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Chemical and Thermal Effects of Trace Components in Hydrogen Rich Gases on Combustion

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The production of carbon-neutral fuels through clean energy has been defined as a target by the European Union and by several international institutions. If the concepts are available, hydrogen, in particular, is considered to be one of the most target-oriented, ecologically and economically realizable approaches. In terms of safety, long-time storage and long-distance transport of hydrogen are still under development. However, pipeline systems similar to those for natural gas are being considered. Gas quality criteria will have to be developed for this case. The effects of trace components in the hydrogen on chemical and thermal aspects are not yet sufficiently understood and need to be characterized more precisely. For these reasons, this work presents a detailed analysis for a more complete understanding of the phenomena involved. More specifically, the flame structure, temperature profile and overall reactivity were first determined for gas mixtures analyzed under four varying dilutions of carbon dioxide, carbon oxide, nitrogen and methane in hydrogen. The characterization of the total reactivity and the laminar burning velocity offers an appealing solution to quantify the effects of dilution. The most distinctive effects of the operating conditions on the ignition phenomena have been worked out numerically for the lower and upper boundaries and have been discussed. The results collected in this work provide a robust feature for a detailed evaluation of normal operation as well as the accidental release of the hydrogen-rich fuels.

1. Introduction

In the future, carbon-free fuels such as hydrogen and ammonia will play a major role in energy production. As a compressible gas, hydrogen can have a significant role in supplying Europe because of the actual infrastructures, although its different properties with respect to the mixture currently employed. For this purpose, the existing gas transport grid will have to be adapted. On the one hand, existing pipelines will have to be prepared for the new challenges, and on the other hand, they will have to meet the high safety standards and be able to supply the end customers with a consistently high quality of fuel. For this reason, international regulations are being established to control the changes in the gas network for 100 % hydrogen as well. Currently, in Europe, both in France and in Germany, 2 vol.-% dilution in hydrogen is under discussion, whereas worldwide also 5 vol.-% are assumed. This change in trace gas concentration is to be investigated about its influence on fundamental combustion properties. Among the others, the laminar burning velocity offers the possibility to disregard turbulence by physic-chemical phenomena. Indeed, this parameter is commonly adopted for the evaluation of the overall reactivity, severity of explosions, and characterization of accidental scenarios in computational fluid dynamics (Skjold et al., 2018). Several approaches can be used for the evaluation of this fundamental parameter, including either experimental or numerical strategies. As a way of example, counter flow flame (Eckart et al., 2021c), heat flux burner (Eckart et al., 2017), or spherical vessel (Eckart et al., 2021b) can be used to measure it. Additional information on practical and theoretical aspects involving these systems can be found elsewhere (Konnov et al., 2018). However, it is worth reporting that the heat flux burner represents the only option where extrapolation is not needed to obtain stretch-free data, with a considerable reduction in uncertainties associated with the measurements (van den Schoor et al., 2008). Indeed, the heat flux burner has been largely adopted to measure the laminar burning velocity of different fuels, including hydrogen, under a

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wide range of conditions (Alekseev and Konnov, 2018). On the other hand, the numerical estimation of laminar burning velocity mostly relies on the accuracy of detailed kinetic mechanisms, usually consisting of hundreds of species and thousands of reactions (Egolfopoulos et al., 2014). The strategies implemented for the genesis of a detailed kinetic mechanism can variate by several aspects. Indeed, these models can be produced by automated or expert-driven procedures or can use different target species, sources for thermodynamic and kinetic parameters (Curran, 2019). Besides, an additional source of differences in kinetic mechanisms is represented by the approach adopted for the realization of transport models. Among the others, the Soret diffusion affects the mass burning rate also in the case of mono-dimensional flames (Zhou et al., 2017), especially if hydrogen is directly involved in the unburned mixture (Law, 2010). Each possible approach can potentially generate different mechanisms regarding accuracy and size, suggesting the comparison with experimental data for the sake of validation.
In this work, both the influence on the burning velocity and the Wobbe number are investigated in more detail. Finally, the findings will be substantiated numerically to shed more light on the chemical changes.

