Feasibility of a methane reduced chemical kinetics mechanism in laminar flame velocity of hydrogen enriched methane flames simulations

Ridha Ennetta[*1], Ali Yahya[2] and Rachid Said[2]

[1]*Higher Institute of Industrial Systems (ISSIG), Gabes University, Salaheddine El Ayoubi Street,*
6011 Gabes, Tunisia
[2]*Ionized and Reactive Media Studies (EMIR), Preparatory Institute of Engineers Studies of Monastir (IPEIM),*
Monastir University, Avenue of Ibn El Jazzar, 5019 Monastir, Tunisia

Abstract.   The main purpose of this work is to test the validation of use of a four step reaction mechanism to simulate the laminar speed of hydrogen enriched methane flame. The laminar velocities of hydrogen-methane-air mixtures are very important in designing and predicting the progress of combustion and performance of combustion systems where hydrogen is used as fuel. In this work, laminar flame velocities of different composition of hydrogen-methane-air mixtures (from 0% to 40% hydrogen) have been calculated for variable equivalence ratios (from 0.5 to 1.5) using the flame propagation module (FSC) of the chemical kinetics software Chemkin 4.02. Our results were tested against an extended database of laminar flame speed measurements from the literature and good agreements were obtained especially for fuel lean and stoichiometric mixtures for the whole range of hydrogen blends. However, in the case of fuel rich mixtures, a slight overprediction (about 10%) is observed. Note that this overprediction decreases significantly with increasing hydrogen content. This research demonstrates that reduced chemical kinetics mechanisms can well reproduce the laminar burning velocity of methane-hydrogen-air mixtures at lean and stoichiometric mixture flame for hydrogen content in the fuel up to 40%. The use of such reduced mechanisms in complex combustion device can reduce the available computational resources and cost because the number of species is reduced.

Keywords: laminar burning velocity; reduced mechanism; methane; hydrogen

1. Introduction

With increasing concern about the energy shortage and environmental protection, research on improving engine fuel economy and reduction of the exhaust emissions have become a major research aspect in combustion community and engine development. Due to limited crude oil reserves, the development of the alternative fuel engines has attracted more and more interest in the engine community (Huang *et al.* 2006a). Natural gas, as an alternative fuel, is considered to be one of the favorable fuels for engines. It has emerged as a solution to depleting crude oil resources

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∗Corresponding author, Ph.D., E-mail: ridha_ennetta@yahoo.fr

as well as to the deteriorating urban air quality problem. As a gaseous fuel, gains from natural gas have already been established in terms of low emissions of carbon monoxide, hydrocarbon and particulate matter (Kirtli *et al.* 2005). However, due to the slow burning velocity of natural gas and the poor lean-burn capability, the natural gas spark-ignited engine has the disadvantage of low thermal efficiency, large cycle-by-cycle variations, and poor lean-burn ability. These will decrease the engine power output and increase fuel consumption (Rousseau *et al.* 1999, Ben *et al.* 1999).

One of the effective methods to solve the problem of slow burning velocity of natural gas is to mix the natural gas with a fuel that possesses a fast burning velocity. Hydrogen is regarded as the best gaseous candidate for natural gas due to its very fast burning velocity (Blarigan and Keller 2002, Akansu *et al.* 2004).

Addition of hydrogen to natural gas has been shown to have a beneficial effect in terms of improving combustion properties and reducing polluting emissions (Hu *et al.* 2009a, b, Huang *et al.* 2009b, c, Liu *et al.* 2008). Furthermore, the broad flammability limits and fast flame propagation velocity of hydrogen aid complete combustion of mixtures of hydrogen and natural gas in internal combustion engines of both spark and compression types, and allow the engines to be operated at the lean-burn ranges. Lean-burn operation maintains emission of nitrogen oxides, carbon monoxide and total hydrocarbons at a much lower than that for natural gas only. Internal combustion engines operating at or near the lean limit are a possible technology for solving environmental problems due to pollutant emissions from vehicles in urban areas (Itsuki 2008).

