Explosion characteristics of synthesised biogas at various temperatures

L. Dupont *, A. Accorsi

Institut National de l'Environnement Industriel et des Risques, Parc Technologique Alata, BP2, Verneuil-en-Halatte, France

Abstract

Biogas is considered as a valuable source of renewable energy. Indeed, it can be turned into useful energy (heat, electricity, fuel) and can contribute to reduce greenhouse gas emissions. Knowledge of its safety characteristics is a very important practical issue. Experimental investigation of synthesised biogas explosion characteristics was conducted in a 20-L sphere at various temperatures (30–70 °C) and at atmospheric pressure. The studied biogas was made of 50%[1] methane (CH_4) and 50% carbon dioxide (CO_2). It was also saturated with humidity: this composition is frequently met in digesters during waste methanisation. There are two inert gases in biogas: water vapour and carbon dioxide. Its vapour water content rises along with temperature. The presence of these inert gases modifies considerably biogas characteristics compared to the ones of pure methane: explosion limits are lowered and beyond 70 °C, water vapour content is sufficient to inert the mixture. Furthermore, explosion violence (estimated with the maximum rate of pressure rise values, $(dp/dt)_{max}$) is three times lower for biogas than for pure methane at ambient temperature.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Biogas; Explosion characteristics; Explosion limits; Explosion pressure; Rate of pressure rise

1. Introduction

Biogas results from the anaerobic digestion of organic matter (domestic waste, purification water treatment sludge, agricultural effluents, . . .).

There are two main types of biogas: "landfill gas", which is formed spontaneously in domestic waste landfills and "digester gas", which is induced in bioreactors or digesters.

For environmental reasons waste methanisation has been growing for the last years to upgrade domestic solid waste: output biogas is clean (when sulfur compounds are removed) and useful. Organic matter undergoes a step-by-step degradation (hydrolysis, acidogenese, methanogenese), and thus becomes more easily assimilable by micro-organisms.

According to thermal conditions, different micro-organisms are responsible for the methanisation process: psychophilic below 20 °C, mesophilic between 20 and 45 °C or thermophilic beyond.

So, there is a great variability in biogas composition. However, it is mainly composed of methane (CH_4) and carbon dioxide (CO_2).

Due to the presence of methane, biogas is a combustible gas. Thus, its handling can cause fire and explosion hazards. These hazards can be found not only nearby waste discharges or digesters but also at remote distances because of lateral migration. Hence it is fundamental to know biogas explosivity characteristics in order to undertake adequate risk assessment and to run biogas plants safely.

Today biogas characteristics are assumed to be similar to those of methane [1]. This assumption can hardly complicate explosive atmospheres prevention and protection measures: for example, it is sometimes impossible to apply reasonable explosion vent sizing when methane explosive characteristics rather than those of biogas are used.

The aim of this study is to measure experimentally explosion characteristics (explosion limits LEL and UEL, maximum explosion pressure p_{max} and maximum rate of pressure rise $(dp/dt)_{max}$) of quiescent synthesised biogas/water saturated air mixtures at atmospheric pressure and from ambient temperature up to 70 °C in a 20-L sphere device.

The detailed knowledge of the explosivity region as a function of the fuel, air and diluent ratios is fundamental for

---

* Corresponding author. Tel.: +33 3 44 55 66 46; fax: +33 3 44 55 65 65.
E-mail addresses: laurent.dupont@ineris.fr (L. Dupont),
antoinette.accorsi@ineris.fr (A. Accorsi).

[1] All gas and vapour concentrations are given in vol.%.

the prevention of explosion and fire hazards: the triangular flammability diagram helps to determine for which ratio a mixture is flammable. This diagram shows the flammability envelope.

Maximum explosion pressure and maximum rate of pressure rise are both useful, either for sizing protection systems such as vents or to estimate the required structural resistance of a confined enclosure in which a deflagration can occur.

Table 1
Water vapour concentration (%) of the tested mixtures

20 °C	2.3
30 °C	4.2
40 °C	7.4
50 °C	12.3
55 °C	15.7
60 °C	19.9
70 °C	31.2

2. Experimental

2.1. Experimental apparatus and procedures

Fig. 1 shows a schematic diagram of the experimental 20 L Spherical Explosion Vessel (20-L sphere) in accordance with prEN 14460 and EN 1839 [12,13]. This stainless steel 20-L sphere was purchased from Adolf Kühner AG. It can withstand a maximum pressure of 40 bar. Test mixtures were prepared by the mixing flows method: methane, carbon dioxide and air were released by means of three mass flow controllers.

