zero in all investigated cases. The measured results show a reasonable agreement at the near stoichiometric concentrations with the previous studies. At a concentration of degas  $\Phi = 1.0$  is the  $P_{\max}$  value 7.2 bar that is close to the  $P_{\max} = 7.0$  bar at concentration  $\text{CH}_4/\text{CO}_2$  (1:1) reported by Wang et al. (2014) and not far from the 7.1-7.7 reported for pure methane by (Mittal, 2017). This is true until the initial gas temperature is equal to the atmospheric temperature. Increasing the initial temperature up to 150 °C the  $P_{\max}$  value decrease substantially to the value 4.9 bar. The combustion time are influenced by the initial temperatures in explosion chamber. The variation of  $t_c$  with temperature is shown in Table 1. The measured pressure-time records were analysed for determination of rate of pressure rise and deflagration index presented in Figure 4.

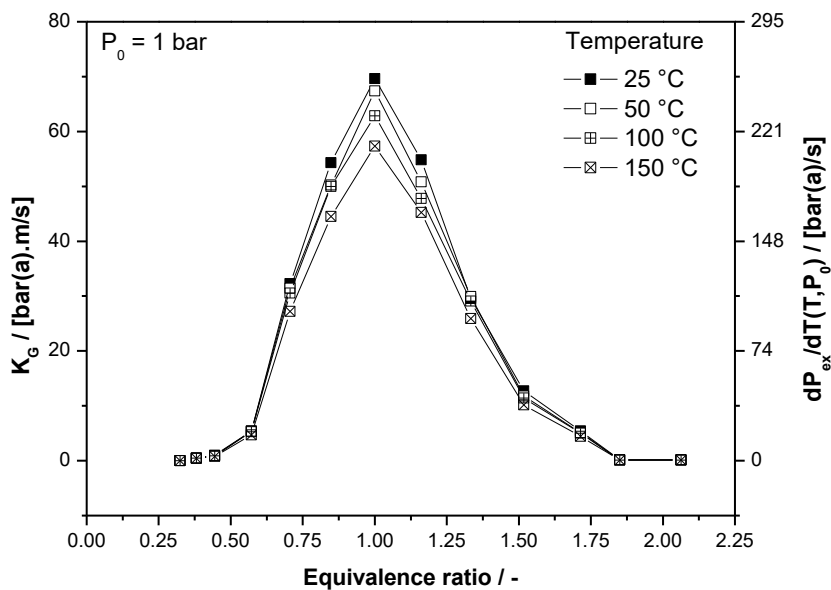


Figure 4:  $K_G$  and  $dP_{\text{ex}}/dt$  at various degas/air equivalence ratios ( $\Phi$ ) and initial temperatures ( $T$ ) for ambient initial pressure ( $P_0 = 1\text{ bar}$ ).

Figure 4 shows the variation of  $K_G$  with equivalence ratios ( $\Phi$ ) and initial temperatures ( $T$ ) for degas as measured in 0.02 m<sup>3</sup> spherical test vessel. The  $K_G$  value was calculated from the experimentally determined  $(dp/dt)_{\text{ex}}$  values. At all initial temperatures, the  $K_G$  has been observed at equivalence ratio where  $P_{\max}$  has been found. The experimental values of  $K_G$  are determined in a spherical vessel for all temperatures. The data on  $K_G$  presented in Figure 4 shows that the experimental values decrease with increase of temperature.  $K_G$  value ranges from 69.7 to 57.4 bar.m/s for stoichiometric mixture and for initial temperatures 25 to 150 °C. Deflagration indexes have maximum at  $\Phi=1.06$ , and their values decrease going to lean and rich mixtures.  $K_G$  gives the similar peak value at varied initial temperatures, indicating that  $K_G$  are less sensitive to the variation of temperature than  $P_{\max}$ . The resulting values are summarized in Table 1, where the measurement uncertainties are determined by the test method.

Table 1: Average values of the explosion characteristics at  $\Phi = 1.06$  and  $P_0 = 1\text{ bar}$ .

Characteristic	Unit	$T_0 = 25\text{ °C}$	$T_0 = 50\text{ °C}$	$T_0 = 100\text{ °C}$	$T_0 = 150\text{ °C}$
$P_{\max}/P_0$	[-]	7.2±0.4	6.3±0.3	5.4±0.3	4.9±0.2
$(dp/dt)_{\max}$	[bar/s]	257.2±12.9	248.7±12.5	232.1±5.2	211.8±4.7
$K_G$	[bar. m/s]	69.7±6.1	67.4±5.7	62.9±5.2	57.4±4.7
LEL	[%]	6.0-0.2	5.5-0.2	5.5-0.2	5.0-0.2
UEL	[%]	19.5±0.2	19.0±0.2	19.0±0.2	18.5±0.2
$t_c$	[ms]	9.6	10.7	15.0	17.0

