CHEMICAL ENGINEERING TRANSACTIONS

VOL. 53, 2016

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

Guest Editors: Valerio Cozzani, Eddy De Rademaeker, Davide Manca

ISBN 978-88-95608-44-0; **ISSN** 2283-9216

DOI: 10.3303/CET1653002

Explosion Parameters of Coke Oven Gas in 1 m^3 Explosion Chamber

Jan Skrinsky*, Jan Veres, Vaclav Peer, Pavel Friedel, Jana Travnickova, Andrea Dalecka

Energy Research Center, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava - Poruba
jan.skrinsky@vsb.cz

Coke oven gas is highly rated as a valuable by-product of coal carbonization to produce coke in the steel industry. For the assessment of process hazards and the safe design of process equipment handling coke oven gas, the knowledge of safety parameters, such as maximum pressure, maximum rate of pressure rise and burning velocity, is required. In this work, the explosion behavior of coke oven gas/air mixtures is studied. Experimental tests are carried out in a 1 m^3 closed explosion chamber adopted for the explosion tests.

1. Introduction

All process industry accidents fall under three broad categories fire, explosion, and toxic release. Of these fire is the most common, followed by explosions. Within these categories explosion make the immediate damage potential (Skřínská et al., 2015). Coke oven gas (COG) is highly rated as a valuable by-product of coal carbonization to produce coke in the steel industry. Typically, a single ton of coke generates approximately 360 m^3 COG (Razzaq al., 2013). Although COG is regarded as a non-standard gaseous fuel, it still has a reasonable energy content and calorific value, which depend on the nature of coal and the type of carbonization and have been widely used together with blast furnace gas and converter gas in the steel industry in Moravian-Silesian region of Czech Republic.

1.1 Coke oven gas

COG, sometimes simply called ‘‘coke gas,’’ is a by-product of the coke-making process, where volatile coal matter is generated as COG, leaving carbon intensive coke behind. Coke is a very strong macro-porous carbonaceous material produced by the carbonization of a specific coal grade or of different coal blends at temperatures 1400 K. Approximately 90% of coke produced from blends of coking coals is used to maintain the iron production process in a blast furnace (Xianga et al., 2015).

1.2 Gas explosion severity parameters

COG is a flammable and explosive substance. Gas explosion severity parameters are the explosion pressure, P_{exp}, defined as the highest pressure reached during an explosion in a closed volume at a given fuel concentration, and the maximum explosion pressure, P_{max}, found as the highest P_{exp} over the flammable range. The maximum pressure rise rate, dP/dT_{max}, during gas explosions in enclosures and the deflagration index, K_{st}, are important explosion characteristics of premixture. 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. Beyond safety devices, the values of these parameters are useful for emergency planning especially for developing scenarios where emergency relief or external heat transfer may be inadequate.

1.3 Previous studies

Few data at standard conditions are available in open literature. As reported in literature (Zhang et al., 2013), measurements of COG explosion parameters were performed in 20 L stainless steel cylinder. The maximum explosion pressure and the maximum rates of pressure rise reach maximum around the stoichiometric concentration of 20 vol. %. Otherwise, they tend to decrease if their concentration is lower or higher than the

Please cite this article as: Skrinsky J., Veres J., Peer V., Friedel P., Travnickova J., Dalecka A., 2016, Explosion parameters of coke oven gas in 1 m3 explosion chamber, Chemical Engineering Transactions, 53, 7-12 DOI: 10.3303/CET1653002

stoichiometric concentration. In the presented paper these characteristics have been systematically examined and determined in the ISO 1 m^3 explosion chamber for the first time.

2. Experiment

2.1 Experimental device

For years the 1 m^3 has been considered the “gold standard” for combustible gas explosion testing. The first part of this article is the description of the heated 1 m^3 explosion chamber (OZM Research s.r.o., Czech Republic) situated at ERC, VŠB-TU Ostrava, and its evaluation by $CH_4/O_2/N_2$ and $H_2/O_2/N_2$ gas mixtures. The 1 m^3 explosion chamber is described in Figure 1.

