NUMERICAL STUDY OF SPONTANEOUS IGNITION OF PRESSURIZED HYDROGEN RELEASE INTO AIR

B. P. Xu[1], L. EL Hima[1], J. X. Wen[1*], S. Dembele[1] and V.H.Y. Tam[2]
[1]Faculty of Engineering, Kingston University
Friars Avenue, London, SW15 3DW, UK
[2]EPTG, bp Exploration, Chertsey Road, Sunbury-on-Thames, TW16 7LN, UK

ABSTRACT

Numerical simulations have been carried out for spontaneous ignition of pressurized hydrogen release directly into air. Results showed a possible mechanism for spontaneous ignition due to molecular diffusion. To accurately calculate the molecular transport of species, momentum and energy in a multi-component gaseous mixture, a mixture-averaged multi-component approach was employed in which thermal diffusion is accounted for. To reduce false numerical diffusion, extremely fine meshes were used along with the ALE (Arbitrary Lagrangian-Eulerian) method. The ALE method was employed to track the moving contact surface with moving clustered grids. A detailed kinetic scheme with 21 elementary steps and 8 reactive chemical species was implemented for combustion chemistry. The scheme gives due consideration to third body reactions and reaction-rate pressure-dependant "fall-off" behavior.

The autoignition of pressurized hydrogen release was previously observed in laboratory tests [2-3] and suspected as possible cause of some accidents. The present numerical study successfully captured this scenario. Autoignition was predicted to first take place at the tip region of the hydrogen-air contact surface due to mass and energy exchange between low temperature hydrogen and shock-heated air at the contact surface through molecular diffusion. The initial flame thickness is extremely thin due to the limiting molecular diffusion. The combustion region extends downward along the contact surface as it moves downstream. As the hydrogen jet developed downstream, the front contact surface tends to be distorted by the developed flow of the air. Turbulence plays an important role in mixing at the region of the distorted contact surface. This is thought to be a major factor for the initial laminar flame to turn into a final stable turbulent flame.

Keywords: Spontaneous Ignition, Diffusion Ignition, Shock, Mach Disk, Molecular Transport, and ALE.

1. INTRODUCTION

It is well known that the combustion of fossil fuels is responsible for the majority of the greenhouse gas emission and a significant fraction of pollutant emissions in the world. The natural reserves of fossil fuels are also diminishing quickly. Hydrogen is one of the most promising substitutes of hydrocarbon fuels, due to the absence of carbon-cased pollutants, the abundance of hydrogen in nature, and the ability to generate hydrogen from sustainable energy sources. The future widespread use of hydrogen demands research on safety issues in relation to the production, transportation, storage and utilization of hydrogen.

As an energy carrier, hydrogen has some unique properties compared to other combustible gases. Because of its low density, storage of hydrogen at pressures as high as 100MPa is being considered for transportation applications. The low viscosity and small molecular size of hydrogen give it a greater propensity to leak than other common gaseous fuels. Hydrogen is also more diffusive and more buoyant which mean that hydrogen can disperse more easily and rapidly than other fuels after an accidental

[*] *Corresponding author e-mail: j.wen@kingston.ac.uk*

release. However this also produces a detrimental effect of enabling deflagration and diffusive combustion of hydrogen to proceed rapidly in ultra-lean mixtures. Hydrogen has a much wider range of flammability in air (4% to 75% by volume) and the minimum ignition energy is about an order of magnitude lower. These two properties make hydrogen easier to be ignited. The autoignition temperature of hydrogen is only around 800K. It also has a stronger chain branching in its chemical reaction and reacts rapidly at a location where the temperature exceeds 1000K, while for hydrocarbon fuels rapid reactions only occur until temperatures is greater than 1500K. The radiation from a hydrogen flame is very low which makes the flame nearly invisible and also hotter than a hydrocarbon flame.

The risk for pressurized hydrogen release to auto-ignite is of great safety concern. Historically, there were incidents where sudden releases of high pressure hydrogen were ignited with no clearly identifiable ignition sources [1]. Several ignition mechanisms have been examined in the literature [1,2]. Among them there are reverse Joule-Thomson effect, static electricity, diffusion ignition, sudden adiabatic compression, hot surface ignition, mechanical friction and impact ignition. Although more than one mechanism might be responsible for the autoignition in a hydrogen release accident, the principal concern in this paper is diffusion ignition.

The mechanism of diffusion ignition was first proposed by Wolanski and Wojciki [3]. In their experiments, high pressure hydrogen driven by a detonated oxygen-hydrogen mixture was released into a cylindrical chamber of 20 cm in diameter filled with oxygen. The hydrogen release into oxygen produced a shock wave which caused an auto ignition even though the overall temperature of hydrogen was below the ignition temperature. They found that the ignition was caused by a temperature increase of combustible mixture due to the mass and heat diffusion between hydrogen and shock-heated oxygen, and they referred to this phenomenon as diffusion ignition.

Very recently, Dryer et al. [2] demonstrated diffusion ignition of compressed releases of hydrogen into air by experiments. The experiments were conducted by administrating rapid ruptures of burst disks under different release pressures and internal flow geometries downstream the disks. Autoignition occurred for release pressures above 20 bar. It was found that flow geometry downstream of the burst disk has a strong influence on autoignition especially for lower release pressures. In their experiments, the rupture of the burst disks resulted in multi-dimensional transient flows involving shock formation, reflection and interactions. It was speculated that the multi-dimensional shock-boundary and shock-shock interactions played a key role in producing short mixing time scales for the autoignition to occur.

