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Flammability Limits of Methane (Lng) and Hydrogen (Lh2) at Extreme Conditions

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In the recent years the growing interest for cleaner and low carbon content energy sources has addressed the development of several industrial and civil applications based on methane, hydrogen, and their mixtures. The use of these gases rises, however, several technological issues for the storage and the transportation systems. Among others, cryogenic liquefaction (as liquified natural gas, LNG and liquified hydrogen, LH2) and cryo-compressed gases are considered among the most promising potential solution. On the other hand, when low and ultra-low temperature are considered, several questions regarding the safe use of such gases are raised, including the behaviour of the cold vapour phase in air after the release of liquid or cryo-compressed gas from containment system. In this work, the flammability limits of hydrogen, methane and their blends at low and ultra-low temperatures were estimated by using the laminar burning velocity obtained by means of detailed kinetic mechanism. Numerical results were compared with experimental data and empirical correlations commonly adopted for this purpose. The data agreement demonstrates the applicability of the developed procedure for the estimation of safety parameters at low and ultra-low temperature and for future technological applications, even at cryogenic conditions.

1. Introduction

The growing concern on the environmental issues has led to renewed interest in low carbon-fuels. In particular, liquefied natural gas (LNG), liquefied hydrogen (LH2) and cryo-compressed hydrogen have been demonstrated to be attractive for both civil and industrial applications due to their elevated specific energy density, reduced greenhouse gases emissions, and cost per amount of produced energy if compared to conventional fuels. Furthermore, recent studies on the technical feasibility and economic aspects concerning the hybrid engines for aviation (Rao and van Buijtenen, 2014; Withers et al., 2014) and road transportation (Osorio-Tejada et al., 2017) have further confirmed the potentiality of cryogenic and cryo-compressed fuels. The massive use of these fuels has however raised several questions regarding the safe use of such gases. More specifically, few studies have been addressed to the analysis of accidental scenarios occurring when these gases are released from the containment system at low and ultra-low temperature. An example has been performed e.g. by Schmidtchen et al. (1997) for aircrafts and connected infrastructure. Besides, although the innovative solutions for large scale LH2 storage systems, including the potential zero boil-off methods developed by NASA (Notardonato et al., 2017), the dispersion of vaporized hydrogen and its potential ignition still represent a complex issue. In this framework, a first advancement is represented by the determination of flammability limits of gaseous mixture at low temperatures. Hence, the aim of this work is the estimation of the effect of initial temperature on the flammability limits of methane/hydrogen/air mixtures at temperature varying from the ultra-low values (100 K) up to room temperature (300 K) by means of detailed and simplified approaches.

2. Methodology

The numerical analysis has been carried out by implementing the open-source code Cantera (Goodwin 2003) with the detailed kinetic mechanism developed for light hydrocarbons oxidation in previous work (Pio et al.,

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2018) by a combination of University of California, San Diego mechanism (UCSD) (University of California at San Diego, 2018) and Lawrence and Livermore National Laboratory (LLNL) mechanism (Sarathy et al., 2012). This mechanism, now referred as KIBO (Kinetic Modelling at University of Bologna), is composed by 76 species and 322 reactions. KIBO has been already validated for the estimation of the reactivity of methane/hydrogen/air mixture at low temperature (Pio and Salzano, 2018a) and compared with experimental data obtained by the heat flux burner at room conditions (Salzano et al., 2018). The laminar burning velocity (S_u) and the critical adiabatic flame temperature (CAFT), i.e. the adiabatic flame temperature calculated at the flammability limits composition, were evaluated by modelling one-dimensional flames under the assumption of perfectly adiabatic conditions, by using Newton iteration technique to solve mass and thermal balances. Simulations were carried out by using as grid parameters slope equal to 0.07 and curve equal to 0.14, a total grid points number of about 170-230, relative error criteria (RTol) and absolute error criteria (ATol) equal to $1.0 \cdot 10^{-9}$ and $1.0 \cdot 10^{-14}$ for steady-state problem and $1.0 \cdot 10^{-5}$ and $1.0 \cdot 10^{-14}$ for time stepping problem (used by the code as first attempt solution), respectively. These parameters were adopted by optimizing the results accuracy and computational time required to perform the simulation (Pio and Salzano, 2019). The effect of equivalence ratio (φ), as defined in Eq (1), and hydrogen ratio (Eq 2) on S_u and CAFT was studied at room temperature at first (300 K).

