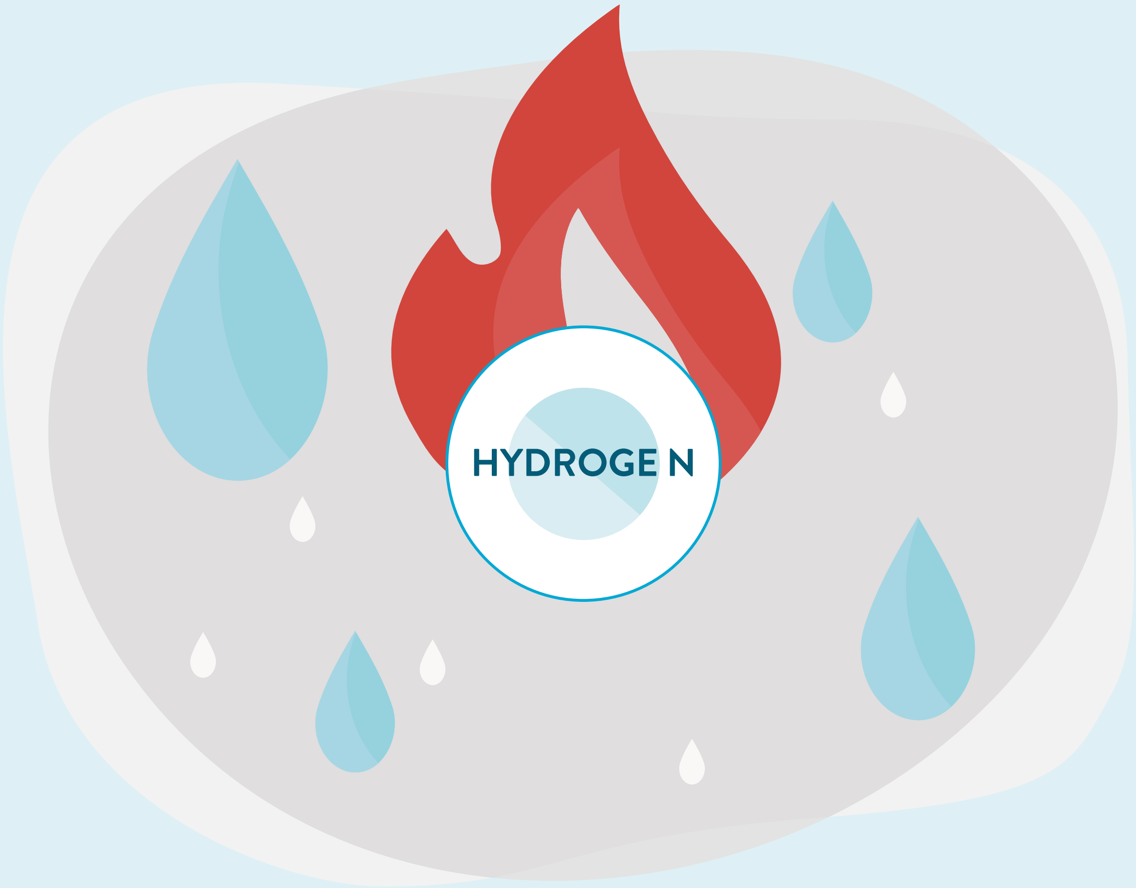
Hy4Heat
demonstrating
hydrogen for heat

Department for
Business, Energy
& Industrial Strategy

WORK PACKAGE 2

Colourant



Foreword for WP2 Colourant Report

This foreword / covering note is intended to supplement the Hy4Heat Colourant Report and inform the reader of the progress that has been made, in relation to the consideration of colourant within a hydrogen gas network, since the report was drafted.

Introduction

As part of Work Package 2 (WP2) of the Hy4Heat programme, DNV produced a substantive report regarding colourant within a potential hydrogen gas network within the UK [1]. Considering the advances within the hydrogen industry over the past year, this covering document provides an update to the results as presented by DNV, based on current industry progress and research.

Advancements have been made in the understanding of key topics:

- Flame visibility and supervision
- Health and safety of colourant additives
- Production of Nitrogen Oxides (NO_x)
- Likelihood of ignition from domestic electrical installations
- Nature of gas escapes

These are addressed below.

Flame visibility and supervision

As outlined in the report, in certain conditions, the visibility of hydrogen flames is limited. However, manufacturers of domestic hydrogen gas appliances in Work Package 4 (WP4) have developed designs to overcome this without the need for a centrally added colourant.

All hydrogen burning appliances must comply with the Gas Appliance Regulations (GAR) and appropriate Building Regulations (ADJ in England). This includes demonstration of all reasonable use (and misuse) by the user. This requires that any hot surfaces and zones likely to cause burns must be clearly identifiable by the user. This might include lint flammability tests. Suitable tests must be carried out by certification bodies prior to placing on the market of such appliances. Manufacturers and certification bodies are aware of these tests and apply them diligently. It will therefore be the responsibility of all appliance manufacturers to include such features into appliance designs, as the WP4 manufacturers have, to meet the certification requirements.

Examples of the solutions used include:

The use of small visual indicators connected to thermocouples have been used on cooker hobs, which illuminate as soon as a change in temperature (e.g. the hob is lit) is detected, similar to existing electric hob technology. These thermocouples are also interlocked with a gas solenoid valve that will cut off the gas supply in the event of a power cut.

High temperature ceramic materials used in gas fire appliances have also been shown to produce an ‘appealing glow’ and may be a preferred method to any flame additive.

In some appliances such as boilers, the need for flame visibility is negated; however, flame detection and supervision are paramount. Manufacturers are using UV and temperature detection in place of conventional ionisation devices to identify ignition failures. In this scenario there is no requirement for a colourant to be present.

Thermocouples have also been linked to flame failure devices (FFDs), within appliances so if a gas ignition on a burner does not occur, the gas supply is cut and the risk of an unchecked gas release, or delayed ignition is removed.

The report also considered the potential to use salt (sodium chloride (NaCl)). Appliance manufacturers under WP4 have not pursued this option and any manufacturer in the future who considered doing so would need to consider both the safety of the combustion products and the process by which the salt was to be replaced, without compromising the safety of the appliance, in order to achieve certification.

Health and safety of colourant additives

As identified by DNV, the addition of a colourant to the pipeline network results in operational difficulties which leads to high CAPEX and OPEX. Non-ignited escapes from high pressure pipelines are almost always detected through smell or sound; and in the event an underground release is ignited, the entrainment of dust and other material will result in a visible flame. Swain [2] also identified that hydrogen flames are more visible where air has high concentrations of particulate matter containing sodium, for example in coastal areas [3]. It is therefore concluded that adding colourant to the network at significant cost and operable complexity would not reduce risk and is not appropriate.

DNV also identified that the addition of substances such as salts, gases or reactive metals to produce a flame colour downstream of the Emergency Control Valve (ECV), has the potential to result in harmful by-products (including CO_2 if adding hydrocarbon gases to the hydrogen) during appliance operation. This was supported by university research under WP4, whereby NaCl (salt) was tested for use on cooker hobs and found to result in Na (sodium) deposition, which was thought likely to lead to corrosion.

The exception to this was when considering the use of NaCl reservoirs on gas fires, whereby any salt deposits were thought to escape from the appliance through the flue gases. However, other gas fire manufacturers are seeking alternative methods, such as flame impingement on high temperature materials, which if successful are likely to be the preferred choice.

It should be noted that currently (March 2021) no manufacturers appear to be using sodium chloride or any similar colourant as an indicator of flame presence. If a manufacturer were to identify an entirely novel system, they would still need to convince Certification Bodies of the long-term safety of their approach (probably for the projected longevity of the appliance). It would be unlikely that an approach which would require routine intervention by the householder and/or a Gas Safe fitter would pass this criteria. All manufacturers and certification bodies are aware of the potential health risks associated with chemical colourants.

NO_x

The production of NO_x has been in question throughout the Hy4Heat programme, with suggestion that the higher flame temperatures of hydrogen would result in greater NO_x production. However, evolving research and feedback from appliance manufacturers has shown that in practice, engineering can be put in place to reduce NO_x emissions compared to the equivalent natural gas appliance:

- In a similar way to biomass boiler operation, additional excess air can be introduced into the combustion chamber to reduce temperatures and thus, inhibit NO_x production.
- The residence time of hot combustion gases can be minimised to ensure they enter the heat exchanger and thus start to cool shortly after combustion. This reduces time for NO_x formation and is particularly appropriate for boilers, although can also apply to gas fires.

- Hydrogen flame length is shorter than methane, therefore the residence time at high temperature for a properly designed burner is reduced. This has the effect of reducing thermal NOx production.
- If a colourant were to be added to the hydrogen, the quantity would be very low (similar to odorant at ppm level). Therefore, any effect on the production of NOx would be negligible.
- NOx levels will have to demonstrate compliance with the Ecodesign directive.

Likelihood of ignitions from domestic electrical installations

It is widely acknowledged that the ignition energy of hydrogen is lower than natural gas; especially at high hydrogen gas in air concentrations [4]. However, in practice most domestic appliances provide sufficient energy to ignite both gases in appropriate conditions. This risk would not be reduced by the addition of colourant but will be considered in the WP7 risk assessment.

Nature of gas escapes

The Hy4Heat focus is risk downstream of the ECV. Steer Energy has carried out a series of experimental testing within Work Package 7 (WP7) safety assessment to determine leak rates and characteristics of hydrogen compared to methane for a range of typical domestic gas escape scenarios. The key findings were that a non-leaking fitting with methane is non-leaking with hydrogen, likewise a leak with methane will result in a leak with hydrogen. The volume of hydrogen will be greater (x1.2 for a laminar leak and x2.8 for a turbulent leak) but the much greater dispersion of hydrogen means that increases in concentration around the leak are much less than proportionate. Typical measured concentrations for hydrogen are x1.3 to x1.7 of those for methane from the same size (turbulent) hole

For most unattended escape scenarios, such as leaking fittings due to poor installation or pipe movement, the resulting gas escapes were found to be small, likely leading to low gas in air accumulations detectable through smell. Severe defects such as holes or fractures, almost always occur in occupied situations, e.g. a nail driven through a pipe. Therefore, the gas escape is likely to be detected through odour or sound at the time of event, and mitigation actions taken, before an accumulation of gas occurs.

In most domestic situations where a gas escape occurs outside of an appliance (e.g. is not a faulty part within a gas appliance), the likelihood of ignition of a gas escape is low due to proximity of sources of ignition to the position of the gas escape (e.g. a pipe within a wall or under the floor is not often close to a source of ignition). Within WP7, data was collected from First Call Operatives (FCO) following gas incidents, which detailed the nature of the call out. When only considering internal gas escapes, none of these incidents resulted in the ignition of the escaping gas. There are about 50 Natural Gas fires per year in GB; current studies indicate this number is unlikely to change with any re-purposing to hydrogen. As noted in this report, hydrogen leaks and flames tend to be louder than natural gas leaks, and so there is an increased likelihood of hearing a leak with hydrogen, along with the reduced likelihood of seeing a hydrogen flame. It is only in fires arising from exposed pipes where the reduced luminosity of the flame increases the risk of injury.

If the gas escape does ignite, in such a fashion as to cause a continuous flame, then damage to nearby objects such as scorching of surfaces provides clear indication of fire, and in these circumstances colourant in the gas does not provide additional risk reduction. Large leaks creating large flammable gas clouds will create general deflagrations; again, the risk from these would not be affected by colourant. In the unlikely event of a very small domestic leak igniting, the flame will remain on the leak. In this instance there may be a small increase in the likelihood of injury, however, the severity of injury from a small flame would be minor.

Further work as part of Hy4Heat WP7 safety assessment and Testing and Purging report indicate that larger gas escapes (from holes greater than 2 to 3 mm) are nearly always associated with 3rd Party intervention/damage; large leaks very rarely arise from spontaneous corrosion or building structural failure. In this context odorant or hydrogen alarms will be more effective than the addition of a colourant, which only becomes apparent if the gas escape ignites.

It is noted that the concept of ATEX Zone2NE has not yet been accepted by the HSE with regard to hydrogen. This area of work is important and should be progressed.

Leakage control from the gas network is outside the remit of the Hy4Heat programme and is the responsibility of the GDNO's as part of their safety case under the Gas Safety (Management) Regulations. It will therefore be for the GDNOs to develop safe systems of work but it should be noted that the addition of any chemical colourant is unattractive from the perspective of internal air quality (flueless appliances) and appliance corrosion/deposits (flued appliances).

Recommendations

It is concluded that adding colourant to a future hydrogen gas network for use within buildings is not necessary if engineering measures are put in place to enable safe appliance operation. These engineering measures may include:

- A means of identifying if an appliance is operational and the location of hot surfaces/zones. as currently required by the GAR and Building Regulations e.g. visual indicators.
- A means of displaying a decorative flame picture through in-appliance flame impingement, high temperature materials or entirely innovative approaches, again all GAR compliant.
- It is not felt that a centrally added chemical colourant is required to ensure visibility of fires arising from leaks on the gas network, however, this is not within the scope of Hy4Heat but is a matter for the GDNOs to consider as part of their Safety Case work for submissions under the Gas Safety (Management) Regulations. This work has been undertaken by the GDNOs and they have concluded that a centrally added colourant would not need to be added. [5].
- If such a colourant were ever thought necessary, a holistic risk analysis should be carried out on the additive including its possible effect both on appliances and the users of both flued and flueless appliances.