In a very recent paper, Golub et al. [4] numerically and experimentally investigated the shock-induced ignition of high-pressure hydrogen releases. Their numerical results revealed that the auto ignition of the jet release was related to the hole size and no combustion occurred for the hole diameter less than 2.6mm. In their experiment, the high-pressure hydrogen was released through a tube of constant area into a large chamber. The minimum required release pressure for autoignition to occur was found to be dependant on the tube length. As the length was increased, the minimum required pressure dropped.

Liu et al. [5] conducted two-dimensional numerical simulations of high pressure hydrogen release into an oxidizer. The scenarios considered were the direct release into air of high pressure hydrogen through a small hole with a diameter of 1mm. Three tank pressures were considered, i.e. 10, 40 and 70 MPa. The predictions showed that autoignition occurred at the tip region of the contact surface separating hydrogen and air after 10 μs for the 40MPa and 70MPa cases. However, the local combustion was quenched quickly due to the cooling effect of under-expansion of the hydrogen jets.

In a recent paper [21], we reported on the numerical simulation of high pressure hydrogen release through a section of tube into air. The predictions have captured the autoignition scenario experimentally observed by Dryer et al. [2], and numerically demonstrated that hydrogen will auto-ignite inside the tube if the tube

length is sufficiently long and the release pressure sufficiently high. In the present study, neglecting the effects of wall boundaries and multi-dimensional pressure boundary failure, we conducted numerical simulations to investigate the diffusion ignition mechanism when high pressure hydrogen is released directly into an open ambient environment. Molecular diffusion is a key factor in diffusion ignition. To accurately calculate the molecular transport of species, momentum and energy in a multi-component gaseous mixture, we have adopted a mixture-averaged multi-component approach [6] which also accounts for thermal diffusion.

2. NUMERICAL METHODS

Only early stage of the release was simulated. During this stage, the flow can be treated as invicid, although a large scale vortex ring is generated after the release [7]. The production of the vorticity is closely tied to the baroclinic torque, i.e. the misalignment of the pressure and density gradients instead of viscous effects [7]. Mass diffusion and heat transfer inside the contact surface were considered in the simulations. The simulations were performed by solving the unsteady Navier-Stokes equations of a chemically reactive multi-component mixture of ideal gases using the KIVA-3V code [17]. Considerable modifications have been carried out by the authors to introduce higher order numerical schemes, overcome false numerical diffusion and facilitate accurate calculations of the molecular transport of species, momentum and energy in a multi-component mixture [19-20]. For chemistry, the detailed chemical-kinetic mechanism developed by Saxena and Williams [9] for hydrogen combustion is implemented. It involves 8 reactive species and 21 elementary steps. Due consideration is given to third body reactions and the reaction-rate pressure dependant “fall-off” behavior.

The numerical scheme is based on the ALE method [8]. Each time cycle is divided into two phases: a Lagrangian phase and a rezone phase. In the Lagrangian phase the cell vertices move with the fluid velocity, so there is no convection across cell boundaries. In the rezone phase, the flow field is frozen, the vertices are moved to new user-specified positions, and the flow field is rezoned onto the new computational mesh. This rezoning is accomplished by convecting material across the boundaries of the computational cells, which are regarded as moving relative to the flow field.

In the Lagrangian phase, a second-order Crank-Nicolson scheme is used for the diffusion terms and the terms associated with pressure wave propagation, a two-stage, second-order MacCormack method [16] is used in the rezone phase to solve convective terms. The coupled semi-implicit equations are solved by a method similar to the SIMPLE algorithm, with individual equations being solved by conjugate residual method [17]. For spatial differencing, a second-order TVD scheme [18] is used for convection terms and second-order central differencing scheme for all the other terms.

3. PROBLEM DESCRIPTIONS

The simulations were set up on the basis of the experimental set up of Wolanski et al. [3]. The effect of solid wall roughness was ignored and the walls were assumed smooth and free slip boundary condition was applied. A sector of 0.5 degree was taken as the computed domain and the front and derriere were set to periodic boundaries. Compressed hydrogen initially entered the computational domain through an inflow boundary where a local hydrogen sound speed was applied with convection of pure pressurized hydrogen through the boundary. The gases left the computed domains by a continuous outflow boundary. The right boundary of the simulated open space was set to a solid wall boundary to help ensure numerical stability. Since only the early stage of release was simulated in the current simulations and the right boundary was unaffected by the release before the resulting semi-spherical shock reaches the boundary. This treatment of the boundary has little influence on the predictions. The computational domains were filled with still air in the beginning.

One benefit of the ALE method is allowing moving grids. At the start of the release, the contact surface is nearly flat and of a high local pressure [7]. As molecular diffusivity is inversely proportional to the pressure, the diffusion at the contact surface inside the tube is small at the start phase of the release. To prevent false numerical diffusion to smear out the real molecular diffusion, the moving contact surface was tracked by a number of clustered moving grids with grid spacing as small as 4 microns during this phase. Since the tracking grids moving with the contact surface, almost no convention is computed in the second phase of the ALE method for this part of mesh and the false numerical diffusion can be controlled to a very low level.

Several scenarios involving different release pressures were computed to study the effect of pressure on the autoignition. The computational grids were clustered around the jet exit and a minimum grid spacing of 20μm was used to resolve the reaction zone. The relevant input and boundary conditions and key parameters are listed in Table 1. Grid sensitivity study was conducted for Case 4.

