Theoretical analysis of explosion behavior for CO/O2/N2, CO/O2/N2/H2O and CO/O2/N2/CO2 mixtures

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Teoretická analýza výbuchových charakteristik směsí $CO/O_2/N_2$, $CO/O_2/N_2/H_2O$ a $CO/O_2/N_2/CO_2$

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hořlavé látky   plyny   směsi   výbuchové charakteristiky   výbuchy   požáry

Abstract

Gas mixture explosions and fires are responsible for most of the largest property loss events worldwide in the chemical and power industry. In this contribution, a theoretical analysis was performed of explosion behavior for $CO/O_2/N_2$, $CO/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$ mixtures. Presented explosions based on real scenarios of accidents associated with transport and storage facilities with flammable chemicals. While explosions of pure flammable chemicals are well described in the literature, the information about explosions of toxic flammable substances is rather scarce. This work aims at studying the explosion behavior of pure mixture and of the inerted carbon monoxide-air mixtures at different initial temperatures and pressures. The results of mathematical modeling of the calculated maximum explosion pressure are presented.

Keywords: Gas explosion; Explosion modeling; CO

Abstrakt

Výbuchy a požáry hořlavých plynů v chemickém a energetickém průmyslu způsobují většinu z největších majetkových ztrát po celém světě. V tomto příspěvku je prezentována teoretická analýza chování výbuchu pro směsi $CO/O_2/N_2$, $CO/O_2/N_2/H_2O$ a $CO/O_2/N_2/CO_2$. Prezentovaná data k výbuchům jsou založena na základě reálných scénářů havárií spojených s dopravou a skladováním zařízení s hořlavými látkami. Zatímco výbuchy chemicky čistých hořlavých látek jsou v literatuře popsány velmi dobře, informací o výbuších toxických hořlavých směsí látek je poměrně málo. Tato práce je zaměřena na studium chování výbuchu čisté směsi a inertizované směsi $CO/O_2/N_2$ a vzduchu za různých počátečních teplot a tlaků. V příspěvku jsou vůbec poprvé prezentovány výsledky matematického modelování

maximálního výbuchového tlaku tohoto plynu.

Klíčová slova: Výbuchy plynů; Modelování výbuchů; CO

1. Introduction

Oxidation of solid, liquid and gaseous fuels either in oxygen atmosphere is surely attractive in the worldwide challenge for zero emission technology and in chemical process intensification. However, this opportunity raises several issues not only in terms of costs, but also in terms of safety. Indeed, in the case of loss of control, explosion consequences can be dramatic. Safety is a primary concern when dealing with flammable gases mixtures and the study of explosion pressures is an important consideration in addressing this issue (Lees, 2012). This work aims at studying the explosion behavior of $CO/O_2/N_2$ at different initial temperature and pressure and with one of two inerts H_2O (vapor) and CO_2 (gas). Nowadays, experimental tests are carried out in a closed cylindrical vessel. Experiments could be, however, expensive and time consuming, especially at elevated conditions of temperature and pressure, at which many industrial processes occur (Pekalski et al., 2005). Therefore, approximate calculation methods are being sought with which approximate values of explosion pressure can be calculated in reasonable time.

2. Analysis

Due to the complexity of the involved physical phenomena and to the lack of an adequate amount ofreliable experimental data, a number of different models and calculation procedures for estimating the physical consequences following the physical explosion of a gaseous state are presently reported in the literature. Due to the consistency of the input phys.-chem. data used in this study were chosen those from standard database (DIPPR, 2012) based mostly on experimental values with standard errors according to AIChE. The recommended values and temperature correlations are based on a critical, comprehensive evaluation by experts of the available data including inter-property relationships, inter-chemical relationships, and predicted/expected values.

Element balanced equation:

$$a_j = \sum_{i=1}^{l} n_i A_{i,j} \qquad (1)$$

where a_j are moles of j-th element (atom); n_i are moles of i-th species; $A_{i,j}$ number of j-th element in i-th species; l is the number of elements; j is the number of species.