References

[1] DNV, “Hydrogen Colourant - Final Report,” Hy4Heat, 2019.

[2] M. R. Swain, “Fuel Leak Simulation,” in *Proceedings of the 2001 DOE Hydrogen Program Review. NREL/CP-570-30535*, Florida, 2001.

[3] C. E. Junge and R. T. Werby, “The Concentration of Chloride, Sodium, Potassium, Calcium and Sulfate in Rain Water over the United States,” *Journal of Meteorology,* vol. 15, no. 5, pp. 417-425, 1958.

[4] Pacific Northwest National Laboratory, “Hydrogen Compared with Other Fuels,” H2Tools, [Online]. Available: https://h2tools.org/bestpractices/hydrogen-compared-other-fuels. [Accessed 2 April 2020].

[5] SGN, H100 Colourant Report, 2021.

[6] HM Government, *Approved Document J; Combustion appliances and fuel storage systems,* Crown Copyright, 2015.

[7] Steer Energy, “Hy4Heat Work Package 7 - Lot 1. Safety Assessments for the Suitability of Hydrogen in Existing Buildings. Final Report,” Hy4Heat, 2019.

HY4HEAT (WP2) HYDROGEN PURITY & COLOURANT

Hydrogen Colourant – Final Report

Department for Business, Energy & Industrial Strategy

Report No.: 10123173-FINAL COLOURANT, Rev. 04
Date: 2019-11-15

Project name: Hy4Heat (WP2) Hydrogen Purity & Colourant
Report title: Hydrogen Colourant – Final Report
Customer: Department for Business, Energy & Industrial Strategy
1 Victoria Street,
London SW1H 0ET,
United Kingdom
Customer contact: Steve Loades
Date of issue: 2019-03-25
Project No.: 10123173
Report No.: , Rev. 04
Document No.:

GL Industrial Services UK Ltd
Holywell Park
Ashby Road
Loughborough
LE11 3GR
Tel: +44 (0)1509 282000

Objective:

The objective of this study was to determine if there is a requirement for adding a colourant to hydrogen to ensure that safe burning and user acceptance is achieved and to investigate the optimum solution if a colourant is required.

This aspect of the work also focuses on low pressure hydrogen leaks and makes recommendations to undertake further work to mitigate potential risks from hydrogen leakage.

Prepared by:

Martin Brown
DNV GL

Verified by:

Colin R Heap

Colin Heap
DNV GL

Approved by:

M J Pritchard.

Michael Pritchard
DNV GL

Stephen Graham
HSL

Rui Chen

John Gordon and Rui Chen
Loughborough University

DNV GL Distribution:

☐ OPEN. Unrestricted distribution, internal and external.

☐ INTERNAL use only. Internal DNV GL document.

☒ **CONFIDENTIAL. Distribution within DNV GL according to applicable contract.***

☐ SECRET. Authorized access only.

*Specify distribution: BEIS, Arup+, NPL, Element Energy, HSL, Loughborough University

Rev. No.	Date	Reason for Issue	Prepared by	Verified by	Approved by
1	2019-11-15	Final Report	Martin Brown Stephen Graham Rui Chen John Gordon	Colin Heap	Michael Pritchard
2	2019-12-11	Final Report	Martin Brown Stephen Graham Rui Chen John Gordon	Colin Heap	Michael Pritchard
3	2019-12-20	Final Report	Martin Brown Stephen Graham Rui Chen John Gordon	Colin Heap	Michael Pritchard
4	2020-03-25	Final Report	Martin Brown Stephen Graham Rui Chen John Gordon	Colin Heap	Michael Pritchard

Table of contents

1 EXECUTIVE SUMMARY

1.1 Summary

Hydrogen is considered to be one potential option to support the UK Government's approach to the decarbonisation of energy use. As domestic and commercial heat provision is a significant contributor to the UK's overall carbon dioxide emissions, it is timely to evaluate the options for this sector.

To support the overall aims of the Hy4Heat programme in evaluating the technical viability of distributing hydrogen to decarbonise heat supply for domestic and commercial users, an in depth understanding of the system implications for using hydrogen gas is required.

The Hy4Heat programme is divided into several Work Packages and the requirement of this Work Package (WP2) is to consider the flame colourant requirements for hydrogen, to ensure that safe burning and user acceptance is achieved. The recommendations as set out in this report will support the use of hydrogen in an unoccupied trial (Hy4Heat Work Package 8) and potential future occupied trialling (Hy4Heat Work Package 9).

This report makes up only part of the Hy4Heat Work Package 2, with hydrogen purity and hydrogen standards also contracted out under this work package and reported separately.

1.2 Project Objectives

The objective of this study was to determine if there is a requirement for adding a colourant to hydrogen to ensure that safe burning and user acceptance is achieved and to investigate the optimum solution if a colourant is required.

There is background information available that shows that hydrogen flames have low luminosity and are difficult to see. From an end-use safety view point it is important to have "visible flames" (especially for cookers and fires), and this aspect of the work programme will focus on options to maintain safe end use through the potential addition of a colourant or additive.

1.3 Scope of Work

1.3.1 Hydrogen Characteristics

- Describe existing hydrogen flames and burners
- Describe light emission from hydrogen flames
- Describe the challenges for hydrogen burners for domestic appliances
- Compare the appearance of hydrogen flames with those from natural gas to identify any safety implications.

1.3.2 Stakeholder Consultation

- Is a colourant required?
- What form should the colourant be in?
- Where should the colourant be added (upstream into the gas distribution network or downstream at the user appliance)?
- Who should maintain the colourant addition process?

1.3.3 Assess Hydrogen Colourant Types

- Review of colourant options
- Test odorant to see if it can have a dual role as a colourant as well
- Evaluate potential impacts and risks associated with introduction of colourants
- Liaise with key industry stakeholders

1.3.4 Investigate Hydrogen Colourant Addition

- Report on the practical and economic feasibility and the desirability of adding a colourant at distribution network level

1.3.5 Quantify the Risks and Hazards

- Understand the implications of Low Visibility Flames on the Network
- Understand the implications of odorant on flame colour
- Identify the risks to appliance performance

1.3.6 Undertake Hydrogen Leakage Testing

- Undertake burner simulation testing
- Undertake comparison tests – traditional natural gas flames and colourant containing gas
- Recommend further testing that may be required to determine if hydrogen is safe with no colourant.
- Report on the above experiments, referencing existing literature as required

Note: The scope was adjusted after the initial results from the colourant study highlighted that colourant may not be required in the hydrogen pipeline network. Additional test work on hydrogen leakage was agreed and tests were performed on leakage from copper pipes to mimic examples of the possible damage mechanisms that may result in internal pipework.

1.4 Methodology

The methodology adopted was initially based on literature review and critical assessment of available, openly-published information. This was then added to through a stakeholder consultation. The output from this highlighted some possible colourants, and these were then evaluated from the point of view of an efficacy, ease of introduction and maintenance, compatibility and health and safety for both the end-users and the network engineers.

In addition, a series of laboratory-based experiments were undertaken to evaluate the effects of no colourant and the potential for ignited hydrogen leaks to be established. The stability of these ignited leaks, the ease of ignition and the overall flame visibility provided further evidence to support the overall aims of this project, focusing on colourant requirements.

In summary:

1.4.1 Key Stakeholder Consultation

We issued a stakeholder questionnaire to gauge the views on colourant from gas distribution network operators and appliance manufacturers. The stakeholder questionnaire focused on understanding the nature of the colourant and whether it would it be beneficial or detrimental to the performance of the appliance.

1.4.2 Colourant Type

We looked at hydrogen flame colourant compound types to establish the range of options available. A structured approach was taken to provide a selection of the best forms of colourant (gas, liquid or solid), consider the impacts on flame stability and consider the potential by-products formed from the combustion of the colourant material.

1.4.3 Addition of the Colourant

We considered where to add the colourant. This could be into the pipeline network or at the appliance, and we also considered whether a colourant was needed at all.

We considered a number of important factors

- Colourant type
- Compatibility with network operations, maintenance and materials
- Injection process and point of injection
- Number of injection points required
- Quantity of colourant to add
- Impact of releases

1.4.4 Colourant Quantity

The quantity of colourant to add to a network is not known at present and here the parallel with odorant may diverge. Odorant quantities are in the parts-per-million range, but the likelihood is that higher quantities of colourant may be required. This would result in the requirement for larger storage facilities and more delivery activities (i.e. increased tanker movements), which would lead to a higher risk.

1.4.5 Risks and Hazards Review

We considered the implications of low visibility hydrogen flames on the network, identified the risks to appliance performance and also considered the implications of odorant on flame colour.

- The presence of odorant NB (an 80/20 mix of TBM and DMS) was investigated, as the presence of hydrocarbon components or fragments and sulphur may give rise to increased flame luminosity.
- Tests using odorised and unodorised hydrogen were performed and a comparison made “by-eye”. A diffusion flame was used in the first tests and photographs of the flames obtained.
- The odorant concentration was chosen to be similar to that found in natural gas, and the overall odour intensity was confirmed by standard rhinology checks.

1.4.6 Hydrogen Leakage Testing

We undertook hydrogen leakage testing by setting up a selection of copper pipe test pieces to mimic domestic pipework. Initial information from industry contacts suggested that nail holes in pipework or badly soldered joints could be the main leak types to focus on.

- We carried out initial tests on ignited releases from these layouts
- We undertook tests on the location of igniter, impact of distance from the leakage point and supply pressure
- We undertook comparison tests with methane and natural gas

- We focused on no impingement or secondary heating - photographic records and additional data were gathered
- We investigated ignited releases adjacent to a number of surfaces to evaluate the impact on flame visualisation. Material types included blocks, bricks, terracotta block, metallic surface, painted surface, wooden surface, MDF/chipboard, and various coloured tiles

We presented the results through photographic records with additional commentary on observations by eye. These results are supported by IR camera images to provide additional insight into the leak ignition and extent of the hydrogen flame.

1.5 Key Findings

1.5.1 Key Stakeholders gave their view

Eleven companies responded to our stakeholder questionnaire,

- Nearly 50% of respondents believed that a colourant is required, but nearly 60% don’t know what form the colourant should be in (gas, liquid or solid). A gaseous colourant was the highest category although this could be from addition of a volatile liquid.
- Approximately 60% of the replies believed that addition of the colourant into the pipeline was the best approach, although several highlighted that not all appliances need to have a visible flame.
- Just over 50% of the responses advised that the homeowner should be able to maintain the colourant addition but in others there was a strongly held view that this should be undertaken by a qualified engineer.
- The main view from domestic cooker and fire manufacturers is that some colourant system will be required if the design of the appliance remains similar to the current ones for natural gas.

The results demonstrated a wide spread of views and it was clear from the replies that more knowledge is required on the options for colourants before an optimum method can be selected.

1.5.2 Suitable colourants were identified

The information from the literature review and background studies on flame colour and flame photometry, highlighted that a wide range of components could be considered as colourant options. Some of these compounds may be hazardous to health, especially some of the metal species and as the final outcome was a combustion process that could lead to emission into the home environment, a decision was made to focus on substances that could be classified as “non-hazardous” (at the expected concentrations within the network or following combustion). The evaluation highlighted that the following were possible options for “Non-hazardous” colourants:

Colourant	**Advantages**	**Disadvantages**
Carbon Dioxide	Carbon dioxide addition can lead to a flame that has a more distinct blue colour. Readily available and addition could be a straightforward process	The quantities required are significant (potentially up to 20% by volume). This addition would result in significant reduction in Wobbe Index, reduced calorific value and lead to carbon dioxide emission as the point of use, impacting on the decarbonisation benefits from the use of hydrogen.
Methane, Propane	Has the potential to give a similar flame colour (albeit slightly less intense). Easy to handle and introduce. Readily available	Hydrocarbon species (including the alkanes and ketones) will need to be present in reasonably high concentrations (possibly in the range 5 – 10% by volume) to impart a blue colour, and carbon dioxide too if it can produce a light blue colour. This could be at odds with the overall aims of decarbonisation as it is adding carbon-containing species, and will also impact on the control of the fuel to the burner as it will affect the Wobbe Index.
Nitrous oxide	Hydrogen / nitrous oxide flames have been described as having an apricot-coloured appearance in some flame types or green/grey colour. Detailed spectra suggest visible emission from red to violet light	To get significant colour, the amount of nitrous oxide added may be prohibitive. It is anticipated that several percent by volume of nitrous oxide would be required. Also nitrous oxide is an oxidant and high concentrations in the fuel gas may not be appropriate.
Water	Water could be a simpler colourant option as humidification of the fuel (or the combustion air) may enable pink flames to be produced. Some studies have shown that the increase in luminosity is small but significant.	Water could impact on flame temperature and increase the moisture content from cooker hob burners.