Glass evaporator tube is surrounded by an helical electrically heated steel tube. The gas mixture carries water into the tube, where it is vaporised. The saturated mixture is then fed into the sphere. The 20-L sphere is heated up at the required temperature with a water jacket. The entire sphere is isolated to prevent water condensation. Before each test the sphere is emptied and purged 10 times with the saturated mixture. The ignition system is an electrical arc generated by a fusing wire located at the centre of the sphere. It delivers an ignition energy of 20 J. This energy level is sufficient to ignite all potentially explosive atmosphere and to avoid any effect of pressure rise inside the sphere.

Pressure is recorded during the tests with two independent piezo-electrical pressure transducers.

The explosion criterion is a measured pressure rise above 50 mbar after the ignition in accordance with EN 1839.

2.2. Gas composition

Biogas composition depends considerably on waste nature and processes and also varies in time. However, it is mainly composed with methane (CH_4) and carbon dioxide (CO_2) [1] in variable proportions between 50–60% of methane and 50–40% of CO_2.

It also contains traces of many other compounds, especially hydrogen sulfur (H_2S) or/and organosulphur (mercaptans) in small contents that do not significantly influence explosivity characteristics of biogas.

The studied synthesised biogas is composed of 50% of CH_4 and 50% of CO_2 and is water saturated. The vapour concentration matches the saturated vapour pressure. It is therefore growing along with temperature. Table 1 shows water vapour concentration in the mixtures over the temperature range.

Beyond carbon dioxide and water vapour, nitrogen in the air also contributes to inert the mixture. These inert gases can considerably lower the biogas explosivity.

The presence of multiple inerting agents hinders the prediction of the whole flammability envelope [2] since each inert gas has its own inerting power when mixed with methane.

Nowadays, no model is universally recognised to predict correctly the flammability envelope of such mixtures. Therefore, it is crucial to experimentally determine these data.

Inert gases are responsible for lowering explosivity characteristics by decreasing flame temperature below a certain threshold
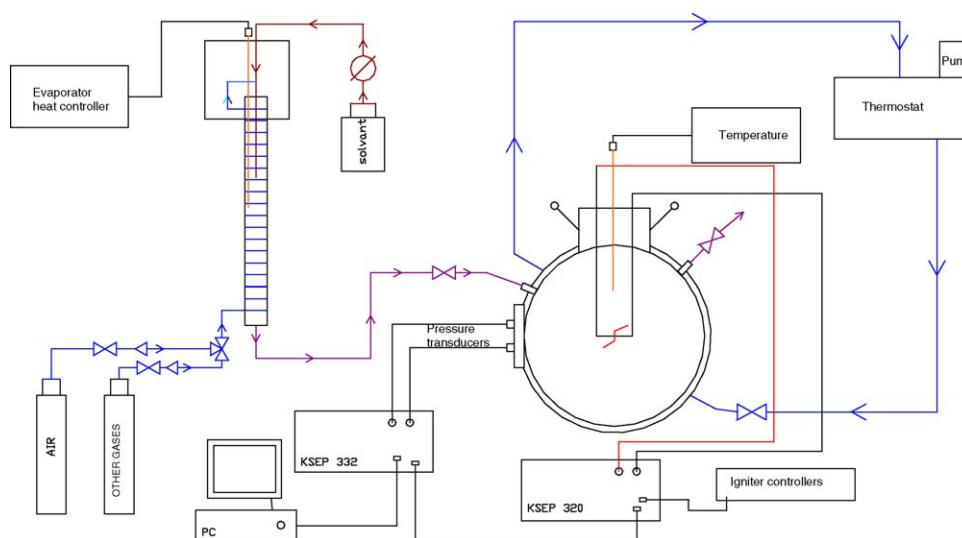

Fig. 1. Schematic diagram of the 20-L sphere apparatus.

Table 2
Thermal capacity C_p at 50 °C from diluent gases

Diluent gas	Thermal capacity C_p at 50 °C (J/mol/K)
CO_2	38.3
H_2O	33.7
N_2	29.1

value [3]. Their inerting ability depends on their heat capacity [4]. The inerting efficiencies of these diluents is as follow: $CO_2 > H_2O > N_2$ (Table 2). To compare and investigate the effect of the different inert gases on the explosivity characteristics, experiments were conducted with dry synthesised biogas at different temperatures. For each temperature level, CO_2 was added to the dry biogas/air mixture at a concentration equivalent to that of water vapour for saturated mixtures.