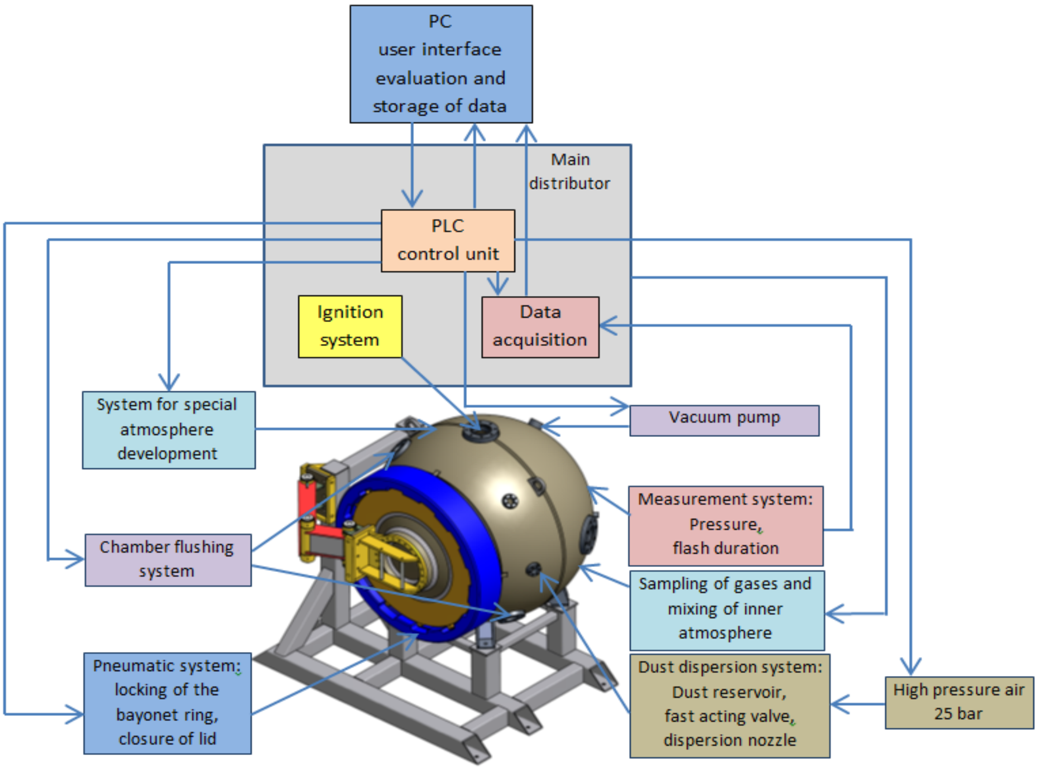

Figure 1: General diagram of the testing system adopted for the COG/O2/N2 tests.

The spherical explosion chamber with the internal volume of 1 m3 allows the measurement of parameters of explosive gas dispersion in accordance with the terms and specifications in EN 1839. In comparison with conventional 1 m3 vessel, a new 1 m3 vessel allows the measurement of gases, dust dispersions and liquid vapour at the same time. The present part focused on description for measurement of gaseous COG mixture. The mixing process proceeds inside the explosion chamber. The gases are dosed into the chamber from the dosing vessel equipped by three inputs for connection to cylinders with nitrogen and oxygen and line for free suction of air from outside. The ignition source is located in the geometrical centre of the cylinder. In the experiment, ignition was performed with hot wire between stainless steel electrodes. Explosion tests have been performed at different initial concentration of COG with the air at standard initial temperature and pressure (T_{init} = 298.15 K, P_{init} = 1 bar). The $CH_4/O_2/N_2$ and $H_2/O_2/N_2$ mixtures were obtained by using the partial pressure methodology. After vacuum, the combustion vessel was filled by injecting one mixture component. For validation tests the Siad gases have been used (purity above 99.9 vol. % for both CH_4 and H_2 fuel). 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 closing in the shape of spherical segments. Lock is locking by hydraulic actuator with safety position sensing "locked." Explosion chamber is made of structural steel. The material and components comply with the use of equipment for experiments at atmospheric initial pressure and initial laboratory temperature (15-30 °C). The system is sealed to the extent that the occurrence of an explosive atmosphere during normal operation outside the delivered system is not supposed. The chamber is also equipped by the glass window to allow a monitoring of the processes inside the chamber by camera.

