On the explosion limit of syngas with CO_2 and H_2O additions

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ABSTRACT

In this study, the pressure-temperature explosion limits of $H_2/CO/O_2/CO_2/H_2O$ mixtures are analyzed computationally and theoretically. The result indicates that with the increase of H_2O and CO_2 mole fractions, the explosion temperatures are increased around all the three explosion limits. Furthermore, the increase of the explosion temperature is higher with the addition of H_2O compared with the addition of CO_2 near the second explosion limit. In addition, the increase of the explosion temperature near the first and third explosion limit is almost the same for the addition of these two inter gases. The single-limit expression analysis shows that the first explosion limit is mainly controlled by the changing of the oxygen concentration with the addition of inert gas; the changing of the second explosion limit is caused by the changing of the reaction rate of $H + O_2 (+M) \rightarrow HO_2 (+M)$, which is indirectly through the Chaperon efficiency of the third body recombination reaction, and the effect of inert gas addition on the third explosion limit is mainly caused by the changing of the hydrogen concentration.

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Introduction

With increasing demand on energy resources and concerning on air pollution, researches on clean reformed fuels have attracted more and more attentions in the past decade. Among these fuels, synthesis gas offers a promising opportunity for sustainable development in the energy and transportation sectors. Synthesis gas, produced from coal, biomass, waste, landfill and alcohol fuels via gasification, pyrolysis or fermentation processes, has been widely used in power plant or internal combustion engines [1–3]. The combustion characteristics of syngas in those applications are the most attractive and promising research field in recent years. However, the big challenge in syngas utilization is the control of NOx emissions. Consequently, the EGR (Exhaust Gas Recirculation) or water injection strategies are frequently used to reduce NOx emissions, where plenty of CO_2 or H_2O will be presented in the mixture [4,5].

In order for flames (deflagrations) or detonations to propagate, the reaction kinetics must be fast. That is, the mixture must be explosive. The explosive characteristics of different mixtures with various concentrations, initial pressures and temperatures were experimentally investigated and analyzed on the basis of combustion pressure history in constant volume confined vessels [6–8]. The explosion limits of a given fuel-oxidizer mixture are the pressure-temperature boundaries of the mixture that separate the regimes of explosion and non-explosion [9–11]. It will determine properties of interest, such as ignition and extinction limits, flame propagation, etc. In particular the explosion limits of H_2–O_2 mixtures,

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which exhibit a characteristic Z-shaped curve in the pressure-vs-temperature space, with the three segments of this curve referred as the first, second and third explosion limits, have been studied extensively [12–16]. It was well established that the first explosion limit was controlled by the gas-phase chain branching reactions competing with radical deactivation reactions at the wall [17]. At low pressure, the radical wall destruction reactions dominated over the chain branching reactions, accordingly no explosion will happen in the system. As the pressure was raised to a point, the rapid increase of the concentration of chain carriers leaded to the increase of reaction rate and finally to explosion. The second explosion limit (medium pressure branch) was controlled by the H–O_2 branching and termination chemistry, and the third explosion limit was determined by the HO_2 and H_2O_2 chemistry competing with radical wall deactivation [18].

Tschirschwitz et al. studied the explosion limits of different mixtures in a cylindrical steel autoclave. It was found that a combination of a pressure rise criterion of 2% and a temperature rise criterion of 100 K was a suitable criterion for the determination of explosion limits [19]. Sher et al. obtained a single analytical expression for the upper and intermediate explosion limits of H_2–O_2 mixtures by employing the Le-Chatelier rule [20]. Li et al. investigated the effect of CO_2 addition on the explosion characteristics of flammable gases and their explosion limits. It has been proved that CO_2 had a better suppression effect on the explosion of flammable gases [21–23]. Tong et al. studied the H_2 addition on the explosion limits of combustible gases based on the numerical calculations. The results proved that the upper explosion limit of a combustible gas mixture will increase considerably with increasing the amount of H_2 [24]. Van den Schoor et al. determined the explosion areas of the ethylene/hydrogen/nitrogen/air mixtures at typical production process conditions in a closed spherical vessel [25]. Addai et al. examined the lower explosion limit of methane/hydrogen mixture blended with dust. However, the proposed mathematical formulas to predict the lower explosion limit were not reliable for some mixtures [26].