Developments of such systems are today increasingly performed using simulation tools. Indeed, experimental campaigns, being often expensive, technically-limited or even prohibited in some fields, are more and more replaced by numerical simulations. The main difficulty is then to develop predictive models accounting for reacting flows including both chemistry and turbulence effects. The evaluation of the laminar flame speeds is consequently crucial as these data is among the most critical parameters of turbulent combustion models (Bougrine *et al.* 2011).

Turbulent combustion models taking into account the fully detailed descriptions of combustion chemistry are still numerically expensive. As a result, it is important to minimize the dimension while retaining essential features of the detailed chemistry (Ennetta *et al.* 2009).

Reduced chemical kinetic mechanisms that can represent important aspects of the behavior of these detailed mechanisms using few enough scalars that they can be implemented into CFD simulations offer large potential improvement in the modeling of practical combustion devices (Montgomery *et al.* 2002, Glassman and Yetter 2008).

The present research was intended to demonstrate the feasibility of a reduced reaction mechanism in one-dimensional simulations of the laminar flame speed of premixed hydrogen enriched methane flames.

In the present study, chemistry is described by the four-step chemical kinetic mechanism of Jones and Lindstedt (1988). This mechanism was chosen thanks to its good results in 1-D laminar and turbulent propagating methane flames (Jones and Lindstedt 1988, Truffin 2001) and in internal combustion engine simulations (Ennetta *et al.* 2008).

Simulations were carried out using the Flame Speed Calculation (FSC) model of the chemical kinetics code CHEMKIN4.0.2 (Kee *et al.* 2004).

A wide number of conditions are investigated. Equivalence ratio is then varied from 0.5 to 1.5, and hydrogen content in the fuel from 0 to 40%. Results of simulations were tested against an extended database of laminar flame speed measurements from the literature (Di Sarli and Di Benedetto 2007, Huang *et al.* 2006b, Haniff *et al.* 1989, Yu *et al.* 1986). Good agreements were obtained.

The results show that the four step reaction mechanism of Jones & Lindstedt can well reproduce the laminar burning velocity of methane-hydrogen-air mixtures at lean and stoichiometric mixture flame for the whole range of hydrogen percentages as well at rich mixture flame in the case of high hydrogen percentage.

2. Numerical model

Laminar flame speed is often used to characterize the combustion of various fuel-oxidizer combinations and in determining mixture flammability limits. Therefore, the ability to model chemical kinetics and transport processes in these flames is critical to flammability studies, interpreting flame experiments, and to understanding the combustion process itself.

To study the effect of hydrogen addition on methane laminar flame simulations were carried out using the Flame Speed Calculation (FSC) model of CHEMKIN4.02 software (Kee *et al.* 2004). CHEMKIN is a powerful set of software tools for solving complex chemical kinetics problems. It is used to study reacting flows, such as those found in combustion, catalysis, chemical vapour deposition and plasma etching. CHEMKIN consists of rigorous gas-phase and gas-surface chemical kinetics in a variety of reactor models that can be used to simulate detailed kinetics in important industrial systems by predicting the reacting flow conditions or chemical state based on operating conditions (Kee *et al.* 2004).

The FSC model involves a freely propagating flame. This configuration is used to determine the characteristic flame speed of the gas mixture at specified pressure and inlet temperature. In this case there are no heat losses (by definition) and thus the temperatures should be computed from the energy equation.

For these equations, we assume 1-D flow with uniform inlet conditions. The governing conservation equations reduce to:

Continuity:

$$\dot{M} = \rho u A \tag{1}$$

Energy:

$$\dot{M}\frac{dt}{dx} - \frac{1}{c_p}\frac{d}{dx}\left(\lambda A \frac{dt}{dx}\right) + \frac{A}{c_p}\sum_{k=1}^{K}\dot{\omega}_k h_k W_k = 0 \tag{2}$$

