Impact of Detailed Molecular Transport on Ammonia/Hydrogen Ignition Delay Time Measurements in Rapid Compression Machines

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1 Introduction

The dependence of ignition delay time (IDT) on pressure and temperature is an important characteristic of any fuel. For the case of ammonia(NH_3)/hydrogen(H_2) mixtures, there is a paucity of ignition delay time measurements. This contrasts with the importance of these mixtures in their potential as alternative fuels. More experimental IDT data for these substancey are desired. IDTs can be measured in Rapid Compression Machines (RCM, see e.g. [1]). Accurately reproducing experimentally measured IDT by kinetic mechanisms under varying conditions remains a significant challenge [2]. Simulations of the auto-ignition in RCMs often rely on homogeneous reactor models, which do not include a detailed description of critical factors such as in-cylinder flow and heat transfer to the cold wall. Still, such effects can influence the ignition process observed in experiments; e.g., [6] classify the relative influence of these factors to form a regime diagram dedicated to RCM experiments. In a similar way, mass transfer by diffusion can become an important factor. For instance, in hydrogen-containing mixtures, the low molar mass and high diffusivity of H_2 (see e.g. [3]) can cause an ”un-mixing” of hydrogen at temperature gradients. This can effectively result in a stratified fuel-air ratio field, and thus affect ignition behavior.

In this study, a one-dimensional model was employed to model auto-ignition in a system that evolves under detailed chemical kinetics and detailed molecular transport. The model simulates a laminar layer of fuel/air mixture which extends from the center of the chamber to the wall. We used detailed transport model to show the effect of differential diffusion and thermo-diffusion on the ignition. Results show that effects of detailed transport can notably alter the mixture before and during the induction phase, so that conditions at ignition can deviate from those in the initial compressed mixture. These alterations can become notable within the typical time scales of ignition delay in RCM experiments (say, several 10 ms), and their neglect may lead to a bias in reported experimental ignition delay time curves.

2 Methodology

The impact of detailed molecular transport on the auto-ignition during a typical RCM experiment is studied by numerical simulations of species- and temperature profiles in a laminar layer of the reacting

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gas mixture in the RCM-chamber. Attention is given to full spatial and temporal resolution; in particular, the interplay of detailed molecular transport processes (transport of energy by heat conduction and species diffusion, transport of chemical species by diffusion and by thermo-diffusion, regarding different diffusivities among species and between mass and energy) with detailed chemical kinetics is modeled.

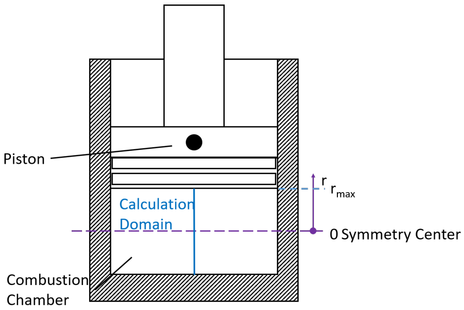


Figure 1: Schematic of the calculation domain.

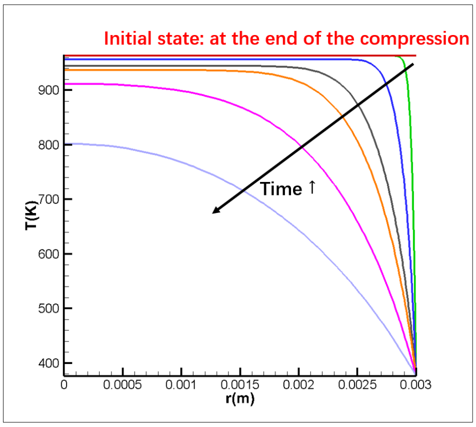


Figure 2: Temperature profile of an inert gas mixture in the simulation.

This is achieved with the in-house code INSFLA [4]. This solves the detailed equations for reaction and molecular transport for a reacting ideal-gas mixture on a 1D region, applying automatic grid adaption and time stepping with error control on the solution. The simulated region is a line in the center of the RCM chamber, spanning the axial distance from the piston surface to the cylinder head (Fig. 1). Since that in RCMs in compressed state axial distance is typically an order of magnitude smaller than the cylinder diameter, the temperature gradient in the axial direction are significantly steeper than those in the radial direction. As a result, molecular transport in the axial direction becomes more pronounced. Therefore, a one-dimensional simulation along the axial direction can qualitatively describe the impact of molecular transport on the calculation of the ignition delay time (IDT). The thermo-chemical evolution on this line is simulated from the time where the compression in the modeled RCM process is just finished. This causes the gas to have high temperature T_c and pressure p_c. Initially (at time $t = 0$), all fields (species and temperature) are homogeneous. The inner boundary is set at the symmetry center, while the outer boundary is set at the cold wall with $T_w = 376K$.