The explosion chamber is equipped with measurement of time depended dynamic pressure using two pressure sensors (Kistler type 701A, accuracy: 0.00125 MPa), data rate acquisition system (sampling data rate: 400 ks/s, 4 channels) and also by 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. Pressure range is up to 25 MPa calibrated for the range up to 2.5 MPa. Working temperature is up to 200 °C. The entire control of explosion chamber and management of the experiments is concentrated in the main distributor. Control of the mechanical parts of the chamber, dispersing system control, ignition system, the system for the preparation of initial internal atmospheres other than air, including homogenization, data acquisition system to record the data will be connected to the main distributor. Control will be ensured through the programming logic controller (PLC) Siemens S7-1200 (high-speed counters, 1 MHz). The signals from the main distributor are transmitted to the auxiliary distributor located directly on the chamber stand. This auxiliary distributor is used to distribute the signals to individual action elements. The control program contains a procedure enabling the evaluation of the measured data and generating output protocol. Evaluation of pressure curves in terms of the maximum achieved pressure, maximum rate of pressure rise and duration of a flash is done automatically. The evaluation of a whole series of tests with a single dust will be done for the output protocol and values P_{max} and $(dp/dt)_{max}$ are recorded together with the concentration at which the maximum values were reached.

2.2 Coke oven gas used in the experiment

The gases used in the experiment included coke oven gas (main components given in Figure 2 and Table 1), air (O_2 and N_2). The compositions of coke oven gas for the experiments are taken from the month averages of real coke oven gas concentration from industrial by-product of coal carbonization.

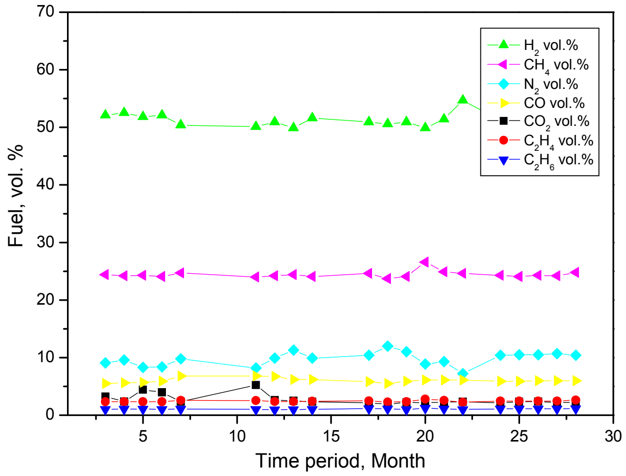

Figure 2: Relationship between the individual ingredients vol.% concentration in coke oven gas produced in Moravian-Silesian region of Czech Republic.

Table 1: The average compositions of coke oven gas for the experiments

Ingredients	H_2	CH_4	CO	C_2H_6	C_2H_4	CO_2	N_2
Content %	51.2	24.4	6.0	1.2	2.4	2.6	12.2

COG–air mixtures were obtained by the partial pressure method in gas cylinders and were ignited at once after mixing the components. The experimental procedure was as follows: (a) the air in the explosion vessel was evacuated to a vacuum of 0.1 mbar; (b) mixing gases were added into the vessel at different ratios; (c) the mixture was admitted at the desired pressure, then ignited at once; (d) after ignition and the capture of the signals by the acquisition system; (e) the burned gas was completely evacuated. Then, a new cycle was repeated.

3. Results and discussion

In the following, the experimental results on coke oven gas explosion severity parameters are presented.

3.1 Maximum explosion pressure

The adiabatic pressure, P_{ad}, calculated by GASEQ is shown as the approximate prediction for the maximum explosion pressure, P_{max}, from experiments. Explosion pressures are calculated using the species and their thermodynamic values from the GRIMECH 3.0. The discrepancy between the results of experiment and calculation mirrors the degree of conversion of the initial mixture and the degree the explosion can be considered adiabatic. Efforts were made to identify the main cause of the discrepancy in the combustion regimes of pure $CH_4/O_2/N_2$ and $H_2/O_2/N_2$mixtures and $COG/O_2/N_2$.The pressure histories of $COG/O_2/N_2$ mixture for the ten analyzed fuel concentrations are shown in Figure 3.