Colourant	Advantages	Disadvantages
Propanone / butanone	Readily vaporised liquids like propanone or butanone could be used a colourant and would produce a light blue flame, due to their carbon content.	Quantities of additive may need to be relatively high (possibly around 5 – 10% by volume) and this will add to the overall carbon emissions
Halocarbons	Readily available Often easily vaporised	Halocarbons could be introduced but they could impact on flame stability as many are flame retardants, and the overall impact is not known. They could also form hazardous combustion products.
Potassium / Sodium / Rubidium / Cerium / Bismuth chloride	Aqueous solutions containing these metal chlorides could be a better approach rather than using powders, as powders could encourage particulate formation in the combustion products.	Although these species are known to impart colour they will produce solid deposits in the post-combustion region and this could impact on surfaces (pans, cooker, etc) and lead to increased corrosion or negative aesthetics for the process. The metal ions may give rise to particulate production and this is an unwanted side effect that could impact on indoor air quality and affect human health in the home
Borax	Borax can be used as a powder or an aqueous solution. It is sodium borate and can give a blue/green colour to a hydrogen flame (and also some orange colour from the presence of sodium)	May form solid deposits or small particles that could be considered as a negative end-user impact.

Table 1: Non Hazardous Colourants

The above materials cover three physical states, highlighting that colourant could be added as a gas, liquid or solid. The efficiency of any colourant option is influenced by its concentration, but there are no clear best options, and the suitability is influenced by the location and nature of the colourant addition (as discussed below).

1.5.3 Colourant addition options were investigated

The location of any colourant injection is a key aspect and it affects the quantity required, colourant type and management of the addition process. The addition locations considered included the high-pressure distribution network, the domestic pipework and at the point of use in utilisation equipment. These are considered below:

Network addition of colourant

Adding a colourant into the network raised the following issues:

- Network addition of the colourant requires the pipeline operator to provide additional management and control of operations to ensure that the process is managed safely and efficiently.
- The physical state of the colourant is constrained by the requirement to deliver a gaseous hydrogen product to end-users. This limits the colourant options to gases or volatile liquids, and almost certainly excludes the options to add liquid or solid material.

  From a network operation viewpoint, it is important to avoid liquids and solids in pipelines as they can affect pressure and flow control, especially through pressure reduction installations.

  Throughout the network, filters are used to trap liquids and solids and if the colourant is added close to the point of production then this would limit the colourant options to gases only.
- Colourant may not be required for parts of the system operating at the highest pressures but may be a requirement for some appliance types (fires and cookers) where a visible flame is preferable from an aesthetic viewpoint.
- Odorant injection quantities are typically in the parts-per-million range, but the likelihood is that higher quantities of colourant injection may be required. This would result in the requirement for larger storage facilities, more delivery activities and higher risk.
- Pipeline network operators would incur high CAPEX and OPEX costs to provide large-scale facilities for the injection of colourant, especially as the requirement is for a limited number of end-user types, and not needed in the main domestic use from condensing boilers.
- High pressure hydrogen releases from the network will be audible and if they ignite, will entrain surrounding solid material (dust, soil, etc) that will result in a visible flame.

The benefits through addition of colourant into the high-pressure pipeline distribution system are difficult to quantify and the conclusion from the stakeholder discussions is that there may not be any risk reduction. The addition of colourant may add to the overall risk, as it introduces additional factors to control and manage. The colourant will not improve the detection of unignited leaks from the network, and the odorant provides the safety control measure for this event. Ignited releases have been shown to be visible through entrainment of dust and other material and any colourant impact may only be a slight increase in flame luminosity. Overall network addition of colourant does not appear to be an optimum approach.

Internal pipework and appliance addition of colourant

Adding colourant after the ECV (within the property) was also considered. There are two options: either within the internal pipework to provide colourant to all appliances or within a specific appliance. The following points resulted from consultation with stakeholders:

- Low pressure hydrogen releases within internal pipework (between the ECV and the appliance) may result in hydrogen flowing through the ground material and then igniting at the point of entry to atmosphere where a flammable mixture could be generated and an ignition source is present.

  If the hydrogen flow ignites, the flame produced in these circumstances may be small and potentially invisible depending on the location and the surroundings.
- The process of low pressure release, tracking and ignition is not well understood, and although the potential to form a flammable mixture is present, in practice it may not occur.

- The onus for the management of the colourant is placed on the appliance manufacturer (from the viewpoint of introducing a system whereby colourant can be added) and the homeowner (appliance operator) to ensure that the colourant addition process is operating correctly.
- There are implications for end users that don't require a colourant e.g. fuel cell applications, and this would mean additional clean-up or filtration would be needed.
- The colourant additive will need to be food-safe as, in hobs and ovens, the products of combustion may be in direct contact with food.
- If the combustion products are released into the room, then the colourant and any chemical reaction products will need to be non-toxic.
- The wider environmental impact of flue emissions containing the colourant and any combustion products needs to be investigated.
- The impact of the colourant on hydrogen flame properties will need to be considered, including flame temperature, NOx emissions and flame stability.
- Colourant is only required for cookers and fires, where a visible flame is required / desired. Colourant is not required for boilers, which will contribute to the majority of future hydrogen gas use in the home.
- Colourant types considered will be either liquid or solid compounds and will be introduced by some unspecified process either into the fuel gas stream or into the flame. Any material added to the hydrogen fuel gas stream has the potential to cause blockages and potentially impair the overall combustion process.
- For boilers, the introduction of a colourant could increase deposits on the heat exchangers, change flue gas emissions, alter condensate pH, affect the fluid properties of the condensate (i.e. more water vapour) and/or generate particulate emissions from the flue.
- Cooker hobs discharge into the kitchen atmosphere and the impact of the possible trace emissions are considered in the future stages of the project. Colourant may also affect the material where flame impingement occurs, this could be pans or supports.
- New (safe) burners have been developed by manufacturers that remove the need to "see" a visible flame, therefore a visible flame is no longer an essential requirement.
- Where a visible flame is a desirable requirement as part of the aesthetics of an appliance, the onus should be placed on appliance manufacturers to develop products that provide a visible flame.
- A key consideration when deciding whether or not to add colourant is to ensure that the overall impact of the colourant should not result in increased maintenance of appliances or reductions in lifetime.

As the aim of colourant addition is to provide a more visible flame, the requirements for addition were considered from the point of view of improved operability or reduced risk. For appliances, colourant is only required for exposed flame burners like those on cooker hobs and fires. It is not required by boilers, and from a material resource aspect adding colourant where it is not required from a safety or operability reason is potentially increasing risk due to additional emissions, adding further points of equipment failure or additional process malfunction/misuse.

1.5.4 Hydrogen low pressure leakage testing was undertaken

Through the extended scope, additional practical tests were performed to determine the level of flame luminosity and visibility. Comparison with natural gas flames was made and the general result was that hydrogen flames are less luminous than natural gas flames, and also that in many instances natural gas flames could not be established at the leak point whereas ignited hydrogen would attach to the leak point. Outline results from the test work are shown below:

Preliminary leakage testing using a reverse pitot tube:

- The visibility of the flames is greatly enhanced when they are in front of a darker background.
- For white (melamine or painted) and wood backgrounds, it is evident just how difficult it is to see the established flame especially at lower pressure
- For methane, no flame could be stabilised at a pressure greater than 25 mbar. For hydrogen, a flame could be established easily at 80 mbar

Leakage testing from a copper pipe:

- The hydrogen flame becomes more visible (noticeable) at higher pressures due to the extended flame length and overall flame volume.
- There is a large difference in visibility of the flame as the hole diameter decreases as seen when comparing the results for the 0.5 mm and 0.3 mm drilled hole in copper pipes at 10 mbar.
- Attention is drawn to the difference between the IR and digital images, in particular the flame tip as this is the region that is virtually invisible to the naked eye. In this region temperatures can still be high enough to cause harm or initiate a secondary fire if it impacts on combustible material although occupants may not be able to see the full extent of the flame.
- An interesting result that was found during these tests is that a methane flame could not be established regardless of hole diameter, over the pressure range from 10 to 80 mbar.

Leakage testing from an unsoldered end cap:

- A different leakage and flow orientation was observed with the hydrogen issuing from the full circumference of the pipe in the annulus between the pipe and the connector
- A hydrogen flame could be established on the unsoldered end cap.
- A methane flame could also be established on the unsoldered end cap arrangement and the flame luminosity was greater than that for hydrogen.

Audible sound levels from leaks:

- For typical gas supply pressures (c20mbar), it is possible to hear an ignited hydrogen leak from a 0.5 or 1.0 mm hole but not from the 0.3 mm drilled hole. If the leak was unignited then only the 1.0 mm hole leak was detectable. Unignited leaks were best described as a hiss and the ignited ones more of a “roar”. The sound intensity was perceived to be greater for hydrogen than methane for unignited releases from the same hole sizes.

Flame Length

- A hydrogen flame was established for all leak testing, except for leakage from a 1mm hole in copper pipe at 80mbar. This was not the case for methane, where a number of leak tests did not establish a methane flame (See table 12).
- In all cases where a methane flame and hydrogen flame could be compared (5 x leak tests), the hydrogen flame was shorter in length.

Ignition distances

- It has been determined that methane is unable to be ignited for drilled holes in copper pipe test pieces. It could be ignited for some conditions in the initial set-up study of the reverse pitot tube and for the unsoldered joint.
- Hydrogen leakage ignition is possible for all leak sizes and flows studied here, and the ignition point can be reasonably distant from the leak point.

Although hydrogen flame luminosity is low in many instances, the flames can be observed in most tests depending on the background light level and the colour of the background material. The hydrogen flames can become more luminous if they entrain dust or other material. Also, the ignited release could be detected by secondary effects such as smouldering or scorching of material close to the leak point if the flame impinges on the surface. Secondary indicators are not dependent on the presence of a colourant.

The tests have highlighted that ignited releases from domestic pipework connections is an additional risk factor for hydrogen delivery compared to natural gas, and this is not dependent on the presence or absence of a colourant.

1.6 Conclusions

The overall conclusion of this work is that a colourant is not required at all as it does not offer any additional benefit in relation to safety or network operations when compared to natural gas. Adding a colourant would incur additional costs, may have negative impacts on appliances and network operations, and may lead to potential health impacts.

More detail is given as follows:

1.6.1 The addition of a colourant into the network

- **High pressure flames** - High pressure hydrogen flames (typically > 2bar) can have increased luminosity if they entrain dust, solid particles or humidified air. This tends to result in an orange flicker and glow.
- **Network Operations** - Network operators have highlighted that addition of any colourant material to the hydrogen gas could result in network operational issues and could impact on some end users, in particular fuel cell users, which are not covered within the scope of this work. These effects may include drop-out of liquid or solid, material integrity impacts and may possibly lead to detrimental effects on flow measurement, pressure control and other network operations.
- **Risk vs. benefit** - The technical and logistic problems with introducing a colourant into a network may introduce additional risk without significant benefit. Here, the nature of the colourant was considered with solids eliminated and water too from the viewpoint of network integrity. Volatile liquids could be added but the quantities required could result in liquid collection in the pipelines.

Our conclusion is that a colourant should not be added into the network:

  - High pressure flames from ignited releases from the pipeline network (> 2bar) will be visible due to the entrainment of dust or other material so a colourant is not required.
  - Network operators do not want to add colorant due to increased operational activities, potential increased risk to operatives working on the network and potential reduced performance on network equipment.
  - Adding colourant could add risk due to the additional process plant required, handling or processing of colourant to add, and potential failure modes of any colourant injection equipment.

1.6.2 The addition of a colourant into internal pipework or at the appliance

- **Flame visibility -** The ability of the eye to detect low luminosity hydrogen flames is influenced by the background surrounding to a far greater extent than for natural gas. Natural gas flames and burners can be surrounded by stainless steel, white enamel painted surfaces or other coloured material and are nearly always visible even if the burner is operating at a low (turn-down) rate.

  This is not the case for hydrogen in that white or light coloured backgrounds can render the flames nearly invisible. Even against black backgrounds it is sometimes difficult to distinguish hydrogen flames, especially if there is a bright, surrounding light level.

  Where the flame is in an area which can be seen, there is therefore an increased risk when using hydrogen. However, where a flame is produced behind a kitchen cabinet or in a void where it cannot easily be seen, adding a colourant will not decrease the risk.

- **Supply pressure** - Flame visibility is also dependent on the supply pressure. A higher supply pressure produced a larger flame, and this increased flame "volume" assisted with visual detection. Although the guidance from the Hy4Heat team is that the preferred network and delivery pressures for hydrogen will be similar to those for the natural gas system, the lower calorific value of hydrogen may necessitate a slightly higher supply pressure. Slight increases on pressure will not significantly impact the flame luminosity

- **Coloured flame desirability** - If a colourant is required or desired for the indication of a flame at a cooker or decorative fire then there is a wide range of materials for the appliance manufacturers to choose from (from a practicality, ease of delivery and user operability perspective, an aqueous salt solution may be a suitable candidate).

  Thermochromic materials can also be used for thermal detection of flames. These materials contain a pigment which when exposed to heat, will cause a colour change on the surface of the material. This option could provide manufacturers with a desired flame colour for fires and cookers.

- **Appliance risks** - Alongside the practicality of adding colourant at the appliance, we have also considered the main risks (deposition on metal surfaces, enhanced corrosion rates and potential production of particulates in the combustion products).

- **Flame detection** - Thermal flame detectors can be used to detect a hydrogen flame but must be placed directly above the site of the flame. However, if a leak occurs, a flame can develop in a different position which is not detected by the instrument. This is an increased risk which must be considered fully by the appliance manufacturers.

  UV and IR radiation detectors can also be used as alternative methods of flame detection. Since hydrogen flames emit UV radiation, photo-electrons are emitted which create an electrical impulse.