2. Methodology

2.1 Theoretical background

The trace gases carbon dioxide, nitrogen, carbon monoxide, and methane were considered in the studies. In each case, 0 to 5 vol.-% were added to hydrogen. The mixture compositions are summarized in Table 1.

Table 1. Mixture composition of the trace gases in pure hydrogen at p = 1 bar and T = 298 K.

CO [%v/v]	CO_2 [%v/v]	CH_4 [%v/v]	N_2 [%v/v]
1-5	0	0	0
0	1-5	0	0
0	0	1-5	0
0	0	0	1-5

Further, the Wobbe number is a gradiometer of the interchangeability of gases and is frequently defined in the specifications of gas supply, transport utilities and heat load of fuel gas consumers with different gas compositions. The Wobbe number expresses both the energy content and the flow velocity-determining variables (density and pressure loss). It is the central key figure in several international technical rules. Gases with the same Wobbe index can be exchanged without design changes to the burner or conversion of the burner nozzle. The fluid mechanical principles are derived from the Bernoulli equation for the pressure drop across a burner nozzle which discharges the gas from a line into a room with ambient pressure. The pressure drop Δp across the burner nozzle corresponds in a first approximation to the line overpressure p_l. Via the continuity law, the ratio of the velocities (u) in line and nozzle can be derived from the diameter (d) ratio.

$$\frac{\pi}{4} d_l^2 \cdot \rho_g \cdot u_l = \frac{\pi}{4} d_d^2 \cdot \rho_g \cdot u_d \tag{1}$$

From this follows for the pressure drop

$$\Delta p = \frac{\rho_g}{2} \cdot u_d^2 \cdot \left(1 - \frac{d_d^4}{d_l^4}\right) \tag{2}$$

Thus, if the general conditions at the burner nozzle (pressure drop as well as line and nozzle diameter) remain unchanged, the exit velocity inevitably increases as the fuel gas density decreases. The following then applies to the heat load $\dot{Q}_B$ of a burner or end device.

$$\dot{Q}_B \approx \alpha \frac{\pi}{4} d_d^2 \cdot \sqrt{\frac{2\Delta p}{\rho_g}} \cdot H_s = C \cdot \sqrt{\Delta p} \cdot \frac{H_s}{\sqrt{\rho_g}} \tag{3}$$

With the introduction of the density ratio k, the Wobbe index is obtained as a parameter:

$$\dot{Q}_B \approx \frac{C}{\sqrt{\rho_{luft}}} \cdot \sqrt{\Delta p} \cdot \frac{H_s}{\sqrt{\frac{\rho_g}{\rho_{luft}}}} = C^* \cdot \sqrt{\Delta p} \cdot \frac{H_s}{\sqrt{k}} = C^* \cdot \sqrt{\Delta p} \cdot W_s \qquad \text{or} \qquad \dot{Q}_B \sim \sqrt{\Delta p} \cdot W_s \tag{4}$$

As an option for the technical adaptation of gas appliances (burners) to a gas type, the nozzle inlet pressure (pressure drop ∆p) can be used, from which the Extended Wobbe Index $\sqrt{\Delta p} \cdot W_s$ is then derived.

2.2 Numerical Approach

In this work, laminar burning velocity was estimated through several detailed kinetic mechanisms existing in the current literature under different initial conditions and gaseous compositions of interest for the investigated system and representative of the experimental data collected.
The freely propagating, steady and one-dimensional flames were investigated in a doubly infinite domain using the premixed laminar flame-speed code of the Chemkin-PRO 2020R2 software. Using the multi-component transport coefficients and thermal diffusion option the LBV the final results were calculated. A typical number of grid points of around 1000 with respect to the gradient and curvature adaptive mesh parameters of GRAD = 0.02-0.04 and CURV = 0.05-0.08 were used. Further details are explained in Eckart et al. 2021 (Eckart et al., 2021a). A shortlist of kinetic mechanisms considered in this work is reported in Table 2.