In this study, dry oil-free synthesised air was used. Commercial carbon dioxide and methane were used as inert gases. Gases purity was above 99.8%.

3. Results and discussion

3.1. Explosion limits and limiting oxygen concentration

The lower explosion limit (LEL) and the upper explosion limit (UEL) of methane, dry biogas, and vapour-saturated biogas were studied.

Most authors from the literature agree with Le Chatellier's Theory [4], which postulates that explosion limits rely on intrinsic mixture parameters. From this theory, flame propagates through a flammable mixture by thermal diffusion, heating the unburned gas up to a critical temperature, T_{inf}. T_{inf} corresponds to the ignition temperature of the mixture. Below this temperature unburned gases are too cold to allow the flame to propagate.

Explosion limits of the dry and the water-saturated biogas are shown in Fig. 2.

At 20 °C, the presence of CO_2 did not raise significantly the lower limit of pure methane: 5.2% in methane for water-saturated biogas versus 4.6% for pure methane. However, the upper limit is drastically reduced by the presence of CO_2: 11.4%

versus 16.8%. At this temperature the moisture influence is negligible.

As for methane [3] within this temperature range, an increase in temperature widens very slightly the explosion range of dry biogas. With increasing temperature, the moisture influence on the lower limit remains negligible while the upper limit is drastically reduced. On one hand, it is well known that explosion range widens with increasing temperature by reduction of LEL and by increase of UEL [4]. This influence of temperature variation on explosion range of methane/air mixture was extensively studied by Coward and Jones [3].

On the other hand, it is also well known that addition of inert gases shortens LEL and UEL of fuel–air mixture [3] by reducing the burning velocity.

In our case, the presence of CO_2 in biogas cools the methane/air flame. Furthermore, as the temperature increases, the water vapour concentration rises. These conditions should shorten the explosion range. In opposition temperature rise can counterbalance this decrease. Thus, temperature rise has a double and contradictory influence on explosion limits.

In water-saturated biogas/air mixture there are simultaneously three inert gases, N_2 from the air, water vapour and CO_2 contained in the biogas.

These contradictory effects of inert gases and temperature rise are illustrated in Fig. 2.

There is a progressive dilution of the biogas-air mixture with water vapour or CO_2. When oxygen concentration is less than a critical value, known as the limiting oxygen concentration (LOC), the reaction cannot generate enough energy to heat up the surrounded gas mixtures to allow the propagation of a self-sustained flame [5,6].

Fig. 3 shows the influence of temperature rise on explosion limits for water-saturated biogas and dry biogas with added CO_2. As mentioned before, for a given temperature, the added CO_2 concentration is equivalent to the saturated water vapour concentration. So, except the nature of the inert gas, compositions of both mixtures are identical at each test temperature. One should note that the dry biogas with added CO_2 corresponds to a simple CH_4/CO_2 mixture.
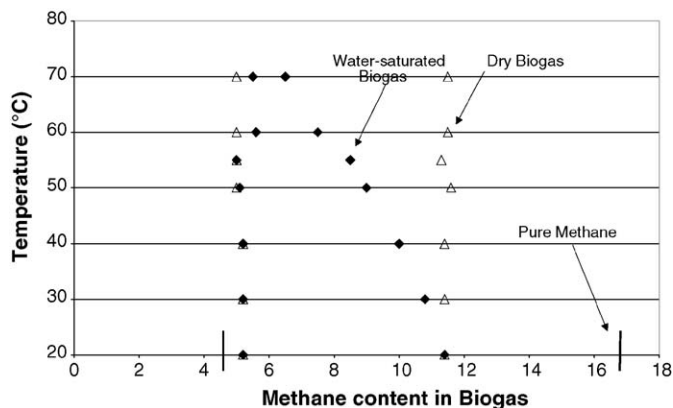

Fig. 2. Influence of temperature and humidity on the flammability limit of the biogas (50 vol.% methane and 50 vol.% CO_2) at atmospheric pressure.
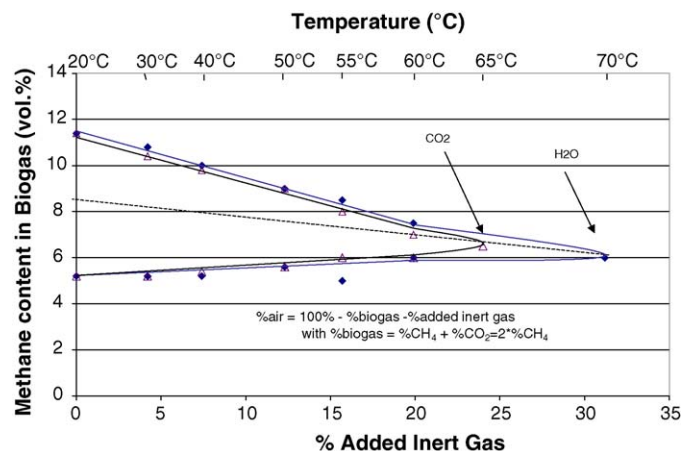