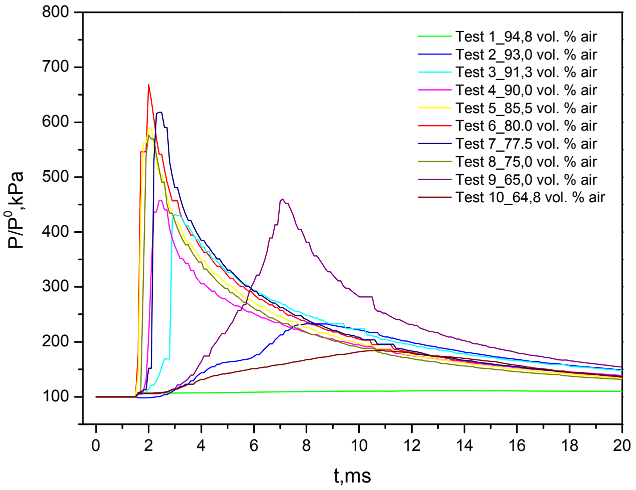

Figure 3: Relationship between the maximum explosion pressure of coke oven gas and its concentration.

Figure 3 shows that the measured explosion pressure increases with the increase of initial fuel concentration from 64.8 vol.% up to 80.0 vol.% (peak explosion pressure). From 80.0 vol.% of COG this trend reversed up to the upper explosion limit (between 93.0 and 94.8 vol.% of COG).

3.2 Deflagration index and maximum rate of pressure rise

The maximum pressure rise rate during gas explosions in enclosures, $(dP/dt)_{max}$, and the deflagration index, K_G, are important explosion characteristics of premixture. They are used to quantify the potential severity of an explosion. The maximum pressure rise rate, $(dP/dt)_{max}$, depends not only on the mixture properties (such as mixture composition, initial temperature and initial pressure) but also on the volume of the vessel in which gas explosion takes place. Unlike $(dP/dt)_{max}$, the deflagration index is an intrinsic property of the premixture and it is independent of the volume of the vessel used in experimental measurements. The relationship between K_G and $(dP/dt)_{max}$ is given by Eq(1):

$$K_G = \left(\frac{dP}{dt}\right)_{max} V^{1/3} = (36\pi)^{1/3}(P_{max} - P_0)\left(\frac{P_{max}}{P_0}\right)^{1/\gamma} S \tag{1}$$

in which K_G is the deflagration index (bar.m/s), V is the vessel volume (m^3), $(dP/dT)_{max}$ is the maximum rate of pressure rise (bar/s), P_{max} is the maximum explosion pressure (bar), P^0 is the initial pressure (bar), and γ the adiabatic coefficient of the unburned gas (-).

3.3 Burning velocity

In order to capture the intrinsic reactivity of COG/mixture, the burning velocity has been obtained from time pressure records of explosions occurring in 1 m^3 closed explosion chamber. In (Dahoe, 1996), the burning velocity has been calculated from the pressure time history by using the time derivative of flame radius, r_f, as given by the correlation in Eq(2):

$$r_f = \left(\frac{3V}{4\pi}\right)^{1/3}\left[1 - \left(\frac{P^0}{P}\right)^{1/\gamma}\left(\frac{P_{max}-P}{P_{max}-P^0}\right)\right]^{1/3} \tag{2}$$

in which r_f is the flame radius (m), V is the vessel volume (m^3), P^0 is the initial pressure (bar), P is the actual pressure (bar), P_{max} is the maximum explosion pressure (bar) and γ the adiabatic coefficient of the unburned gas (-).

$$s = \frac{1}{(P_{max}-P^0)}\frac{1}{3}\left(\frac{4\pi}{3V}\right)^{-1/3}\left(\frac{P}{P^0}\right)^{1/\gamma}\left[1-\left(\frac{P}{P^0}\right)^{1/\gamma}\left(\frac{P_{max}-P}{P_{max}-P^0}\right)\right]^{-2/3}\frac{dP}{dt} \tag{3}$$

in which s is burning velocity (m/s), r_f is the flame radius (m), R is specific gas constant (J/kg.K), V is the vessel volume (m^3), P^0 is the initial pressure (bar), P is the actual pressure (bar), P_{max} is the maximum explosion pressure (bar), γ the adiabatic coefficient of the unburned gas (-) and dP/dT is the rate of pressure rise (bar/s).