$$\varphi = \sum \frac{\left(\frac{n_f}{n_{ox}}\right)}{\left(\frac{n_f}{n_{ox}}\right)_{st}} \tag{1}$$

$$\mathrm{R_{H_2}} = \frac{\mathrm{n_H}}{\mathrm{n_C} + \mathrm{n_H}} \tag{2}$$

where n is the mole at feeding composition, the subscripts f, ox, H and C represent the generic fuel, the oxidant, hydrogen and methane, respectively whereas st stands for the stoichiometric conditions with respect to the reaction of fuel complete oxidation. The lower flammability limit (LFL) and upper flammability limit (UFL) were estimated within the temperature interval 150 K – 300 K, by means of the limiting burning velocity ($S_{u,lim}$) theory reported by Hertzberg (1984), since previous studies have indicated this technique as suitable for the estimation of safety parameters of light hydrocarbons (Pio and Salzano, 2018b). $S_{u,lim}$ was calculated for the investigated conditions by using the Eq (3).

$$S_{u,lim} = \sqrt[3]{2\alpha g \frac{\rho_b}{\rho_u}} \tag{3}$$

where α represents the effective diffusivity, g the gravitational acceleration, ρ_b and ρ_u are the burned and unburned gas density, respectively. The obtained results were compared with experimental data, when available, and with the results obtained either by the empirical correlation by Chatelier (Eq 4) for binary fuel mixtures, which is based on the additivity effect of pure components, or by the Zabetakis correlations (Eq 5 and Eq 6), which is based on the energy balance and the assumption of constant values of the adiabatic flame temperatures at flammability limits:

$$FL_{mix}(T) = \frac{1}{\sum \frac{y_i}{LFL_i(T)}} \qquad FL = LFL\ or\ UFL \tag{4}$$

$$LFL_{mix}(T) = LFL_{mix}(T_0) + \frac{c_{p,u}}{-\Delta H_c} \cdot (T - T_0) \tag{5}$$

$$UFL_{mix}(T) = UFL_{mix}(T_0) - \frac{c_{p,u}}{-\Delta H_c} \cdot (T - T_0) \tag{6}$$

where y_i indicates the mole fraction of the i-th compound in the fuel mixture, T_0 is the reference temperature, ΔH_C the theoretical heat of combustion and $c_{p,u}$ the heat capacity of unburned gaseous mixture.

3. Results and discussion

In this section the effect of initial low and ultra-low temperature on the flammability limits of pure hydrogen and methane in air are first presented (Figures 1 and 2). The experimental data for methane/air mixture collected by Siu et al. (1998), Li et al. (2011) and Cui et al. (2016) have been included for the sake of comparison

(Figure 1). For hydrogen/air mixtures, the LFL data reported by Karim et al. (1984), and both the LFL and UFL measured by Wierzba and Wang (2006) were compared with numerical results (Figure 2). The correlations proposed by Zabetakis (Eq.5 and 6) were only considered at this stage, being the most accurate for the estimation of the effects of temperature on the flammability limits of lower hydrocarbons ($<C_5$) among the simplified approaches proposed in the literature (Liaw and Chen 2016). The $S_{u,lim}$ of pure methane was found to be strongly dependent on the initial temperature and weakly affected by the mixture composition, since either rich or lean mixtures show similar properties. On the contrary, the calculated $S_{u,lim}$ of hydrogen is strongly affected by both the gaseous composition and initial temperature, being almost double for rich conditions with respect to lean conditions. Discrepancies among methane and light fuels $S_{u,lim}$ were already reported by Ronney and Wachman (1985) and can be attributed to larger equivalence ratio of the rich hydrogen mixtures with respect to the UFL methane mixture, leading to both larger thermal diffusivity and density ratio in the first case, because of the reduced air content in the initial mixture.

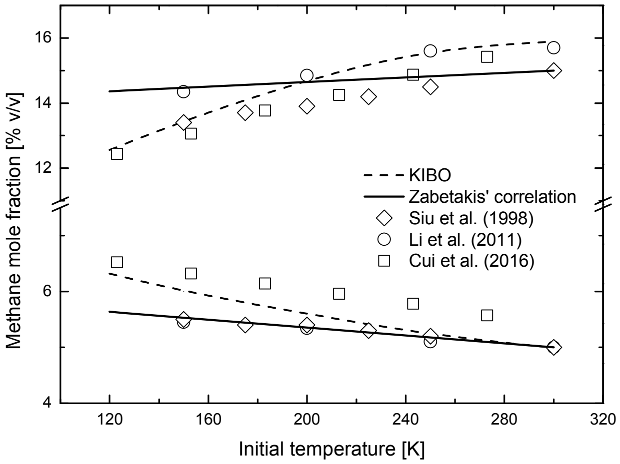

Figure 1: The effect of initial temperature on the LFL and UFL of methane/air mixtures.