Table 1 Computational parameters of direct release

	Case 1	Case 2	Case 3	Case 4
Release Pressure [bar]	40	100	250	250
Dimensions in Diameter [cm]	1(hole)/16(open space)			
Height of Open Space [cm]	10			
No. of Grids	1,600,000			800,000
Minimum Grid Spacing [μm]	20			40

To expedite the simulations, once the contact surface becomes curlier and the local pressure drops to below a certain level, the clustered tracking grids were removed from the computational domain. This process was carried out without affecting the conservation of mass and energy.

4. RESULTS AND ANALYSIS

4.1 Estimation of contact surface thickness

The contact surface or diffusion surface between pure hydrogen and air is extremely thin and its thickness is varied with time and local pressure. Here the local pressure is the pressure inside the contact surface, which is much lower than the release pressure due to flow acceleration and expansion. To estimate the varying trend of the surface, a diffusion computation was performed for a one-dimensional domain filled with still hydrogen and air and the initial contact surface was situated in the middle of the domain with zero thickness. The diffusion equation was solved by a fourth order Runge-Kutta method with a uniform grid spacing of 1 micron. The initial temperature was 500K for both hydrogen and air. The diffusion coefficient was computed according to the methods described in Section 2.

The time-varying thickness of the contact surface under different pressures is shown in Fig. 1. The thickness is defined as the depth of the mixing region with a volume fraction within the range of 1%-99%. The contact surface grows with time and its changing rate is larger in the beginning due to the large species gradients. The thickness strongly depends on pressure since the diffusivity is inversely proportional to pressure. It is only 120 μm under 50bar at t=100μs and increased to 850μm under 1bar.

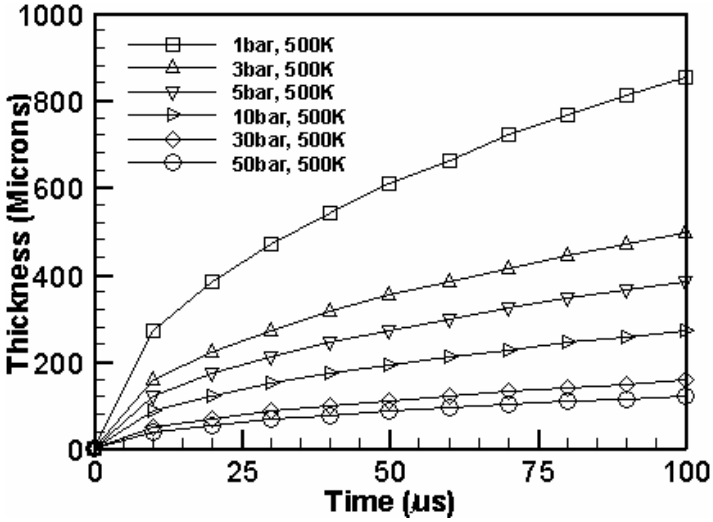

Fig. 1 The thickness of contact surface versus time under different pressures.