Fig. 3. Explosion diagram of vapour-saturated biogas and dry biogas/CO_2 mixtures at atmospheric pressure for various temperatures.

Table 3
Experimental LOC of vapour-saturated biogas and dry biogas/CO_2 mixtures

	Vapour-saturated biogas/air ($CH_4/CO_2/H_2O$/air)	Dry biogas/air/CO_2 (CH_4/CO_2/air)	
		This work	Zabetakis
LOC (%)	11.1	13.2	13.4
Corresponding temperature (°C)	70	65	20
Equivalence ratio	1.0	1.0	1.1

Coordinates of both axis from Figs. 2 and 3 represent temperature versus volumetric percentage of the methane content in biogas or the added inert gas (H_2O or CO_2) in the whole mixture. The dashed line in Fig. 3 corresponds to the stochiometric mixtures.

The vapour-saturated biogas mixture is not flammable beyond 70 °C, which corresponds to a water vapour concentration of 31.2%. At this temperature, only a 6% in methane of biogas mixture is flammable with a small explosion pressure p_{max} (2.5 bar). Results are presented in Table 3.

Carbon dioxide is clearly more effective in inerting the mixture than water vapour. Beyond 24% CO_2 none of the mixtures are flammable whatever the fuel content.

Table 3 shows the LOC for the two studied mixtures. The LOC for the dry biogas/air/CO_2 mixture is compared with literature data reported by Zabetakis [7]. Data were obtained using the explosion burette method of US Bureau of Mines. The LOC determined in this study agrees well with there results.

3.2. Maximum explosion pressure (p_{max}) and maximum rate of explosion pressure rise (dp/dt)$_{max}$

Figs. 4 and 5 show, respectively, explosion pressure (p_{ex}) and rate of pressure rise curves (dp/dt)$_{ex}$ for the water-saturated biogas at studied temperatures. These curves go through a maximum which corresponds to p_{max} and (dp/dt)$_{max}$. These peak values are obtained for the same concentration, slightly above stochiometry.

We did not use the deflagration index K_G, often used in similar studies: K_G is deemed to be a normalised volume-independant
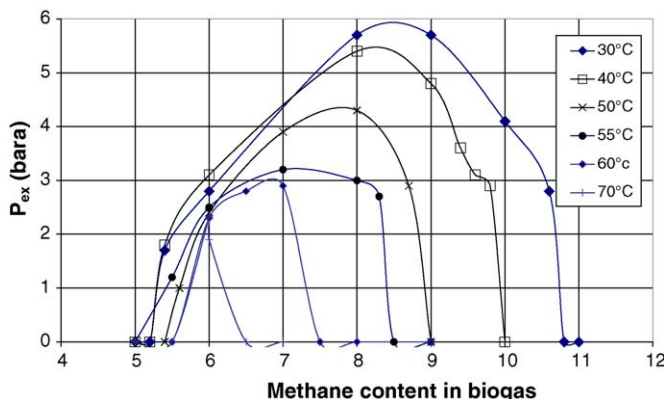

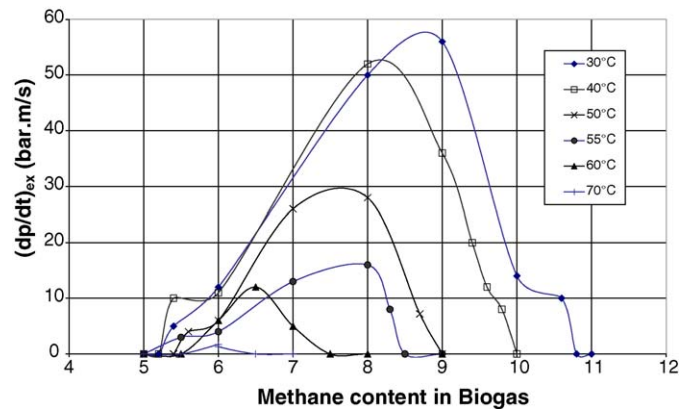Fig. 4. Explosion pressure of vapour-saturated biogas at different temperatures.

