Explosion Characteristics of Coke Oven Gas – Theoretical study

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Abstract

The present contribution presents absolute explosion pressures (in terms of bar(a)) of stoichiometric $H_2/CH_4/CO/C_2H_6/C_2H_4/CO_2/O_2/N_2$ *coke oven gas mixtures with air calculated for various initial temperatures and pressures. The aim of this contribution is to evaluate the influence of the temperature on the explosion parameters and the role of development of flame on maximum explosion pressure. The primary outcomes are: explosion parameters at ambient conditions and elevated temperatures and pressures.*

Keywords: *Maximum Explosion Pressure; Constant Volume Adiabatic Temperature*

1. Introduction

The characteristic safety parameter of coke oven gas in a closed vessel explosion, so called explosion characteristic, discussed in this contribution is the maximum explosion pressure and constant volume adiabatic temperature. The maximum explosion pressure is the highest explosion pressure over the flammable range in a closed volume at a given fuel concentration (Eckhoff, 2005).

This explosion characteristic is 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. At the same time, the maximum explosion pressure that the explosion reaction can generate is one good measure of the magnitude of the hazard associated with the reaction (CCPS, 1995).

The present contribution presents absolute explosion pressures (in terms of bar(a)) of stoichiometric $H_2/CH_4/CO/C_2H_6/C_2H_4/CO_2/O_2/N_2$ ***coke oven gas mixtures with air mixtures with air calculated for various initial temperatures and pressures. The contribution has been focused on the characterization quantification of the key role of elevated temperatures and pressures.***

2. Basic description of the reactivity of the mixture

The mixture composition investigated in this contribution is given in Table 1.

Table 1 The compositions of coke oven gas for analysis

Ingredients	H_2	CH_4	CO	C_2H_6	C_2H_4	CO_2	N_2
Content vol. %	51.18	24.41	6.00	1.190	2.410	2.60	12.21

When a typical hydrocarbon fuel reacts with air, the kinetic of the combustion reaction is ruled by the generation and propagation of radical species. As it regards CO combustion, in the absence of hydrogen containing species, the reactions involving $O^\cdot$ radical and CO are very slow. Indeed it is extremely difficult to ignite and to have flame propagation in such mixtures. As H_2 molecules or other species hydrogen containing (as H_2O for instance) are added to CO, the reaction rate rises considerably because hydrogen radicals diffuse very rapidly through propagation reactions, which involve $H^{\cdot}$ atoms (Kuo, 2005). The kinetic models for $CO/H_2/O_2$ combustion reaction are fundamental for the understanding of combustion chemistry. One of the first validated kinetic study was that of Yetter et al. (1991), which elaborated a reaction scheme for gas/air combustion system and developed a detailed kinetic mechanism, which has been confirmed and further developed in several following studies. A study by Richards et al. (2005) have showed how the oxidation rate of CO in the gas/air system is reduced by the presence of CO_2 in the reacting mixture, hence determining longer residence time for the complete combustion. This effect can be attributed to either thermal effects, due to the lower adiabatic temperature or the slower laminar flame speed due to the kinetic role of CO_2. A study by Di Benedetto et al. (2009) has evaluated the effect of CO_2 addition to $CH_4/O_2/N_2$ and $H_2/O_2/N_2$ at stoichiometric conditions and at different levels of oxygen-enrichment. The presence of CO_2 has been shown to affect significantly the laminar burning velocity up to flame extinction. The simulations have shown that the main role of CO_2 is to induce changes in the heat capacity of the mixture, hence lowering the flame temperature. The presence of CO_2 has been found to play also a kinetic role. Lieuwen et al. (2010) state that technical development are hindered by the lack of fundamental data on burning velocity for diluted gas oxy-combustion, even if several experimental and numerical studies are available in the literature when using air as oxidant. A review of the influence of H_2/CO ratio, initial pressure and preheat temperature, dilution and flame stretch on the laminar flame speed of gas fuel mixtures in air is largely analyzed. A study by Bouvet et al. (2011) carried out laminar flame speed measurements at atmospheric pressure and ambient temperature by using spherically expanding flames. Mixture compositions ranging from H_2/CO = 5%/95% to H_2/CO = 50%/50% and equivalence ratios from 0.4 to 5.0 have been investigated. ***Due to the complexity of the involved physical phenomena and to the lack of an adequate amount of reliable experimental data, a very limited number of different models and calculation procedures for estimating the physical consequences following the explosion of a gaseous state mixture as coke oven gas are presently reported in the literature. The following model was used to investigate and quantify the role of initial temperature and pressure in affecting the explosion behavior of coke oven gas mixture.***

3. Analysis

Mathematical model used in this study computes adiabatic flame temperatures and constant volume adiabatic explosion pressures at various initial temperatures and pressures, taking into account ***26 species*** (chemkin format). It has been shown that the model is able to predict, with a reasonable accuracy in different fuel-enriched conditions, for different types of gaseous mixtures explosions. Detail description of calculation is in (GASEQ, 2004). Detail description of the theory is in (Kuo, 2005).

