Soret Diffusion Effects on the Exergy Losses in Hydrogen-Air Laminar Premixed Flames

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1 Introduction

Hydrogen will play an important role in the ongoing process of energy transition, which is based on the capability to produce new fuels and energy carriers and use them in the most efficient manner. The aim of this contribution is to investigate which level of details must be employed in the numerical simulation of hydrogen-air mixtures when a proper assessment of the efficiency when adopting a combustion process. The evaluation of exergy losses is an effective tool for evaluating second-law irreversibility in energy conversion systems [1, 2]. Determining how the thermodynamic efficiency changes by changing the system's parameters, as illustrated in [3], can help the designer to select the most efficient design point.

Som and Datta [2] have shown that the greater amount of exergy loss in power generation systems is due exactly to combustion phenomena. Following the previous investigation [3], a simple configuration of a laminar one-dimensional premixed flame propagation will be adopted in this first study to evaluate the contribution that the Soret diffusion, often neglected in the simulation models of combustion systems, adds to the entropy production and so to total exergy losses.

The entropy generation in a combustion process is linked to four irreversible phenomena: chemical reactions, heat conduction, mass diffusion, and viscous dissipation [5]. Particularly, mass diffusion is an essential phenomenon in laminar flames. Indeed, it affects ignition, flame propagation, and extinction [6]. In a multicomponent mixture, mass diffusion depends on three contributions associated with the mechanical driving forces and a contribution associated with the thermal driving force [7]. This latter contribution describes the chemical species diffusion under the influence of a temperature gradient; it is known as the Soret effect or thermal-diffusion effect. Usually, it is negligible because the thermal diffusion coefficient is typically significantly smaller than the mass diffusion coefficient [7]. Nevertheless, it can be quantitatively significant at times and must be taken into account [8] especially if light or heavy fuels are considered [6]. The Soret effect drives light species towards hot regions of the flow and heavy species away from them [9]. Conversely, the companion effect, i.e. the energy flux due to a mass concentration gradient (also known as the Dufour effect) generally has a weak influence in laminar flame [8, 10].

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Both Yang et al. [11] and Faghih et al. [12] show that thermal diffusion may appreciably affect the laminar flame speed in premixed hydrogen/air flames. These results are adopted as the reference and the starting point for the present study. Particularly, the results reported in figure 3 of Yang et al. [11] and in figure 2 of Faghih et al. [12] are used as reference conditions for performing the exergy loss analysis.

2 Methodology

The laminar flame speed of a premixed hydrogen/air mixture is calculated by using the CHEMKIN software package [13]. The model used is the freely-propagating flame (a detailed mathematical formulation of this model can be found in [14]). The final computational domain is set to 0.12 m (120 mm) from -0.02 to 0.1 m, the adaptive grid controls based on, respectively, curvature and gradient are set to 0.005 and 0.002, the tolerance parameters are set to $1\mathrm{e}{-9}$ for the absolute one and $1\mathrm{e}{-6}$ for the relative one, and the maximum number of grid points allowed is set to 10000. The transport properties are evaluated using the multicomponent transport model (see for details Kee et al. [14]). In agreement with both Yang et al. [15] and Faghih et al. [12], the detailed chemical mechanism consisting of 9 species and 20 reactions developed by Li et al. [16] is used to model hydrogen combustion.

The local entropy generation γ in laminar premixed flames, under the following assumptions:

1. radiative heat transfer is negligible
2. gas mixture is ideal
3. pressure is constant throughout the flowfield
4. Dufour effect is negligible
5. contribution due to viscous effect is negligible
6. gravity is the only body force
7. flow is steady, plane, and one-dimensional in the adopted frame of reference

can be quantitatively evaluated as:

$$\begin{aligned}\gamma_{tot} = &\frac{\lambda}{T^2}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2 + \rho R_m \sum_{k=1}^{N_s} \frac{D_{km}}{X_k}\left(\frac{\mathrm{d}X_k}{\mathrm{d}x}\right)^2 + \sum_{k=1}^{N_s} \frac{R_k D_k^T}{X_k T}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)\left(\frac{\mathrm{d}X_k}{\mathrm{d}x}\right) + \\ &- \frac{1}{T}\sum_{k=1}^{N_s}\sum_{j=1}^{N_r} \mu_k(\nu_{kj}^P - \nu_{kj}^R) r_j\end{aligned} \tag{1}$$