Species:

$$\dot{M}\frac{dY_k}{dx} + (\rho A Y_k V_k) - A\dot{\omega}_k W_k = 0 \tag{3}$$

Equation of State:

$$\rho = \frac{P\overline{W}}{RT} \tag{4}$$

In these equations x denotes the spatial coordinate, $\dot{M}$ the mass flow rate (which is independent of x), T the temperature, Y_k the mass fraction of the kth species (there are K_g species), the P pressure, u the velocity of the fluid mixture, ρ the mass density, W_k the molecular weight of the kth species, $\overline{W}$ the mean molecular weight of the mixture, R the universal gas constant, λ the thermal conductivity of the mixture, c_p the constant-pressure heat capacity of the mixture, c_{pk} the constant pressure heat capacity of the kth species, $\dot{\omega}_k$ the molar rate of production by chemical
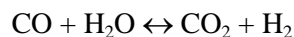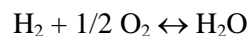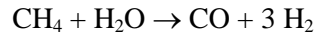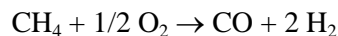
reaction of the kth species per unit volume, h_k the specific enthalpy of the kth species, V_k the diffusion velocity of the kth species, and A the cross-sectional area of the stream tube encompassing the flame (normally increasing due to thermal expansion) normalized by the burner area.

3. Properties of mixtures and chemical kinetics

Complete chemical kinetic descriptions of hydrocarbon combustion may require the tracking of hundreds of chemical species and thousands of reaction steps. Despite the great progress in computer hardware it still very hard to implement such complex reaction schemes into CFD combustion simulations. As a result, it is imperative to minimize this number while retaining essential features of the detailed chemistry.

Reduced chemical kinetic mechanisms that can represent important aspects of the behavior of these detailed mechanisms using, few enough scalars that they can be implemented into CFD simulations, offer large potential improvement in the modeling of practical combustion devices (Montgomery *et al.* 2002).

In the present study, the four step reaction mechanism of Jones and Lindstedt (1988) was chosen thanks to its good results in 1-D freely propagating flame (Truffin 2001, Ennetta *et al.* 2008) and in ICE simulations (Truffin 2001):

$$CH_4 + 1/2\,O_2 \rightarrow CO + 2\,H_2$$

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

$$H_2 + 1/2\,O_2 \leftrightarrow H_2O$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

The laminar flame velocity of hydrogen-methane mixtures was calculated by implementing the Jones & Lindstedt four step reaction mechanism in the flame propagation module of the CHEMKIN software (Kee *et al.* 2004). A wide range of global fuel equivalence ratios (from 0.5 to 1.5) and of hydrogen contents in the mixture (from 0% to 60%) was explored.

4. Results and discussions

The effects of hydrogen addition on the laminar flame velocity, S_L, at atmospheric pressure are shown in Fig. 1. Hydrogen content in the fuel is varied from 0% to 40% in volume. For a given equivalence ratio, when the hydrogen fraction in the fuel increases, the laminar flame speed increases, as expected. This is due to the high mass and thermal diffusivity of hydrogen and its high reactivity. Between 0 and 40% of H_2 at stoichiometry, S_L increases from 37 to 56 cm/s, an increase of about 50%. This increase of laminar velocity would lead to very different performances in real combustion systems. For the different hydrogen fractions, the variation of laminar flame velocity with equivalence ratio is qualitatively the same. In the studied range of hydrogen fraction, the maxima of SL are found near stoichiometry (from 1 to 1.1).

Fig. 2 shows numerical and experimental data of the laminar flame velocities of stoichiometric methane-hydrogen-air flames as a function of the hydrogen content.
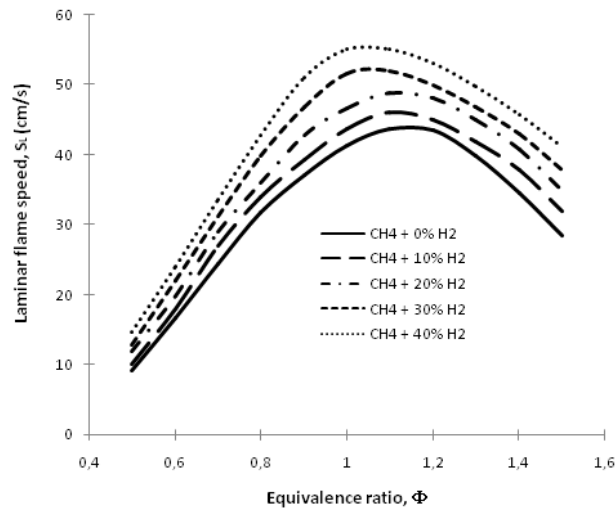
Fig. 1 Laminar flame velocity as a function of equivalence ratio for methane hydrogen mixtures
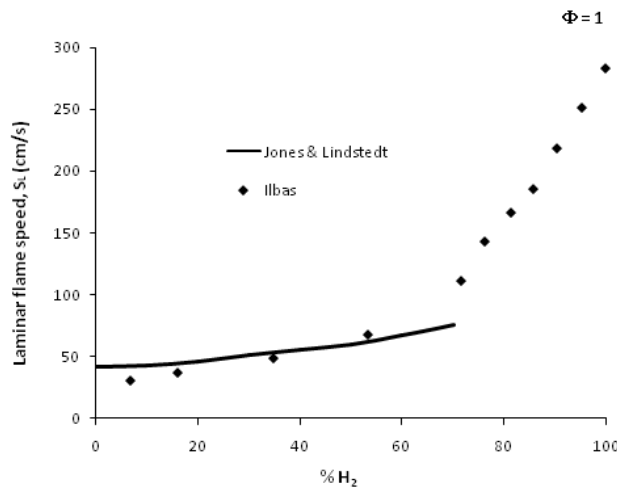