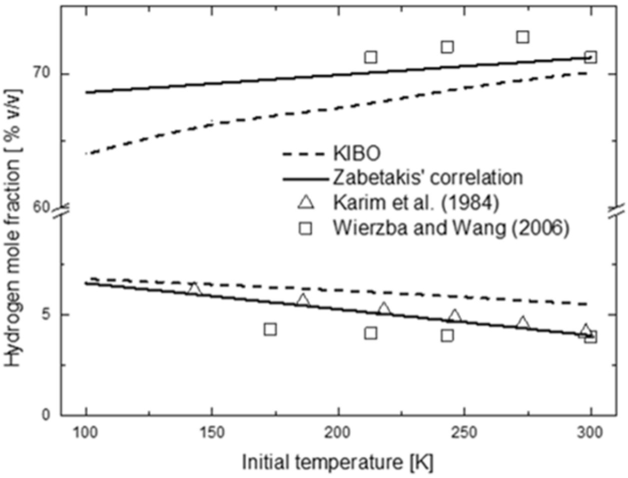

Figure 2: The effect of initial temperature on the LFL and UFL of hydrogen/air mixtures.

Noteworthy, the UFL of methane is well estimated by the limiting burning velocity theory, thus suggesting the need of detailed kinetic models for the prediction of the phenomena involved at the conditions analyzed in this work. Indeed, although the absolute values are under predicted, the obtained trend of hydrogen UFL with respect to the initial temperature matches with experimental data. On one hand, Zabetakis assumptions seem to be not applicable to the rich methane case, being the LFL trend with respect to the initial temperature far from the linearity. On the other hand, the Zabetakis correlation is more accurate than the proposed procedure in the estimation of the flammability limits of hydrogen, especially for the UFL. However, it should be considered that the estimation quality of Zabetakis correlation is strongly enhanced by the adoption of the average values for the initial temperature of the experimental data, whereas the limiting burning velocity theory is based on mixture thermal properties and reaction parameters obtained by generic kinetic mechanism suitable for different fuels. Moreover, the lack of a comprehensive experimental database, including more recent data for hydrogen/air mixtures, makes the comparison and the evaluation of numerical results less effective.

The obtained results for hydrogen enriched methane are compared to the experimental data reported by Miao et al. (2011) and Van Den Schoor and Verplaetsen (2007) at ambient temperature in Figure 3.

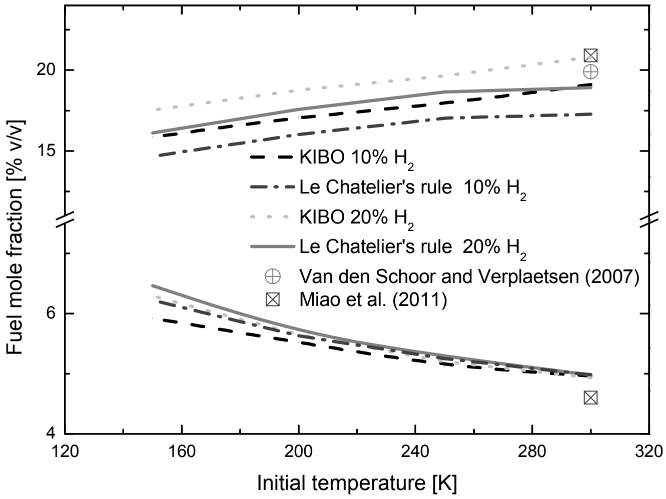

Figure 3: Numerical evaluation of the flammability limits of hydrogen enriched methane/air mixtures with respect to temperature. A comparison with existing correlations is reported.

The LFL obtained by using the Le Chatelier's rule are in line with the one obtained by means of the limiting burning velocity. However, discrepancies were found for the UFL, where the effect of additional fuel is stronger due to the larger mole fraction in the mixture. The parabolic trend with respect to hydrogen content of the methane/hydrogen LFL at room temperature reported by Miao et al. (2011), cannot be predicted by empirical correlations, such as Le Chatelier's rule, where a monotonic trend is assumed. On the other hand, this behavior can be explained by the dual aspect considered in the limiting burning theory, i.e. the enhancement of the S_u due to the hydrogen addition makes narrower the flammability area and the variation in the mixture properties leading to higher $S_{u,lim}$ enlarge this zone, the combination of these opposite trends makes the approach suitable for the prediction of LFL even at higher hydrogen content. It should be noted that the kinetic approach is more conservative on the safe side than Le Chatelier's rule, indicating larger flammability area for all investigated conditions, but makes narrower the flammability area respect to the assumption of constant flammability limits, making possible further refinement and optimization in the design process of storage systems. Even at low temperature, where the reaction rates are reduced and so the discrepancies among the different approach should be limited, the results obtained by means of kinetic-based approach disagree with empirical correlations. Additional information on the combined effect of initial temperature and fuel composition can be obtained by comparing the CAFT at LFL ($CAFT_{LFL}$) and UFL ($CAFT_{UFL}$), commonly adopted as analytical criteria for the evaluation of safety parameters (Shebeko et al., 2002), at different initial temperature for hydrogen enriched methane, as reported in Table 1.

