State-of-the-Art and Research Priorities in the Hydrogen Safety

Kotchourko, A.[1], Baraldi, D.[2], Bénard, P.[3], Jordan, T.[1], Kessler, A.[4], LaChance, J.[5], Steen, M.[2], Tchouvelev, A.[6], Wen, J.[7]

[1]IKET, Karlsruhe Institute of Technology, Karlsruhe, Germany
[2]IET, European Commission DG-JRC, Petten, The Netherlands
[3]Hydrogen Research Institute, Université du Québec à Trois-Rivières, Québec, Canada
[4]Fraunhofer ICT, Pfinztal, Germany
[5]Risk & Reliability Analysis, Sandia National Laboratories, Albuquerque, USA
[6]A.V. Tchouvelev & Associates Inc. Mississauga, Ontario, Canada
[7]School of Engineering, University of Warwick, Coventry United Kingdom

Research Priorities Workshop

- The International Association for Hydrogen Safety - HySafe - is globally the focal point for all hydrogen safety related issues. It is an international non-profit organization that currently has more than 30 members from industry, research organizations and universities representing 14 countries worldwide.

- HySafe and the Institute for Energy and Transport (IET) of the Joint Research Centre of the European Commission partnered to organize a Research Priorities Workshop in Berlin on October 16-17, 2012 hosted by BAM (on behalf of HySafe).

- The participating experts were carefully selected according to their experience/expertise, number of scientific publications and participations to International Conferences, seminars, workshops as well international and European funded projects.

By performing a consultation with industry and a broader research community as well as a state of the art review on hydrogen safety issues (including of CFD modelling), a consensus was reached among the experts as to the remaining gaps in the field and on the priority of the research needs.

RP Workshop mission

- The Workshop is aimed to become a regular meeting point for researchers/scientists and technical (including industry) experts working in the area worldwide on the biennial basis.

- Identifying the remaining knowledge gaps is a logical necessary step for making decisions on the next steps to carry out the full and safe utilization of hydrogen.

- It is also a welcomed contribution for the Fuel Cell and Hydrogen Joint Undertaking and for other funding bodies/organizations that must make decisions on research programmes and during the selection/choice of projects to be financially supported pursuing the safe use of hydrogen within Horizon 2020 framework.

- The performed analysis and recommendations are expected to work as a catalyst to accelerate both the improvements of existing research programmes and the developments of new engineering guidelines and industrial practices, as well as supporting formulation of and compliance with RCS requirements.

RP Workshop participants

The authors would like to express their special appreciation and thanks to all participants of the RP Workshop as making this work possible by their valuable contributions

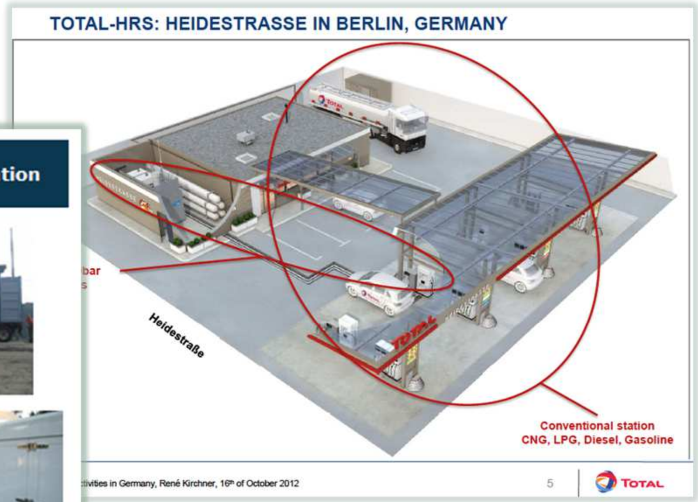
- **Baraldi, Daniele (Joint Research Centre - Petten, the Netherland)**
- **Barthélémy, Hervé (AirLiquide, France)**
- **Bénard, Pierre (HRI/UQTR, Canada)**
- **Carcassi, Marco (Pisa University)**
- **DeVaal, Jake (Ballard Power System, Canada)**
- **Ekoto, Isaac (Sandia National Laboratories, USA)**
- **Hooker, Phillip (HSL, UK)**
- **Jordan, Thomas (Karlsruhe Institute of Technology, Germany)**
- **Kessler, Armin (Fraunhofer ICT, Germany)**
- **Kamiya, Shoji (Kawasaki Heavy Industries, Japan)**
- **Kirchner, René (Total Deutschland, Germany)**
- **Keller, Jay (Zero Carbon Energy Solutions, USA)**
- **Kotchourko, Alexei (Karlsruhe Institute of Technology, Germany)**
- **LaChance, Jeff (Sandia National Laboratories, USA)**
- **Marangon, Alessia (Pisa University, Italy)**
- **Markert, Frank (Technical University of Denmark)**
- **Middha, Prankul (GexCon, Norway)**
- **Molkov, Vladimir (University of Ulster, UK)**
- **Oyama, Suguru (Kawasaki Heavy Industries, Japan)**
- **Paraschivoiu, Marius (Concordia University, Canada)**
- **Ruban, Sidonie (AirLiquide, France)**
- **Schmidtchen, Ulrich (BAM, Germany)**
- **Siegel, Kay Kimberly (H2SAFE, USA)**
- **Steen, Mark (Joint Research Centre - Petten, the Netherland)**
- **Tchouvelev, Andrei (AVT, Canada / IA HySafe)**
- **Vågsæther, Knut (Telemark University, Norway)**
- **Vendra, Madhav Rao (Kingston University, UK)**
- **Wen, Jennifer (University of Warwick, UK)**

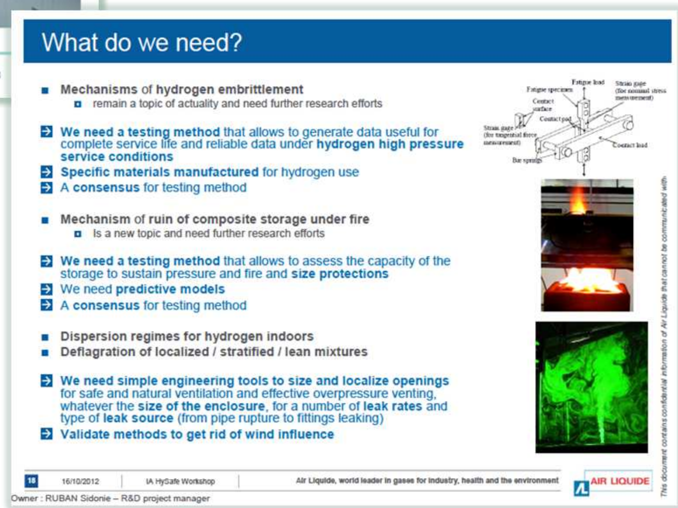
INDUSTRIAL PERSPECTIVES

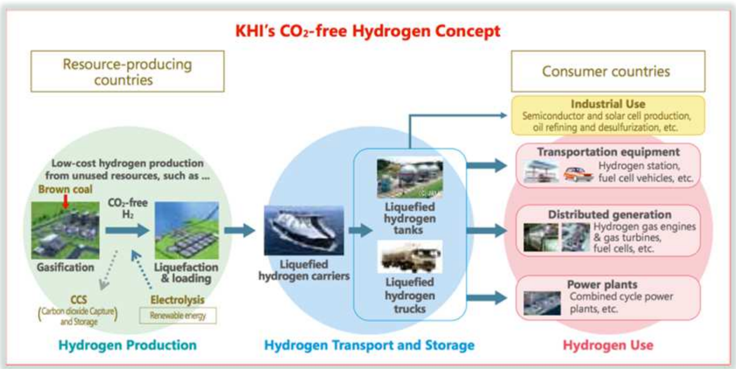
Consultations with industry stakeholders constitute a critical component in setting research priorities.

For this reason, the companies operating within different market segments of the hydrogen and fuel cell sector were invited to share their experiences and needs as well as their perspectives on research priorities in the field of hydrogen safety and standardization.

Hydrogen fuel cells developer and provider – Ballard Power Systems, Canada
Global industrial gas company – Air Liquide, France
International fuel and refuelling provider – Total, Germany
Multi-industrial corporation – Kawasaki Heavy Industries, Japan







Ballard Power Systems Inc, Canada

BALLARD®

Jake DeVaal

Ballard is a dominant player in automotive fuel cell development since early 2000's (e.g., their stacks were used in Daimler and Ford demonstration programs, European CUTE bus demonstration project)

From the field of commercialization of bus and distributed generation products, the following specific areas for near-term hydrogen safety research are identified:

- Improved fuel flow monitoring for hydrogen leak detection in Bus and Distributed Generation (DG) products,
- Tools and approaches for addressing the H_2/N_2 start-up discharge-emission hazards,
- Improved understanding of fuel cell recombination effectiveness, where recycling leaked H_2 through stacks is highly effective at recombining fuel but can also cause crossover leaks,
- Improved understanding of cathode air filtration effectiveness and H_2 fuel quality issues (e.g., biogas quality), and
- Qualify/use risk analysis tools and develop more meaningful standards.

Air Liquide, France

AIR LIQUIDE

Sidonie Ruban

Air Liquide is a world leader in gases for industry, health and environment. More than 40 years in H_2 field and 10 years in FC development and deployment. AL built globally an infrastructure with more than 200 H_2 production plants, distribution assets >1,850 km, trucks and cylinders.