Table 2. Kinetic mechanisms used in this study.

Model	reactions	species	source
Glarborg	1407	154	Glarborg et al., 2018
USC II	784	111	Wang et al., 2007
Shrestha	1125	129	Shrestha et al., 2018
KiBo	321	73	Pio et al., 2019
GRI 3.0	325	53	Smith et al., 2000

More specifically, the detailed kinetic mechanism developed by the Gas Research Institute, GRI 3.0 (Smith et al., 2000), was adopted since it has been largely considered as a benchmark for the description of the main combustion-related phenomena of light hydrocarbons. Besides, the detailed kinetic model developed at the University of Bologna (KIBO) was adopted since previous studies have indicated KIBO as a suitable mechanism for light hydrocarbons at the investigated conditions (Pio et al., 2019). Further, for comparison the Shrestha mechanism (Shrestha et al., 2018), Glarborg mechanism (Glarborg et al., 2018), and the USC 2016 (Wang et al., 2007) were included, as well. Eventually, the effect of different approaches for the generation of transport models were compared, as well.

3. Results and discussion

A comparison of the experimental and numerical laminar burning velocity of pure hydrogen, obtained at 298 K and 1 bar, is presented in Figure 1. Figure 1 shows that for pure hydrogen combustion, the measured data for LBV scatter significantly; this was also discussed extensively in Konnov et al. (Konnov et al., 2018). In the upper graph, a 95 % confidence interval was entered. The simulations with the three different transport mechanisms can predict within this interval. Nevertheless, the complex multi-component approach considering the Soret effect for thermal diffusion gives the best results and was used for the comparison in the lower graph for all mechanisms. Although the detailed reaction mechanism for hydrogen-air flames among each other shows a variation in the range up to 40 cm/s, this is comparable to the variations in the experimental data (Konnov et al., 2018). The maximum deviation between the predictions of the mechanisms is 20 %. This should be considered for further evaluation and improvements. As well-known, the hydrogen is highly reactive with respect to the given conditions, as confirmed by higher values of LBV at an equivalence ratio ϕ, defined as the fuel to oxygen ratio in feeding stream to the ratio of the stoichiometric coefficients of fuel to oxygen, higher than 1.0 (stoichiometry). Thereby, the Glarborg mechanism shows higher values over the whole range than the other four. The USC II from ϕ > 0.8 shows the lowest values. The KIBO mechanism shows over a wide range a good average value between these two and we will show for the following considerations.

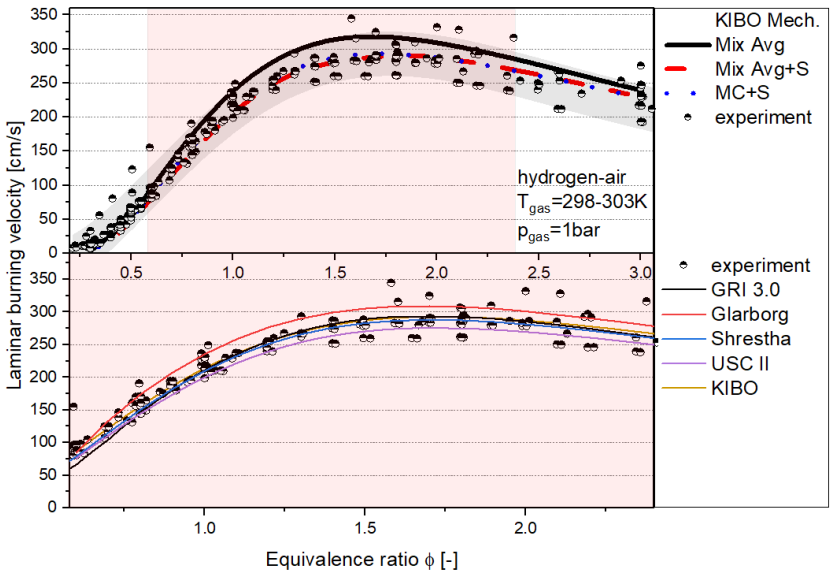

Figure 1 Comparison of experimental data (Konnov et al., 2018) for 100 % hydrogen with numerical results of different reaction mechanisms, Top: comparison mixed average, mixed average+ Soret effect and multi-component + Soret effect, Bottom: compare the mechanisms USC II, Shrestha, GRI 3.0, Glarborg and KIBO for T=298 K and 1 bar.