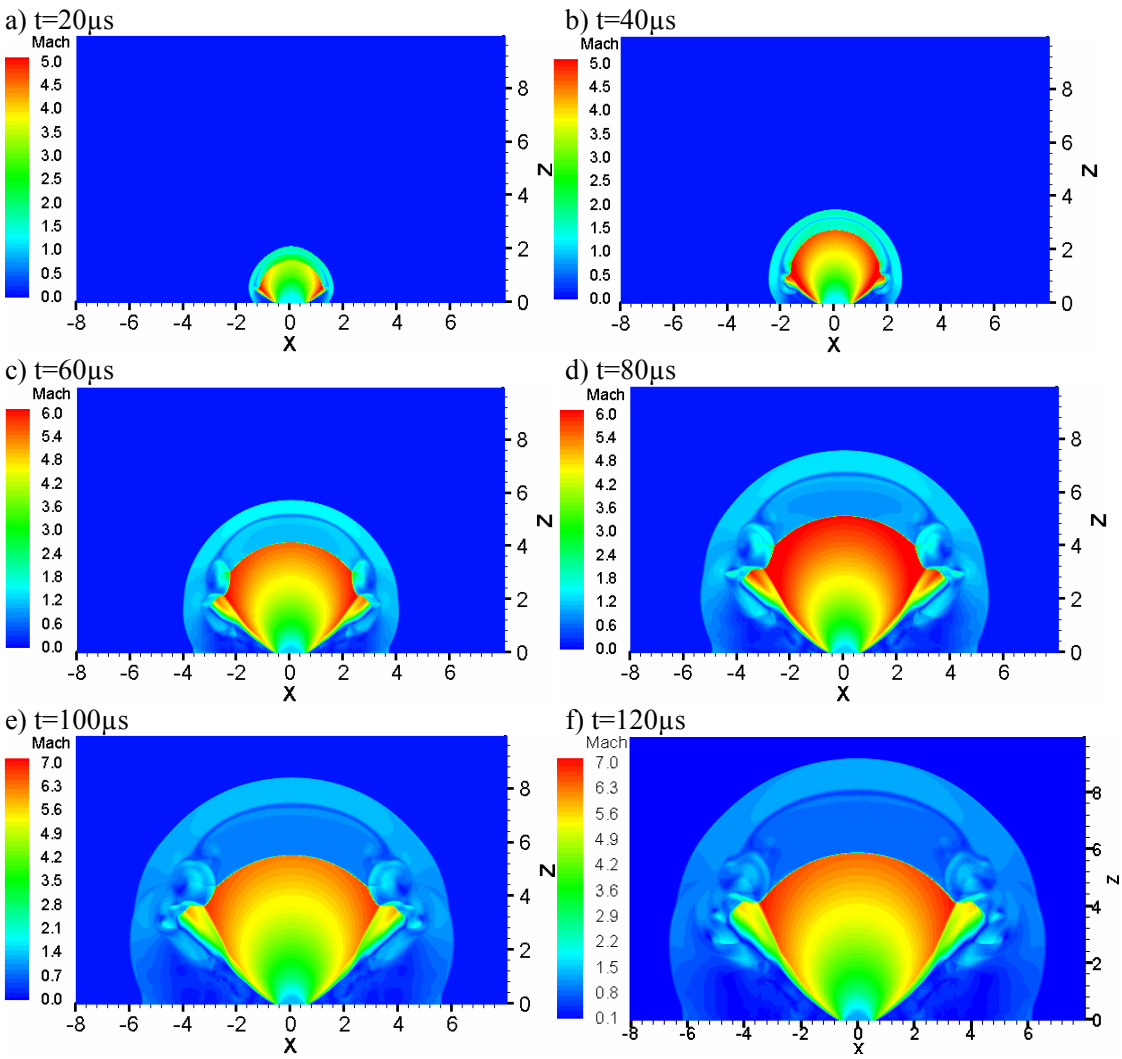

Fig. 2 Contours of Mach number at six different moments for a release pressure of 250 bar.

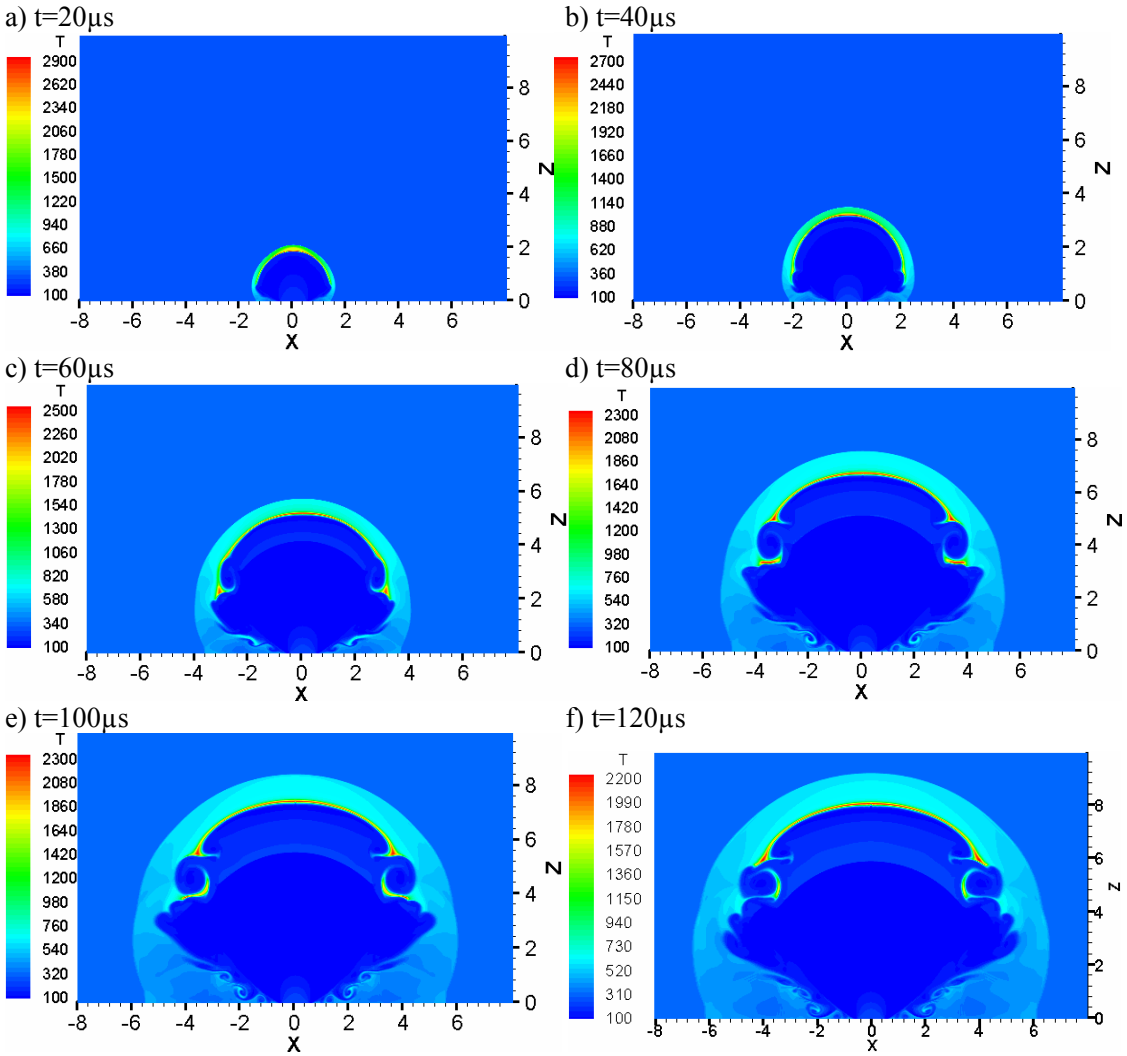

Fig. 3 Contours of temperature at six different moments for a release pressure of 250 bar.