For dedicated refuelling infrastructure (as high priority task) the safety-related challenges:

- High pressure and specific mechanical loading
  - Leak tightness
  - Material compatibility (incl. hydrogen embrittlement)
  - Intelligent depressurizing tap
- High capacity of H_2 mobile composite storage
  - Failure mechanisms
  - Fire resistance
- 'Indoor' use (enclosed environment):
  - Natural ventilation
  - Structural strength of enclosures

Knowledge gaps addressed last years:

- pipeline steel microstructure and fatigue enhanced embrittlement in addition to material composition;
- sizing release flow rate for fire protection of H2 composite cylinder taking into account pressure peaking effect, flame effects and storage leak
- opening size and position for an efficient natural ventilation of enclosures strongly affecting dispersion regimes

Total Germany, Hydrogen/E-Mobility

Total Germany acquired experience in hydrogen refuelling since 2002 (first station for gaseous H_2 for Berlin buses) via 7 H_2 stations projects, as e.g., public H_2 dispensing combined with a conventional station in Berlin in 2006; another HRS in Berlin in 2011 with a was new design with other fuels like CNG, gasoline, diesel and LPG.

TOTAL

René Kirchner

Specific Total's learning experience:

- local authorities need to be informed and involved as much and as early as possible;
- need for an overall guideline for HRS permitting (DIN, EN or ISO) to feel comfortable with and accelerate the process;
- knowledge dissemination within local authorities in Germany is inevitable and needed;
- exchange of experience within industry (CEP is a good example);
- key open issues as barriers to HRS commercialization;
    - hydrogen metering;
    - hydrogen quality sampling; and
    - refuelling protocol, particularly for 700 bar dispensing.

Kawasaki Heavy Industries, Japan

Kawasaki Heavy Industries, Ltd. (since 1878), is a leading global diversified manufacturer of transportation equipment and industrial goods: ships, rolling stock, aircraft and jet engines, etc, including consumer products such as motorcycles and personal watercraft.

Suguru Oyama
Shoji Kamiya

Highest priority request relates to appropriate/optimized safety distances. Existing methods for calculation of safety distances for liquid hydrogen are based on data obtained in early 1960-1970's. Those correlations did not anticipate such significant amounts and as such cannot be used for reliable calculations. New correlations are needed.
A similar situation is with the shipment of large quantities of LH_2. Large bulk transportation is not covered by any code or standard.

In summary, more knowledge is required related to

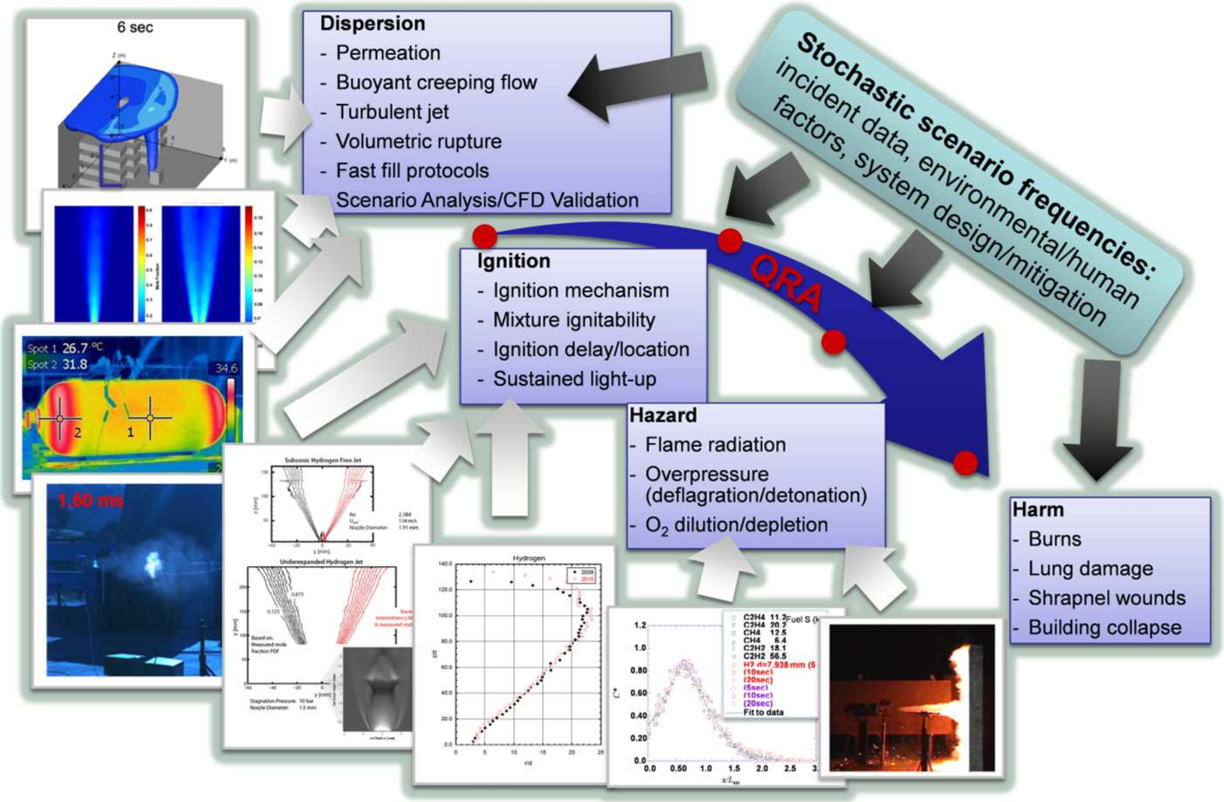
- spillage of large quantity of LH_2 on ground or seawater;
- cloud dispersion of cold hydrogen from vent and its ignition;
- performance of various thermal insulation options;
- safety distance as function of LH_2 quantity and re-assessment of the scientific basis for existing correlations;
- evaluation of related hazards and their consequences; and risk assessment of typical accidents.

RISK-INFORMED SAFETY SCIENCE

Hazards Deficiencies

The safe use of any technology requires that the hazards and associated risk be understood and minimized, which is the task of quantitative risk assessment (QRA).

Although the general methods for performing a QRA are well established, there are significant gaps in the data utilized to establish the frequency of accidents and in the models used to evaluate the resulting consequences.



QRA: hazard identification

In order to quantify the accident sequence models, data for the modelled events must be obtained:

- frequency of accident initiating events (e.g., hydrogen leaks)
- component failure probabilities, conditional events
- human error events
- the probability of certain accident phenomena

Little hydrogen-specific data available:

- current data collection efforts such as in the HySafe *Hydrogen Incident and Accident Database* and the U.S. DOE's *Hydrogen Incident Reporting and Lessons Learned* database are not sufficient for utilization in a QRA and
- no requirements for collecting data (the exception U.S. Department of Energy's technology validation program)

Thus, data from other industries, primarily the oil and gas industry has been utilized in hydrogen QRAs. A different approach (Bayesian process) to combine H_2 data with others was used by LaChance. Without hydrogen-specific data, the fidelity of H_2 QRAs is less than desirable: it is important to begin planning and testing an industry-wide framework for QRA data collection activities and to begin serious efforts for collecting failure data.

QRA deficiencies

- Human errors are often significant contributors to accidents. Currently, human errors have not been explicitly included in hydrogen facility QRAs (one recent exception Groth), which may result in a significant under prediction of the risk. In future QRAs, accident models must be expanded to include it. There are many useful Human Reliability Assessment methods that can be utilized for H2 (evaluation of their capability in Forester).
- A key parameter in H2 accident scenarios is the probability of ignition. There are much work on self-ignition and jet delayed ignition, but the knowledge is not yet translated into a QRA probabilistic model. Some efforts were made to develop a non-mechanistic ignition probability models based on literature searches, empirical data, and some experimental data (HySafe by DNV), but more work is required.
- The consequence calculations should predict the physical circumstances resulting specifically from the accident (e.g., explosion overpressure and thermal radiation levels). The consequences are usually quantified using mathematical models; these may be either simple engineering models or CFD models. For QRAs, where the consequences from a large number of scenarios should be evaluated, there is a need to develop more simple engineering models for evaluating the consequences of hydrogen releases.
- The results of consequence evaluations must be translated into a probability of causing damage to an individual, component, or structure for use in a QRA. This can be done using Probit functions which provide a statistical correlation between the magnitude of the consequence (e.g., thermal heat flux) and the resulting potential for damage (summary of Probit functions by LaChance). Available Probit functions for predicting damage from a thermal heat flux are not hydrogen specific and thus introduce uncertainty in the risk results which can be evaluated using sensitivity studies.
- For utilization of QRAs to make a risk-informed decision, it is desirable to establish risk acceptance guidelines or criteria. Although there are different types of risk criteria and each country has its own risk criteria, Tchouvelev has suggested uniform risk acceptance criteria for use in the hydrogen industry.
- Necessary clear understanding the sources of uncertainties in the QRA model that could be affected, and ultimately the results from the QRA model that may be impacted. Guidance on making decisions in light of uncertainties is needed and can potentially be adapted from other industries