## 6. Conclusions

Energy Research Centre, VŠB-TU Ostrava is aimed at fundamentally improving the understanding of gas oxidation processes, the risk assessment of such processes, their environmental efficiency and safety (Skrinsky et al., 2016). The focus of this paper is to quantify the explosive properties of the degas mixture for different initial temperatures. The main conclusions are summarized as follows:

- 1) Determination of maximum explosion pressure ( $P_{max}$ ), deflagration index ( $K_G$ ) and time to reach  $P_{max}$  ( $t_c$ ) of degas-air mixtures ( $\Phi = 0.32 - 2.10$ ) on various initial temperatures and gas concentration.
- 2) Explosion pressure, rate of explosion pressure rise, and deflagration index of the degas-air mixture reach maximum values near the stoichiometric concentration with an equivalent ratio  $\Phi = 1.06$  within the studied range, i.e. 0.32 - 2.10 at temperatures of 25 - 150 °C.
- 3) The explosion pressure varied between 7.2 to 4.9 bar, the rate of explosion pressure rise 257.2 to 211.8 and the deflagration index 69.7 to 57.4 bar. m/s for initial temperatures 25°C to 150 °C.
- 4) LEL values slightly decrease with increasing temperature from 3.5 % to 3.0 %.
- 5) UEL values slightly increase with increasing temperature from 13.0 % to 13.5 %.
- 6) The data reported lead to an extension of the current data for methane/CO<sub>2</sub>-air mixture found in literature.

The explosion severity has been determined as maximum explosion pressure, maximum rate of pressure rise, time to reach the maximum explosion pressure of degas/air mixture. All parameters have been measured in an enclosed spherical vessel of 0.02 m<sup>3</sup> with a central initiation and calculated in various initial conditions of temperature and fuel/air ratio. The highest values have been evaluated at degas/air equivalence ratio corresponding to 1.06 that is above the stoichiometric concentration. The results support comparative studies on the explosion characteristics of methane/carbon dioxide/air mixtures at ambient temperatures. Present values of explosion characteristics can be practically used in designing explosion protection techniques, such as 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 degas/air mixture.

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## Reference

- Di Benedetto, A., Di Sarlia, V., Salzano, E., Cammarota, F., Russo, G., 2009, Explosion behaviour of CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub> and H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>/CO<sub>2</sub> mixtures, *International Journal of Hydrogen Energy*, 34, 6970-6978.
- Explosion Pressure, 2004, The program for calculation of maximum pressure of explosion for chemical equilibrium conditions. <[www.morechemistry.com/SAFEKINEX/deliverables/21.Del%20No.16%20ExplPress\\_Exe-15-11-2004.zip](http://www.morechemistry.com/SAFEKINEX/deliverables/21.Del%20No.16%20ExplPress_Exe-15-11-2004.zip)>, accessed 13/06/2018.
- GASEQ, 2005, A Chemical equilibrium program for Windows. <[www.c.morley.dsl.pipex.com](http://www.c.morley.dsl.pipex.com)>, accessed 13/06/2018.
- Knoef, H.A. M., Angrill, L.S., Bennekom, J., Bräkow, D., Blasi, C., Brown, R.C., 2012, *Handbook biomass gasification*. BTG Biomass Technology Group BV, Enschede, the Netherlands.
- Mittal, M., 2017, Explosion pressure measurement of methane-air mixtures in different sizes of confinement. *Journal of Loss Prevention in the Process Industries*, 46, 200-208.
- Seitz, S., Westphal, F., 2016, Design of Pressure Relief Devices for Chemical Reactors on the Basis of Adiabatic Tests – Is this always Conservative? *Chemical Engineering Transactions*, 48, 571-576.
- Skřínský J., Skřínská M., 2014, Calculation of maximum explosion pressure for gaseous C1-C3 oxidiser mixtures with different initial temperatures in a spherical closed volume. *CHISA*, 9, 2412.
- Skřínská M., Skřínský J., Dolníček P., Lukešová P., Přichystalová R., Serafínová C., 2015, BLEVE - Cases, Causes, Consequences and Prevention, *Material Science Forum*, 811, 91-94.
- Skřínský J., Vereš, J., Peer, V., Friedel, P., Travníčková, J., Dalecká, J., 2016, Explosion parameters of Coke oven gas in 1 m<sup>3</sup> explosion chamber, *Chemical Engineering Transactions*, 53, 7-12.
- Wang, Z.R., Ni, L., Liu, X., Jiang, J.C., Wang, R., 2014, Effects of N<sub>2</sub>/CO<sub>2</sub> on explosion characteristics of methane and air mixture, *Journal of Loss Prevention in the Process Industries*, 31, 10-15.