4.2 Release directly into air

As compressed hydrogen is abruptly released into air, a semi-spherical shock is generated. The flow structures are depicted in Fig. 2 by contours of Mach number for a release pressure of 250 bar. The air immediately behind the shock is heated by the shock wave. As the shock wave propagates away from the exit, its strength becomes weaker due to flow divergence. Meanwhile another semi-spherical shock wave is developing inside the expanding hydrogen jet. As the shock wave propagates downstream, it intensifies due to the strong under expansion of hydrogen and its front tends to be flat. Finally, a well-known shock structure, Mach disk is formed and its position is nearly fixed only oscillating around its average position. Behind the Mach disk, the temperature is extremely low; ahead of it, it is elevated to a high level. As the jet leaves the exit, expansion waves originate around the circular edge. The expansion waves propagate downstream and reflected back as compression waves by the outer boundary. The coalescence of these compression waves results in a barrel shock structure surrounding the highly supersonic region behind the Mach disk. The flow inside the region between the flow boundary and the barrel shock is still supersonic, but its Mach number is much lower than that inside the barrel shock.

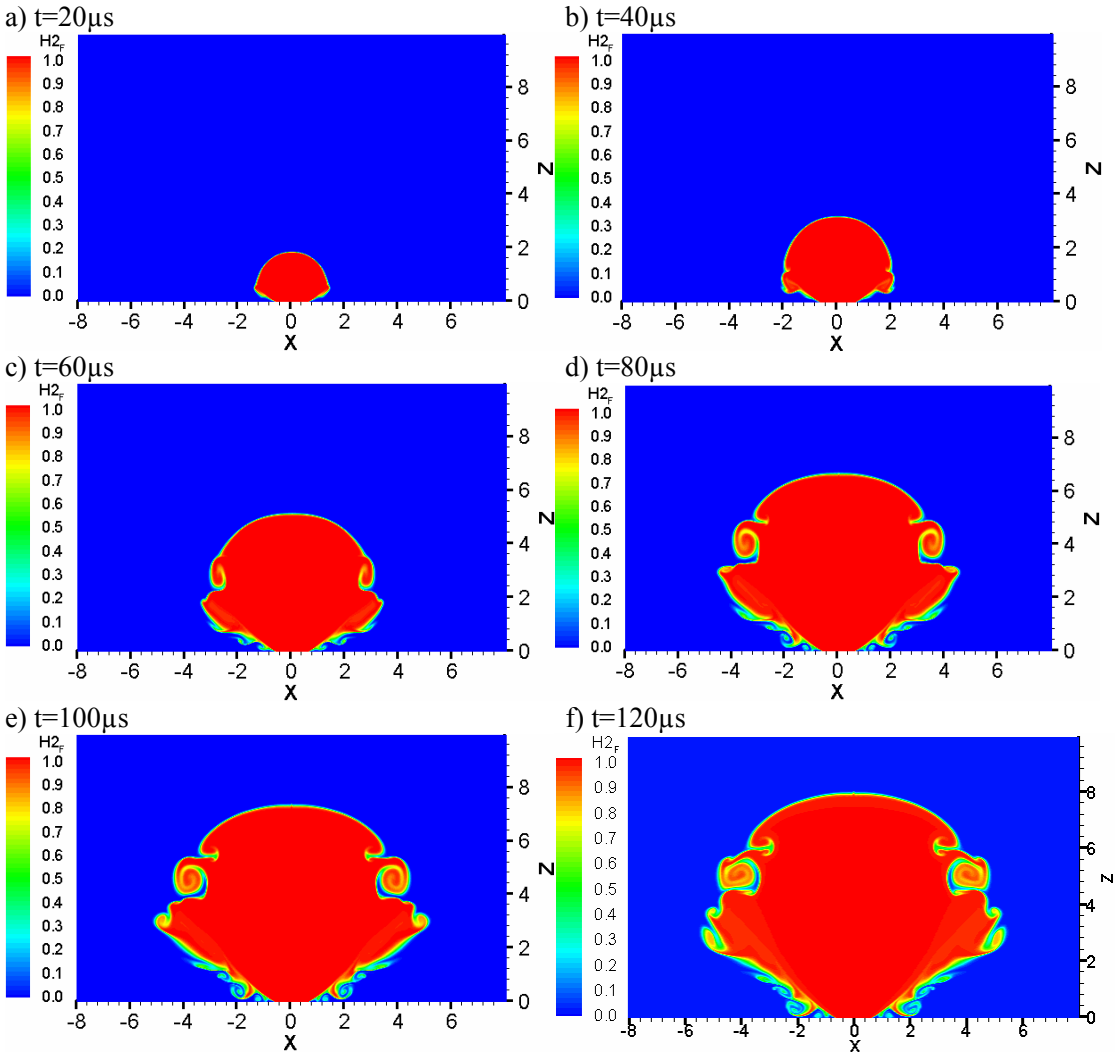

Fig. 4 Contours of hydrogen mass fraction at six different moments for a release pressure of 250 bar.

The contours of temperature at different moments are displayed in Fig. 3 for a release pressure of 250 bar. Autoignition first takes place at the tip region of the contact surface before t=20μs and the initial flame thickness is extremely thin with very high temperature because of the high pressure. The combustion region extends downward along the contact surface and the flame temperature drops with the expansion. The contact surface grows thicker as the pressure drops and also distorted by the developed flow at the end of the front surface where turbulent diffusion plays an important role in mixing as shown in Fig. 4 by the contours of hydrogen mass fraction. Turbulent diffusion greatly enhances the mixing and played a key role for the initial laminar flame to turn into a stable turbulent flame downstream. Large scale turbulence also develops at the jet boundary region close to the exit; however no combustion occurs there because of the low temperature.