SIMPLIFIED TOOLS

Simplified Toolkit requirements

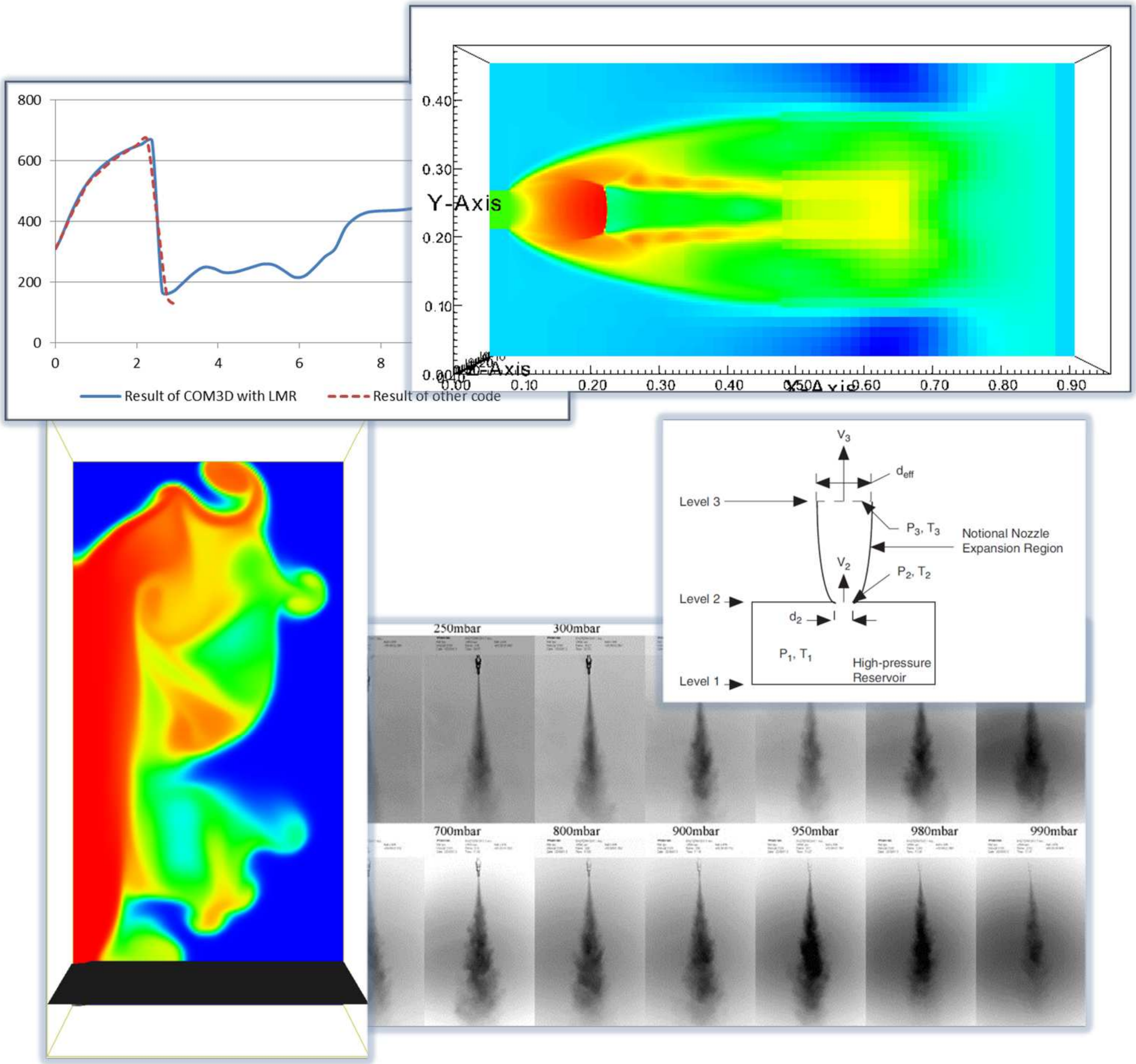
Content: all kind of empirical correlations, criteria, statistics and models based on robust, published, state-of-the-art correlations having target users, as: design and process engineers form industry, standard development experts, risk analysts and QRA professionals, and technical authorities. It should be based on modular design including:

- probabilistic component with an agreed set of failure frequency data, ignition probabilities and a set of appropriate Probit functions allowing a user to preform QRA;
- the toolkit shall be maintained by the hydrogen safety research community itself, the toolset should be an open and free software system, which is well documented and quality assured in a cooperative manner. International Energy Agency Hydrogen Implementing Agreement seems as suitable host for such collaboration (HySafe could serve as maintainer).
- Each tool shall be described in detail, the valid range of input parameters has to be controlled appropriately, literature references should be given and model tests have to be provided.
- Users with appropriate rights may edit tools or define new tools. New tools might use existing ones by calling them in a specific sequence or even recursion should be possible.
- Web-based implementation is envisaged. A system which allows for immediate testing and on-the-fly editing of the tools is e.g., the Smalltalk dialect Squeak based dynamic web development framework Seaside.
- A typical use case will consist of a user defining explicitly a new scenario by giving the inventory or hydrogen flow, geometrical settings like confinement and/or congestion, mitigation measures, up to a leak size. For a statistical analysis a probability distribution can be defined.
- The user might choose a tool to act on the scenario. The input, which was not yet defined but required by the selected tool, shall be input by the associated tool interface. If any of the input parameter lies outside the models validity range an appropriate reaction shall be taken. Appropriate measures are warnings or even an exception. Any output defined before the execution of the model, shall be overridden by the model. A warning will be issued.

SOURCE, RELEASE AND DISPERSION FOR GASEOUS H_2

Jet releases
Notional nozzle
Attachment

The evaluation of the safety of hydrogen systems requires methods to characterize the release of hydrogen and the determination of the extents of the flammable clouds, which are very important parameters in the establishment of the safety distances and sizes of hazardous zones. Jet and plume releases constitute the most common mechanism of release and dispersion. As such, their properties have been studied extensively by hydrogen safety researchers.

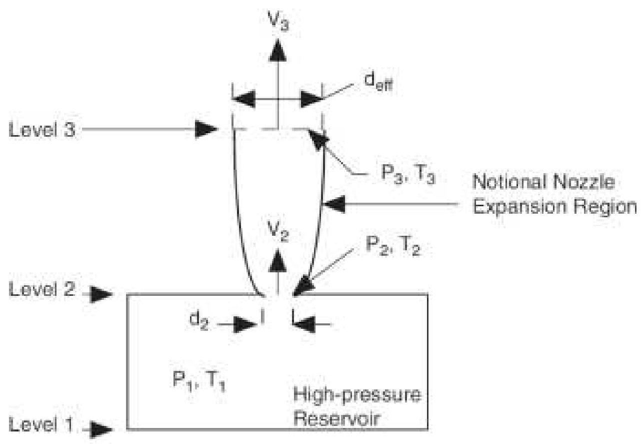


Jet releases

- Jet releases have been the object of intense R&D activities. An overview of the properties of neutrally buoyant turbulent jets (compressible and incompressible) is presented in the classic work of 60's (Abramovich et al.)
- The scaling properties of buoyant vertical turbulent jets are detailed in a monograph of 80's by Chen and Rodi.
- Despite numerous data, there is a lack of detailed studies
  - Detailed validation of notional nozzle theory (proximity to a surface, buoyancy, nozzles with small diameters)
  - Effects of the shape of a nozzle on the release (slits, elliptic orifices, rectangular orifices, effects of the aspect ratio of asymmetric orifices on the scaling laws)
  - High pressure releases in enclosed areas (with natural or forced ventilation)
  - Effect of wind on unignited jets, Interaction of multiple jets, behavior of jets from flapping sources, cryogenic jets
- Detailed studies of the orifice shape effect on the H_2 concentration in the expanded region are still rare (Paraschivoiu, Molkov) despite the fact that realistic sources are not likely to be circular
- Buoyant jet releases occur for small, often subsonic releases, which do not in principle follow the scaling laws. Their behaviour can however be predicted numerically.
- Low momentum H_2 jets (forced plumes) have been studied (Houf, Schefer). They measured the jet mass fractions (Froude numbers of 99, 152, and 268) and compared the results with their integral model accounting momentum and buoyancy contributions.
- A non-Boussinesq engineering model (Xiao) for fully turbulent horizontal jets.
- Deviations from the scaling behaviour of expanded jets along the centreline of the jet for subsonic low momentum horizontal jets exist are discussed by Hourri et al in their omputational study of horizontal subsonic free jets of hydrogen
- General correlation for the length of hydrogen flames normalized by the nozzle diameter as a function of the product of the ratio of the density of hydrogen at the nozzle to the ambient density of the environment by the cubic power of the Mach number (Molkov, Saffers 2011). This correlation was shown to be applicable to all flow régimes, including both buoyancy and momentum-dominated. In view of the fact that there are indications that the flame length may be correlated to the size of an unignited jet, it would be interesting if a corresponding correlation could be derived for the flammable size of a hydrogen release.