Fig. 2 Experimental and numerical data of the laminar burning velocities of stoichiometric methane-hydrogen-air flames as a function of the hydrogen content

Experimental data of Ilbas *et al.* (2006) shows the existence of two regimes. The first regime occurs at low hydrogen contents, $H_2 < 50\%$. In this regime the laminar velocity increases slightly as a linear function of the hydrogen content.

We can note that this regime is clearly shown by the numerical study using the Jones & Lindstedt reaction mechanism.

In the second regime, for $H_2 > 50\%$, the laminar burning velocity increases significantly and non-linearly.

This increase is probably due to the increase of the hydrogen radical H in the mixture. This result was recently shown by Di Sarli and Di Benedetto (2007) who found that there exists a strong coupling between the laminar burning velocity and the H radical concentration, when
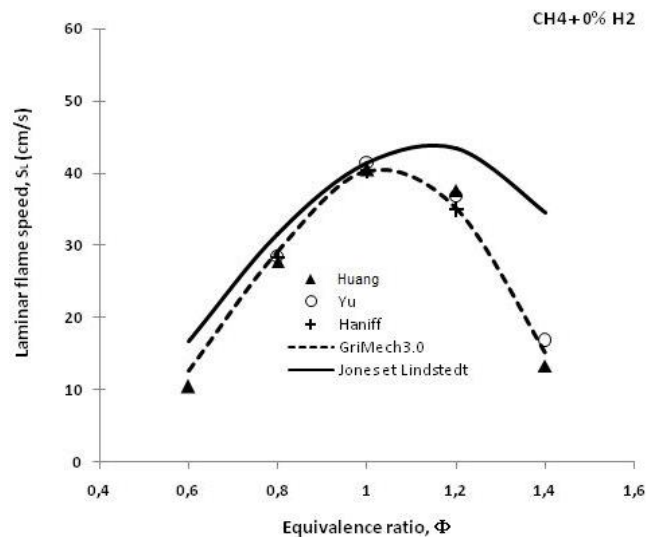
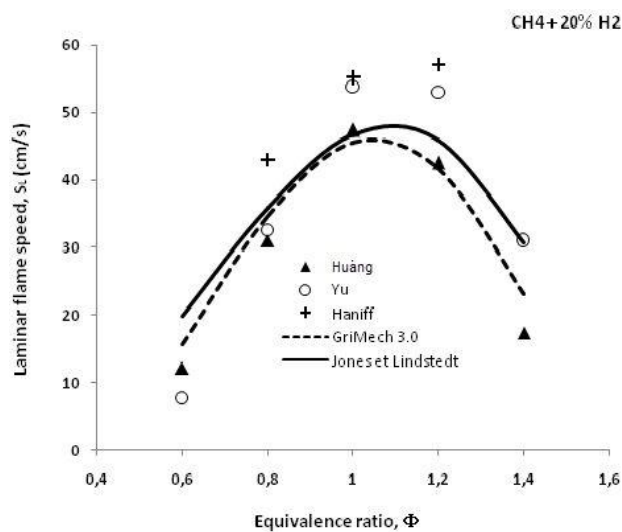Fig. 3 Calculated laminar flame velocity of $Ch_4+0\%H_2$ mixtures, and comparison with experimental data from literature

Fig. 4 Calculated laminar flame velocity of $Ch_4+20\%H_2$ mixtures, and comparison with experimental data from literature

adding hydrogen the overall rate of combustion accelerates due to the increasing H radical concentration.