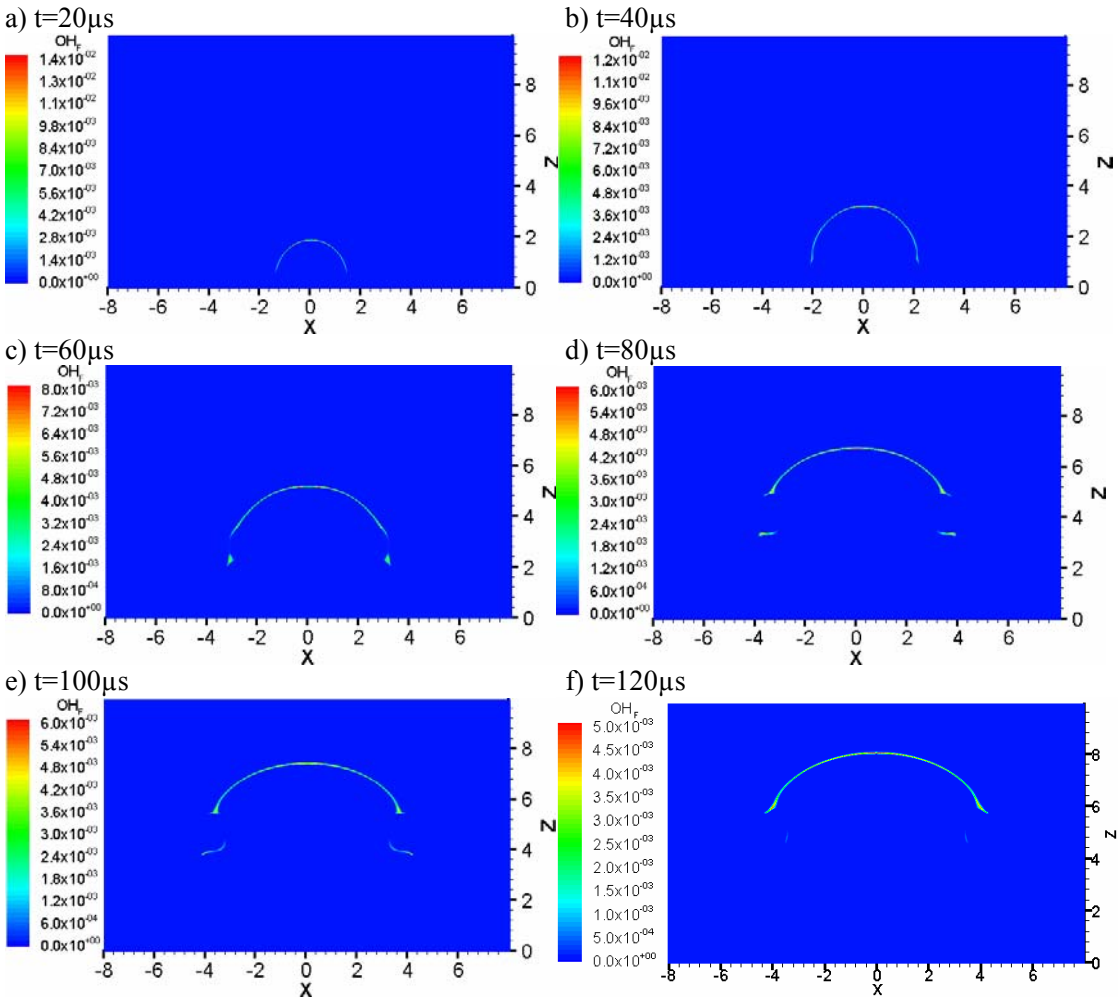

Fig. 5 Contours of OH mass fraction at six different moments for a release pressure of 250 bar.

The contours of mass fraction of OH are shown in Fig. 5 for a release pressure of 250 bar. The chemical reaction rate can be judged by the concentration of OH. It is seen that although the reaction rate decreases with time, there still remains a high OH mass fraction of 0.005 at t=120μs. This proves that combustion still continues. Three reasons may account for the decrease in reaction rate: firstly the temperature drop due to flow divergence, secondly the dilution of the mixture by combustion products; and finally relatively slow mass and heat diffusion at the contact surface. However, when turbulence starts to play a role in mixing as mentioned above, the reaction rate will pick up because of turbulence enhanced diffusion. The turbulence enhanced diffusion is therefore considered as the key factor for the initial laminar flame to transit into a final stable turbulent flame.