The free energy (Helmholtz function) of the system F equation:

$$a_j = \sum_{i=1}^{l} n_i A_{i,j} \qquad (2)$$

where F is the free energy (Helmholtz function) of the system; n_i are moles of i-th species; f_i is free energy of i-th species.

$$a_j = \sum_{i=1}^{l} n_i A_{i,j} \qquad (3)$$

where f_i is free energy of i-th species; λi are the Lagrangian multipliers for each element (j=1 to J); $A_{i,j}$ number of j-th element in i-th species.

$$a_j = \sum_{i=1}^{i} n_i A_{i\_j} \quad (4)$$

where g_i is the Gibbs free energy for single i-th species; ΔH_f is the enthalpy of formation of the i-th species at standard conditions;

$$a_j = \sum_{i=1}^{i} n_i A_{i\_j} \quad (5)$$

where g_i is the Gibbs free energy for single i-th species; R is the universal gas constant; T is temperature; n_i is the number of moles of every species; V is the volume.

$$a_j = \sum_{i=1}^{i} n_i A_{i\_j} \quad (6)$$

where a_j are moles of j-th element (atom); n_i are moles of i-th species; $A_{i,j}$ number of j-th element in i-th species; l is the number of elements; j is the number of species; g_i is the Gibbs free energy for single i-th species; λi are the Lagrangian multipliers for each element (j=1 to J); R is the universal gas constant; T is temperature; n_i is the number of moles of every species; V is the volume.

$$a_j = \sum_{i=1}^{i} n_i A_{i\_j} \quad (7)$$

where g_i is the Gibbs free energy for single i-th species; $A_{i,j}$ number of j-th element in i-th species; l is the number of elements; λi are the Lagrangian multipliers for each element (j=1 to J); R is the universal gas constant; T is temperature; n_i is the number of moles of every species; V is the volume.

It has been shown (Skřínský et al., 2015) that the model is able to predict, with a reasonable accuracy in different fuel-enriched conditions, for different types of gaseous mixtures explosions. The equations 1-7 were used to investigate and quantify the role of initial temperature and pressure in affecting the explosion behavior of $CO/O_2/N_2$, $CO/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$ mixtures.

3. Results and discussions

CHARACTERISTIC	ABBREVIATION	UNIT	CO
Maximum explosion pressure	P_{max}	bar(a)	8.2[G]
			8.3[CO]
			8.0[D]

Table 1: Explosion characteristics of flammable gas component

G = GESTIS-Substance database (IFA); CO = Compendium of Environmental Standards (CES); D = Design Institute for Physical Properties (AiChE).

Table 1 compares the theoretically derived data for the maximum explosion pressure of the studied gas mixture components. The values were adopted from the databases as the IFA and the AiChE, and from the literature as the Compendium of Environmental Standards (CES). In Table 1, for example the values of the P_{max} adopted from IFA,

AiChE and CEI (8.2 bar(a), 8.3 bar(a) and 8.0 bar(a), respectively) clearly appear to be quite different. All values were obtained by using standard testing conditions.

A) Adiabatic temperatures and explosion pressures for $CO/O_2/N_2$

Calculated adiabatic temperatures, T_{ad}, and explosion pressures, P_{ex}, for $CO/O_2/N_2$ were determined at various initial temperatures and ambient initial pressure. The results of calculations are given in Table 2 and Figures 1a-2a.

FUEL FRACTION [VOL.%]	INITIAL TEMPERATURE (K)							
	298		358		418		478	
	P_{EX}	T_{AD}	P_{EX}	T_{AD}	P_{EX}	T_{AD}	P_{EX}	T_{AD}
15.0	5.94	1912	5.05	1953	4.41	1993	3.94	2033
30.0	7.98	2705	6.67	2710	5.74	2717	5.05	2724
45.0	7.78	2618	6.55	2647	5.68	2675	5.02	2701
60.0	6.43	2090	5.46	2133	4.77	2175	4.25	2218
75.0	4.76	1498	4.08	1542	3.60	1588	3.24	1633

Table 2: Computed explosion pressures for $CO/O_2/N_2$ mixtures at $p_0 = 1$ bar(a)

From the numerical results presented in Table 2 it is possible to identify that the increase in the initial temperature lowers the maximum explosion pressure (37% for 30.0 vol. %). The value of the explosion pressure with varying $CO/O_2/N_2$ concentration is similar at all investigated initial temperatures. The maximum value of the explosion pressure is found close to 35 vol. % of CO for all fuel fraction vol. % (see Figure 1a). Further, in Table 3, we reported simulations on the explosion properties of $CO/O_2/N_2$ mixtures at various initial pressure and ambient initial temperature.