In 1-D simulations using INSFLA, detailed molecular transport was applied. The initial conditions consisted of homogeneous fuel/air mixtures with an initial temperature T_c. In this study, stoichiometric mixtures containing $40\,\%\,\mathrm{NH_3}$ and $60\,\%\,\mathrm{H_2}$ were investigated. Since the inner boundary is set at the symmetry center, Neumann boundary conditions are applied. The outer boundary is positioned at the cold wall, where Dirichlet boundary condition is imposed on the temperature, maintaining an isothermal wall condition at the outer boundary. The outer boundary condition of the species is $j_i = j_i^M + j_i^T = 0$, where j_i^M denotes the mass flux of species caused by concentration gradient and j_i^T denotes the mass flux of species caused by temperature gradient.

An example of simulated temperature profiles $T(t, r)$ is shown in Fig. 2. The simulation begins at the end of compression with a spatially uniform initial temperature T_c. After that, the outer boundary is fixed at the cold wall with $T_w = 376$ K, leading to a decrease in the temperature within the domain due to heat conduction toward the cold wall.

2 Evaluation procedure for the simulated RCM process

The simulated data (notably, T_c, p_c and the resulting pressure trace $p(t)$) are used like experimental RCM data as the basis for a data evaluation procedure to obtain ignition delay time and the temperature and pressure associated with an ignition event.

Moreover, 0-D homogeneous reactor simulations of the ignition event are performed to investigate the impact of detailed molecular transport. Firstly, inert 1-D simulations were performed to obtain the inert pressure trace $p(t)$ corresponding to inert gas measurements in RCM experiments. Then, under the isentropic assumption, the volume trace $v(t)$ was calculated from the conservation equations and the ideal gas law. The volume trace $v(t)$ was then used as the input for homogeneous reactor simulations.

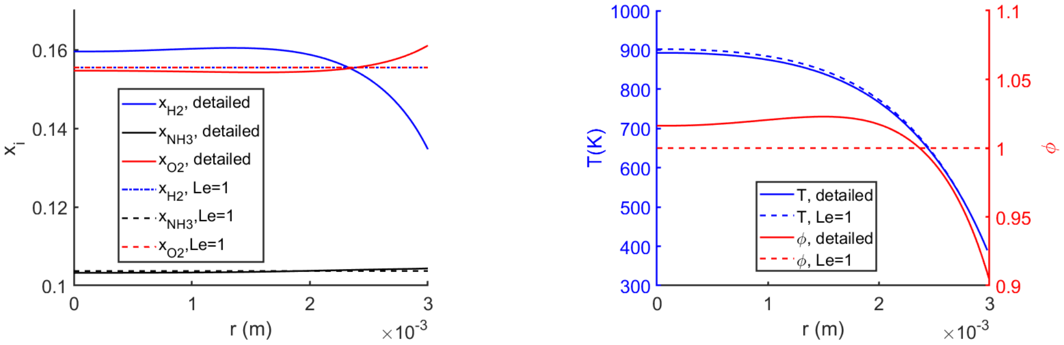
In both 1-D simulations and homogeneous reactor simulations, detailed chemical kinetics with the mechanism for NH_3 and H_2 developed by Shrestha et al. were applied [5]. The ignition delay time (IDT) in both simulations was defined as the duration from $t = 0$ to the point where the pressure gradient reaches its maximum.

3 Results and Discussion

3.1 Results

Non-reacting case First, a non-reacting $40\,\%\,NH_3$/$60\%\,H_2$ (mol/mol) / air at $\phi = 1$, $T_c = 960$ K, $p_0 = 15$ bar was simulated. To achieve this, the chemical reactions were "shut off", so that only molecular transport processes affect the system. Fig. 3 shows the resulting profiles of species mole fractions, temperature, and equivalence ratio after 40 ms. The equivalence ratio was calculated using the H/O atom ratio: $\phi = \frac{w_H/w_O}{(w_H/w_O)_{\text{stoich.}}}$. Due to heat transfer to the cold wall, a thermal boundary layer at the outer boundary (formed by the cylinder top) has formed. The temperature gradient at this layer wall causes diffusion of species by thermo-diffusion. Fig.3 shows this effect, both for simulations with a detailed transport model (solid lines) and for simulations with equal species diffusivities and a unity Lewis number assumption (dotted lines). Since the diffusivity of hydrogen is larger than that of ammonia, H_2 diffuses faster into the high-temperature region in the detailed transport model. The differential diffusion, therefore, causes an un-mixing of the initially homogeneous gas mixture, resulting in a space-dependent equivalence ratio. At the outer boundary, the temperature is lower, and the mixture is "leaner" compared to the center.