There are several motivations for the present study. Firstly, the intrinsic chemical interaction between H_2 and CO, and its effect on the explosion limits of syngas need to be clarified with different hydrogen mole fractions. Secondly, recognizing that the CO_2 and H_2O species are frequently presented in syngas utilization to reduce NOx formation, it is thus of both fundamental and practical interest to investigate the effect of these two inert gases addition on the explosion limits of the syngas-O_2 mixture, particularly in identifying the intrinsic chemical interaction and its effect on the explosion limits. Thirdly, whether the eigenvalues method of the reaction rates matrix is capable of predicting the explosion limit of syngas with various inert gas mole fractions is not very clear. Consequently, further research work should be done to extend this theory.

Numerical approach

The SENKIN code was used to investigate the explosion limits of syngas-oxygen-inert gas (H_2/CO/O_2/inert gas) mixture [27].

The calculation pressure range was from 3.5 to 3.2×10^7 Pa and the temperature was from 0 to 2500 K, which was selected to cover all the possible conditions. Curran's mechanism, which consists of 15 species and 45 elementary chemical reactions with associated rate coefficient expressions, was used in this study [28]. The fuel/oxygen mole fraction ratio was kept constant at 2:1, which stands for stoichiometric condition. In order to study the effect of inert gas addition on the explosion limit, two different mole fractions of inert gas were added into the stoichiometric syngas-oxygen mixture with mole ratios of 2:1:2 and 2:1:4 for the fuel:O_2:inert gas. The initial mole number of the fuel, oxygen and inert gas in the mixture can be found in Table 1.

The kinetic approximation was made in that diffusion of the radicals to the chamber wall was assumed to be much faster than the absorption by the wall since only a small amount of the radicals that reach the wall were absorbed. Furthermore, concentrations of the radicals at the wall were assumed to be the same as those in the gas phase. As such, the reactive system was treated to be spatially homogeneous.

The radicals were destroyed at the wall according to the following reactions:

$$H, O, OH, HO_2, H_2O_2 \xrightarrow{k_H, k_O, k_{OH}, k_{HO_2}, k_{H_2O_2}} \text{wall destruction} \quad (1)$$
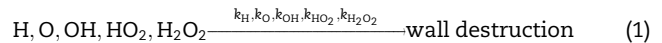
With the equivalent reaction rate constants per unit volume $k_H, k_O, k_{OH}, k_{HO_2}$, and $k_{H_2O_2}$ given by:

$$k = \frac{1}{2} \varepsilon \bar{v} \frac{S}{V} \quad (2)$$

Here, $\bar{v} = \sqrt{8k_B T/\pi m}$ is the average velocity of the thermal motion of the radicals at temperature T, m is the molar mass of each radical, and k_B is the Boltzmann constant. The destruction efficiency of the radicals in the collision with the wall is measured by the sticking coefficient ε, and usually $\varepsilon \approx 10^{-5}$ to 10^{-2} for glass and quartz [13]. S/V is the surface area/volume ratio.

The main parameters that control whether the system explode or not are the shape and size of the chamber, the wall sticking coefficients of the radicals, the pressure and temperature, total gas concentration, and hydrogen and oxygen molar fractions. A spherical chamber is used to account for the radical wall destruction, with diameter $2r = 0.074$ m and surface area/volume ratio $S/V = 3/r$. The sticking coefficient is set as 10^{-3} for each radical.

Table 1 – Initial mole number of the fuel, oxygen and inert gas in the mixture.

Gas mixture	Initial mole number			
	fuel		O_2	Inert gas (CO_2 or H_2O)
	H_2	CO		
5% H_2	0.1	1.9	1	0
25% H_2	0.5	1.5	1	0
50% H_2	1	1	1	0
pure H_2	2	0	1	0
25% H_2+inert gas	0.5	1.5	1	2, 4
Pure H_2+inert gas	2	0	1	2, 4