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Determination of Rate Coefficient for Para-Orthohydrogen Conversion in Cryogenic Vortex Tube

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Abstract **-** Raising efficiency of the cooling process for cryogenic hydrogen and minimizing hydrogen boil-off during storage and transportation of liquid hydrogen are critically important factors for widening implementation of hydrogen-based clean energy systems. One novel approach involves utilization of relatively simple catalyzed vortex tubes, where hydrogen in primarily para form is converted into ortho isomer while consuming a significant amount of heat. To design such systems effectively, better understanding is required about catalyst-assisted para-orthohydrogen conversion rates in high-speed vortical flows. In this study, a computational fluid dynamics simulation has been set up to model an experimental system with cryogenic hydrogen vortex tubes. Mesh-verification and validation study has been conducted first for a non-catalyzed tube. Then, the rate coefficient of the para-ortho conversion of cryogenic hydrogen has been determined by matching numerical results with experimental data available for a catalyzed vortex tube. The presented information can help design and optimize cryogenic hydrogen cooling devices with vortex tubes.

Keywords**:** Vortex tubes, Hydrogen systems, Para-ortho conversion, Cryogenics, Computational fluid dynamics

1. Introduction

Since hydrogen does not produce harmful emissions when reacting with oxygen, it is often believed to be a major clean fuel for future economy. However, producing, storing and transporting hydrogen in its energy-dense liquid form requires more economical cryogenic storing and cooling than currently used. One of innovative cooling approaches involves catalyzed vortex tubes [1], where hydrogen initially heated near the walls in high-speed swirling flow can undergo transition from its quantum parahydrogen form, which is dominant at very low temperatures, to the orthohydrogen form, which equilibrium fraction increases with temperature. This para-ortho transformation is accompanied by large heat consumption of about 703 kJ/kg. As this reaction is very slow when unassisted, catalysts placed on the inside walls of vortex tubes can accelerate this conversion. Such vortex tubes can potentially replace conventional Joule-Thomson valves in existing hydrogen liquefaction cycles (Linde-Hampson, Claude) or be used in thermal-shielding systems to reduce hydrogen boil-off [2].

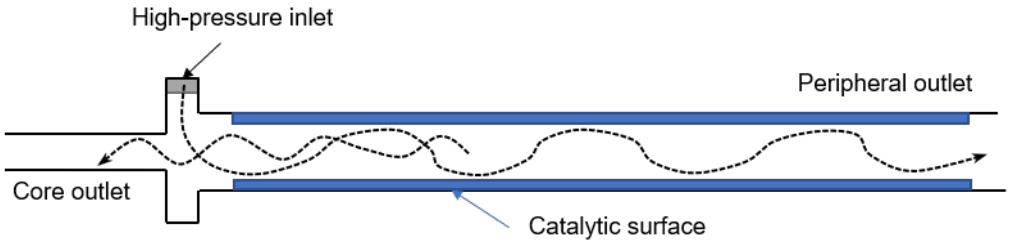

Fig. 1: Schematic of catalyzed vortex tube schematic.

The original and most common application of vortex tubes, also known as Ranque-Hilsch devices, is for temperature separation and refrigeration of atmospheric air at normal temperatures [3]. However, in the present analysis, the vortex tube primary role is to serve as a vortical reactor for assisting para-orthohydrogen conversion accompanied by significant cryogenic cooling while not involving moving parts. The present study is a continuation of previous efforts aimed at developing this technology [4,5]. The main goals of the current investigation are to set up a computational fluid dynamics

(CFD) simulation of a hydrogen vortex tube, to validate this modelling against experimental data, and to determine the effective rate coefficient for para-orthohydrogen conversion in vortex tubes.

2. Computational Aspects, Geometry, and Reaction Modelling

Computational simulations of cryogenic hydrogen vortex tubes are carried out in this study using CFD program STAR-CCM+. The coupled, finite-volume solver was employed for unsteady simulations, but only steady-state results are reported here. For computational efficiency, the RANS approach was utilized. Several turbulence models were tried, and the realizable k-ε model showed better agreement with experiments. Because of large variations of flow properties inside vortex tubes, the two-layer, all-Y+ (blended) option of the turbulence model was adapted. It relies on wall functions at larger Y+ values while resolving more detailed structure of the boundary layer at small Y+ values. Specifics of numerical methods in the employed CFD program are provided in STAR-CCM+ manual [6]. Properties of both ortho- and para-isomers of hydrogen are incorporated into simulations via tables obtained from REFPROP [7].

The vortex tube geometry in the numerical setup originates from the experimental study [5] and is illustrated in Fig. 2. It has an inlet maintained at high pressure from which hydrogen enters tangentially into the tube via three nozzles of combined cross-sectional area of about 0.5 mm^2. There are two outlets at the opposite ends of the tube. The core outlet extracts fluid near the tube centreline close to the inlet, whereas the periphery outlet is located far from the inlet. While most vortex tubes have smooth surfaces on the inside, the current setup employed a rifled tube to maximize the surface area covered by catalyst and help maintain the vortex further along the tube away from the inlet. The length and averaged diameter of the rifled portion are 180 mm and 3.3 mm, respectively.