Infrared detectors use IR sensor filters to enable visualisation of the flame but need to be designed to detect the low levels of infrared emitted. As for thermal flame detectors, this is an increased risk which must be considered fully by the appliance manufacturers.

Our conclusion is that a colourant should not be added into the internal pipework or at the appliance:

- A colourant cannot help to detect a flame that cannot be seen (i.e. produced behind a kitchen cabinet or in a void).
- A colourant may impact on the performance and safety of an end-use appliance.
- A colourant may impact on the potential use of the hydrogen in fuel cell systems.
- A colourant will only be required for decorative fires and cookers (not for boilers). Where a coloured flame is desired, this can easily be provided by the manufacturer through use of additives or inserts.
- Flames detection methods are readily available to appliance manufacturers to detect hydrogen flames, and UV sensors may provide the most appropriate approach.

Addition of colourant into the domestic pipework does not appear to produce a reduction in risk for unignited or ignited releases. Any addition of colourant has the potential to add additional risk factors including material handling problems and failures in the addition process.

As colourant may be required only for exposed flame burners (cookers, hobs or fires) it is proposed that methods to add colour at the point of use are considered to be the best option.

1.6.3 Alternative methods to create a coloured flame or provide a flame indication at the appliance should be considered where desirable

Where a coloured flame is desirable at the end use appliance (for a fire or cooker), there are a number of ways this can be achieved safely, and these are being investigated by appliance manufacturers

- Use of temperature sensors and indicators, possibly LED systems, especially for cooker hobs as there are parallels with current hot surface indication for ceramic/electric hobs.
- Consideration of a coating on decorative coals for use in fires. This could take up some of the information on flame colouration using metal salts, recognising that the flue products will be discharged external to the home.
- Consideration of flame inserts that could radiate when hot or provide additional flame colour.

1.6.4 Additional risks have been identified through leakage testing

- **Ease of ignition** - A key finding from the leakage test work undertaken was the ease of ignition of small hydrogen leaks from holes in domestic copper gas supply pipework. Pin holes in the pipe give rise to gas leakage and hydrogen can be ignited easily to form a flame that attaches to the pipe at the point of release whereas natural gas did not form a stable flame. Also, hydrogen could be ignited at a significant distance from the pin hole.

  These different characteristics of hydrogen and natural gas highlight that further comparative studies are required to evaluate the potential change to the evaluation of risk.

  This will also need to consider the impact on the frequency or probability of a leak resulting in an ignition which could then give rise to a secondary fire, if the flame impinges on a combustible surface.

- **Ignition distances** - Ignition of the flames could occur at a significant distance from the hole, dependent on the pressure and the hole diameter. For example, for a 1 mm hole diameter with a hydrogen supply pressure of 20 mbar, a flame can be established with a spark ignition from a piezo igniter held at around 12 cm above the pipe.

  This example highlights that a risk evaluation is required to understand the probability that a hydrogen leak could develop into a flame and cause a secondary fire if it impacts on combustible material. This phenomenon is not observed for natural gas flames which would not ignite or produce a stable flame. The lack of ignition will also allow the build-up of hydrogen in poorly ventilated spaces and this could be included in further studies to support the QRA.

- **Flame retention** - Leakage testing from holes in the copper pipework all produced stable hydrogen flames when the leak was ignited and these flames were attached to the pipe at the leak point. This was not the case for methane flames. So for both hydrogen and methane leaks there is the possibility that the leak into a poorly ventilated space could build-up and lead to additional risk. If an ignition source s present, then this could give rise to an ignited release for hydrogen but not for methane. The ignited release could then lead to a secondary fire if the flame impinges on neighbouring combustible material. The relative risks of a hydrogen leak producing a hydrogen flame vs. a methane leak not producing a flame needs to be considered. And should be included in the Hy4Heat QRA.

- The unsoldered joint leak test demonstrated that both hydrogen and natural gas can be ignited and retained around a badly assembled joint. The natural gas leak produced a visible yellow flame around the joint whereas the hydrogen flame was not very luminous.

Our conclusion is that there are additional risks that need to be further investigated:

  - Hydrogen can be ignited more easily than natural gas to form a flame. Further comparative studies should be undertaken to evaluate the potential change to the evaluation of risk.
  - Ignition of a hydrogen flame could occur at a significant distance from the point of leakage. A risk evaluation is required to understand the probability that a hydrogen leak could develop into a flame and cause a secondary fire if it impacts on combustible material
  - Hydrogen forms a stable flame that attaches to the pipe at the point of release whereas natural gas does not form a stable flame. The relative risks of a hydrogen leak producing a hydrogen flame vs. a methane leak not producing a flame needs to be investigated.

1.7 Recommendations

In order to mitigate the risks and hazards identified in this report, the following recommendations are made:

- **An extended study on ignition of leaks from different hole sizes and their potential to establish hydrogen flames should be undertaken (and be aligned with other work underway from the Hy4Heat programme to establish the range of possible leak types)**, to include:
  - Other pipework types and failures (including connection hoses to cookers).
  - Extracts from installed domestic copper carcass to extend the study from idealised holes to ones that may be present in the wider population.

- **Combined studies on leak rate, ignition and gas tightness testing should be carried out** to increase the level of understanding on existing approaches for leak detection. In particular with establishing a maximum permissible leak rate (MPLR) for hydrogen in the same manner as that for natural gas. (This will combine aspects from Hy4Heat Work Packages 2 and 7 and support the development of the Quantitative Risk Assessments (QRAs)).
- **The impact of ignition energy and ignition location on the potential to form a stable hydrogen flame on leaks from domestic pipework should be quantified**
    - Extend the current work to provide supporting information on flame development as a function of distance from the leak point and the ignition energy. (Again, with the aim of providing data for the QRAs.)
    - To increase the level of knowledge and understanding, further work on the ignition and flame stabilisation processes is required, focusing on minimum ignition energy linked to distance from the point of release.
- **Further studies are required to investigate if degradation of the copper surface affects the overall integrity of the pipework infrastructure.** There is clear heat impact to the pipes near the holes as a consequence of the heat from the flames. As the hydrogen flames seem to “attach” to the pipe surface, there is darkening and oxidation caused by the elevated surface temperatures.
- **Additional work should be undertaken to investigate techniques to reduce NOx** (and provide flame colourisation) through the addition of water (addition of water prior to combustion, humidification, or transducer mist introduction).
    - An advantage of this approach is that as NOx is dependent on flame temperature, by adding water the temperature will decrease and hence the amount of NOx produced should reduce.
    - The presence of hydroxyl radicals in hydrogen flames can also lead to increased luminosity. The addition of water into the combustible mixture has been suggested as a means of providing colour to a hydrogen flame [17]. This adds more OH and H radicals into the system which will react further and increase the emission intensity.
- **The differences in flame characteristics should be explicitly explained during training of GDNO staff and other people potentially coming into contact with hydrogen leaks/fires** (First Call Operatives, Fire Brigade employees, Police, Paramedics and other support services). As has been shown through the experimental work undertaken in this study and the supporting research literature, the visibility of hydrogen flames will often be lower than that of hydrocarbon flames. In particular, such training should include witnessing both small and fairly large hydrogen fires; it is an area where (by the nature of colour images) only sight and sound of a real flame is likely to be remembered and retained.

2 INTRODUCTION

Hydrogen is considered as one of the potential future options to support the UK Government's approach to decarbonisation of energy use. As domestic heat provision is a significant contributor to the UK's overall carbon dioxide emissions, it is timely to evaluate the options for this sector.

The Hy4Heat programme is extending the current knowledge base to understand the practicality and costs for utilisation of hydrogen for domestic applications focusing on space heating (central heating and fires) and cooking. The programme is divided into several sub-parts and the requirement of Work Package 2 is to develop and document evidence on hydrogen purity and colourant that will enable the subsequent Work Packages to use this to assist with domestic appliance development.

There are many areas where hydrogen can be used as a fuel which includes the automotive market using hydrogen fuel cells, electricity generation and household appliances such as boilers, but the focus of this study is the utilisation in traditional domestic appliances using established burner technology.

This report considers the characteristics of hydrogen combustion and highlights the potential requirement for a colourant to be added as hydrogen flames have low levels of light emission (luminescence). The location of the colourant addition is considered focusing on a centralised large scale addition to the network, or targeted addition in appliances where a visible flame is needed. Different colourant options are discussed, and future work highlighted to evaluate best technical options and also high level cost implications.

2.1 Hydrogen Combustion Characteristics

Hydrogen is one of the simplest gaseous fuels, and it has been the focus of many studies. It is an extremely useful reference fuel and one that is used in many University research applications.

The combustion characteristics are significantly different from those of natural gas and some of these are highlighted in Table 2 below.

Characteristic	Units	Hydrogen	Methane
Gross Calorific Value	MJ/m^3	12.10	37.78
Gross Calorific Value	MJ/kg	141.95	55.57
Flammability range (LFL – UFL)	Vol%	4 – 75.6	5 - 15
Stoichiometric fuel % in air	Vol%	29.5	9.5
Minimum spark ignition energy (in air)	mJ	0.02	0.29
Maximum Adiabatic Flame Temperature	K	2318	2148
Maximum Laminar Burning Velocity	m/s	3.1	0.4
Autoignition temperature	K	833	873

Table 2: Selected combustion characteristics of hydrogen (compared to methane)

As hydrogen has significantly higher burning velocity, wider flammability range and lower ignition energy, these characteristics impact on the overall options available for burner stabilised flames.

There are three broad classes of flame depending on the way that the fuel and air are combined. These are diffusion (non-aerated), partially-premixed (like a Bunsen burner) or fully premixed (like those used in modern domestic boilers). These are shown pictorially in Figure 3.

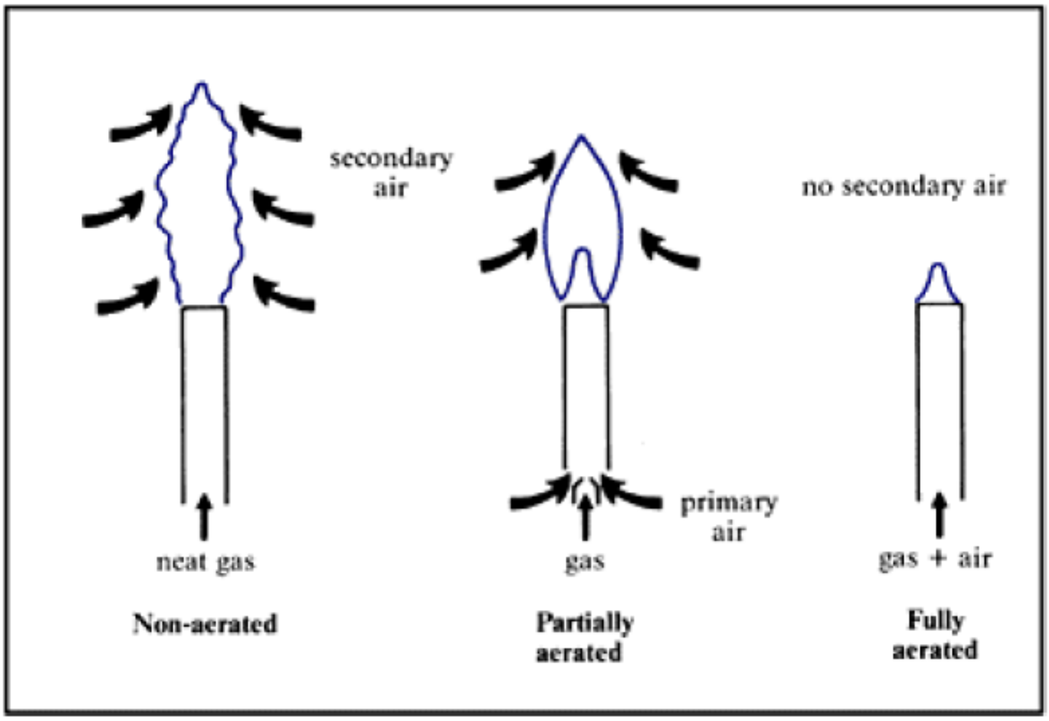


Figure 3: Representation of different flame type [1]

As well as the overall flame stability, the different flame types give rise to different flame colours. For natural gas, non-aerated flames are yellow, partially premixed flames have a light blue inner cone and a darker blue outer cone, and fully premixed flames have a concentrated light blue appearance.

2.2 Existing Hydrogen Flames and Burners

Although hydrogen is a key component of Towns Gas and many burners are available for a wide range of domestic appliances for this fuel, there are fewer burners developed for pure hydrogen. In the main this is due to the fact that hydrogen was not historically thought of as a bulk fuel for widespread utilisation, but also as a consequence of the different combustion characteristics listed above.

There are few commercially available burners for domestic appliances that are capable of using hydrogen.