where λ is the thermal conductivity, D_k^T, X_k, and D_{km} are the thermal diffusion coefficient, the mole fraction, and the Equivalent Fickian diffusion coefficient of species k respectively, and R_m and R_k are the mixture and k-th species gas constant. For a detailed explanation of all symbols please see [4]. In Eq. 1, four contributions can be distinguished, in the order: heat conduction (thereafter indicated as γ_{hc}), mass diffusion (γ_{diff}), mass diffusion by Soret effect ($\gamma_{\text{diff,Soret}}$), chemical reactions ($\gamma_{\text{react}}$). These quantities are evaluated, in order to investigate the relative importance of the Soret effect, in post-processing (from the flame numerical results) by using our own Matlab functions, based on Cantera open-source suite [17]. The exergy loss is obtained by using the Gouy-Stodola theorem [18]:

$$\dot{E}_{loss} = T_0 \gamma \tag{2}$$

Here, the subscript 0 refers to the exergy reference environment that is assumed to be, in accordance with Moran et al. [19], an ideal gas mixture modeling Earth's atmosphere as defined in [20]. The exergy loss ratio is calculated as [21]:

$$E_{loss} = \frac{T_0 \int \gamma \mathrm{d}x}{e_f} \tag{3}$$

where e_f is the chemical exergy flux density carried by the unburnt mixture. It is defined as the product between the standard chemical exergy per unit mass of the unburned mixture e_u and the volumetric mass flux entering the flame $\rho_u S_L$:

$$e_f = e_u \rho_u S_L \tag{4}$$

3 Results and Discussion

Effect of Soret diffusion as a function of the equivalence ratio. Yang et al. [11, 15] show that the Soret diffusion decreases the laminar flame speed in the entire range from lean to rich mixtures due to the downstream diffusion of H radicals. Computing the relative difference between the results obtained with and without the Soret effect:

$$\text{Relative difference}(S_{L,\text{Soret}}, S_{L,\text{noSoret}}) = \left| \frac{S_{L,\text{Soret}} - S_{L,\text{noSoret}}}{0.5(S_{L,\text{Soret}} + S_{L,\text{noSoret}})} \right|$$

allows for identifying the equivalence ratio in which this effect is more significant. Figure 1 shows that the maximum effect of the Soret diffusion on the laminar flame speed is at an equivalence ratio of 0.7. The entropy generation rates due to the four contributions identified are reported in Figure 1, left, at $\varphi = 0.7$, $P = 1\text{atm}$, and $T_u = 300\text{K}$. This figure shows that, despite the contribution due to the Soret effect sharply rises at the main reaction zone in a similar way to the other contributions, it is an order of magnitude lower than the entropy generated by mass diffusion. The low importance of the Soret effect in the entropy generation and, hence, in the exergy loss is confirmed by computing its relative weight with respect to the total mass diffusion (the sum of the mass diffusion and Soret diffusion) and with respect to the total entropy generation (Figure 4) by adopting the following relations:

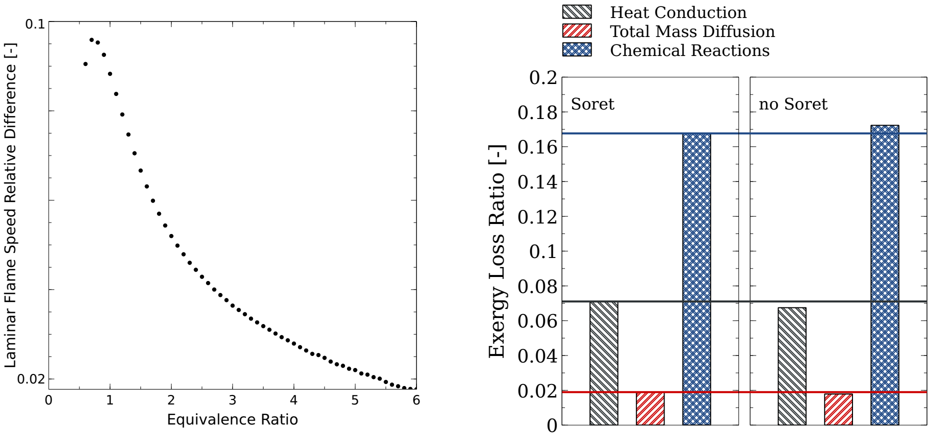

Figure 1: Left: Relative difference between laminar flame speed computed with and without the Soret effect. Right: Comparison between results obtained with and without Soret effect at $\varphi = 0.7$, $P = 1\text{atm}$, and $T_u = 300\text{K}$.

$$RW_{\text{diff}} = \frac{\gamma_{\text{diff, Soret}}}{\gamma_{\text{diff, Soret}} + \gamma_{\text{diff}}} * 100$$

$$RW_{\text{tot}} = \frac{\gamma_{\text{diff, Soret}}}{\gamma_{\text{diff, Soret}} + \gamma_{\text{diff}} + \gamma_{\text{hc}} + \gamma_{\text{react}}} * 100$$

Clearly, it appears that the Soret diffusion is negligible with respect to the other contributions. However, this is not a conclusive answer. Indeed, it is still needed to verify if neglecting the Soret diffusion in the laminar flame simulations may significantly affect the exergy loss due to other contributions.

In order to carry out this verification, a comparison between the exergy loss ratios obtained with the Soret effect and without this phenomenon is presented in Figure 1, right. The results presented show that the Soret diffusion appreciably affect the exergy losses due to chemical reactions and to heat conduction. This effect is not so small. If Soret diffusion is neglected, the contribution of chemical reactions is overestimated by 13.1%, those of total mass diffusion by 3.8%, and the one due to heat conduction by 4.5%. The total exergy loss evaluation will result affected by an error of 10.1%.

Effects of Soret diffusion under engine-relevant conditions. In [12] it is shown that, for hydrogen/air mixtures, the Soret diffusion reduces the laminar flame speed by around 10% in premixed flame under engine-relevant conditions mainly due to the Soret diffusion flux of H radicals and H_2 molecules. The relative weight with respect to the entropy generation by total mass diffusion (the sum of contributions due to the mass diffusion and Soret diffusion) and with respect to the total entropy generation (Figure 2) suggest to investigate the Soret diffusion effects at $P = 6$ atm, and $T_u = 579.03$ K where RW_{diff} is maximum, and at $P = 19$ atm, and $T_u = 792.30$ K where RW_{tot} is maximum. The comparisons between the exergy loss ratios obtained with the Soret effect and without this phenomenon are presented in figure 3 for the three conditions identified. The results presented show that there is an appreciable

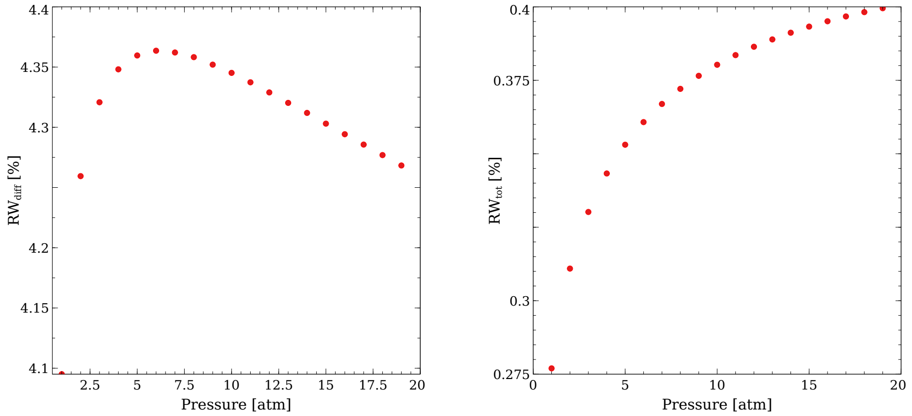

Figure 2: Relative weight of the entropy generated by Soret effect with respect to the entropy production by total mass diffusion (left) and the total entropy generation (right) at $\varphi = 1$. The temperature of the unburned mixture changes with pressure following the isentropic compression relationship with the initial values of $P = 1$atm, and $T_u = 350$K.