Notional nozzle models

- Notional nozzle models:
  - Birch et al. (1984): Conservation of mass, temperature at notional nozzle equal to atmospheric
  - Birch et al. (1987): Conservation of mass, conservation of momentum, temperature at notional nozzle equal to atmospheric
  - Ewan and Moodie (1986): Conservation of mass, temperature at notional nozzle equal to the one at the actual release nozzle
  - Schefer et al. (2007): Conservation of mass, conservation of momentum, real gas (Abel-Noble equation of state), temperature at notional nozzle equal to atmospheric
  - Harstad and Bellan (2006): Conservation of mass, conservation of momentum, conservation of energy, location just after the Mach disk (Low flow speed)
  - Adding Mach disk conditions (Winters 2007, GexCon 2008)
- Detailed evaluation of notional nozzle models for free-shear under-expanded H2 jets (Papanikolaou) for k-ε, k-ω, and SST turbulence models (Schefer 2007 with Abel-Noble EOS is the best)
- Despite the successes of the notional nozzle approximation
  - unclear to what degree such approaches can be applied to the description of the attached or confined jets
  - detailed analysis of the effect of this approximation on the transverse velocity distribution should also be performed
  - the applicability of notional approximations to different shapes of the orifice of the release has not yet been looked in details
- Validation for the combustion i.e.,
  - not only concentration and flow speed
  - but also turbulence.
- Validation with broader range of conditions:
  - very high pressure(500-700 bar),
  - different diameter size,
  - jet impingement with
  - obstacles/walls.
- Definition of criteria to help to identify the best modelling strategy
  - for each application: which notional nozzle? notional nozzle or
  - real nozzle?

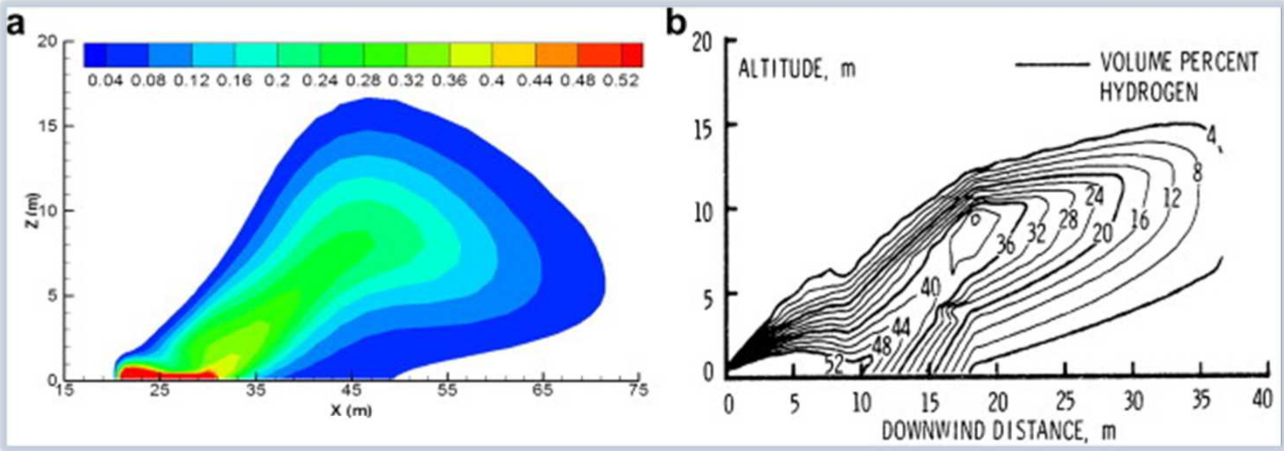


Jet confinement and attachment

- In the enclosures numerical and experimental studies show that H_2 accumulates either as a stable, stratified distribution of concentration or as a homogeneous layer if the convective flows at the top of the enclosure are high enough.
- Engineering model (Cleaver, Zhang, Worster-Huppert, Peterson) deficiencies:
  - Release direction (existing models mostly for vertical)
  - Momentum / Buoyant (most engineering models assume buoyant) regimes should be proved
  - Linearity of the distribution for stratified case can be violated
  - Aspect ratio of the enclosure (usually near cubic)
  - Role of natural and forced ventilation including vent sizing methodology
- Simplified mathematical models have been devised to predict the dispersion of hydrogen releases within a confined volume. Recent work (Cariteau 2012) depending on volumetric Richardson number four different distribution regimes identified:
  - $Ri < 2.5 \cdot 10^3$ – homogeneous
  - $2.5 \cdot 10^3 < Ri < 2.5 \cdot 10^3$ – stratified with homogeneous layer
  - $Ri > 3$ - – stratified with non-homogeneous layer (linear or parabolic distribution)
- A study investigating the discharge of H2 from onboard storage tanks through a PRD inside a garage like enclosures with low natural ventilation has been performed (Brennan 2011) with a goal to investigate the relationship between PRD diameter, natural ventilation and volume for releases in enclosures with a single vent from onboard storage tanks of 1, 5 and 13 kg at 350 and 700 bar.
- EC projects: InsHyde-HySafe, HyPer, Dimitrhy, HyIndoor (ongoing)
- The proximity of jets to surfaces will modify the scaling behavior of expanded jet and typically increase their flammable lengths. It may induce a Coanda effect, create a recirculation zone between the nozzle and the surface, and generate transient behavior such as puffing, which may temporarily increase the flammable extent beyond the steady state equilibrium (Benard, 2007) . The properties of attached jets have been studied numerically (Hourri 2001) and to a lesser extent experimentally for unignited and ignited releases (Désilets 2009, Willoughby 2009). These results require experimental confirmation and cross-checking with simulation results obtained using more complex turbulence modeling.

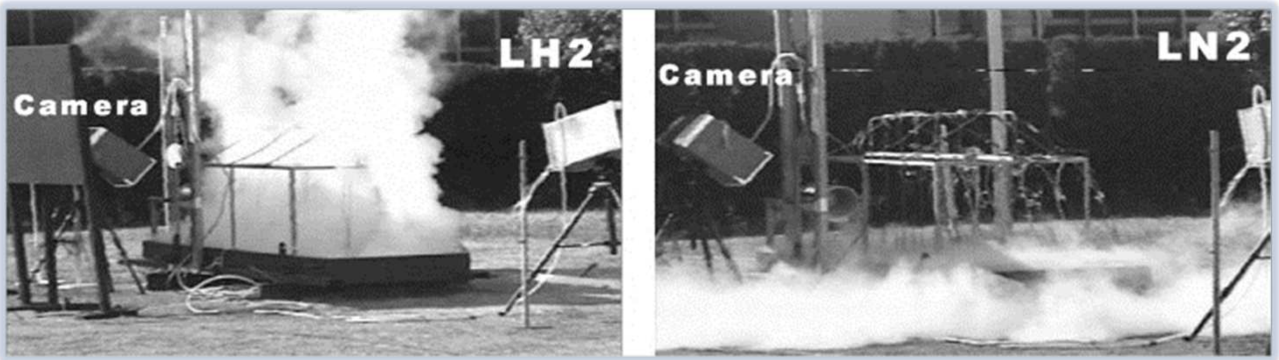
SOURCE, RELEASE AND DISPERSION FOR LIQUID H_2

Experiments
Simulations
Analytical models



Liquid H_2 is one of the promissible possibilities for hydrogen storage and transport thanks due to it larger density (~71 Kg/m^3 at 20 K) in comparison to compressed hydrogen (0.08 Kg/m^3 at 300 K). Pressure vessels contain 2–3 times more fuel than conventional compressed H_2 vessels (Aceves, Kircher).

Liquid H_2 brings additional hazards in comparison with gaseous incidents, but the accidental spillages and/or leaks are poorly understood, particularly the initial stages of pool spread and vaporisation (Pritchard & Rattigan)



Experiments with LH_2

- Several groups starting in 80's performed experiments of liquid hydrogen spillages and the data are available in the scientific literature: Witcofski, Chirivella, Schmidtchen, Dienhart, Verfondern, Nakamichi with colleagues.
- Existing experiments provide confirmation that a pool can be formed if a liquid release is made on the ground and the ground surface is sufficiently cooled. Moreover oxygen and nitrogen freeze, forming a solid deposit on the ground.
- However the quantity and the level of details of the experimental data that are available in the scientific literature are limited. The available data do not allow for the complete accurate quantification and modelling of the phenomena and for the validation of the models
- Because of safety reasons, liquid helium was used as replacement for liquid hydrogen by Proust and co-workers, which validity should be further approved.
- More recent experiments of liquid hydrogen spillage were carried out at HSL/HSE (Royle and Willoughby, Hooker at al.)
- Experiments of release and combustion of cryogenics hydrogen jets (Friedrich) provided an estimate of safety distances and an extrapolation model for other jet conditions. In the ICEFUEL cable study (integrated cable energy system for fuel and power), they investigate the possible accident in delivering liquid hydrogen and superconducting electric power simultaneously in the same cable (Friedrich et al., 2012).
- Other major hazards related to LH2 are the very low temperature (20.28 K) which can cause severe tissue frostbite and the enhanced embrittlement of material (Rigas & Sklavounos)

- In general in the experiments in the literature, mainly the liquid hydrogen release and dispersion are investigated while experiments with the entire sequence of release and dispersion followed by explosions and/or fires are rare (Hooker et al., 2005).

Numerical simulations for LH_2

Numerous physical phenomena is to be modelled in CFD for LH_2 release and dispersion:

- two-phase release sources, multi-phase jets, phase changes and gas behaviour at low temperatures,
- pool formation and spreading, heat transfer with the surrounding environment,
- effect of weather conditions e.g. temperature, humidity, wind and atmospheric stability, effect of ground and roughness/obstacles configuration,
- effect of turbulence and buoyancy on all the above phenomena.