Hydrogen burners and flames are available for selected applications including Flame Ionisation Detectors (FIDs) and flame photometric detectors for gas chromatographs, FIDs for selected gas detection equipment, and small burners for bespoke applications such as brazing, soldering and jewellery work (see Figure 4 for example) [2]

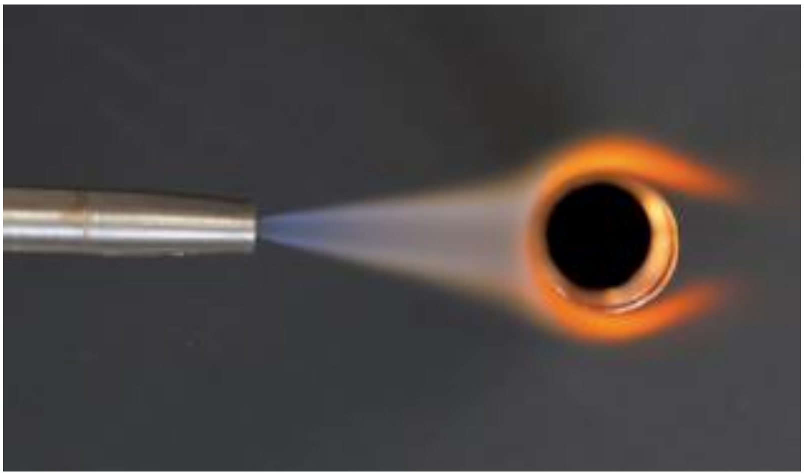


Figure 4: “Safeflame” hydrogen torch. [3]

Global industry is estimated to use about 50 - 60 million tonnes of hydrogen per year as a chemical feedstock. Ineos uses the hydrogen by-product from chlor-alkali production as a support fuel to natural gas for its gas boilers. The Sabic ethylene plant on Teesside uses hydrogen and hydrogen mixtures generated as a by-product of ethane cracking to fuel the burners on cracker furnaces. [4]

Several industrial burner manufacturers have products that can use hydrogen as fuel gas, and Toyota has announced that it plans to replace 1,000 natural gas burners with hydrogen across its production plant in Japan. The burner designs are different to conventional industrial burners, with the aim being to develop a flexible burner with low NOx emission rates. The controlled mixing of the hydrogen and oxygen enables the flame temperature to be lower with concomitant reduction of NOx emissions as shown in Figure 5 below.

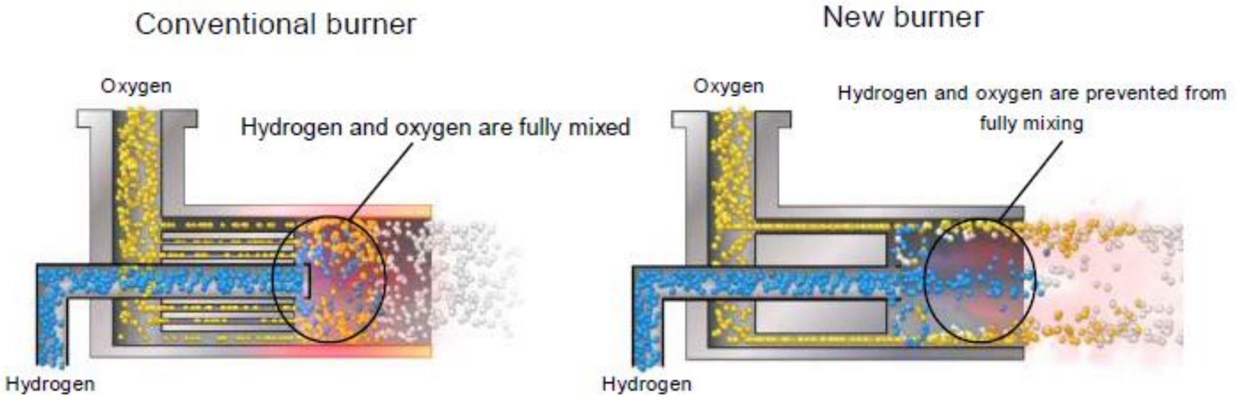


Figure 5: Schematic of Toyota burner concept. [5]

2.3 Light Emission from Hydrogen Flames

Several reports have commented on the low light emission levels from hydrogen flames. This is dependent on the flame size and application, but for small domestic scale burners hydrogen flames are almost completely invisible to the human eye compared to natural gas flames.

Ding et al [6] have recently published an analysis of the light emission from a domestic natural gas burner from a typical gas boiler. There are several spectral features, and these are shown in Figure 6 below.

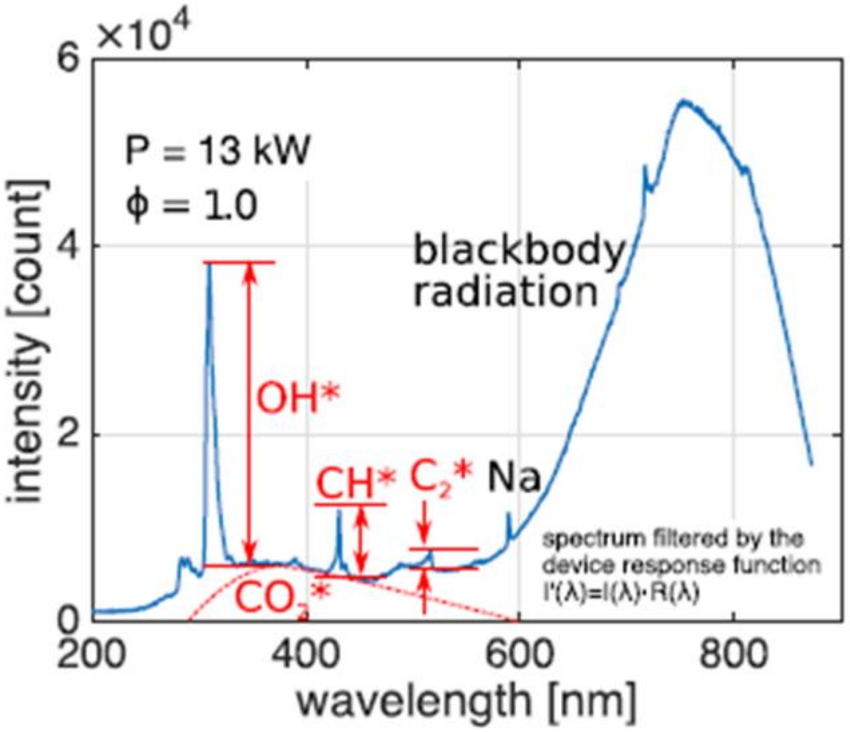


Figure 6: Light emission spectrum from a natural gas fuelled premixed gas burner. [7]

The light emission shows distinct bands from excited radical and molecular species, and then a continuous black-body radiation from the hot burner surface. The variation of the emission across the spectral range manifests as a change in flame/burner colour. The burner appears orange/red from the black body radiation and the flames are blue from the electronically excited CH and C_2 radicals together with emission from OH radicals (although this emission is primarily in the UV region).

The emission spectrum from the natural gas flame can be compared with one from a study on hydrogen flames [8] shown in Figure 7. The absence of carbon-based fragments means that there are no strong blue light emitters (400 – 500 nm) and the visible spectrum from a hydrogen flame is one of a faint blue continuum together with red light emission from water in the flame (around 700 nm).

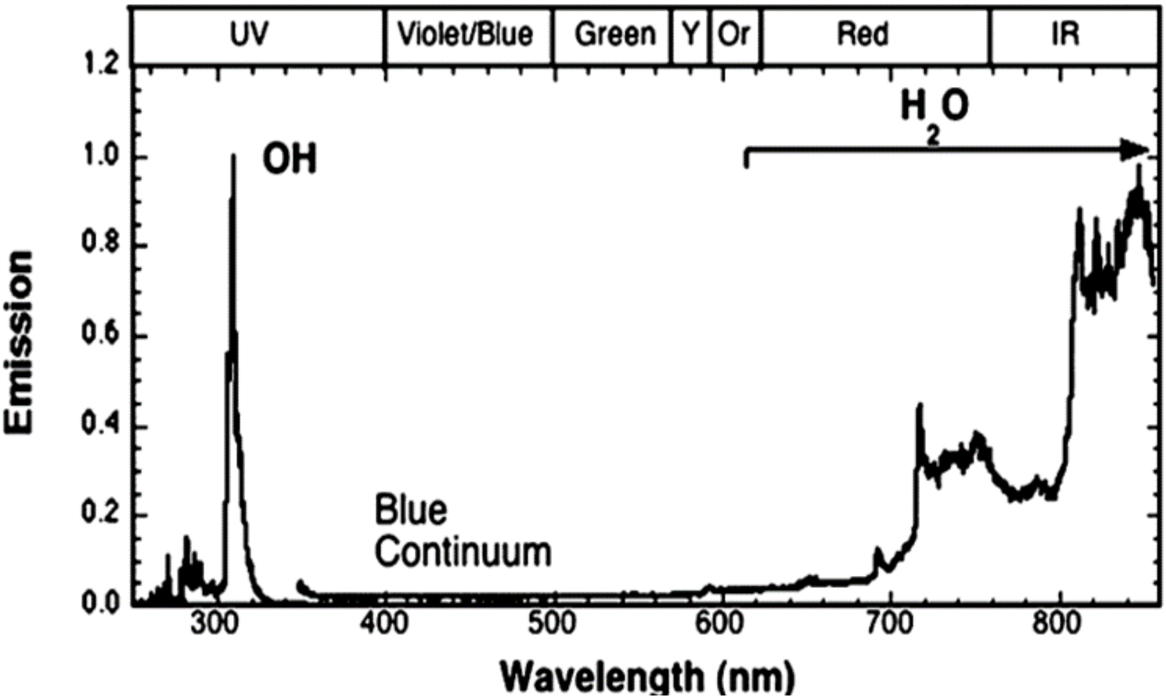


Figure 7: Light emission spectrum from a hydrogen flame. [8]

The faint blue and red emission from a hydrogen flame is shown in Figure 8.

Figure 8: Photograph of light emission from a hydrogen flame. [8]

2.4 The Challenges for Hydrogen Burners for Domestic Appliances

Hydrogen burners for domestic appliances (and the resulting hydrogen flames) can be broadly categorised into two types:

- Ones that traditionally need to be visible (cookers and fires)
- Ones that may not need to be visible (e.g. Boilers with no viewing port)

The visible flame requirement relates to either safety or aesthetics and is primarily a requirement for gas cooker hobs and gas fires. Modern condensing gas boilers do not require a visible flame and in many instances there is no optical access to the combustion chamber.

If there is a requirement for a visible flame then a suitable colourant may be needed to provide an indication of the efficacy of the burner operation particularly with regard to:

- **Stability -** A visible indication of **flame movement** or **flame loss** on gas cooker ports can provide the user of an indication of burner performance
- **Turn-down -** Many users use the visible appearance of a flame to gauge turn-down and input settings for both gas cooker hobs and gas fires
- "**Look and feel**" to give the same appearance and operation as natural gas burners. For hydrogen burners to have a similar outward appearance to natural gas burners it is important to consider flame colour.

The low luminosity (chemiluminescence) of hydrogen flames is independent of the type of combustion, and so applies to both premixed, partially premixed and diffusion flames

As hydrogen flames burn colourlessly, it has become more of a safety aspect with regards to household appliances such as cookers and fires, to find methods of highlighting and identifying the extent of hydrogen flames easily. Colourant additives will provide a direct link with the high temperature flame envelope, but other alternative methods could be considered including:

- **Hot surface indication -** Here a simple LED indication may be practical as an indicator of a hot surface in a similar manner to current ceramic hobs
- **Thermochromic materials -** Paints or coatings could be used to provide an indication of a hot surface although they may not be able to be placed directly in the path of the hydrogen flames.

  A US Patent exists for thermochromic cookware (ref: US 20060O81639A1) which states that the invention will provide "*a visual indication to a user to suggest if a surface of the cookware is at an elevated temperature above room temperature.*"

  A European patent (EP3189117A1), explores a similar approach with an artefact including "*a cookware item coated with the thermally colour-changeable ceramic coating composition, and to the use of the thermally colour-changeable ceramic coating composition for coating an artefact, in particular a cookware item*."

  Also, researchers from the University of Toulouse have investigated "visible thermochromism in vanadium pentoxide coatings".
- **Thermal detection -** An approach could be adopted whereby a surface thermocouple could be included in the design to provide a signal for a display to indicate the presence of a hot surface.

- **UV or IR detection -** Hydrogen flames are known to emit both UV and IR frequencies (see the spectrum in figure 7). If low cost sensors are available, then they may be able to be accommodated into an appliance design to provide an indication of the presence of flame or heat.
- **Flame inserts to indicate the presence of a flame -** Injector ports in the burner or metal bars around the burner could be positioned to be in the flame and glow if the flame is present

It may also be possible to re-engineer the burner designs to eliminate the need for an open visible flame.

Significant R&D is required to evaluate all options and determine the key aspects for hydrogen use in domestic appliances, including new burner designs and the use of indicators to show the presence of a flame.

Research by Almaas Technologies [9] on a modified standard atmospheric cooker hob burner (with the primary air ports blocked off) results in a flame picture akin to that for a hydrogen diffusion flame as shown in Figure 9 below.

Figure 9: Hydrogen flame on a modified cooker hob burner

An alternative indication of the presence of a flame could be through the use of a metal gauze approach as shown in Figure 10.