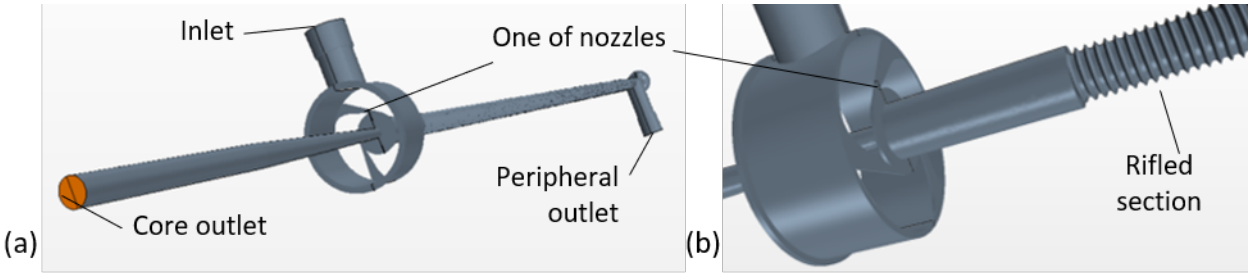

Fig. 2: (a) Vortex tube schematic, (b) geometrical details near inlet and transition to rifled section.

In the catalysed vortex tube experiments, the rifled portion of the internal surface was covered with hydrous ruthenium catalyst [5]. For simplified modelling of catalytic conversion between para and ortho states of hydrogen, a thin zone (0.25-mm-thick) in the vicinity of the tube surface was chosen as the reaction zone (Fig. 3a). The rate of conversion was modelled inside this zone using a relaxation-type equation,

$$\frac{d\rho_{ort}}{dt} = k\rho_{par}\left[y_{ort,\,equil} - y_{ort,\,actual}\right] \tag{1}$$

where ρ_{ort} and ρ_{par} are the densities of ortho- and para-hydrogen, respectively, t is the time, $y_{ort,\,actual}$ and $y_{ort,\,equil}$ are the actual and equilibrium (at a local temperature) mass fractions of orthohydrogen. The reaction coefficient k was not known in advance. It was determined by matching the CFD prediction of the peripheral temperature to a value recorded in the experiment. According to Eq. (1), the ortho-hydrogen production rate is proportional to the local density of parahydrogen and depends on how far the mixture is from the equilibrium.

2. Mesh Verification and Reaction Coefficient Determination

To establish a suitable numerical grid, a mesh verification study was accomplished using numerical results for the peripheral temperature obtained at three numerical grids of different density in the non-catalyzed tube. The experimental conditions included

the inlet and core-outlet pressures 56.60 psia and 16.13 psia, respectively, the total mass flow rate of 0.159 g/s, and the inlet and peripheral-outlet temperatures of 53.71 K and 52.70 K, respectively. The constructed numerical grids were of polyhedral type with prism layers near solid surfaces. An illustration of a numerical mesh is shown in Fig. 3b. The computationally predicted reductions of the peripheral temperature with respect to the inlet state were found to be 1.19 K, 0.93 K, and 1.04 K for the coarse, medium and fine grids, respectively. These results demonstrate oscillatory numerical convergence. Using the Richardson extrapolation [8] and the factor of safety [9], the numerical uncertainty was estimated as 0.10 K. Since this value is greater than the difference between test and computational results for the peripheral temperature (0.03 K), the present numerical approach has been validated.

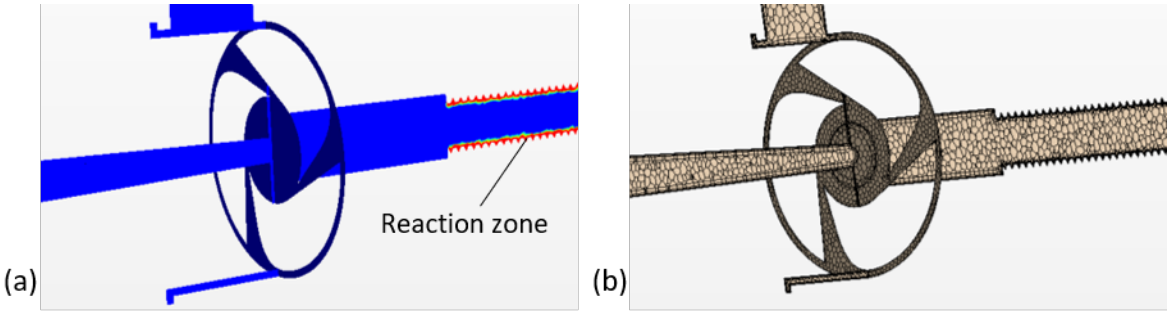

Fig. 3: (a) Reaction zone (shown in red) and (b) numerical grid in cross sections of the vortex tube.