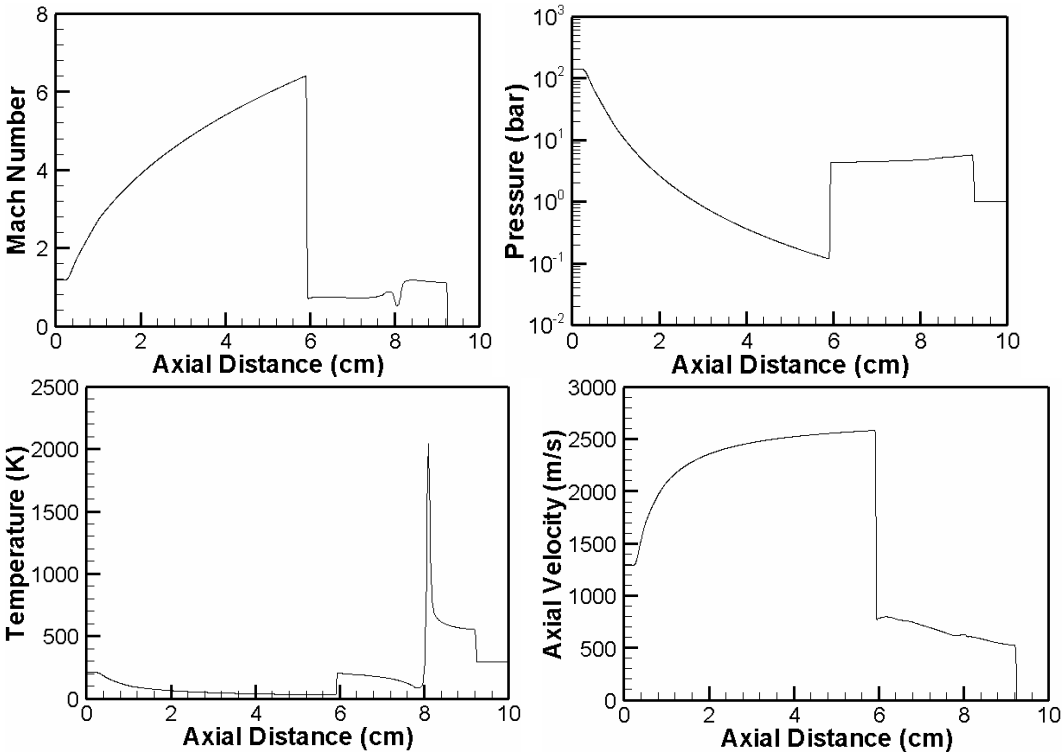

Fig. 6 The changing patterns of Mach number, pressure, temperature and axial velocity on the axis for a release pressure of 250 bar at t=120μs.

The changing patterns of Mach number, pressure, temperature and axial velocity on the axis are depicted in Fig. 6 for a release pressure of 250 bar at t=120μs. Since expansion wave originates from the exit edge, there is a short unexpanded region on the axis immediately downstream of the exit. After this region, the jet undergoes strong expansion. Owing to the expansion, pressure and temperature drop and axial velocity and Mach number increase. The expansion generates a strong shock at position of z=6cm leading to a sharp increase in pressure and temperature and a steep decrease in axial velocity. After the shock, the axial velocity slowly decreases and pressure recovers slightly. There exists another shock at z=8.6cm, which is the first generated shock when hydrogen is released into air. The air behind the shock is heated up to a high value and ahead of the shock it is the undisturbed. The temperature spike at the contact surface is caused by the heat release from chemical reactions, and the high temperature is also responsible for the low Mach number near the contact surface. The gentle decrease in temperature behind the contact surface is due to flow divergence.

The autoignition of compressed hydrogen release is significantly affected by the release pressure. The contours of temperature and OH mass fraction are shown in Fig. 7 for a release pressure of 100 bar at t=100μs. The chemical reaction rate and laminar flame temperature decrease with a decreasing release pressure and the end of the front contact surface is also less disturbed by the developed flow. As the release pressure drops to a certain level, no autoignition will occur as seen in Fig. 8 for a release pressure of 40 bar since the temperature of the shock-heated air can not reach sufficiently high.

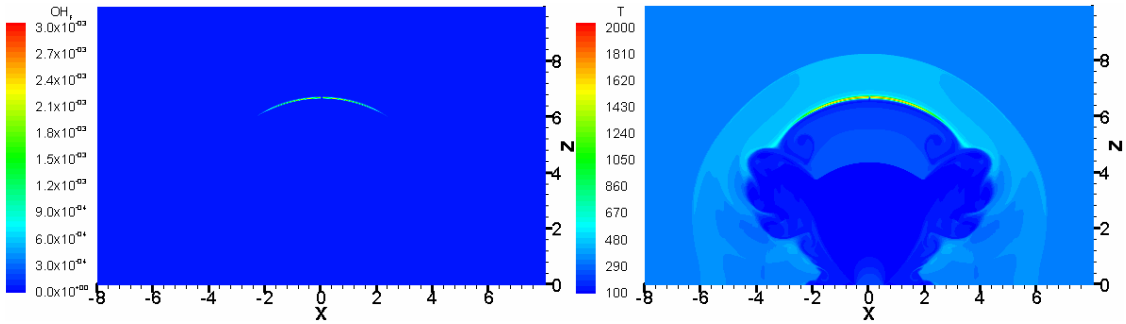

Fig. 7 Contours of temperature and OH mass fraction for a release pressure of 100 bar at t=100μs.

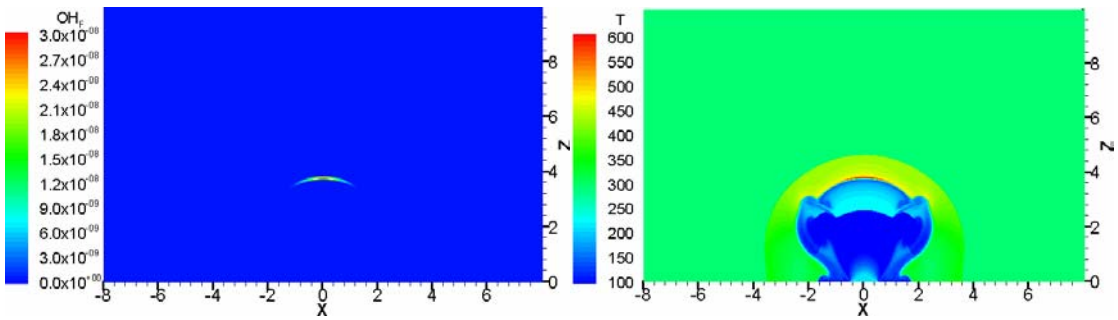

Fig. 8 Contours of temperature and OH mass fraction for a release pressure of 40 bar at t=60μs.