Fig. 5. (dp/dt) for vapour-saturated biogas at different temperatures.

explosion pressure rise value. Based on experimental measures, it is calculated from the following formula:

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

However, some authors [8,9] recently found that K_G values increase with vessel size. Consequently, (dp/dt)$_{max}$ is solely used in this study to compare explosion violence among mixtures. We can note that K_G is still referred in international standards (NFPA 68 and prEN 14994) for gas deflagration venting.

Mashuga and Crowl [10] demonstrated that (dp/dt)$_{max}$ is very sensitive to parameters like relative humidity or turbulence: they conducted experiments at 25 °C in a 20-L vessel with near stochiometric mixtures of methane and humidified air and found a difference of 52 bar m/s between the dry mixture (276 bar m/s) and the moist mixture (224 bar m/s at 90% relative humidity), while p_{max} was almost not affected by humidity.

Turbulence can be responsible for a very significant (dp/dt)$_{max}$ rise: (dp/dt)$_{max}$ of turbulent pure methane is almost 10 times higher than those of quiescent pure methane [11]. This influence emphasises the need to adequately control turbulence in test vessels before ignition. Effect of turbulence is not taken into consideration into current standards (prEN 14994).

Shift between the curves comes from the stochiometric evolution of mixtures when adding water vapour. Explosion violence was considerably reduced when increasing water vapour content along temperature rise as shown in Fig. 4. It should be noted that the total initial moles number in the sphere decreases with increasing temperature: it also contributes, but to a small extent, to the reduction of the explosion violence.

At temperature close to ambient, we measured a low (dp/dt)$_{max}$ value compare to that of pure methane. Such a low (dp/dt)$_{max}$ value illustrates a low and moderate explosion violence. Besides, illustrates a rapid and important decrease in (dp/dt)$_{ex}$ along with temperature rise. Beyond 55 °C (dp/dt)$_{max}$ is down to a value as low as 4 bar m/s. Trends of (dp/dt)$_{max}$ decrease is much more pronounced than decrease in p_{max} along with temperature increase.

Figs. 6 and 7 illustrate p_{max} and (dp/dt)$_{max}$ variation versus temperature for pure methane, dry biogas, dry biogas
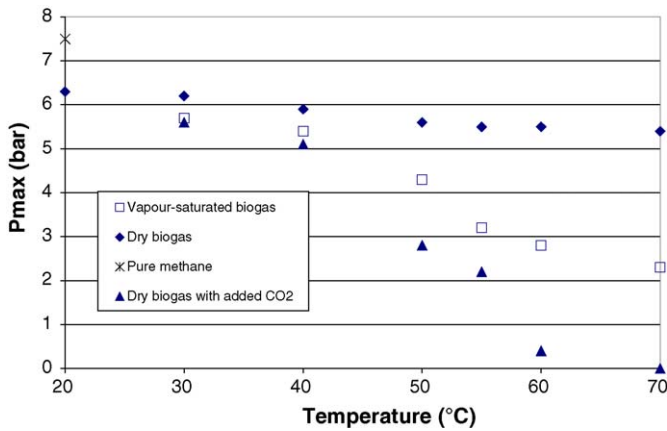
Fig. 6. p_{max} for pure methane, dry biogas, dry biogas with added CO_2 and vapour-saturated biogas at studied temperatures.
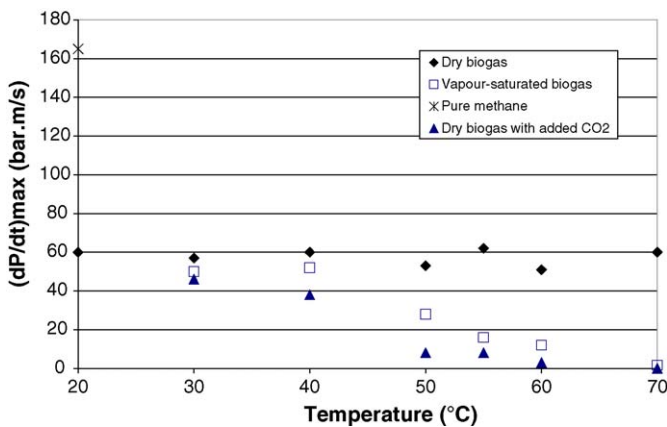

Fig. 7. $(dp/dt)_{max}$ of pure methane, dry biogas, dry biogas with added CO_2 and vapour-saturated biogas at studied temperatures.

with added CO_2 and vapour-saturated biogas at different temperatures.