FUEL FRACTION [VOL.%]	INITIAL PRESSURE (BAR(A))							
	1		5		10		15	
	P_{EX}	T_{AD}	P_{EX}	T_{AD}	P_{EX}	T_{AD}	P_{EX}	T_{AD}
15.0	5.94	1912	29.69	1913	59.38	1913	89.07	1913
30.0	7.98	2705	41.07	2897	83.08	2842	125.40	2864
45.0	7.78	2618	39.10	2633	78.28	2636	117.46	2638
60.0	6.43	2090	32.13	2090	64.26	2090	96.39	2090
75.0	4.76	1498	23.81	1498	47.62	1498	71.42	1498

Fr
ef

increase of initial pressure has significant
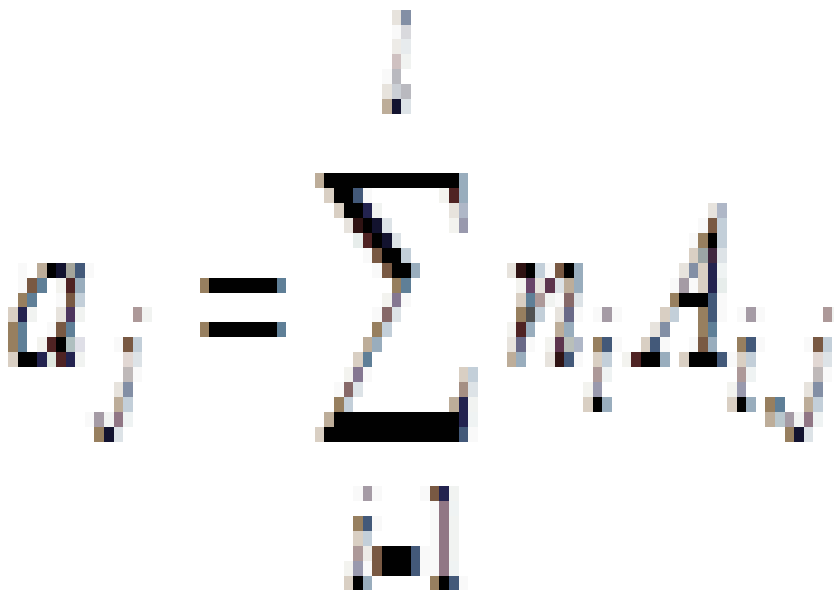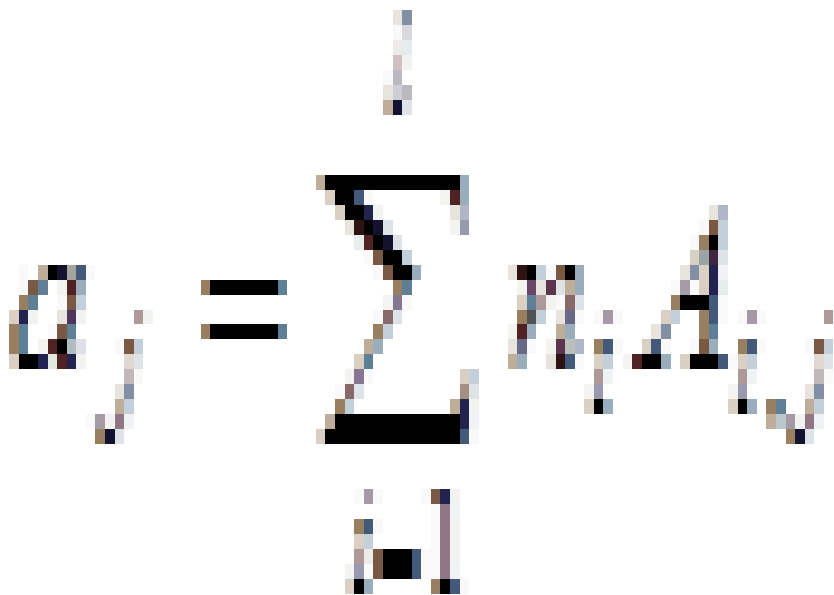
$$q_j = \sum_{i=1}^{I} n_i A_{i,j}$$

a)

$$q_j = \sum_{i=1}^{I} n_i A_{i,j}$$

b)