To determine the effective conversion rate between ortho- and parahydrogen isomers, simulations were conducted for experimental conditions corresponding to a catalyzed tube [5]. In this case, the inlet and core-outlet pressures were 62.03 psia and 15.83 psia, respectively, and the inlet and peripheral-outlet temperatures were 52.81 K and 47.72 K, respectively. While the boundary conditions are similar to those in the non-catalyzed tube, one can notice much larger recorded temperature drop due to para-orthohydrogen conversion. To attain agreement with this exit temperature, the reaction coefficient k in Eq. (1) was varied, and the numerical value of 210 s^{-1} was found to work well.

Illustrations of the pressure and velocity fields inside this tube are given in Fig. 4. The pressure is large at the inlet, whereas most of the pressure drop happens near the nozzles. The velocity is very small at the inlet, but it reaches high values in the nozzles, where Mach number approaches one. Due to tangential orientation of the nozzles with respect to the main body of the tube, a strong swirl is formed at the larger portion of the tube extending to significant distances away from the nozzles.

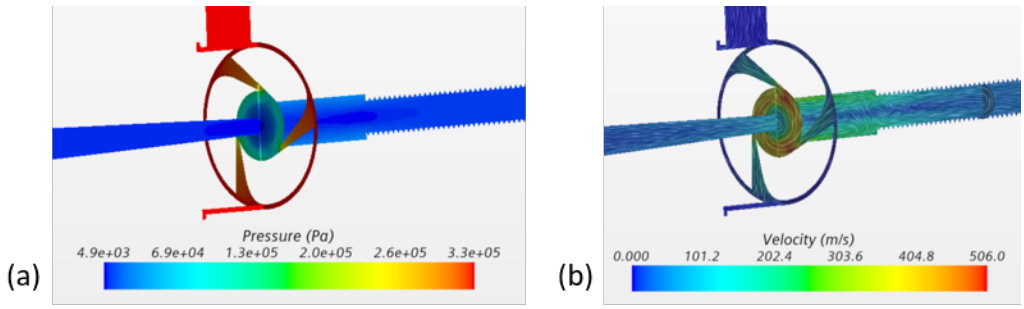

Fig. 4: (a) Pressure distribution and (b) velocity field inside vortex tube.

Temperature varies little upstream of the nozzles, while reaching minimum near the nozzle throats, and then it partially recovers due to flow deceleration (Fig. 4a). However, in the longer portion of the tube, which is covered with a catalyst, temperature starts dropping again due to endothermic conversion of parahydrogen into ortho state. The ortho fraction distribution is given in Fig. 4b, showing how the ortho component increases from the original 2.1% at the inlet up to about 11% at the peripheral exit.

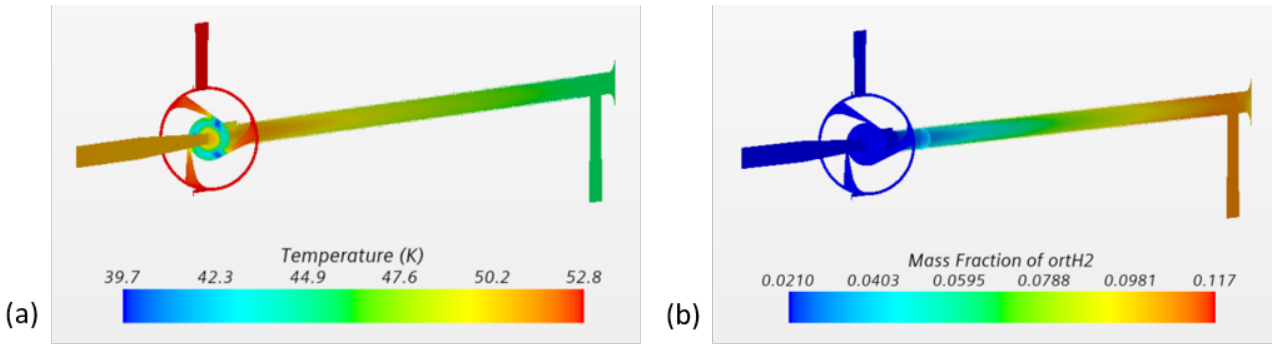

Fig. 5: (a) Temperature distribution and (b) ortho fraction in the flow.

4. Conclusion

High-speed compressible flow of cryogenic hydrogen was successfully modeled inside a vortex tube. Upon verification and validation study in the non-catalyzed tube, a reactive flow inside a catalyzed tube was simulated. By matching the numerical exit temperature to the experimental value, the effective rate coefficient of para-ortho conversion was determined to be 210 s^{-1} for the specific relaxation-type reaction-rate form and the near-wall reaction zone of 0.25 mm. This conversion model can be suggested for approximate simulations of high-speed vortical flow of cryogenic hydrogen undergoing para-ortho transformation. Future extensions of this work can include optimization of practical systems for hydrogen cooling that employ vortex tubes, quantum physics-based modeling of conversion between hydrogen isomers, and validation in broader range of experimental conditions.

Acknowledgements

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