Dry biogas is far less explosive than pure methane: $(dp/dt)_{max}$ is almost three times lower when CO_2 is added and p_{max} is approximately 1 bar lower. These parameters are crucial for vent sizing: when water saturated biogas is handled vents surface can be much smaller for protecting enclosures than when pure methane is handled.

Increase in temperature reduces slightly p_{max} (1 bar over the studied temperature range) and has practically no effect on $(dp/dt)_{max}$ for the dry biogas.

The addition of inert gases (water vapour or CO_2) causes a significant fall in explosion violence compared with pure dry biogas as shown in Figs. 6 and 7. This is particularly noticeable beyond 40 °C.

4. Conclusions

This paper reported experimental study results on explosion characteristics (explosion limits, LOC, p_{max}, $(dp/dt)_{max}$) of syn-

thesised biogas at atmospheric pressure between 20 and 70 °C in a 20-L sphere. Composition of synthesised biogas was 50% in methane and 50% in carbon dioxide. Water vapour content of the studied mixture increases along with temperature according to the saturated water vapour pressure curve.

The following conclusions have been reached:

(1) At ambient temperature whereas the LEL of the methane content in studied biogas is comparable to that of methane (5.1% versus 4.8% for pure methane), its UEL is significantly lower (11.4% versus 16.8% for pure methane).

(2) When temperature increases whereas biogas LEL remains nearly unchanged, biogas UEL decreases rapidly along with temperature rise.

(3) Beyond 70 °C, water vapour content is sufficient to inert the studied biogas. It becomes non-flammable. Since CO_2 is a better inert gas than H_2O the test mixture containing CO_2 is already inerted at 60 °C.

(4) Methane induces more violent explosions than biogas: $(dp/dt)_{max}$ is three times higher for methane than for biogas at ambient temperature.

(5) Finally, increase in temperature reduces considerably p_{max} and $(dp/dt)_{max}$ values for biogas.

This study demonstrated that biogas is responsible for less violent explosions than pure methane. As shown, explosion characteristics strongly decrease with temperature rise. These two safety characteristics are fundamentals for risk assessment and vents sizing.

Acknowledgment

References

[1] David J.V. Campbell, Explosion and Fire Hazards Associated with Landfill Gas. Landfilling of Waste: Biogas, E&FN Spon, 1996.

[2] J. Dwyer, J.G. Hansel, T. Philips, Temperature Influence on the Flammability Limits of Heat Treating Atmospheres, Air Products and Chemicals, Inc., 2003, pp. 1–5.

[3] H.F. Coward, G.W. Jones, Limits of Flammability of Gases and Vapors, Bureau of Mines, Bulletin 503, 1952.

[4] D. Drysdale, An Introduction to Fire Dynamics, second ed., John Wiley and Sons, 1999.

[5] D. Razus, M. Molnarne, O. Fuß, Limiting oxygen concentration evaluation in flammable gaseous mixtures by means of calculated adiabatic flame temperatures, Chem. Eng. Process. 43 (6) (2004) 775–784.

[6] D. Razus, M. Molnarne, O. Fuß, Evaluation of limiting oxygen concentration of fuel/air/inert gaseous mixtures by means of calculated adiabatic flame temperatures and measured fuel/air lower explosion limits, Chem. Eng. Trans. 3 (2003) 69–74.

[7] M.G. Zabetakis, Flammability Characteristics of Combustible Gases and Vapors, Bureau of Mines, Bulletin 627 (1965).

[8] A. Takahashi, Y. Urano, K. Tokuhashi, S. Kondo, Effect of vessel size and shape on experimental flammability limits of gases, J. Hazard. Mater. 105 (1–3) (2003) 27–37.

[9] Determination of the maximum explosion pressure and the maximum rate of pressure rise of gases and vapours, EN 13673, 2003.

[10] C.V. Mashuga, D.A. Crowl, Problems with identifying a standard procedure for determining K_G values for flammable vapors, J. Loss Prev. Process Ind. 13 (3–5) (2000) 369–376.

[11] A. Cleuet, P. Gros, Les mélanges explosifs—Gaz et vapeurs, poussières liquides et solides, INRS, 1994.

[12] Appareil résistant à l'explosion, PrEN 14460, 2002.

[13] Determination of explosion limits of gases and vapours, EN 1839, 2003.