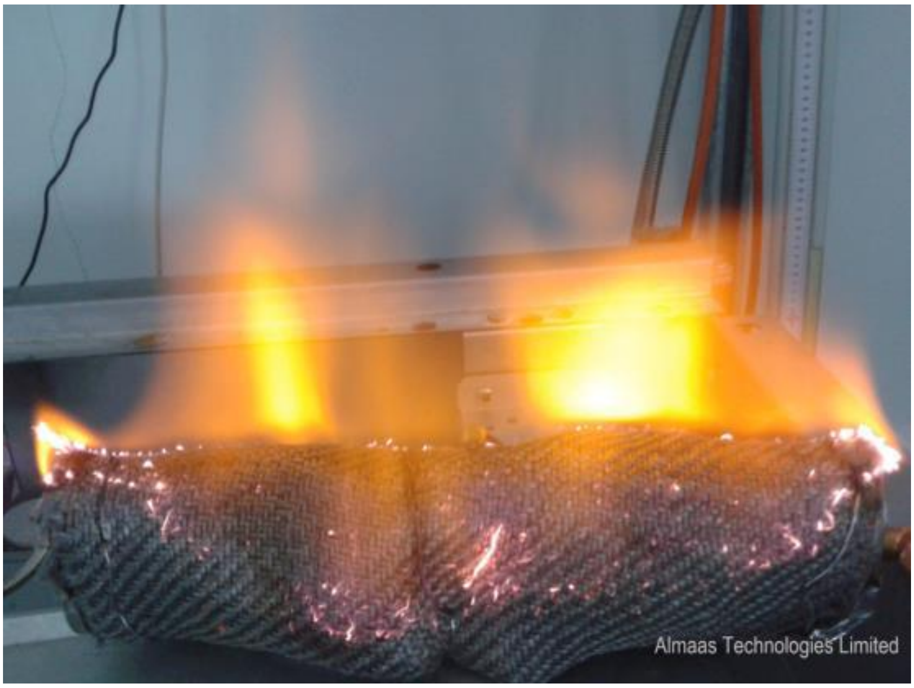


Figure 10: Modified cooker hob burner: hydrogen cooker hob wrapped in metal fibre blanket

3 STAKEHOLDER VIEW

A stakeholder questionnaire was developed and circulated widely through the Hot Water and Heating Industry Council (HHIC) to reach a wide audience of domestic appliance suppliers, Certification and Testing organisations and technical consultancies. Many of these stakeholders will not have witnessed hydrogen combustions before and so many of the views are most likely based on anecdotal information.

In outline this questionnaire has tried to gauge the wider industry awareness of hydrogen as a potential fuel and to encourage feedback and comment on the practical aspects of colourant addition.

The questionnaire output can be summarised by four questions:

- Is a colourant required?
- What form should the colourant be in?
- Where should the colourant be added?
- Who should maintain the colourant addition process?

Figure 11 shows pie charts detailing the collective responses to the questions.

From the responses provided nearly 50% of respondents believe that a colourant is required, but nearly 60% don’t know what form the colourant should be in (gas, liquid or solid). A gaseous colourant was the physical form with the highest response although this could be achieved by addition of a volatile liquid.

Approximately 60% of the replies believed that addition of the colourant into the pipeline was the best approach, although several highlighted that not all appliances need to have a visible flame.

Just over 50% of the responses thought that the homeowner should be able to maintain the colourant addition but in others there was a strongly held view that this should be undertaken by a qualified engineer.

The results demonstrate a wide spread of views and it was clear from the replies that more knowledge is required on the options for colourants before an optimum method can be selected.

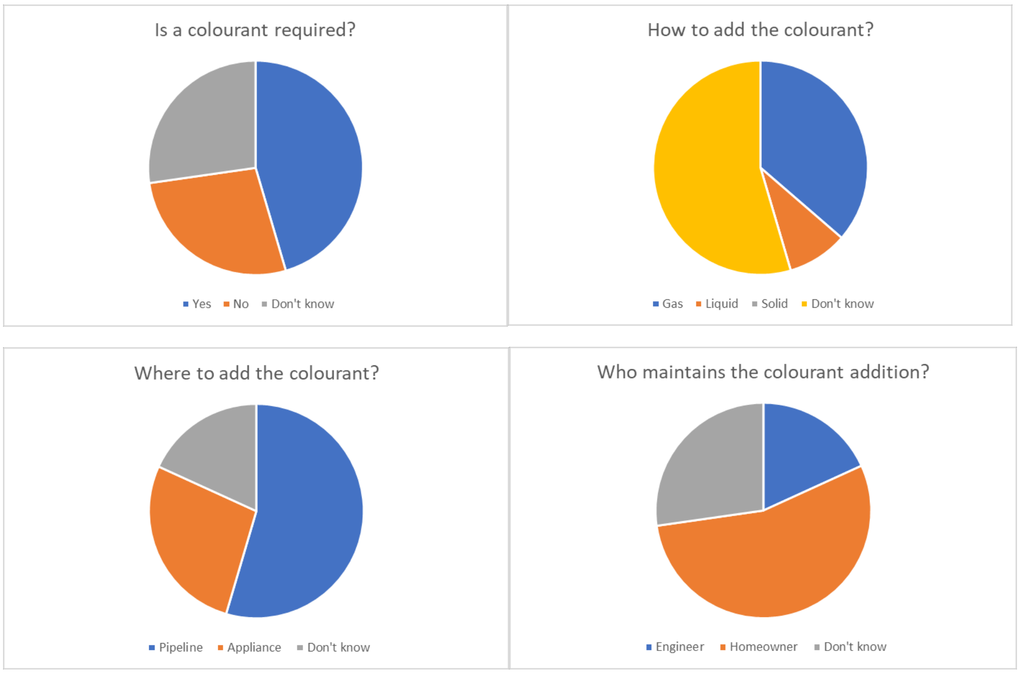


Figure 11: Summary of questionnaire responses

The questionnaire responses came from boiler manufacturers, burner design/development engineering companies, GDNOs, fuel cell equipment development companies and appliance/combustion consultants.

3.1 Consultation with appliance manufacturers

The Hy4Heat programme is focusing on domestic heating and cooking, and the aim is to evaluate options for appliances that could be considered as a like-for-like replacement of a natural gas appliance with a hydrogen-fuelled one.

Here, additional data from the stakeholder engagement questionnaire has been used to gauge the appliance manufacturers view with regard to the colourant. The Heating and Hot water Industry Council (HHIC) has kindly co-ordinated the contact with appliance manufacturers.

Condensing boiler manufacturers do not require the hydrogen fuel to contain a colourant as in many cases a visible flame is not needed or indeed there is no viewing port for flame observation at all. Flame detection by ionisation or temperature could be used for safety, in a similar manner to the current Flame Supervision Device (FSD) or Flame Failure Device (FFD), although it is known that hydrogen flames have low levels of ionisation and this will need to be considered by appliance manufacturers. The comments raised in the consultation focused on understanding the nature of the colourant and if it would it be beneficial or detrimental to the performance of the appliance (see Section 6.2: Risks to appliance performance).

The main views from domestic cooker and fire manufacturers is that some colourant system will be required if the design of the appliance remains similar to the current ones for natural gas.

4 COLOURANT TYPES / ADDITIVES

The physical nature of any colourant will be dependent on the point of introduction, and this dependency is highlighted in the responses shown in Figure 11

Injection of colourant into a pipeline network must be as a gas or volatile liquid, and addition of liquids or solids would impair the operation of the network and also not be consistent with a purity standard that limits the presence of liquid and solid "contaminants". Solid and liquid colourant components in a network could be removed by filtration and so is at odds with the aim of adding colourant.

If the colourant is added at the point of use in the appliances then a wider range of options is possible, and they could be solids, liquids or gases. From a practicality viewpoint, it is likely that colourant added at appliances would be liquid or solid, as gas addition may be harder to control.

The concept of enhancing flame colour has been used for many years in the analytical chemistry method, flame photometry. In this technique metal ions are entrained within the flame and they form electronically-excited ions. These emit light as they revert to the ground state and the wavelength of light (or the colour) is an indication of the metal present. Relatively low concentration levels of metal ions can give rise to highly luminous flames.

Using colourant additives involves introducing more compounds into the combustible mixture to produce an emission of visible light. However, with the addition of these compounds, it must be ensured that they will not react in a way as to produce toxic by-products. Safety is a key factor both from contact with unreacted colourant and also with the products formed by reaction of the colourant in the high temperature flame environment.

This review considers a wide range of colourant options based on literature and historical information in section 4.1, and then considers toxicity of substances in section 4.2 before conclusions are drawn around the most likely candidates for colourant additives.

Many different compounds have been used to cause chemiluminescence with hydrogen flames. The first accounts of monitoring hydrogen flame colours was conducted by W.F Barrett [14] where multiple compounds of solid, liquid and gaseous states were tested. Gaydon [15], has also reported interaction of other compounds and noted their corresponding wavelength and spectrum colours. Nichols and Wilber [16], analysed the luminescence effects of different metal oxides and sulphides on the hydrogen flame. It was found that metal compounds can produce a range of visible spectrum depending on the operating temperature. Additionally, some substances were found to have no effect on the hydrogen flame and were deemed inert [16].

Additive Substance	**Colour of Hydrogen Flame**
Sulphur/sulphates (solid)	Blue
Phosphorous (solid)	Green
Tin (solid)	Scarlet
Sulphuric acid (liquid)	Deeper Blue
Hydrochloric Acid	Reddish-Brown
Ammonia (gas)	Yellow

Carbonic Acid	Pale Lilac

Table 3: - List of Additives tested by W.F. Barrett [14]

Additive Substance	Colour of Hydrogen Flame
Bismuth	Violet
Manganese	Golden Yellow
Lead	Blue
Antimony	Bright Blue
Praseodymium	Pink
Copper	Green
Nitrogen	Green

Table 4: List of additives evaluated by Gaydon [15]

Table 3 and Table 4 show the results of the aforementioned authors. Some of the tables indicate some contradictory data such as those corresponding to Antimony Table 3 (Bright Blue Flame) and Table 4 (Inert). Taking this example, the colour reported for Antimony in Table 3 could be solely due to the hydrogen flame and the hydroxyl radicals present during the reaction, which will be discussed below.

Additive Substance	Colour of Hydrogen Flame	Temperature (°C)	Inert Additives (Oxides)
Calcium Oxide	Strong Yellow	670 – 725	Copper
Calcium Oxide with Bismuth salt	Blue/Green		Lead
Zirconium Oxide	Deep Red	440 – 720	Nickel
	Blue-Green	76 – 372	Manganese
Silicon Oxide	Pale green-White	85 – 367	Cobalt
Aluminium Oxide	Pale Green	52 – 692	Cadmium
Magnesium Carbonate	White	76 – 670	Tungsten
	Blue/Violet	–	Bismuth
Zinc Oxide	Red	568- 700	Antimony
	Blue-Green	700 - 968	Barium
Zinc Sulphide	Yellow – Green	560- 616	Strontium

Additive Substance	Colour of Hydrogen Flame	Temperature (ºC)	Inert Additives (Oxides)
Calcium Sulphide	Blue/Green	60 – 330	Erbium
	Yellow	330 – 737	Cerium
Fluorite	Pale green – White	58 - 310	Lanthanum
Aluminium Oxide (in form of ruby, sapphire etc)	Pale green	52 - 692	Thorium

Table 5: Metal oxides and sulphides tested by Nichols and Wilber [16]

As noted above the presence of hydroxyl radicals in hydrogen flames can lead to increased luminosity. As a result, addition of water has been suggested as a means of providing colour to a hydrogen flame [17]. By adding water into the combustible mixture, more OH and H radicals are essentially being added into the system which will react further and increase the emission intensity. There are advantages and disadvantages for the addition of water. Since NOx is dependent on flame temperature, by adding water the temperature will decrease and hence the amount of NOx produced should reduce.

However, the flame is also susceptible to being quenched and extinguished by using water. The authors of a patent for apparatus to enhance visibility of a hydrogen flame [18] have suggested that hydrogen fuel should be humidified. Described below are methods that have been proposed to do this:

- Addition of water to hydrogen gas before or at point of combustion
- Humidification by introduction of water vapour
- Transducer to add fine water droplets/mist to the mixture upstream or at point of combustion
- Passing of hydrogen through water bath

Water addition at the point of use in the burner does show some promise and is an aspect that should be considered further by other Work Streams in the Hy4Heat programme.

4.1 Flame colourant compound options

To establish the range of options available for colourants, a structured approach was taken to;

- Firstly, provide a selection of best forms, gas, liquid or solid
- Consider the impacts on the flame stability
- and consider the potential by-products formed from the combustion of the colourant material.

This builds on the information presented in Table 5, relating to flame colour options and identifies named compounds to consider from a health and exposure viewpoint.

The modes of exposure will be dependent on how and where the colourant is added, and these are considered in section 5.2: Colourant added at the appliance. The actual requirement for a colourant is dependent on the appliance type and it has been proposed that it is only needed for cookers and decorative fires, and even in these appliances there may be other options rather than introduce a colourant chemical into the appliances to impact on the appliance design and operability.

The rationale for the selection of colourants is set out in Table 6.