For future studies, this range will gain additional high importance, since traces of other gases from 2 vol.-% to 5 vol.-% could be allowed in pure hydrogen networks. Both traces of fuels such as propane, butane or methane are conceivable, but nitrogen or carbon dioxide from biogenic fuel gas production. This would have a considerable influence on the burning velocity, which is expected to be much broader than the admixture up to 50 %. No experimental observations are currently known on this subject. Numerically, the changes in burning velocity were plotted in Figure 2.

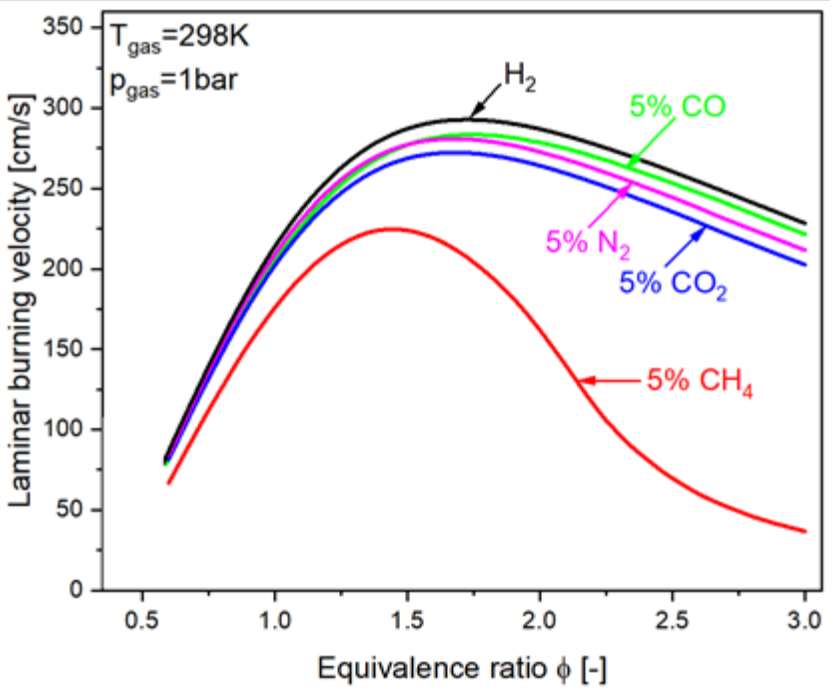

Figure 2. Change in LBV resulting from changes in gas composition, based on a hydrogen flame

It can be seen that CH_4 has the largest effect on LBV followed by CO_2, N_2 and CO. Methane changes the trend of LBV above the equivalence ratio in this case, but the other trace gases do not. As expected, the addition of trace gases influences the laminar burning velocity of hydrogen flames. As shown in Figure 2, CO_2 and N_2 as inert gases as well as CO as fuel do not influence the global trend over the equivalence ratio, whereas methane leads to significant changes.
For the admixture of 5 vol.-% methane, there is already a clear reduction in the burning velocity in the rich region, which leads to a shift of the point of maximum burning velocity to the region around $\phi = 1.3$. It should be noted that the maximum point for methane is around $\phi = 1.1$ (Konnov et al., 2018). The slope of the curve is also more consistent with the common slope for hydrocarbon flames. Likewise, the maximum velocity is also significantly reduced by methane to approx. 220 cm/s. Which still corresponds to factor 6 of the maximum velocity of methane. The operating map of a gas spans between the Wobbe number and the calorific value. This map defines the permissible limits for the distributed gases in an economic area. The characteristic diagram is shown in Figure 3.