Figure 1: Calculated explosion pressure vs fuel fraction for explosions of a) CO/O2/N2 mixture at 298 K (top), 358 K (upper middle), 418 K (lower middle), and 478 K (bottom); b) CO/O2/N2 mixture at 1 bar(a) (top), 5 bar(a) (upper middle), 10 bar(a) (lower middle), and 15 bar(a) (bottom)

$$a_j = \sum_{i=1}^{I} n_i A_{i,j}$$

a)

$$a_j = \sum_{i=1}^{I} n_i A_{i,j}$$

b)

Figure 2: Calculated explosion pressure vs initial temperature for explosions of a) $CO/O_2/N_2$ mixture at 10.00 vol. % (top), 35.00 vol. % (upper middle), 60.00 vol. % (lower middle), and 85.00 vol. % (bottom); b) $CO/O_2/N_2$ mixture at 1 bar(a) (top), 5 bar(a) (upper middle), 10 bar(a) (lower middle), and 15 bar(a) (bottom)

B) CO_2 and H_2O inerting $CO/O_2/N_2$ mixtures

Further, maximum explosion pressure of $CO/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$ at 300 K for four different fractions of H_2O and CO_2 was investigated. The initial ambient temperature profile estimation with different O_2/N_2 atmospheres similar to industrial application conditions was also analyzed. The numerical results of calculation are summarized in Figure 3. The flammability data for $CO/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$ mixtures obtained in the present work provides adequate information for plant design purposes for a range of presented gas atmospheres, ambient temperature and pressures

$$a_j = \sum_{i=1}^{I} n_i A_{i,j}$$

a)

$$a_j = \sum_{i=1}^{I} n_i A_{i,j}$$
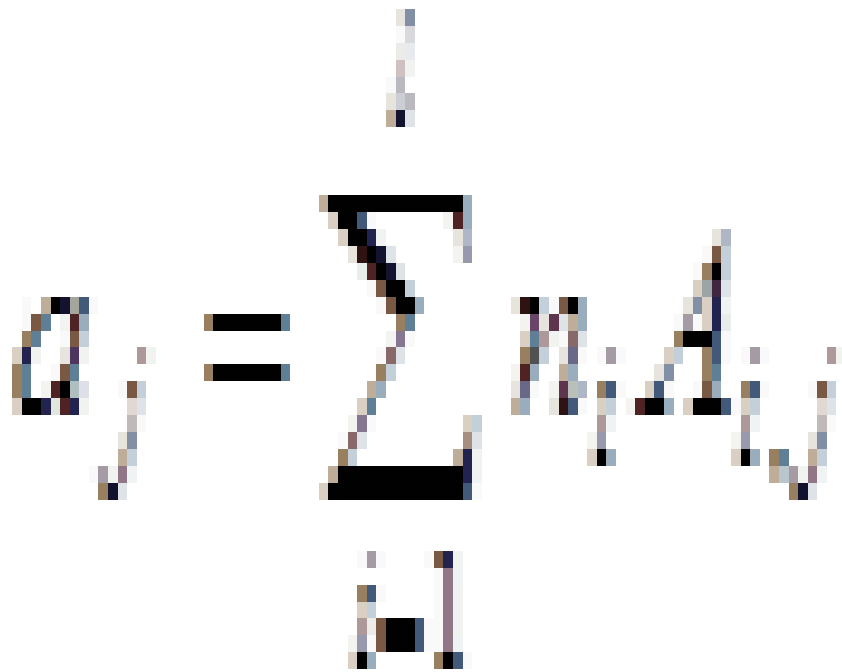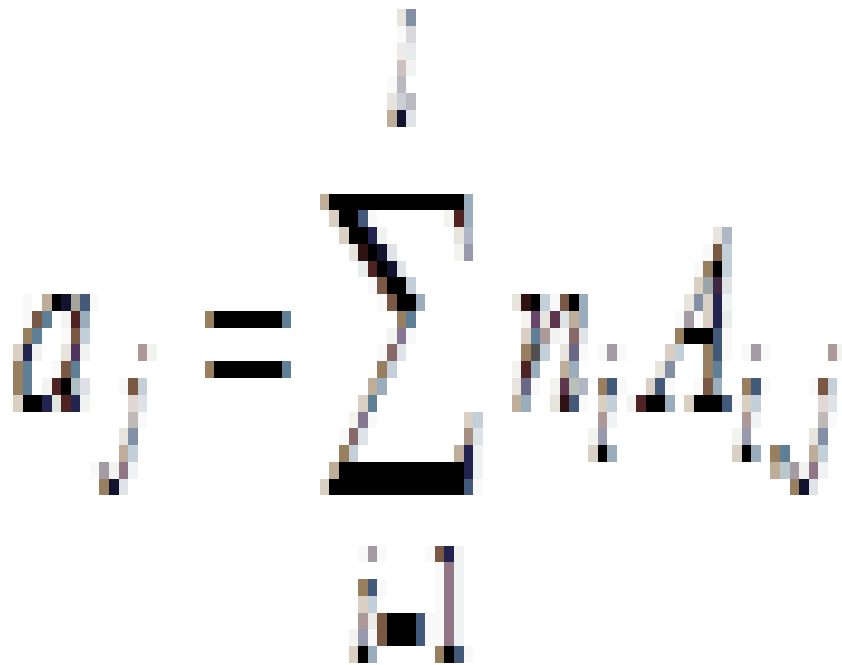
b)