Reacting case To further demonstrate the effect of molecular transport on the auto-ignition process and to estimate the IDT using the 1D model, the simulation was repeated with chemical reactions included. Fig. 4 shows the spatio-temporal evolution of temperature and hydrogen concentration for the auto-ignition in a $40\,\%\,NH_3$ / $60\,\%\,H_2$ / air mixture at $\phi = 1$, $T_c = 960$ K, $p_0 = 15$ bar. During

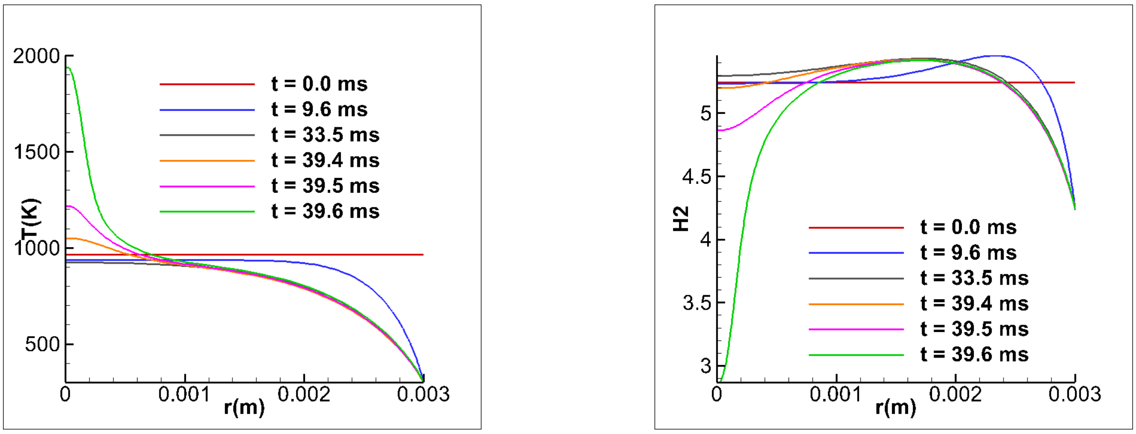


(a) Mole fractions of H_2, NH_3 and O_2, showing effects of thermal diffusion

(b) Temperature and equivalence ratio showing the effect of heat conduction and differential diffusion

Figure 3: Temperature and species profiles for non-reacting mixture of $40\,\%\,NH_3$ / $60\,\%\,H_2$ / air at $\phi = 1$, $T_c = 960$ K, $p_0 = 15$ bar, $t = 40$ ms, $r_{max} = 3$ mm

the ignition delay period, a temperature gradient caused by heat conduction to the cold wall and diffusion of hydrogen into the high-temperature zone can be observed, like in the inert case. Starting at approximately 39 ms, auto-ignition begins to occur. However, unlike in the homogeneous reactor, where auto-ignition occurs simultaneously throughout the entire domain, the temperature rise and auto-ignition in the 1D case initiate in a localized region at the center, while the rest of the mixture remains unignited.



(a) Temperature profile showing auto-ignition in the middle of the calculation domain

(b) H_2 mass fraction showing the reaction and diffusion of hydrogen

Figure 4: Spatio-temporal evolution of temperature and hydrogen concentration for the auto-ignition of mixture of $40\,\%\,NH_3$ / $60\,\%\,H_2$ / air at $\phi = 1$, $T_c = 960$ K, $p_0 = 15$ bar

3.2 Discussion

The detailed molecular transport affects the auto-ignition process in several ways. Differential diffusion alters the equivalence ratio ϕ (mainly due to the different diffusion behavior of H_2 and O_2). It also alters the molar ratio r of the fuel components ($r = H_2/NH_3$). Both effects are notable even in the center of the domain, where the highest temperatures prevail and therefore ignition is occurring (Fig. 4). Fig.5 a) shows the temporal evolution of ϕ and r for one condition. Results for both detailed and simplified transport are shown. This can lead to an assignment of a measured ignition event (and its ignition delay time) in an RCM to physically incorrect values of ϕ and r. The deviation between the nominal and actual values first increases with the time after compression. This is due to the build-up of the "unmixing process" by the different diffusivities of the components in the fuel/air mixture. The deviation then decreases again; this is consistent with the "leveling-out" of the compositional inhomogeneities (which were temporarily created by different diffusivities) on longer timescales. In the example of Fig. 5, the maximum deviation (in the order of 5% for both ϕ and r) is seen near 100 ms after compression. At different conditions (especially, for lean mixtures), one can expect even larger deviations, and also different time scales of the deviations' build-up and decay.