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:

$$F = \sum_{i=1}^{l} n_i f_i \qquad (2)$$

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.

$$f_i = \sum_{j=1}^{J} \lambda_i A_{i,j} \qquad (3)$$

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.

$$g_i^{\circ} = \Delta H_f^{\circ} + \left(h_i - h_i^{\circ}\right) - T s_i^{\circ} \qquad (4)$$

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;

$$f_i = g_i + RT \ln\left(\frac{n_i}{n}\right) + RT \ln\left(\frac{RT}{V}\right) \qquad (5)$$

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.

$$a_j = n \sum_{i=1}^{I} A_{i,j} \exp\left(-g_i^{\circ} + \frac{1}{RT} \sum_{j=1}^{J} \lambda_i A_{i,j} - RT \ln \frac{RT}{V}\right) \qquad (6)$$

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; I 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.

$$1 = \sum_{i=1}^{I} \exp\left(-g_i^{\circ} + \frac{1}{RT} \sum_{j=1}^{J} \lambda_i A_{i,j} - RT \ln \frac{RT}{V}\right) \qquad (7)$$

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; I 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.

Table 2 An example of input parameters for calculation (φ = 1; T = 298,15 K; p = 1,0)

PROPERTY	UNIT	REACTANTS	PRODUCTS
Temperature	K	298,15	1128,15
Pressure	atm	1,0	3,73
H_0	kcal/mol	-0,446	1,187
S_0	cal/mol/K	48,991	59,914
Cp	cal/mol/K	7,031	8,662
Gamma, Cp/Cv	-	1,394	1,298
Mean Molecular Weight	g	30,95	31,42
Density	kg/m^3	1,2656	1,26560
Sound speed	m/s	334,0	622,2
Enthalpy, H	kcal/kg	-14,42	37,79
Entropy, S	cal/kg/K	1582,98	1823,73
Intern Energy, U	kcal/kg	-33,56	-33,56
Free Energy, G	kcal/kg	-486,15	-2019,32
Volume	m^3	24,4537	24,825
Viscosity	kg/m/s	2,03E-05	5,11E-05
Kinematic Viscocity	m^2/s	1,61E-05	4,04E-05
Thermal Conductivity	cal/m/K/s	6,19E-03	1,74E-02
Thermal Diffusivity	m^2/s	2,15E-05	4,97E-05

4. Results and discussions

Computed adiabatic temperatures, T_f, and maximum explosion pressures, p_{max}, for coke oven gas-air mixtures (φ = 0,1-2,0) at various initial temperatures, T_{init}, and ambient initial pressure are given in Table 3.

Table 3 Computed explosion pressures for $H_2/CH_4/CO/C_2H_6/C_2H_4/CO_2/O_2/N_2$ mixtures at p_0 = 1 bar(a)

Stoichiometry [-]	**Initial temperature (K)**			
	298	**358**	**418**	**478**
0,5	10,61	8,867	7,598	6,653
1,0	12,043	10,006	8,562	7,487
1,5	12,416	10,324	8,841	7,736
2,0	11,938	9,963	8,559	7,512

From the numerical results of Table 3 it is possible to identify that the increase in the initial temperature lowers the maximum explosion pressure, and increases the flammability range. The value of the explosion pressure with varying $H_2/CH_4/CO/C_2H_6/C_2H_4/CO_2/O_2/N_2$ concentration is similar at all investigated initial temperatures. The maximum value of the explosion pressure is found close to φ = 1,5 for coke oven gas stoichiometric ratio for all conditions. Further, in Table 4, we reported simulations on the explosion properties of $H_2/CH_4/CO/C_2H_6/C_2H_4/CO_2/O_2/N_2$ mixtures at various initial pressure and ambient initial temperature.

Table 4 Computed explosion pressures for $H_2/CH_4/CO/C_2H_6/C_2H_4/CO_2/O_2/N_2$ mixtures with air at T_0 = 298 K

Stoichiometry [-]	**Initial pressure (bar(a))**			
	1	**5**	**10**	**15**
0,5	10,61	55,145	112,740	170,729
1,0	12,043	63,479	129,688	196,904
1,5	12,416	65,032	132,465	200,711
2,0	11,938	61,299	123,808	186,637

From the data performed in Table 4, it is clear that the increase of initial pressure has significant effect on explosion pressure when only the air as oxidant. This is a good approximation at initial pressures i.e. up to 15 bar(a), but we may assume that will be increasing wrong at higher pressures.

5. Conclusion

The adiabatic explosion pressures $H_2/CH_4/CO/C_2H_6/C_2H_4/CO_2/O_2/N_2$ mixture with air at various initial temperatures and pressures were calculated. The model predictions for the coke oven gas mixtures are compared for four different initial temperatures. 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. As the practical outcome these results will apply for the coke oven gas produced by generator during autothermal gasification in fixed-bed. 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 multicomponent gas mixture explosion scenarios in industry (Skřínský et al., 2015a; 2015b and 2015c).

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