The data in Table 1 indicate that the CAFT values proposed as threshold by Vidal et al. (2006) for the estimation of LFL cannot be applied for the UFL evaluation, since higher values should be considered. Moreover, further refinement - including the dependency on the initial temperature of this parameter - should be beneficial for accurate prediction of the flammability limits, especially for hydrogen enriched mixtures. Indeed, at room temperature the $CAFT_{LFL}$ assumes similar values for all the investigated mixtures, whereas the addition of hydrogen leads to significant variation with linear trend with respect to the initial temperature. Indeed, methane $CAFT_{LFL}$ was found almost constant at 1460 K, whereas hydrogen enriched mixtures $CAFT_{LFL}$ variates up to 84 K. This effect is much more evident for the $CAFT_{UFL}$, where the interval within the $CAFT_{UFL}$ variates is extended at 200 K and the linear trend is not applicable. This phenomenon can be attributed to the elevated difference in the UFL of pure species, i.e. at hydrogen enriched methane UFL composition the adiabatic flame temperature of hydrogen is higher than 2000 K, because of the distance from the UFL of the pure compound.

Table 1: Critical adiabatic flame temperature at LFL and UFL for hydrogen enriched methane in air

	T_0=*300 K*	T_0=*250 K*	T_0=*200 K*	T_0=*150 K*
R_{H_2}= 0.1 $CAFT_{LFL}$ [K]	1466	1453	1440	1422
R_{H_2}= 0.2 $CAFT_{LFL}$ [K]	1467	1435	1407	1383
R_{H_2}= 0.1 $CAFT_{UFL}$ [K]	1692	1653	1597	1494
R_{H_2}= 0.2 $CAFT_{UFL}$ [K]	1709	1661	1602	1508

So that said, it is possible to hypothesize that the thermal aspect rules the LFL at low temperature as well, making the cited correlations suitable for their estimation, whereas they are not sufficient to estimate the UFL where the key role of the radicals kinetic requires more detailed approaches. Nevertheless, the error corresponding to the LFL estimation can be acceptable if the simplicity of the correlation is considered for hydrogen enriched methane up to 20 %v/v of hydrogen. Similar observations were reported for the S_u in a comprehensive literature review on the predictive equations, performed by Basco et al. (2012).

4. Conclusions

The flammability limits of methane, hydrogen and their mixtures at low and ultra-low temperatures were estimated by using a numerical procedure based on detailed kinetic model and the limiting burning velocity theory. The critical adiabatic flame temperature (CAFT) were calculated by using the detailed kinetic mechanism at LFL and UFL composition, as well. For the sake of numerical results comparison experimental data and empirical correlations applied to estimate the effect of temperature of pure species (i.e. Zabetakis' rule) and the effect of composition at the investigated temperature (i.e. Le Chatelier's rule) were considered. The analyzed empirical correlations and the CAFT method were found to be inadequate for the estimation of UFL at low temperature, whereas are mostly in accordance with LFL experimental data. Based on these results the liming burning velocity theory seems to be more accurate than the other correlations considered in this work for the estimation of the effect of low temperature on UFL of the studied mixtures, since the interactions between the pure compounds oxidation mechanism in air can be correctly estimated and considered exclusively by means of this approach. However, further development is required to improve the estimation quality, especially at low temperature. The development and availability of robust and efficient reduced and detailed kinetic models suitable for a wide range of operative conditions, fuel compositions and chemical species, make the application of this procedure preferable, due to its flexibility and accuracy. To this regard, the combined effect of hydrogen addition on S_u and $S_{u,lim}$ has the potential to predict and clarify the reason of the trend reported for elevated hydrogen content in methane flammability limits in air and more in general for the safety operation and storage of methane/hydrogen/oxygen/nitrogen mixtures (Cammarota et al., 2009; Di Benedetto et al., 2009; Salzano et al., 2012). It should be considered that the performed study is strongly affected by the lack of experimental data under the studied conditions, not allowing a comprehensive and effective analysis on the estimation procedure, especially at temperature close to the boiling temperature where large non-idealities should be expected.

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