- Starting from simulations (Statharas 2000) of the tests with a release rate of 0.37 kg/s (BAM test) by accounting the heat transfer to the ground the agreement between experiments and simulations was achieved and the maximum concentration was in most cases predicted within a factor 2.
- Numerical analysis of LH_2 release and dispersion in a mock-up re-fuelling station, investigating the effect of wind direction and the presence of an obstacle on the flammable mass and volume (Baraldi 2009).
- Another challenge in simulations of LH_2 is the modelling of the source term. Experimental observations have indicated that the flow is already two-phase at the exit orifice.
- By modelling the source as a two-phase jet (compared to a pool) and including the heat transfer to the ground (Venetsanos 2007), agreement between experiments and simulations (NASA tests: 9.5 kg/s) was achieved. The observed discrepancies were attributed to wind and to a low value of the heat flux from the ground.
- In CFD sensitivity study (Ichard 2012) of the HSL/HSE experiments (release rate = 0.071 kg/s), they achieved the best agreement with volume fraction equal to 0.99 and in (Middha 2011) the simulated maximum concentrations were within a factor of 2 compared to the experimental data
- Knowledge gaps: a factor 2 for concentration uncertainty for the specific H_2 applications could not be acceptable
- The Fuel Cells and Hydrogen Joint Undertaking (FCH JU) co-funded SUSANA project is starting in 2013 with the target of developing a Model Evaluation Protocol for hydrogen, including a validation matrix for CFD simulations

Analytical models for LH_2

- Beside CFD studies, also analytical models were developed to describe specific stages of the liquid hydrogen release.
- Perturbation method (Kim 2011, 2102) applied to solve a simple physical model that describe the LH2 pool spreading provides nearly identical results to CFD when third order perturbation solutions are considered for the pool volume. The governing parameter is the evaporation rate.
- Epstein and Fauke developed a top-hat jet/plume model to obtain simple closed-form expressions for the total mass and volume of the flammable cloud for a gas or volatile liquid release.
- Harstadt and Bellen investigated the vaporization of a LH_2 pool and developed some analytical expression for the minimum pool evaporation time for the H2 film-boiling rates.
- Verfondern and Dienhart developed a computer model LAUV to simulate the spreading and vaporization of a cryogenic liquid under various conditions e.g. different grounds (solid or water) showing a satisfactory agreement between the model results and the experimental data.
- A homogeneous non-equilibrium, two-phase critical flow model, the homogeneous direct evaluation model (HDE), was developed by Travis. The model was validated with NASA data for liquid and supercritical hydrogen, methane, nitrogen, and oxygen in terms of critical mass fluxes for a range of stagnation conditions.
- Houf and Winters developed a series of models to describe the whole release process of a small and slow leak (at very low Mach number) from a LH_2 storage system based on NIST REFPROP subroutines. Later they developed a similar multi-zones model for high-pressure liquid release, adding a model for the zone of under-expanded flow. The only validation is for the model for gaseous hydrogen leaks, demonstrating a favourable agreement between the model and the experiment for H_2 concentration along the centreline.
- Li used the PHAST software to calculate the harm-effect distances of LH_2 releases and of cryo-compressed hydrogen releases. Their analysis and results have a high level of uncertainties because PHAST is based on simplified models and correlations that do not take into account all the relevant parameters, are not valid for all range of possible conditions and hazardous materials and have very limited examples of results validation for hydrogen.

ACCIDENTAL IGNITION

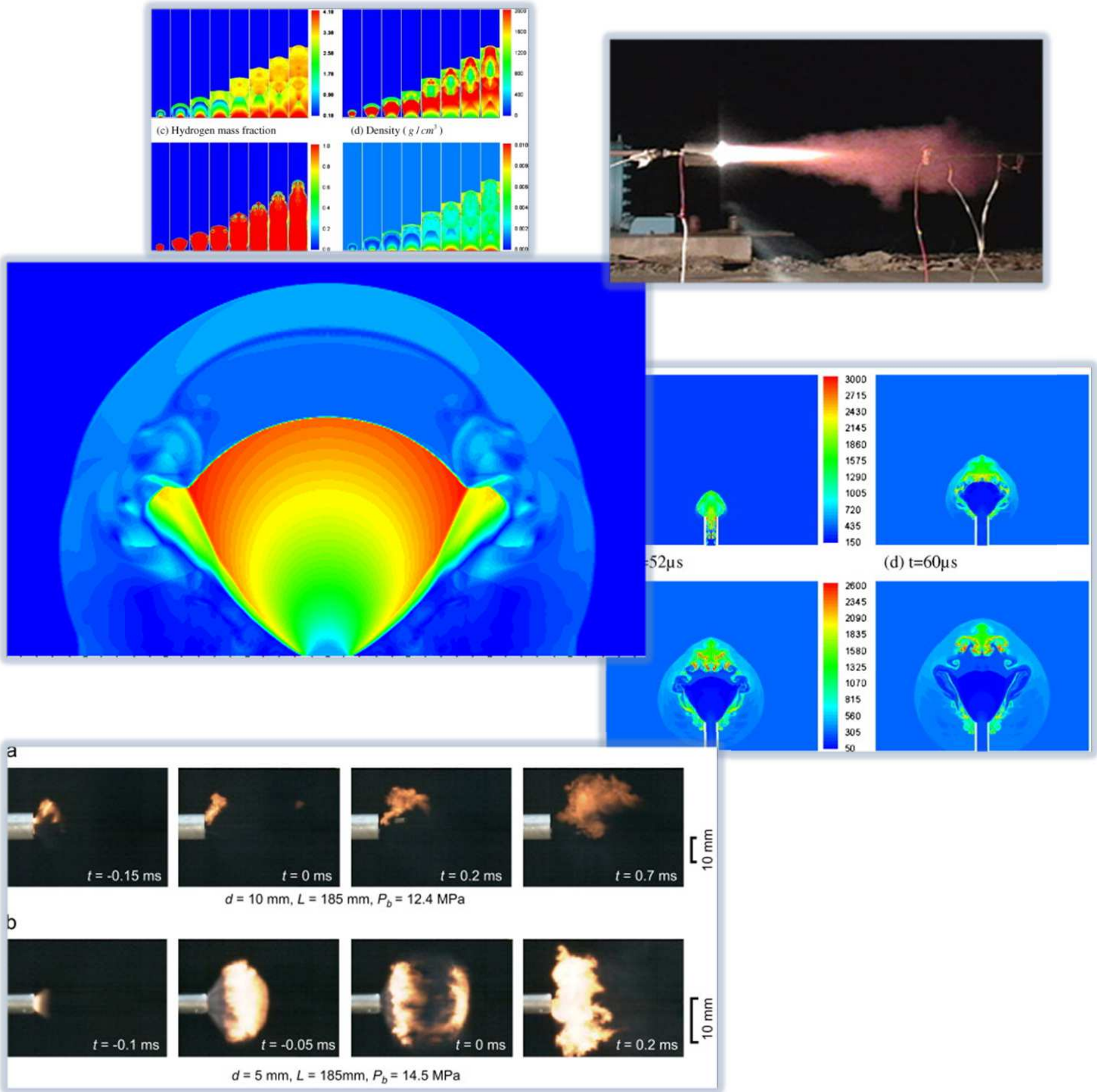
Diffusion ignition Various mechanisms

Four potential ignition mechanisms (Astbury and Hawksworth 2007):

- the reverse Joule–Thomson effect
- the electro-static ignition
- diffusion ignition (ignition behind a shock wave)
- hot surface ignition

Subsequent research excluded the reverse JT effect, but found evidence of all the others.

The majority of the researches has focused on diffusion ignition with few addressing others



Diffusion ignition: experiments

- Since Wolanski and Wojciki's (1972) pioneering experiments of diffusion ignition, little work was done until recent years. Recent experimental studies have been conducted by Dryer, Golub, Mogi, Desilet, Grune, Kitabayashi, Lee with colleagues. While there were variations in the experiments, the releases all passed through a section of tubes and bursting disks.
- Both Golub and Mogi found that the minimum release pressure required for ignition depends on the tube length and diameter. The type of the bursting disks also is important. In general, the propensity to spontaneous ignition increases with the increase of pressure, tube diameter and length. As the tube length increases, the minimum required pressure decreases.
- Cross section shape of the tube is of importance because it affects the flow boundary layer (Golub), narrow rectangular increase probability. At the pressure 1.5–2 MPa, spontaneous ignition was found to occur with the tested rectangular tube.
- It was found that the formation of a complete flame across the tube is important to initiate self-ignition, which sustains a diffusion flame after jetting out of the tube into the air
- Recent tests of Kitabayashi used various tube lengths up to 4.2 m. The required storage pressure is a function of the tube length with characteristic minimum at about 3.8 MPa for tubes with 10 mm ID. Below this critical pressure and with longer or shorter tubes than the length of about 1100 mm, no ignition occurred.
- Golovastov and Bocharnikov studying the influence of rupturing process found that the ignition possibility is defined both by pressure and by diaphragm rupture rate. The faster a shock wave is formed the faster ignition is started. For pressures 5.0–14.0 MPa the rupture rate was varied from 5 to 20 μs. The found dependence is monotonic and practically did not depend on initial pressure. These findings were found to be in line with the numerical predictions (Xu) for release into air without channel.
- Yamada also identified generation of vortices behind the shock in a long tube; the later led them to postulate the possibility of an auto-ignition induced by vortices.
- Dryer provided further insight revealing that the internal geometry downstream of the bursting disk greatly affected the likelihood of ignition, especially for relatively low pressures. They showed that the bursting disk rupture process has an important influence on mixing and ignition through multi-dimensional shock formation, reflection and interactions. However none of the experimental groups investigated in detail the influence of different internal geometries.