Tables 2-3 give the results for $CH_4/O_2/N_2$ and $H_2/O_2/N_2$ mixtures compositions adopted in the validation explosion tests. EN 15967

Table 2: Measured explosion parameters for $CH_4/O_2/N_2$ mixtures of various compositions

Test (-)	Fuel (vol.%)	Air (vol.%)	P_{ad} (bar)	P_{max} (bar)	P_{ad}- P_{max} (bar)	T_{Pmax} (ms)	$(dP/dT)_{max}$ (bar/s)	s_l (m/s)
1	4.0	96.0	5.05	1.81±0.036	3.23	7.87	0.49±0.497	0.09
2	5.0	95.0	5.83	3.39±0.067	2.44	8.27	2.46±0.246	0.09
3	5.2	94.8	5.97	4.48±0.089	1.48	5.62	2.43±0.243	0.05
4	6.5	93.5	6.86	5.54±0.110	1.31	3.38	5.51±0.551	0.07
5	8.4	91.6	7.95	7.89±0.159	0.05	2.24	63.32±6.332	0.42
6	**10.5**	**89.5**	**8.74**	**8.42±0.168**	**2.24**	**2.17**	**76.96±7.696**	0.45
7	11.0	89.0	8.84	6.59±0.131	2.24	2.62	9.31±0.931	0.09
8	12.8	87.4	8.61	6.04±0.120	2.82	3.50	4.61±0.461	0.05
9	14.8	85.2	8.59	5.62±0.112	2.96	5.19	3.44±0.344	0.04
10	15.6	84.4	8.47	5.22±0.104	3.25	6.75	3.07±0.307	0.05

Table 3: Measured explosion parameters for $H_2/O_2/N_2$ mixtures of various compositions

Test (-)	Fuel (vol.%)	Air (vol.%)	P_{ad} (bar)	P_{max} (bar)	P_{ad}- P_{max} (bar)	T_{Pmax} (ms)	$(dP/dT)_{max}$ (bar/s)	s_l (m/s)
1	5.0	95.0	2.76	1.67±0.033	1.08	9.72	0.42±0.042	0.10
2	10.2	88.8	5.30	4.40±0.088	0.89	1.72	45.11±4.511	1.03
3	16.0	84.0	6.75	5.90±0.118	0.84	1.09	226.95±22.695	2.92
4	20.0	80.0	7.60	6.91±0.138	1.69	1.03	524.11±52.411	5.00
5	26.0	74.0	8.60	7.77±0.155	0.82	0.99	842.30±84.230	6.45
6	**29.0**	**71.0**	**8.92**	**8.01±0.160**	**0.90**	**0.98**	**927.77±92.777**	**6.72**
7	30.0	70.0	8.91	7.95±0.159	0.95	0.98	922.72±92.272	6.78
8	35.0	65.0	7.95	7.82±0.156	0.12	0.98	918.10±91.810	6.95
9	37.2	62.8	7.86	7.56±0.151	0.29	1.28	675.28±67.528	5.44
10	45.0	55.0	7.38	6.92±0.138	0.45	1.50	659.29±65.921	6.27

Table 4: Measured explosion parameters for $COG/O_2/N_2$ mixtures of various compositions

Test (-)	Fuel (vol.%)	Air (vol.%)	P_{ad} (bar)	P_{max} (bar)	P_{ad}- P_{max} (bar)	T_{Pmax} (ms)	$(dP/dT)_{max}$ (bar/s)	s_l (m/s)
1	5.2	94.8	4.01	1.04±0.020	2.97	12.87	0.34±0.034	1.83
2	7.0	93.0	4.87	2.36±0.047	2.51	7.75	0.62±0.062	0.05
3	8.7	91.3	5.62	4.30±0.086	1.32	4.01	3.22±0.032	0.07
4	10.0	90.0	6.15	5.45±0.109	0.69	2.04	17.90±1.790	0.24
5	15.0	85.0	7.85	7.57±0.151	0.27	1.50	178.51±17.851	1.28
6	**20.0**	**80.0**	**8.58**	**8.19±0.163**	**0.39**	**1.50**	**180.12±18.012**	**1.11**
7	22.5	77.5	8.47	7.84±0.156	0.63	1.70	97.15±9.715	0.65
8	25.0	75.0	8.25	7.00±0.140	1.25	1.99	41.78±4.178	0.35
9	35.0	65.0	7.02	4.45±0.089	2.57	6.84	26.94±2.694	0.55
10	35.2	64.8	6.59	1.72±0.034	4.87	10.85	0.47±0.047	0.10