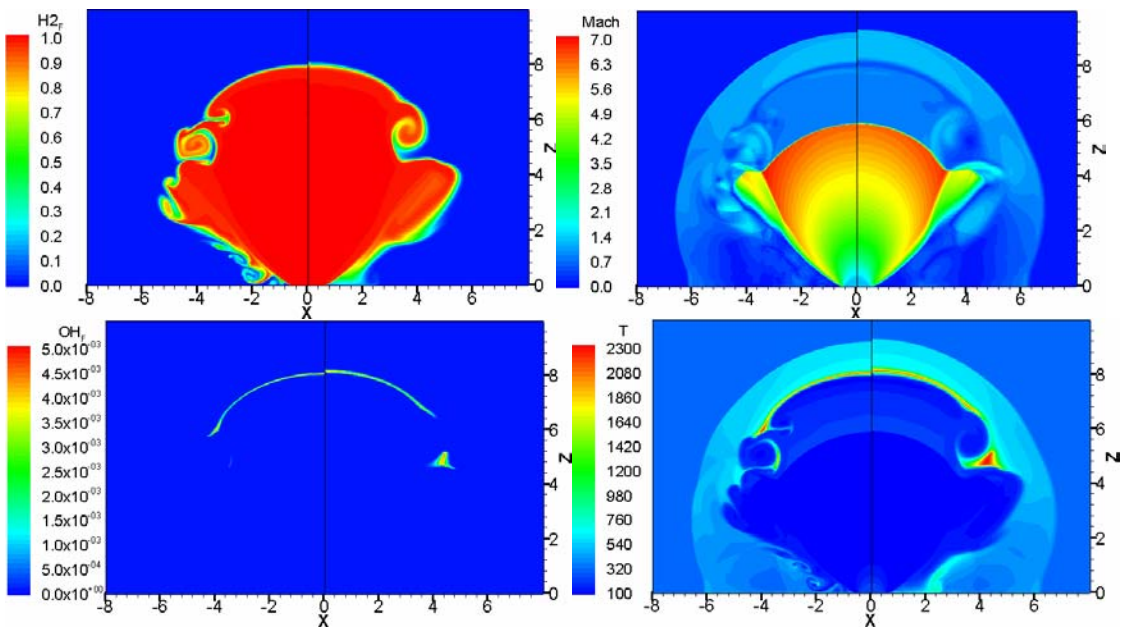

Fig. 9 Contours of hydrogen mass fraction, Mach number, OH mass fraction and temperature for the release pressure of 250bar at t=80μs from fine mesh (left) and coarse mesh (right).

4.3 Grid sensitivity study

Grid sensitivity study was conducted with Case 4 by using only half the grid points as in the previous simulation. Comparison of hydrogen mass fraction, Mach number, OH mass fraction and temperature are shown in Fig. 9 with results from fine mesh displayed on the left and that from coarse mesh on the right. It can be seen that the vortices at the jet boundary are not fully captured by the coarse mesh. The coarse mesh also incurs more false numerical diffusion which artificially increases the thickness of the contact surface and flame thickness.

The changing pattern of maximum temperature with time is shown in Fig. 10. Although the flow field is less well resolved and more numerical diffusion is incurred by the coarse mesh, the maximum temperature is not significantly affected by the current grid resolutions. The maximum temperature is slightly under-predicted by the coarse mesh before the end of the front contact surface is disturbed, and then the temperature is slightly over-predicted due to false numerical diffusion enhanced mixing.

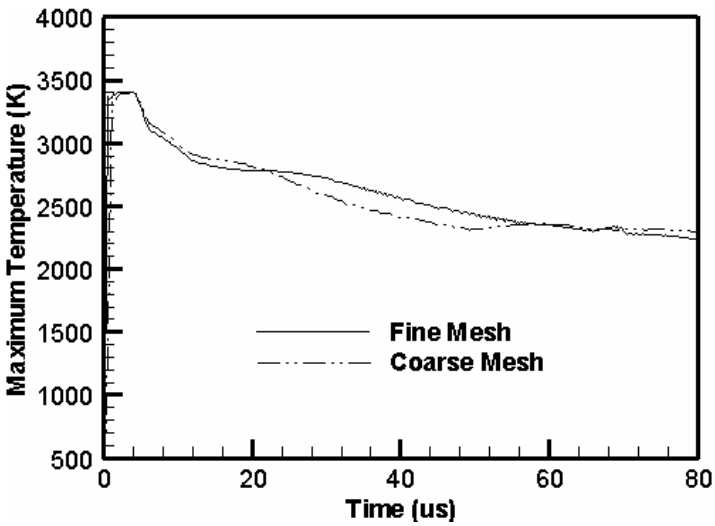

Fig. 10 Maximum temperature versus time of first release scenario (left) and second release scenario (right).

5. SUMMARY

Numerical simulations of direct pressurized hydrogen release into air are described. The experimentally observed autoignition has been successfully captured in the predictions.

Autoignition first takes place at the tip region of the contact surface due to the mass and energy exchange between low temperature hydrogen and shock-heated air at the contact surface through molecular diffusion. The combustion region extends downward along the contact surface and the flame temperature drops with the expansion. The contact surface grows thicker as the pressure drops and also distorted by the developed flow at the end of the front surface where turbulent diffusion plays an important role in mixing. Turbulent diffusion greatly enhances the mixing and played a key role for the initial laminar flame to develop into a stable turbulent flame downstream. Large scale turbulence also develops at the jet boundary region close to the exit. However no combustion occurs there because of the relatively low temperature.

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