Diffusion ignition: numerical studies

- Numerical investigations in 2006 – 2013 were performed by Brady, Sung, Bragin, Molkov, Golub, Lee, Jeung, Radulescu, Shen, Sun, Wen, Xu, Yamada with colleagues.
- The earlier numerical simulations (Liu, Xu) revealed the possibility of spontaneous ignition even when H2 is directly released into air, using important hypothesis that the release was sudden, i.e. infinitely fast. Any accidental releases, in practice, however would often involve releases through a section of a tube and most of studies use such configuration
- Study of several groups identified that the air behind the leading shock is shock-heated and mixes with the released hydrogen in the contact region. Ignition is firstly initiated inside the tube and then a partially premixed flame is developed. Significant amount of shock-heated air and well developed partially premixed flames are two major factors providing potential energy to overcome the strong under-expansion and flow divergence following spouting from the tube.
- Parametric studies (Wen) revealed that the rupture process induces significant turbulent mixing at the contact region via shock reflections and interactions. If the tube length is smaller than a certain value for a given tube diameter, even though ignition could take place inside the tube, is likely to be quenched later. This was later confirmed by the experiments of Golovastov and Bocharnikov
- Xu investigated the effect of a thin flat obstacle on the ignition and found that the presence of the obstacle plays an important role in quenching the flame following spontaneous ignition.
- Xu, Wen examined the effect of local contraction within the tube. They found that a local contraction can significantly increase the propensity of spontaneous ignition by producing elevated flammable mixture and enhancing turbulent mixing from shock formation, reflection and interaction.
- Bragin, Molkov numerically reproduced the experimentally observed phenomenon of flame separation and suggested that the transition to the sustained jet flame is largely dependent on the initial stage, where the developing annular vortex pushes the combusting mixture upstream into the recirculation zone. Once the flame is stabilised near the tube exit, it acts as a pilot flame and ignites a jet fire later on.
- Bauwens and Maxwell investigated theoretically partially confined jets and found that the ignition limits of H_2 releases into confined environments depends strongly on the strength of the shock that is driven into the oxygen/air ahead of the jet and size of the release orifice.

Ignition by various mechanisms

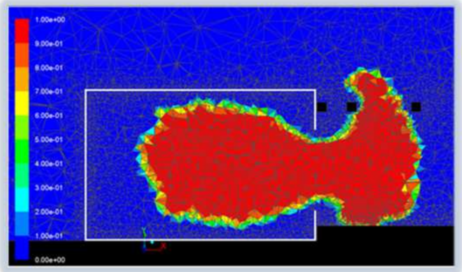
- Experiments on corona discharge (Hooker) showed that H_2-air mixtures can be ignited by the discharges of a potential of several tens of kV. Such situations could be expected at the top of tall vent stacks, tens of meters above ground, in the presence of large atmospheric electric fields (e.g., during snow fall). Therefore horizontal releases of H_2 close to ground level is unlikely to be ignited. They also found that dispersion of dusts up to 160 g with H_2 released from 200 barg did not appear to generate hazardous electric fields.
- A small quantity of entrained particulates can be a source of spontaneous ignition (Merilo). Both electrostatic discharge and corona discharge could be responsible for the ignitions, but typical hydrogen application unlikely will have conditions for ignition. This is consistent with the findings of Hooker et al.
- Imamura et al. investigated the effect of the outlet shape on the possibility of the ignition by electrostatic discharge at a ventilation duct outlet. Four types of outlets were designed: 6.35 mm, 12.7 mm, and 25.4 mm pipe outlet and a tapered porous outlet. If the ventilation duct outlet is grounded, most of the electrostatic charges are not generated, but not all of them can be removed by grounding only.
- Study of the ignition of lean pre-mixed hydrogen/air mixtures at a stagnation-point flow configuration against a catalytic platinum surface (Brady) demonstrated two distinct regimes - catalytic surface reactions and gas-phase ignition and showed dependence catalytic reactions on surface heating. Their findings indicated that ultra-lean hydrogen/air mixtures can be ignited even in the absence of external heat addition, thus confirming a fire safety risk even at room temperature. After ignition, the surface temperatures were stabilized in the range of 600-800 K.
- Welzel investigated the ignition by mechanically generated sources for two different hydrogen/air mixtures. Their work pointed out limiting power densities for the ignition of 10% and 30% hydrogen/air mixtures in friction processes with mild and stainless steel. Limiting values in 10% hydrogen/air mixtures are lower than those in 30% hydrogen. Limiting power densities for stainless steel are lower than those for mild steel.
- Frolov et al. conducted numerical simulations using detailed chemistry on the effect of hydrogen addition on the propensity to spontaneous ignition of homogeneous and hybrid mixtures of heavy hydrocarbons in air. Reactivity of hydrogen-containing mixtures is not always higher than that of pure hydrocarbon air mixtures. At temperatures less than 1050 K, the addition of hydrogen to such mixtures was found to increase the spontaneous ignition delay. At temperatures exceeding 1050 K, hydrogen addition was found to decrease the overall spontaneous ignition delay thus indicating that hydrogen acts as a promoter.

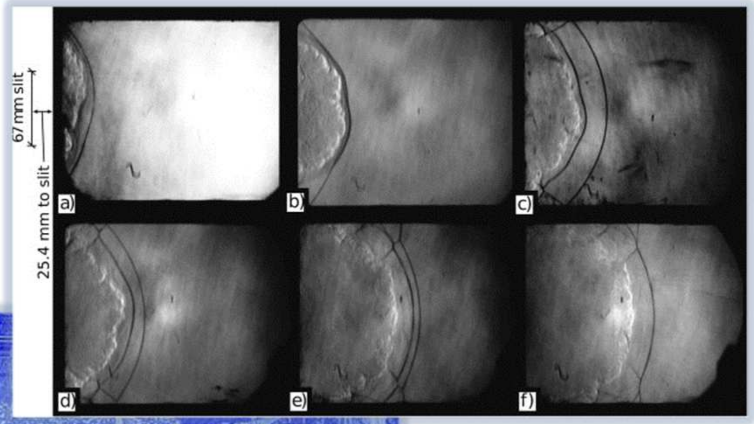
COMBUSTION

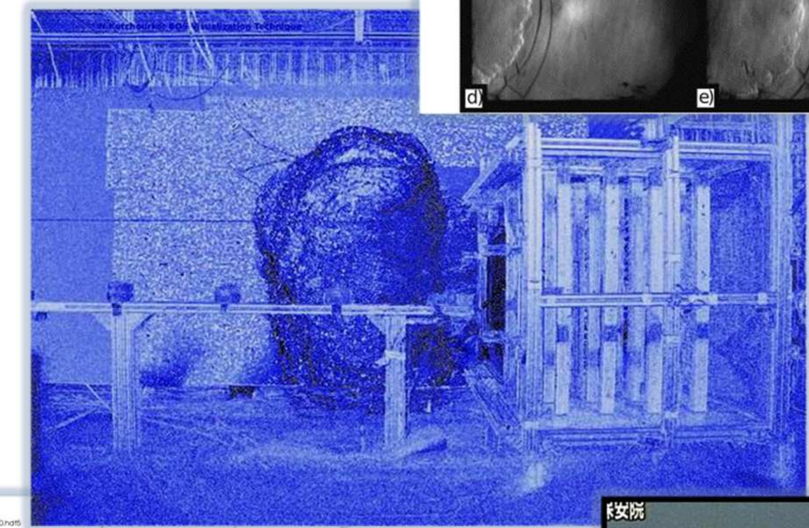
Confinement
Congestion
Mixture

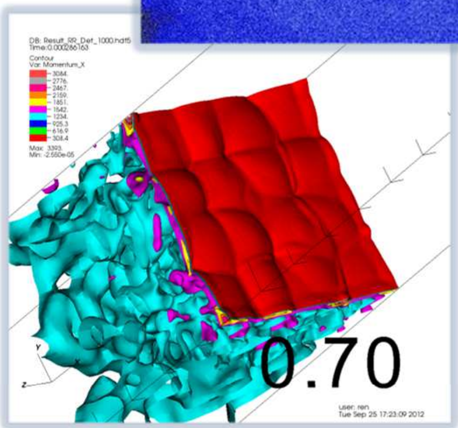
Depending on the hydrogen mixture characteristics, such as concentrations, temperature, pressure, and flow geometry, the combustion process can undergo strong flame acceleration and / or deflagration-to-detonation transition.

Dependence of the potential danger of the combustion process appeared to be very sensitive to the geometrical conditions of the processes, mostly to the confinement and congestion level within the enclosures.