Table 2-4 gives the maximum explosion pressure, P_{max}, (and the corresponding time, t_{Pmax}) for all tests. In the table, the adiabatic pressure (i.e., the maximum theoretical pressure), P_{ad}, is also reported along with the difference P_{ad} - P_{max}. For each fuel composition (i.e., for each fuel composition), P_{max} increases as the initial fuel concentration increases. This trend reflects the increase of P_{ad} with P^o. Owing to heat losses towards the external environment, P_{max} remains lower than P_{ad}. However, the difference P_{ad} - P_{max} decreases with increasing fuel content in the mixture). This suggests that the faster reactivity induced by the hydrogen presence reduces the effect of heat losses on the explosive process. For each value of P^o, minimal differences are observed among the values of P_{ad} and, thus, P_{max} obtained for different fuel compositions. Calculated explosion pressures predictions show a reasonable agreement at the near stoichiometric concentrations. Outside this range the agreement becomes poor, the deviations from the measured values increase when the flammability limits are approached. In all cases, the experimental explosion pressures remain below the calculated values. Based on the pressure time traces three regimes of explosion development or combustion conversion can be identified. In the first one, the pressure increases fast and smoothly to the maximum value, after ignition. This type of pressure development is seen for near-stoichiometric mixtures. Such type of pressure development is present in a narrow fuel lean concentration range and in a wider concentration range with fuel rich mixtures. In the third regime the shoulder disappeared, and the increases are low and slow (Pekalski et al., 2005). From Table 2-4 for $(dP/dT)_{max}$ it can be seen (dP/dt) increases monotonically with P_{max}.

4. Conclusions

Scientific achievements of this article are new 1 m^3 experimental set-up description, validation and determination of COG explosion parameters at ambient conditions. Explosion tests were performed in a closed cylindrical 1 m^3 explosion chamber. Both gas explosion severity parameters and burning velocity have been determined. This work is aimed at fundamentally improving the understanding of gas phase oxidation processes of hydrocarbons mixtures, the risk assessment of such processes, their environmental efficiency and safety (Skřínský et al, 2015). In chemical industry it refers to large-scale hydrocarbon (partial) oxidation processes. These processes form the basis of much of the (petro-) chemical process industry. These activities are of great importance to the improvement and extension of the applicability of standards for the determination of explosion indices such as the maximum explosion pressure, maximum rate of pressure rise and burning velocity. The obtained data allow further advancements on safety for the use of gas fuels mixtures similar to COG.

Acknowledgments

This work would not have been possible without the financial support of Innovation for Efficiency and Environment - Growth, reg. no. LO1403 supported by National Programme for Sustainability and financed by the Ministry of Education, Youth and Sports.

Reference

Skřínská, M., Skřínský, J., Dolníček, P., Lukešová, P., Přichystalová, R., Serafínová, C., 2015, BLEVE Cases, Causes, Consequences, and Prevention, Materials Science Forum, 811, 91-94.

Razzaq R., Li C., Zhang S., 2013, Coke oven gas: Availability, properties, purification, and utilization in China, Fuel, 113, 287–299.

Xianga D., Yanga S., Maia Z., Qiana Y., 2015, Comparative study of coal, natural gas, and coke-oven gas based methanol to olefins processes in China, Computers and Chemical Engineering 83, 176–185.

Zhang Z. Lin B., Li G., Ye, Q., 2013, Coke oven gas explosion suppression, Safety Science 55, 81–87.

EN 15967, 2012. Determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapours. European Standard, Beuth Verlag, Berlin Wien Zurich.

GASEQ, A Chemical Equilibrium Program for Windows. Available at: <http://www.c.morley.dsl.pipex.com/> accessed 15. 3. 2016.

Dahoe A. E., Zevenbergen J.F., Verheijen P.J.T., Lemkowitz S.M., Scarlett B., 1996, Dust explosion in spherical vessels: The role of flame thickness in the validity of the ‘cuberoot law,’, J. Loss Prev. Process Ind. 9, 33-44.

Pekalski A. A., Schildberg H. P., Smallegange P. S. D., Lemkowitz S. M., Zevenbergen J. F., Braithwaite M., Pasman H. J., 2005, Determination of the Explosion Behaviour of Methane and Propene in Air or Oxygen at Standard and Elevated Conditions, Process Safety and Environmental Protection, 83(B5), 421–429.

Skřínský, J., Vereš, J., Trávníčková, J. Dalecká, A. Explosions caused by corrosive gases/vapors, Materials Science Forum, 844, 65-72.