Colourant options	**Comment**	**Colour**	**Combustion products**
Gases			
Carbon dioxide (CO_2)	CO_2 may impart some flame colour (see spectrum in Figure 7). It will impact on flame stability and has a significant impact on Wobbe Index so needs further work to establish if this is possible.	Light blue	N/A (or possibly trace CO)
Methane (or propane)	Addition of methane (or propane) will add hydrocarbon radicals to the flame and this could result in a similar flame colour to natural gas (although slightly weaker)	Light blue	CO_2 and CO
Nitrous oxide	Several studies on hydrogen – nitrous oxide flames have been published and can enhance luminosity. This needs to be confirmed for small N_2O addition but could be considered.	Yellow/green	NO, NO_2
Liquids			
Water / steam	Hydrogen (or the combustion air, or both) could be humidified prior to combustion	Light red/orange	N/A
Ammonia	Probably introduce as a solution	Pale-grey/blue - or possibly orange at higher concentrations	NO, NO_2
Ethanol or methanol	A carbon source but a low cost, easily handled liquid. Vapour could be entrained, and colour obtained in the flame.	Light blue	CO_2 and CO
Propanone or butanone	A carbon source but a low cost, easily handled liquid. Vapour could be entrained and colour obtained in the flame.	Light blue	CO_2 and CO

Colourant options	**Comment**	**Colour**	**Combustion products**
Chloroalkanes Tetrachloromethane Trichloromethane	Easy to handle but possibly not a good option - linked to several health and air quality effects	-	Potential to form phosgene
Triflurobromomethane CF_3Br	Fire retardant so could impact on the flame stability – there is uncertainty regarding the potential to form a hydrogen flame	-	-
Ferrocene $Fe(C_5H_5)_2$	Known fluorescent agent but could be expensive	Red / orange-	FeO, CO, CO_2
Butyrylferrocene $C_5H_5FeC_5H_4COC_3H_7$	Known fluorescent agent but could be expensive	Red / orange-	FeO, CO, CO_2
$Cr(CO)_6$	Used as a flame inhibitor in some academic research and they noted flame colour	Yellow/green	CrO
$Mo(CO)_6$	Used as a flame inhibitor in some academic research and they noted flame colour	-	-
Ammonium heptamolybdate	Used as a flame inhibitor in some academic research and they noted flame colour	Orange/red	-
Solids (or solutions)			
Potassium Chloride	-	Pink/red	Oxide
Rubidium Chloride	-	Red/violet	Oxide
Sodium Chloride	-	Orange	Na_2O / $NaOH$
Calcium Nitrate	-	Orange?	CaO
Boranes (Decaborane)	-	Light green	-
Borax	Boric acid or similar	Blue/Green	-
Barium Chloride	-	Green/yellow	BaO (or the hydroxide)
Lithium Chloride	-	Red	Li_2O (or the hydroxide)

Colourant options	**Comment**	**Colour**	**Combustion products**
Strontium Nitrate	-	Red	SrO
Copper Sulfate	-	Green	CuO
Selenium Oxide	-	Green/blue	Oxide
Cerium Chloride	-	Yellow	Oxide
Bismuth Chloride	-	Pink/violet	Oxide

Table 6: The rationale for the selection of colourants

4.2 Avoidance of Hazards

The United Nations has developed the Globally Harmonised System of Classification and Labelling of Chemicals (GHS). The GHS is a single worldwide system for classifying and communicating the hazardous properties of industrial and consumer chemicals.

In the EU, GHS is implemented through the Classification, Labelling and Packaging Regulations (CLP). Annex VI of the regulations contains a list of 'harmonised substances'. These are substances for which a hazards classification has been agreed by independent experts at European level. Therefore, suppliers of these substances must use, at least, these classifications. However, companies may use a higher (more hazardous) classification if they consider it appropriate.

For non-harmonised substances, suppliers must self-classify them.

Manufacturers of all substances must submit the hazards classification to the European Chemicals Agency (ECHA).

In Appendix C, the tabulated hazard classification is set out for the compounds selected in Table 6. This summarises the classification that suppliers have submitted to ECHA in relation to acute toxicity.

The diagram shown in Figure 12 categorises the acute toxicity classification thresholds for each route of exposure (including three possible physical states for the inhalation route); the values were taken directly from the classification criteria in the GHS/CLP regulations.

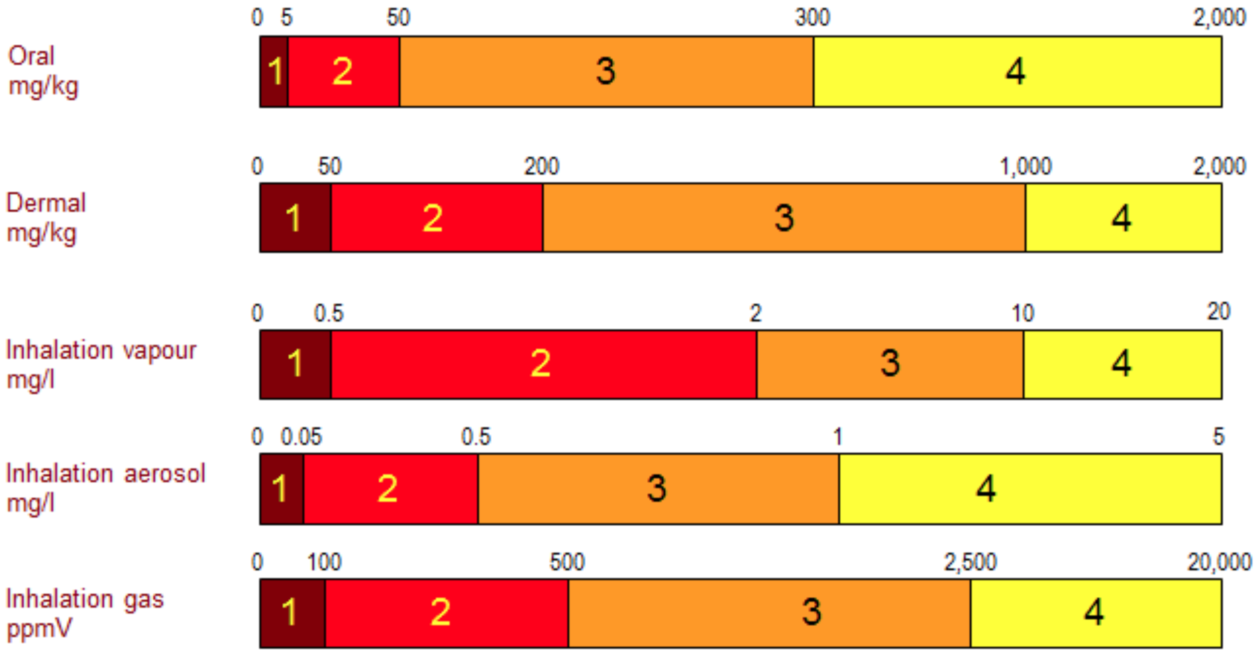


Figure 12: Acute toxicity classification thresholds and categories

In appendices D to H, tables are provided showing the toxicity data has been collected, together with supporting notes in Appendix I, and this information has been collated for the 31 compounds that were nominated from Table 6.

Each Appendix table contains information on the toxicity for each mode of exposure (oral, dermal or inhalation) and the colour coding takes account of all modes based on the categorization:

- Green - Non-hazardous
- Yellow - Toxic Category 4
- Orange - Toxic Category 3
- Red - Toxic Category 2
- Dark Red - Toxic Category 1

From the point of view of colourant selection, category 1 and 2 are automatically discounted from consideration. In addition, all materials falling within categories 3 and 4 would need a strong technical justification for use over non-hazardous alternatives.

This means that only “Non-hazardous” potential colourants are considered, and this study would suggest that the following colourant components are possible contenders:

- Methane, propane (or possibly another light hydrocarbon) - Hydrocarbon species (including the alkanes and ketones) will need to be present in reasonably high concentration to impart a blue colour,
- Carbon dioxide – As described above if it can produce a light blue colour.

This could be at odds with the overall aims of decarbonisation as it is adding carbon-containing species, and also may impact on the control of the fuel to the burner as it will affect the Wobbe Index.

- Nitrous oxide
- Water - Could be a simpler colourant option as humidification of the fuel (or the combustion air) may enable pink flames to be produced.
- Propanone / butanone
- Halocarbons (tetrachloromethane, trifluorobromomethane) - Halocarbons could be introduced but they could impact on flame stability as many are flame retardants, and the overall impact is not known. They could also form hazardous combustion products as noted in Table 6.
- Potassium / Sodium / Rubidium / Cerium / Bismuth chloride - Aqueous solutions containing these metal chlorides could be a better approach rather than using powders, as these could encourage particulate formation in the combustion products.
- Borax

Note: Whilst the above compounds are labelled as non-hazardous, in the event that they are considered as a viable option for hydrogen gas flame colourant, a much more detailed study would be required from a medical perspective, as some of them would not necessarily be desirable for use in the environments described with potential material risk in the long-term.

All of the above materials cover the three physical states, and the efficiency of the colourant options is influenced by their concentrations. If used as a colourant this will depend on the location and mode of colourant addition.

- Network addition may favour gas or volatile liquid injection and may preclude the use of water or powders as these could impact on network integrity. Similarly, colourant addition at appliances may favour water or aqueous solutions of metal chlorides as these are more easily handled than gaseous or organic compounds.

This appears to produce a dividing line between the colourant types and their point of introduction. Added to this is the stakeholder feedback which tends to support the view that colourants should be avoided if safe to do so. These aspects are considered further in Section 6: Risks and hazards of using hydrogen.

5 COLOURANT ADDITION

The overall consideration of the colourant addition requirement for hydrogen has focused on three aspects and these are highlighted in Figure 13 below.

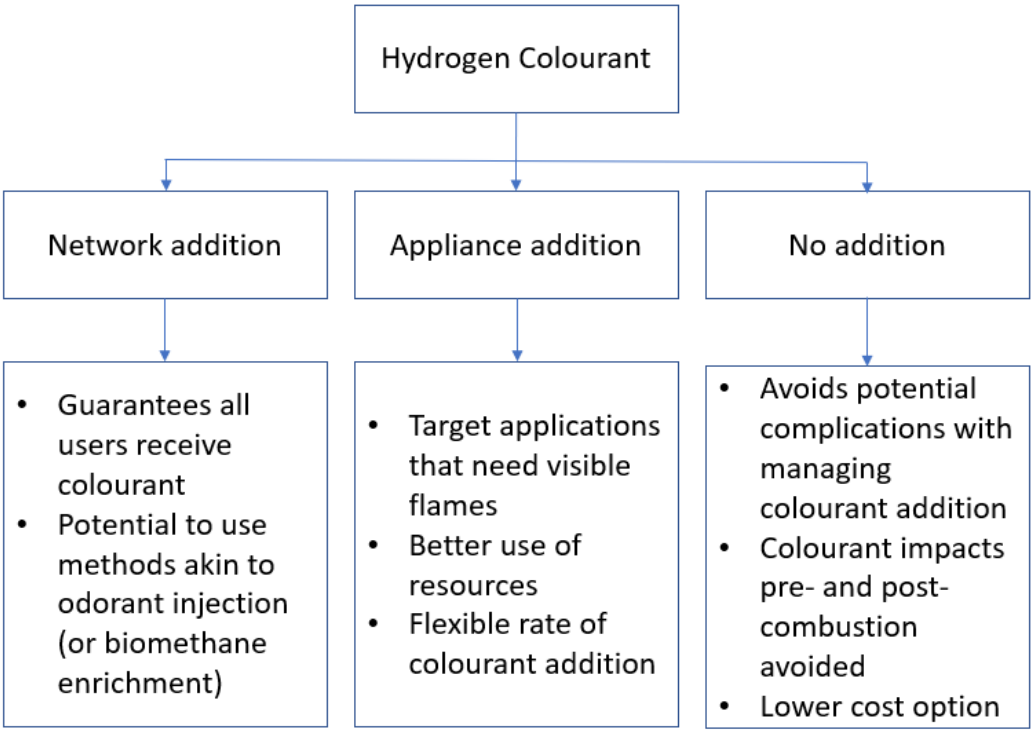


Figure 13: Colourant addition options

5.1 Colourant added into the Network

If the colourant is added into the network, in a centralised manner, then this ensures that all users will receive hydrogen that will produce a coloured flame. Addition of the colourant would need to comply with the pipeline purity specification and be compatible with a gaseous hydrogen flow but in outline this approach could be similar to the propane enrichment of biomethane or the injection of odorant.

Although this would guarantee that the colourant is present for all users, there are implications for end users that don’t require a colourant e.g. fuel cell applications, meaning additional clean-up or filtration processes might be needed.

Network addition of the colourant places the operational management on the pipeline network operator and will require additional management and control of operations to ensure that the process is managed safely and efficiently.

When considering the introduction of the colourant into the network, there are several factors that need to be considered including:

- Colourant type
- Compatibility with network operations, maintenance and materials
- Injection process and point of injection

- Number of injection points required
- Quantity of colourant to add
- Impact of releases

The colourant's sole function is to provide a visible flame colour at point of use (or from ignited releases due to infrastructure failure), but the options are constrained by these other factors.

As mentioned in Section 4: Colourant types / additives, there are a number of different colourant types that can be considered.

First, the physical state of the colourant is constrained by the requirement to deliver a gaseous hydrogen product to end-users. This tends to limit the colourant options to gases or volatile liquids, and almost certainly excludes the options to add liquid or solid material. From a network operation viewpoint, it is important to avoid liquids and solids in pipelines as they can affect pressure and flow control, especially through pressure reduction installations assuming that the hydrogen pipeline infrastructure will be operated in a similar way to the current natural gas network. Throughout the network, filters are used to trap liquids and solids and if the colourant is added close to the point of production then this would limit the colourant options to gases only. Also, the presence of liquids and solids is not compatible with operation of compressors used to move the hydrogen around the network.