As Fig.5 b) shows, the temperature in the center of the simulated region is nearly the same for detailed and simplified [labeled with "Le=1"] in the diagram) transport. The deviation between these curves is overall well below 1 Kelvin over the observed time span (120 ms). The detailed transport, therefore, affects the temperature history hardly any more than the simple transport does. Both temperature profiles are consistent with the isentropic core model in the initial phase, and both deviate in the same way from the isentropic core curve at longer time scales.

Comparable trends were also observed with a 50% NH_2 $/50\%$ H_2 mixture, indicating the robustness of the results.

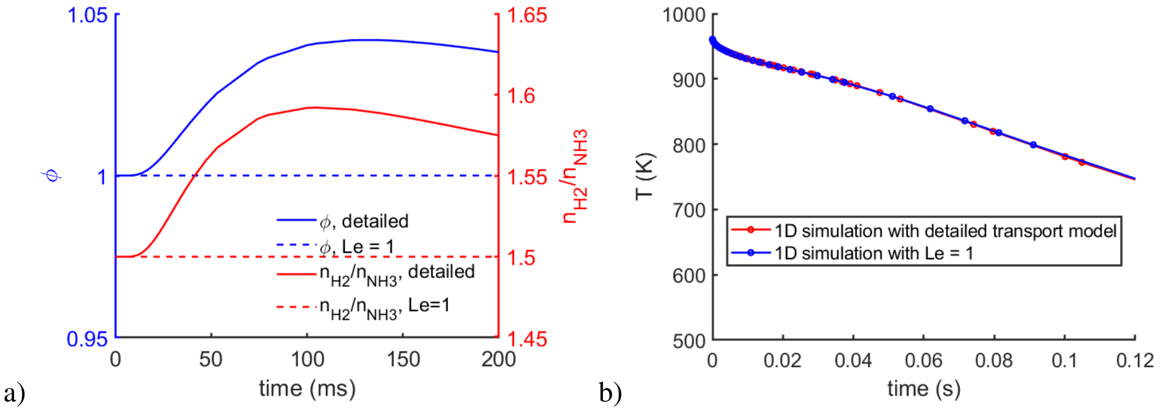


Figure 5: a) Temporal evolution of equivalence ratio and H_2/NH_3 ratio in the center of the domain, as a function of time. b) Same for the temperature in the center. In a) and b) diagram, data for both detailed and simplified transport models are shown.

As described in Sec. 3, the IDT was calculated using both 1-D simulations and homogeneous reactor simulations, with the IDT defined as the duration from $t = 0$ to the point where the pressure gradient reaches its maximum.

While the physical conditions under which the auto-ignition event occurs are affected by detailed transport, the ignition delay time as such is affected only little in the example studied here. This is because near $\phi = 1$, the ignition delay time is not very sensitive with respect to changes in ϕ, and also not with respect to changes in the NH_3/H_2 ratio r near $r = 0.6/0.4$.

Therefore, the evaluation procedure which assigns a temperature and pressure to an ignition event is hardly affected by detailed transport any more than it is by heat transfer (without the complications of detailed transport) anyway. This, however, is the observed behavior in the studied case ($\phi = 1$); it may be different in other cases.

4 Conclusions

This study investigates the impact of detailed transport on auto-ignition in an ammonia-hydrogen mixture for typical conditions of rapid compression machine (RCM) experiments by numerical simulations. The simulations model a laminar gas layer in the chamber of a RCM and incorporate detailed chemical kinetics and molecular transport processes, thus including effects of differential diffusion and unequal diffusivities of heat and species. Mixtures of ammonia/hydrogen with air are considered, in view of their projected significance as fuels for the future energy structure, and in view of the special character of hydrogen in respect to its molecular transport properties.

Results show how, in the fuel/mixture at compressed state, heat conduction to the cold wall creates an inhomogeneous temperature profile, with the maximum temperature occurring at the center, and a steep gradient at the cold wall. The inhomogeneous temperature profile, in turn, leads to an increasingly inhomogeneous mixture composition, driven by unequal diffusivities of species and of thermal energy. This can occur well before chemical reaction significantly alters the mixture composition.

The effect may introduce a bias in practical RCM measurements involving hydrogen as a fuel, when the observed auto-ignition event actually occurs in conditions (e.g., with respect to the equivalence ratio and the molar shares of different fuel components) that are different from the intended, ”nominal” values of equivalence ratio and fuel composition in a multi-component fuel. For similar reasons, the effect may also pose a challenge to comparisons of IDTs from RCM experiments and modeling simulations for validating chemical kinetic mechanisms.

To assess the magnitude of the effect, further studies involving more details of the RCM compression process, the chamber size and geometry, initial mixture composition, compression pressure and temperature will be conducted. It will also be helpful to develop experimental methods capable of assessing the extent of the ”unmixing” effect in an actual RCM-experiment.

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