But in the case of the four steps reaction mechanism of Jones and Lindstedt there is no pathway to produce the H radical. This leads to a poor prediction of the laminar velocity at high hydrogen fraction for the reduced mechanism.

Fig. 3, Fig. 4 and Fig. 5 show laminar burning velocity as a function of equivalence ratio compared with those of the literature (Huang *et al.* 2006d, Haniff *et al.* 1989, Yu *et al.* 1986) for
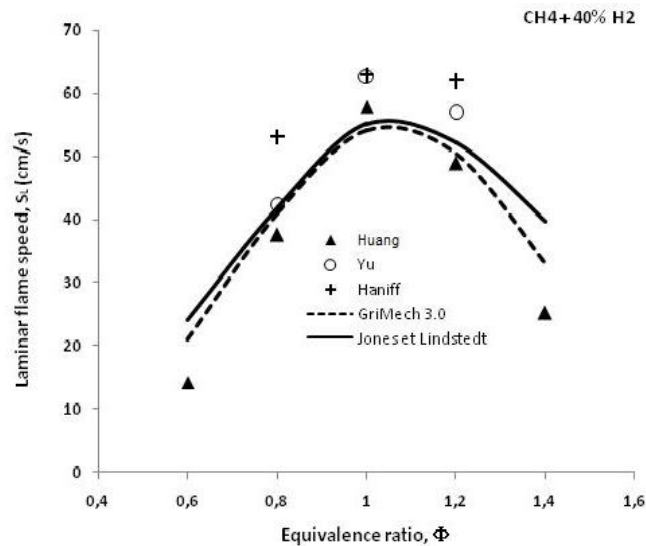
Fig. 5 Calculated laminar flame velocity of $Ch_4+40\%H_2$ mixtures, and comparison with experimental data from literature

different hydrogen contents in the fuel (0%, 20% and 40%).

Our results are very close to those obtained experimentally by Huang *et al.* (2006d) for H_2 mole fractions 0, 20 and 40%. However there is a slight difference with the results of Haniff *et al.* (1989), Yu *et al.* (1986).

A good agreement is also shown with the numerical results of the detailed reaction mechanism Grimech 3.0 (Smith *et al.* 1999) over all the range of H_2 fractions. Grimech 3.0 is considered as a standard for the simulation of natural gas and its compounds. The prediction of the effect of hydrogen addition on the laminar flame velocity is more precise than with the reduced one, because in the case of this detailed mechanism, H_2 has multitude pathways to re act.

The methane based mechanism used in this section for comparison of the laminar flame speed with the experimentally determined data shows some differences. For example for fuel rich mixtures the Jones & Lindstedt mechanism significantly overpredicts the laminar burning velocity compared to the experimental data (for example at $\Phi=1.2$ and $H_2=20\%$, the overpredictions is about 10%), whereas for fuel lean and stoichiometric mixtures this mechanism are close to the experimental data (the overpredictions is generally less than 5%). Note that this difference decreases significantly with increasing hydrogen content.

5. Conclusions

The main objective of this research was to study the laminar burning velocity of hydrogen enriched methane flame using the four step reaction mechanism of Jones & Lindstedt.

Our simulations were carried out in similar conditions to some available experiments and under a wide range of conditions: Equivalence ratio was varied from 0.5 to 1.5, and hydrogen content in the fuel from 0 to 40%.

Results of simulations were tested against an extended database of laminar flame speed

measurements from the literature and good agreements were obtained especially for fuel lean and stoichiometric mixtures.

Our results demonstrated that the four step reduced mechanism of Jones & Lindstedt is feasible for the simulation of laminar flame speed simulations of hydrogen enriched (up to 40%) methane flame.

As we know, the application of such reduced mechanisms can reduce the available computational resources and cost because the number of species is reduced.

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