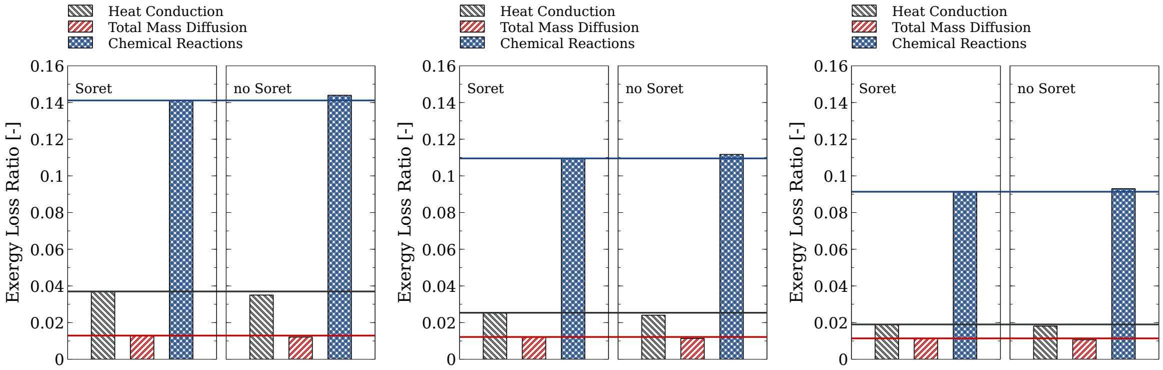

Figure 3: Comparison between results obtained with and without Soret effect at: $\varphi = 1.0$, $P = 1$atm, and $T_u = 350$K(left); $\varphi = 1.0$, $P = 6$atm, and $T_u = 579.03$K(center); $\varphi = 1.0$, $P = 19$atm, and $T_u = 792.30$K(right).

effect due to the Soret diffusion on all three main contributions to the exergy loss. The relative error that would be made in neglecting the Soret effect is summarized in Table 1.

Table 1: Relative error in neglecting the Soret effect

Pressure **Temperature**	$P = 1\text{atm}$ $T_u = 350\text{K}$	$P = 6\text{atm}$ $T_u = 579.03\text{K}$	$P = 19\text{atm}$ $T_u = 792.30\text{K}$
Heat Conduction	3.0%	2.1%	1.9%
Total Mass Diffusion	1.9%	0.6%	0.3%
Chemical Reactions	10.9%	9.7%	9.0%
Total	8.8%	7.6%	7.1%

The reported results show that neglecting the Soret effect significantly affects the exergy loss due to chemical reactions, while the error on the other entropy generation sources remain small. The effect tends to reduce when moving at higher pressures and higher inlet temperatures, but globally it remain significant with a minimum error of 7.1%.

4 Conclusions

The present study computationally investigates the effect of Soret diffusion on the exergy loss in laminar premixed flames using a detailed reaction mechanism and the multicomponent transport model. The results obtained lead to the following conclusions:

- the exergy losses directly due to Soret effect ($\gamma_{\text{diff, Soret}}$) are always negligible with respect to the other contributions;
- even if the Soret effect does not affect the total exergy loss in a direct way, it indirectly affects the other sources of entropy production, whose magnitude modifies appreciably;
- neglecting the Soret diffusion leads to overestimate the total exergy loss by a value ranging from 7.1 to 10.1% for the cases reported, an error comparable to the error it produces on the laminar flame speed.

Hence, the Soret effect, unlike what has been usually assumed, is not negligible in evaluating the exergy loss in flames at least when this effect is known to affect laminar flame speed.

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