Confinement of combustion

- The possibility of the flame to accelerate is very sensitive to the confinement of the volume. The combustion of the fully confined volumes is relatively good understood and its effects can be quite successfully predicted by modern combustion models. The necessity to take into account more practical configurations requires knowledge of the combustion in the volumes with one or more vent areas of varying shapes
- Starting with the channel-like experiments (Sherman) it was found that transverse venting can substantially reduce flame speed and in case of detonation even cause its failure.
- Further results of the influence of the transverse and longitudinal venting in channels were obtained by several research groups (Ciccarelli, Alexkseev, Alexiou) and the criteria for the evaluation of the flame acceleration risk were proposed (Dorofeev).
- Further extension of the vent influence studies involved investigation of the semi-confined volume, such as horizontal flat layer of the H_2 distribution limited from top (Friedrich), and new engineering correlation accounting for the layer thickness, obstacles' interval and blockage ratio was introduced (Kuznetsov).
- Practically important case is *vented explosion*. Experimental data of different scales and boundary conditions (e.g., Pasman, Kumar, Lowesmith) and theoretical models are available since 70's. Proposed by NFPA standard on vent sizing is basically focused on the natural gas and it was found that the model is over-conservative and for the stoichiometric hydrogen mixtures is not directly applicable (Daubech, Molkov)
- Jallais has shown that the later vent sizing recommendations (Molkov, 2008) have limited validity, while their earlier model (1999) globally provides good accuracy with slight overestimation.
- Most of the existing models are targeted to estimate only pressure peak disregarding other parameters, such as ignition location, obstacles, etc. The analytical expression (Bauwens) allows calculation of the both pressure peaks and takes into account other influencing factors. Jallais reported that the correlation is adequate for the hydrogen vented explosion volumes from 1 m^3 to 120 m^3 and H_2 concentrations from 10% to 30% vol.
- Accounting of other confining factors, such as covering vent grid, relative localization of the vent, and particularly important vent cover inertia are still not properly addressed. Molkov produced comprehensive overview of the state-of-the-art on explosions with inertial vent.
- In the currently on-going EC project HyIndoor a systematic study of the venting methodology is undertaken and a formulation of the improved correlations and CFD numerical tools are expected to be proposed.

Influence of congestion

- Details of the obstacle configuration can decisively influence on the regime of the combustion. One of the main parameters which are commonly used for the obstruction characterization is blockage ratio. However other geometrical characteristics can and actually affect the combustion process as well.
  - Starting from 90's the different geometrical forms were studied (e.g., Mayinger: tube bundles, gridiron, plate with rectangular opening) it was shown that flame can strongly accelerate for all blockage ratios.
  - Influence of the variation of blockage ratio, distance between obstacles, imitation of rough walls, etc., were studied in the works of Teodorczyk.
  - Global quenching was observed in the vertical facility with partially obstructed channel (Cheikhravat)
  - Parametric study on the evaluation of limits for effective flame acceleration in obstructed closed geometries (Dorofeev)
  - Deeper understanding of flame acceleration was obtained after remarkably detailed CFD simulation (Gamezo);.
- However full understanding is not yet achieved: thus further efforts are continuously undertaken to improve the knowledge and comprehension of the role of obstacles. Among recent studies, for example,
  - Gaathaug et al. studied experimentally an onset of detonation behind a single obstacle;
  - Heidary and Wen considered a possibility to simulate an onset of detonation using different numerical techniques.
  - On the basis of the experimental work on the flame acceleration in flat layer (KIT), an attempt to generalize utilization of the congestion characteristics using numerical simulations was made (Yanez). It expands earlier correlation (Kuznetsov), which considers dependence on blockage ratio, distance between obstacles and layer thickness, by accounting of most of all possibly significant geometrical parameters of the layout.
  - In the frames of the EC project HyPer a study of leakages and releases followed by combustion inside a generic fuel cell cabinet for a range of leak rates, blockage ratios and vents were investigated.
- Deeper consideration of the boundary layer in un-obsturcted tubes can give rational results (Kuznetsov), keeping in mind that rough tubes without material obstacles and even smooth tubes are able to promote FA and DDT. Further investigations in this direction can have considerable practical outcome.
- Most of the studies are made for artificially created obstacle sets, such as repetitive periodic grids, circular orifices in the tubes at the constant mutual distance, etc., while the real industrial configurations will definitely include the obstacles irregularly placed in the volume with the very different characteristic sizes. Further analyses in this direction is required.

Mixture properties

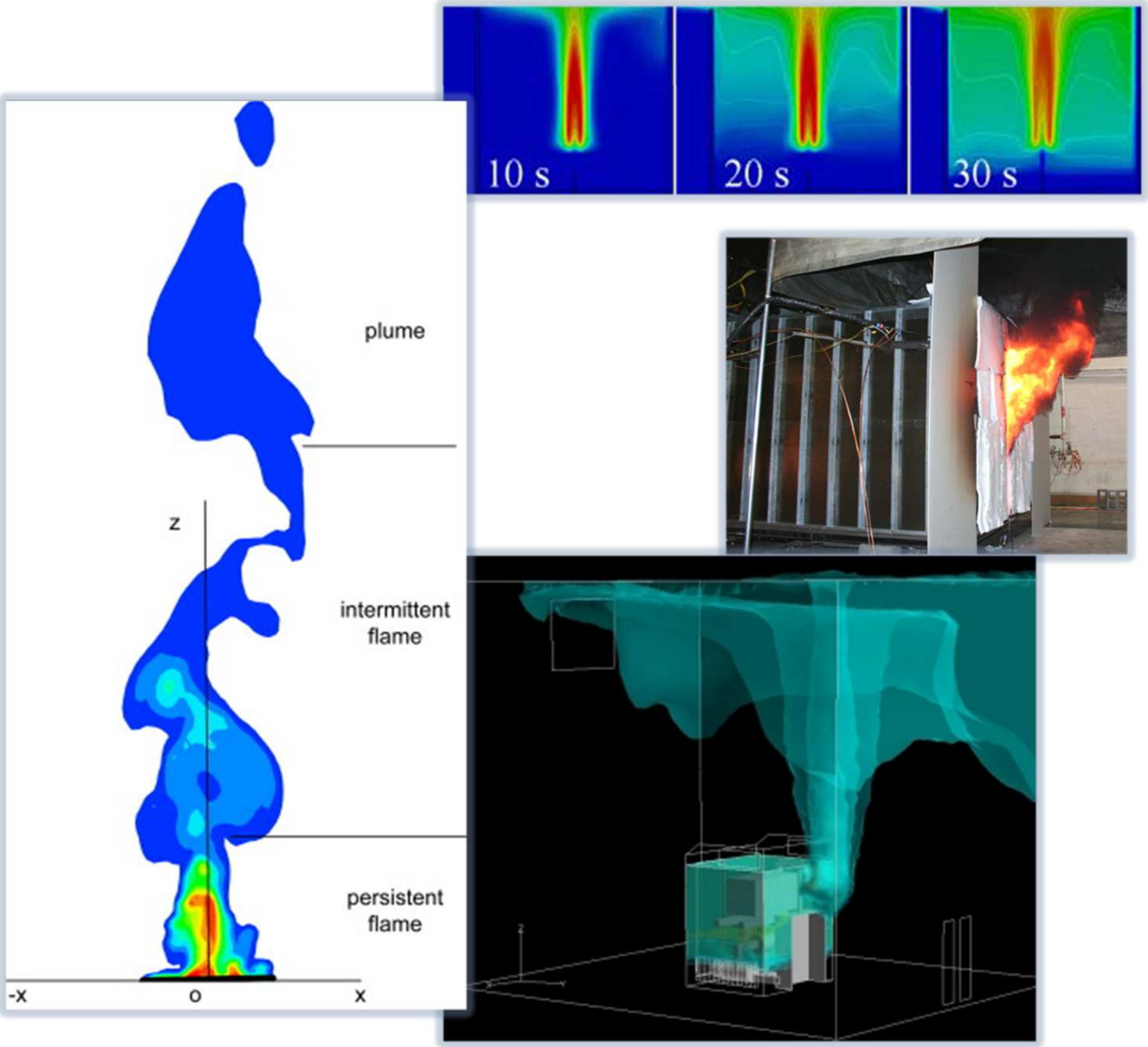
- Non-uniformities of the gas distribution can considerably affect regime of combustion, however, only limited amount of the experimental data are available on the behaviour of the H_2 in the presence of the concentration gradients
- In the recent studies (Bentaib) the data on the flame acceleration of lean H_2-air mixtures with vertical concentration variation and comparison of the obtained flame speeds with those in uniform mixtures were provided.
- Study of combustion regimes in the stratified horizontal layer of H_2-air mixtures (Grune, Kuznetsov) (with a hypothesis of the decisive role of the maximum concentration in the layer) and the numerical study for the corresponding regimes (Kudriakov).
- Large scale cylinder of 60 m^3 with vertically stratified mixtures were experimentally studied by Bengaouer.
- Benchmarking of the different CFD codes (Kotchourko) using data from ENACCEF (Bentaib) demonstrated that most of the codes still have the lack of the predictive capabilities for complicated initial conditions with mixture composition non-uniformity (acceleration and quenching).
- Nature of flames + supplementary events can promote flame instabilities, which lead to the considerably enhanced burning rates. Despite numerous experimental data and considerable theoretical achievements, only limited successes were achieved in the creation of the unified approach to their modelling.
- Recent numerical simulations, which take into account the effect of instabilities, demonstrate that basically successful approaches should be further generalized to provide verified methods for the engineering CFD simulations.
  - Combustion model was proposed (Bauwens) considering additional flame wrinkling which is described by a transport equation of flame surface wrinkling factor. The relative simplicity and transparent physical basis of the method promise high potential for the use in applied simulations, however currently the method requires calibration which reduces the value from the standpoint of the immediate use of it.
  - The existence of spontaneous transition from the acoustic to the parametric instability was demonstrated and their growth rates were evaluated for a set of mixtures typical for hydrogen based applications (Yanez).
  - The accounting of acoustic instabilities was successfully utilized in benchmarking simulations (Kotchourko), although some *backfitting* took place.
  - A SGS combustion model (Molkov), which uses the flame area growth equation based on fractal theory, provided reasonable agreement with experimental data down to ~12.8% H_2 concentrations, although requiring further development for other mixtures.