Figure 3: Calculated explosion pressure vs fuel fraction for explosions of $CO/O_2/N_2$ mixture at a) different initial H_2O volume fractions 2.50 vol. % (top), 5.00 vol. % (upper middle), 10.00 vol. % (lower middle), and 15.00 vol. % (bottom); b) different initial CO_2 volume fractions 2.50 vol. % (top), 5.00 vol. % (upper middle), 10.00 vol. % (lower middle), and 15.00 vol. % (bottom)

Figure 3 shows the calculated explosion pressure behavior of stoichiometric $CO/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$

mixtures. The pressure trends for both mixtures are similar. Depending on the contents of H_2O / CO_2 and fuel fraction, they exhibit a single pressure peak at the maximum pressure. From Figure 3 it appears that the mixture reactivity, as quantified through P_{max}, increases on decreasing the initial H_2O / CO_2 vol. % fraction. Furthermore, it can be noted that the explosion pressure is higher for the mixture with H_2O for the same vol. % fraction values of fuel, in all cases. Therefore, based on equilibrium calculation presented in Figure 3 CO_2 seems to be a better inert for $CO/O_2/N_2$ mixture. The results will be experimentally proofed in 1 m^3 explosion apparatus.

4. Conclusion

The adiabatic explosion pressures and constant volume adiabatic explosion temperatures of $CO_2/O_2/N_2$, $CO/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$ mixtures at various initial temperatures and pressures were calculated. The model predictions for the $CO_2/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$ mixtures are compared for four different initial H_2O / CO_2 vol. % fractions. Finally, the results of simulations are compared to clarify the role of CO_2 and H_2O. Although the results from the evaluation indicate that presented theoretical simulations can become a valuable tool for rough estimation, the modeling requires further improvements to be useful for consequence modeling and design of industrial facilities. Thus, at the first stage, the equilibrium calculations can be used as a rough calculation of a worst case scenario. At the same time, these values will be used as approximate initial values for explosion experiments carried out in heated 1 m^3 explosion apparatus designed by OZM Research s.r.o. at Energy Research Centre, VŠB - Technical University of Ostrava. The experimental data on the flammability of $CO_2/O_2/N_2$, $CO/O_2/N_2/H_2O$ and $CO/O_2/N_2/CO_2$ mixtures can readily be applied to the hazards of handling solutions of carbon monoxide gas mixtures. These conclusions apply only to solutions in closed vessels, but similar calculations based on gas-gas and vapor-gas equilibrium data can be made for solutions in opened vessels. The results represents a continuation of numerous efforts by various research groups, where the key underlying problem has been the understanding of results obtained in laboratory tests for predicting the consequences of gas/vapor explosion scenarios in industry (Skřínský et al., 2015).

5. Acknowledgment

6. Literature

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