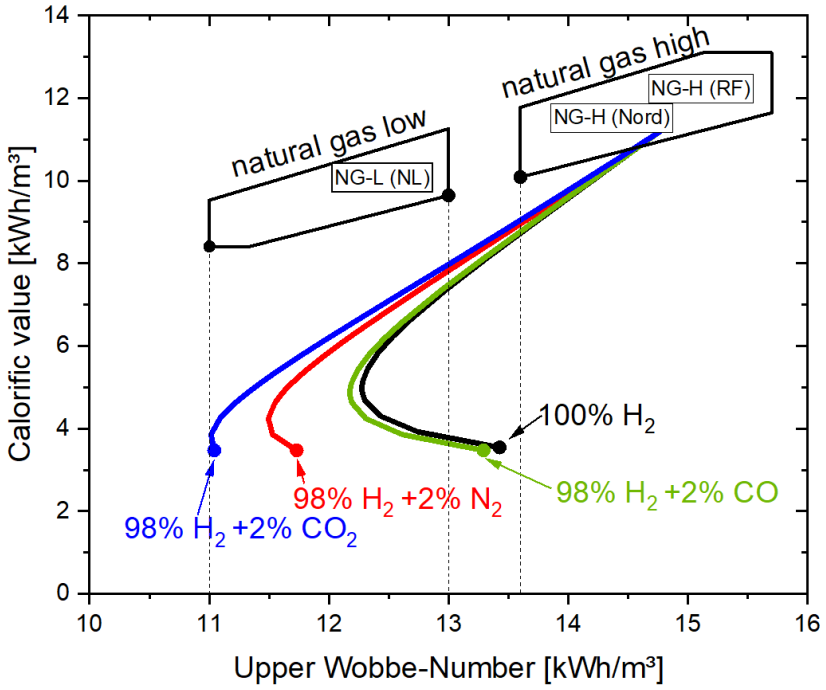

Figure 3 Change in Wobbe number due to changes in gas composition, based on natural gas high

It includes both the fluctuation ranges of typical natural gas sources from the European environment and the characteristic curves for the admixture of hydrogen up to 100 % by volume. Depending on the type of base gas, the mixing characteristic curve covers a wide Wobbe number range. For pure hydrogen, however, the characteristic curve reaches the lower Wobbe number limit of the natural gas H range with a residual deviation from the base gas G 20 (methane) of -9.6 %. For mixtures with a typical natural gas L, there is a deviation from the base gas (natural gas L-Holland) of +5.4 %. For the sake of completeness, the hydrogen gas type A from ISO/DIS 14687:2018 (ISO/DIS 14687, 2018) with permissible inert impurities of up to 2 vol.-% shall also be included in the analysis. Since the effects of trace components have a significantly different density than hydrogen, there is also a non-negligible fluctuation range for this case.

4. Conclusions

The limits of hydrogen and mixtures with minor rarefactions of nitrogen, methane and carbon dioxide were calculated using a numerical method based on a detailed kinetic model. The numerical model was validated against experimental data for pure hydrogen to provide reliable predictions for the dilution cases.
It was shown that the KIBO mechanism, using the MC approach and the Soret effect, was able to reproduce the LBV values for hydrogen-air flames very well. Subsequently, it was shown that all 4 admixtures reduce the LBV. Significant changes in the trend above the equivalence ratio were only seen for CH_4, whereas in the case of CO, CO_2 and N_2 there was only a reduction. It should be taken into account that the study carried out is

strongly affected by the lack of experimental LBV data in the conditions studied. This could be a scientific objective of further interest. Furthermore, the shift in the Wobbe number was calculated for all 4 trace compounds. There are clear shifts in the upper Wobbe number towards lower values due to the addition of trace gases. Here, CO_2 has the greatest influence and CO the least. However, the value for 2 vol.-% CO_2 does not leave the range of the current natural gas low at below 11 kWh/m³.

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