HYDROGEN FIRES

Fires Diagnostics

Leakages, broken fittings or connections as well as openings/holes could act as a continuous source. An ignition is likely for all forms of releases due to the wide range of flammability and low ignition energy, which leads to the occurrence of the resulting fire.

To qualify the possible hazard the characteristic of the flames, such as burning rate, temperature, emitted radiation and the flame envelope should be known. The pure H_2 fire is nearly invisible bringing to the fire investigations additional complications and making development of H_2 fire diagnostic methods quite important.



Jet fires

- Small leakages generate normally low momentum jets and ignition forms sustained laminar or turbulent diffusion flames. Detailed investigations are mostly devoted to determination of burning rates, species and temperature profiles:
  - The data on flame velocities depending on pressure are still limited to relatively low pressures (< 3 MPa) (e.g., Bradley), despite high request for such data exists.
  - UV-Vis emission spectroscopy was successfully applied to small scale turbulent hydrogen diffusion flames (Gore) and P < 3 MPa (ICT) as well as for extremely high pressures up to 200 MPa (ICT).
  - Simultaneous H_20 vapour concentration and T measurements were performed in transient hydrogen flames (Blunck).
  - Still the detection and identification of small hydrogen releases and fires onset are difficult.
- Momentum driven jet fires can be generated from high pressure storage, liquid tanks, or fuel cells. These jets might impinge constructions or humans up to L/D ~ 3000-4000, depending on vessel pressure and mass flow rate. The typical research studies are measuring the length and width of the fire and the radiative properties depending on the initial pressure in the tank and the opening diameter. Recently novel jet flame length correlation was proposed (Molkov) unifying buoyancy and momentum controlled jets.
- Development of jet fire is not completely understood. The H_2 jet after ignition might establish a sustained turbulent flame, developing in two highly transient steps: starting from the ignition point the flame propagates simultaneously downstream and upstream followed by the flame pulsating before flame stabilization. In case of delayed ignition the first phase can develop as a gas explosion. For high initial mass flow rates (> 400 g/s) the apparent flame velocities might approach near sonic speeds and generate substantial pressure waves (KIT, ICT).
- Several studies are performed on the effect of barriers on the fires, e.g. Houf, Willoughby.
- Successful application of numerical modelling enabled the time resolved evaluation of the species concentrations and temperatures, which are close up to 2000 K with transient zones up to 2400 K (similar results by molecular band modelling code BAM from Fraunhofer ICT, and the results of Houf and Schefer from the RADCAL code)
- Poorly studied the exhaust from an opened liquid hydrogen tank led to the initiation of pulsating transient jets subsequently overlapping and lasting some seconds (e.g., Pehr). Generated pressure waves were moderately in the kPa range (Pehr, ICT) with T = 2000 K with some hot spots up to 2400 K (ICT, SNL, KIT).

Contours and radiation from H_2 fires

- Conventional high speed video techniques is mainly applied to record the shapes of emitting fires using seeding tracing material added into the 'invisible' flame, such as sodium or soot. *Schlieren* techniques can make the structures of the flames better visible. The BOS, background oriented Schlieren technique, applicable also in large scales can visualize the shapes of H_2 fires and also their detailed structures, including statistical data of turbulence (ICT, KIT). It can reveal flame structure details similar to *Schlieren* technique, identify air entrainment and blast waves, especially when using additionally brightness subtraction methods. A comparison with detailed imaging spectroscopy and CFD simulations could outline the correlation to real turbulent effects.
- Besides direct flame contact, radiation is the another important injuring effect. Radiation intensity depends on species, duration in the hot zones and T distribution.
  - In laboratory experiment all types of modern spectroscopic methods (UV-Vis-IR-, Raman Spectroscopy, CARS, LIF, PLIV, etc.) can be applied, for large scale H_2 fires the robust methods is preferred. Large fires (ICT studies) are band emitters with temperatures reaching to 2500 K, predominantly bands of OH in the UV-spectral range (band maximum 309 nm) and of H_2O in the NIR and IR spectral range (various bands from 0.64 - 9 µm). Since the different bands approach the intensity of a Black Body radiator at different λ, commonly used pyrometers are useless.
  - To measure the air entrainment, CO_2 with its strong band at 4.25 µm can be used. For measuring turbulent structures or transient phenomena robust FTIR-spectrometers.
  - To study the OH-band in the UV OMAs (Optical Multi-Channel Analyser) is used for more than 30 year with time resolution of 10 ms.
  - The evaluation of the 3-atomic molecules uses the "Handbook Infrared Spectra of Hot Gases" which gave the basis of Hitran, Modtran and Lowtran- code series of NASA, the RADCAL, and the BAM codes.
- The radiation emitted from the fireball strongly interacts with the radical OH, which plays important roles in the reaction mechanism involving H_2O_2 (e.g. Johnson) and HO_2, the reaction fronts being exposed to the intensive radiation of the H_2O fireball interior) and might therefore modify the reaction mechanism used in combustion modelling. The radiation emitted from the fireball interacting with flame front species can contribute also to the effective increase of burning velocity depending on the size of hydrogen-air mixtures (jets and clouds) as compared to self-induced turbulence. Accounting for such factors can contribute to an improved understanding of combustion and DDT events.

IDENTIFICATION OF KNOWLEDGE GAPS

- On the basis of the survey made by the participants of the Research Priorities Workshop held by HySafe the following issues can be qualified as having highest priorities in availability of experimental data, CFD models, and engineering correlations.
- Effects of surfaces on jets (attached jets, impinging jets), multiple jets, and the shape of a nozzle on the release (slits, elliptic orifices, rectangular orifices, effects of the aspect ratio of asymmetric orifices on the scaling laws) including flapping sources.
- Detailed validation of notional nozzle theory (proximity to a surface, effects of buoyancy, effects on the lateral concentration distribution, nozzles with small diameters).
- Effect of weather conditions on the release including cryogenic, e.g. humidity, temperature, wind speed and direction, atmospheric stability class.
- Universal scaling law for the flammable extent of jets.
- The physical properties of liquid hydrogen and gaseous hydrogen at very low temperature (also of O_2 N_2, H_2O – close to saturation) including differences with the ideal gas law, cryogenic jets, effect of buoyancy and turbulence for jets and spills, critical conditions for FA and DDT in cryogenic hydrogen-air mixtures.
- Phase change for cryogenic jets and spills such as the hydrogen evaporation and the condensation and solidification of nitrogen, oxygen, and water in the air.
- Conductive, convective and radiative heat transfer between the cold hydrogen and the surrounding environment including air and the ground.
- Limited studies have been carried out for accidental ignitions caused by mechanically generated sources.
- The effect of tube internal geometries on the propensity to spontaneous ignition.
- The effect of nozzle shape, especially non-circular nozzle, on the propensity to spontaneous ignition.
- A database on the probability of hydrogen spontaneous ignition for typical release scenarios similar to that available for hydrocarbon fuels.

IDENTIFICATION OF KNOWLEDGE GAPS

- Flame acceleration and deflagration-to-detonation transition in a semi-confined to open geometries.
- Vent sizing methodology, including high pressure releases in enclosed areas (with natural or forced ventilation) and effect of vent cover inertia on vented deflagration dynamics.
- Effect of obstruction characteristics on flame dynamics (acceleration/deceleration) and DDT for different confinement, including global and local quenching phenomena in different geometries and scales for premixed and partially premixed cases.
- Effect of hydrogen concentration gradient and stratification on flame dynamics (acceleration/deceleration) and DDT for different confinements.
- Flame instabilities (acoustic, parametric, Rayleigh–Taylor, Kelvin–Helmholtz, Richtmyer-Meshkov, Landau-Darrieus) and their effect on the flame dynamics including scaling conditions.
- Experimental data for the transient pulsating jet fires from liquid hydrogen or tanks at high pressures, further development of high resolution optical method, as e.g., scanning spectroscopy.
- Basic investigations of small scale hydrogen fires with materials, radiation, contact at various distances and large scale hydrogen fires with the view to develop reliable radiation models
- Effective fire ball scales, cooling down and movements, especially for large clouds, where cooling occurs mainly by radiation.
- Investigation of the hydrogen release from various types of currently favoured hydrogen storage materials and the effects of real storage containers, depending on loading status, operational state, ambient temperature etc., including hydride storage facilities.
- Further development of BOS technique: by synchronized 2 cameras, develop 3D BOS video analysis by comparison with CFD simulation, correlate 3D BOS with radiation shapes and CFD modelling including radiation transport.
- Constitution of a validation matrix for CFD simulations (validation against experimental data and inter-comparison), including turbulence modelling, combustion models, accounting of flame instabilities, and mesh sensitivity issues.