If a parallel with the natural gas network operation is drawn, using the odorant addition as the analogy, the colourant may not be required for parts of the system operating at the highest pressures, but will be needed at the lower pressure tiers as the hydrogen is supplied to a myriad of different end-users. The injection process for odorant involves addition of the volatile liquid into the flow, the dose rate being controlled by the gas flow to ensure a consistent concentration of the odorant downstream. A similar approach could be adopted for colourant. The process for propane enrichment of biomethane uses the same general principle with the level of enrichment controlled by the flow rate of the biomethane.

For the odorant injection, fewer larger injection points are used to reduce the number of injection installations required and ensure that the systems are of a scale to be lower cost and avoid issues of flow disparity that may result if the injections are done at lower pressures and more widely dispersed across a pipeline network. It also means that the management of the inventory of odorant is optimised, and clearly this is an important factor for the colourant addition option too.

5.1.1 Colourant Quantity

The quantity of colourant to add to a network is not known at present and here the parallel with odorant may diverge. Odorant quantities are in the parts-per-million range, but the likelihood is that higher quantities of colourant may be required. This would result in the requirement for larger storage facilities, more delivery activities and higher risk. To some extent this has been encountered with propane enrichment of biomethane, where the propane added is a few percent of the total flow. Significant numbers of tanker movements are needed to ensure that the propane inventory at the sites is maintained.

Pipeline network operators would incur high CAPEX and OPEX cost to provide large-scale facilities for the injection of colourant, especially as the requirement is for a limited number of end-user types, and not needed in the main domestic use from condensing boilers.

5.2 Colourant added at the Appliance

If localised (i.e. at the appliance) rather than centralised colourant addition is adopted then the overall usage of colourant material would be substantially lower and present a better use of resources. This approach avoids the impact of colourant on systems where it is not needed but does require correct control to ensure that the rate of colourant addition is suitable for the burners as they are adjusted up and down.

In this case, the onus for management of the colourant is placed on the appliance manufacturer (from the viewpoint of introducing a system whereby colourant can be added) and/or the homeowner (appliance operator) to ensure that the colourant addition process is operating correctly. The colourant could be added to the hydrogen gas in the pipework to the burner or added to the combustion zone itself.

5.3 No Colourant

Another option is to avoid colourant addition through development of new burners or systems that remove the need to "see" a visible flame.

Previous studies and reports by Kiwa [10] and Frazer Nash [11] [12] have highlighted that for cooker hobs there is a safety implication if a visible flame is not present, but this could be reduced if the burner was re-engineered so that a visible flame is not a safety feature and the presence or absence of a flame is indicated by other means.

For example, a recent design development involving catalytic combustion has been published by a Swiss research organisation (EMPA). Here the hydrogen is combusted on a catalyst surface and the burner is mounted under a ceramic glass cover [10] An open flame is avoided, and no colourant is needed as shown in Figure 14 below. Figure 14 shows the main components of the burner without the ceramic top plate.

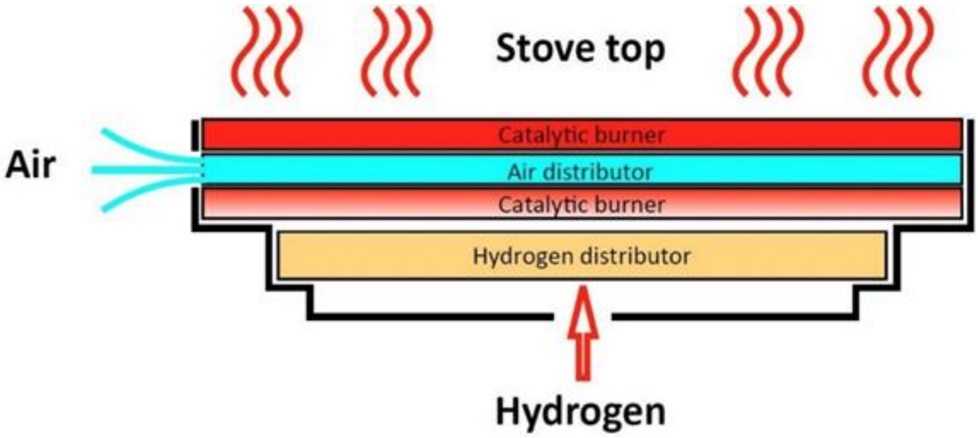


Figure 14: Catalytic burner concept for gas cooker hob

Figure 15 shows the EMPA cooker with the ceramic glass top visible

Figure 15: Catalytic burner under a ceramic glass plate – new hob concept

To date there has been limited research to develop a cooker hob burner, especially one that has the outward appearance of a traditional natural gas burner. It is recognised that for this type of burner a colourant or an additional indication of the presence of a flame will be required. As such, there are a number of considerations that have been highlighted by Frazer-Nash:

- *The colourant additive will need to be food-safe as, in hobs and ovens, as the products of combustion may be direct contact with food [sic].*
- *If the combustion products are released into the room (hobs and ovens) then the colourant and any chemical reaction products will need to be non-toxic within confined spaces.*
- *The wider environmental impact of flue emissions containing the colourant and any combustion products needs to be investigated.*
- *The impact of the colourant on hydrogen flame properties will need to be considered, including flame temperature, NOx emissions and flame stability.*

The report also highlights that the colourant considerations cannot be viewed in isolation and "*should also be combined with hydrogen odorisation to ensure that the solutions obtained are complementary*".

The following sub-sections highlight output from the tasks and activities undertaken by this project to assess the requirement for colourant and the implications of its use.

Returning to the colourant type consideration, if a gas or volatile liquid is required then this would tend to favour addition of a hydrocarbon, as water will need to be avoided in the network. Propane addition, like biomethane enrichment, could be considered but the quantities needed may be substantial. Although no quantitative assessment has been undertaken, from anecdotal information and the flame pictures for methane /hydrogen flames, this addition could be up to 10% by volume.

As the main aim of hydrogen for heat is decarbonisation, the concept of introducing hydrocarbons to act as a flame colourant appears at odds. This would result in significant CO_2 emission and also the management of such large quantities may not be practical.

6 RISKS AND HAZARDS OF USING HYDROGEN

6.1 Implications of Low Visibility Flames on the Network

Hydrogen leakage or releases from a pipeline network may occur and the detection of such releases is an important aspect for network operators. New hydrogen gas detection equipment and methods will be needed but the implication for ignited releases and low visibility flames needs to be considered.

High pressure releases will be audible and if they ignite will entrain surrounding solid material (dust, soil, etc) that will result in a visible flame.

Lower pressure releases may result in hydrogen flowing through the ground material (tracking) and then potentially igniting at the point of entry to the open atmosphere where a flammable mixture in air could be generated and an ignition source is present. If the hydrogen flow then ignites, then the flame produced in these circumstances may be small and potentially invisible depending on the location and the surroundings.

The whole process of the low pressure release, tracking and ignition is not well understood, and although the potential to form a flammable mixture is present, in practice it may not occur. The route to harm for network employees or the general public is not well defined but as this may increase risk it requires further study.

Information from gas network operators is not detailed enough to enable a more complete evaluation to take place but the consequences of such an ignited release requires further investigation.

6.2 Risks to appliance performance

Domestic appliance manufacturers have been consulted with regard to the operation of their appliance designs on hydrogen containing both an odorant and a colourant. The odorant and colourant are added primarily for operational safety, although the colourant will also have the secondary aesthetic appearance role for fires.

The risks to appliance performance cover the introduction of the colourant, the impact of flame stability, the effect on heat transfer surfaces and the emissions that might result. The colourant types considered at this stage are either liquid or solid compounds and introduced by some unspecified process into the flame. The introduction process could be into the hydrogen fuel gas stream or into the flame directly. Any material added to the hydrogen fuel gas stream has the potential to cause blockages and impair the overall combustion process.

For **boilers**, introduction of the colourant is likely to result in changes to the flue gas emissions, impact on the heat exchanger material (or lead to increased deposits on the heat transfer surfaces), alter the pH of the condensate, affect the fluid properties of the condensate and/or generate particulate emission from the flue. The overall impact of the colourant should not result in increased maintenance of appliances or reductions in lifetime.

For **cooker hobs**, the colourant is important in order to assess the extent and size of the flame and the visual aspect is often used as part of the user control of the cooking process. Cooker hobs discharge into the kitchen atmosphere and the impact of the possible trace emissions must also be considered. The colourant may also affect the material where flame impingement occurs, this could be pans or supports.

At the present time, there is no consensus on colourant type or mode of introduction and these factors will impact on the consideration of the risks to appliance performance.

As already discussed, the requirement for and location for injection of colourant is not a straightforward selection. There are different stakeholder views and already the complexity of the process is raising additional tasks that require consideration.

6.3 Implications of odorant on flame colour

As mentioned earlier the presence of odorant (termed NB – an 80/20 mix of TBM and DMS) was investigated, as the presence of hydrocarbon components or fragments and sulphur may give rise to increased flame luminosity. Tests using odorised and unodorised hydrogen were performed and a comparison made "by-eye". A diffusion flame was used in the first tests and the following photographs of the flames obtained as shown in Figure 16.

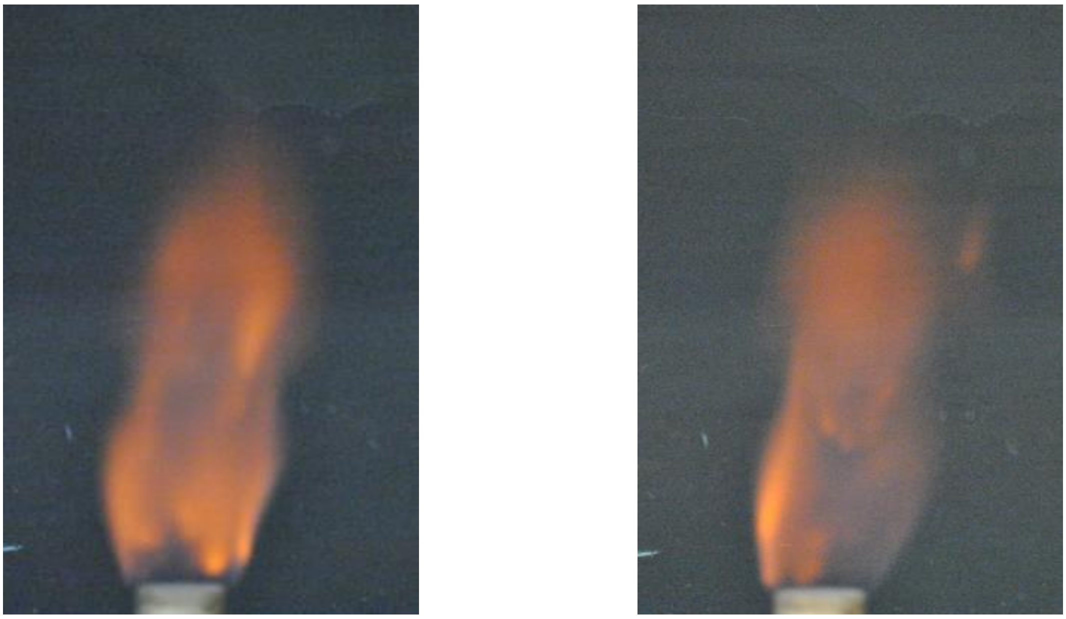


Figure 16: Comparison of hydrogen flames (unodorised - left-hand side; odorised - right-hand side)

The odorant concentration was chosen to be similar to that found in natural gas, and the overall odour intensity was confirmed by standard rhinology checks. The orange glow is typical of this type of flame and the presence of odorant does not appear to increase the flame luminosity. The blue emission near the base of the flame is similar for both and does not appear to show any increase in luminosity due to the odorant.

6.4 Flame detection

Thermal detectors should be placed directly above the site of the flame. However, if a leak occurs, a flame can develop in a different position which is not detected by the instrument. Another thermal device that can be used is a thermocouple for the detecting the presence of heat. Thermochromic materials can be used for thermal detection of flames. These materials contain a pigment which when exposed to heat, will cause a colour change on the surface of the material [19].

UV and IR radiation detectors are an alternative method of flame detection. Since hydrogen flames emit UV radiation, photo-electrons are emitted which create an electrical impulse [20]. Infrared detectors use IR sensor filters to enable visualisation of the flame but need to be designed to detect the low levels of infrared emitted [20].

7 COLOURANT LEAKAGE TESTING (FROM A HOUSEHOLD PIPE)

Although leakage detection relies on the presence of odorant to provide an early indication, small leaks from the domestic supply may go undetected and give rise to additional hazards. These could be related to gas build-up and this aspect was studied in the HyHouse project. The potential for gas accumulation forms part of the work scheduled for Hy4Heat Work Package 7. An additional hazard may result if small leaks of hydrogen can be ignited and may lead to initiation of house fires. This aspect is the focus of the work undertaken here.

In many domestic properties, gas is delivered from the meter to appliances through copper pipework[1]. Some of this pipework may be external to the property but in many cases is internal and often located close to walls, floors, kitchen units, skirting boards and other areas.

If copper pipework is damaged, corroded, or assembled/connected incorrectly then it is possible for gas/hydrogen to leak into the property.

Leakage rates from small holes have been investigated by Steer Energy, through the Hy4Heat Work Package 7 studies. Steer Energy has supported this work through provision of copper test pieces with holes of similar diameter to those used in their study.

The colourant leakage testing comprised several parts:

- set-up of a selection of copper pipe test pieces to mimic domestic pipework

  (initial information from industry contacts suggested that nail holes in pipework or badly soldered joints could be main leak types to focus on; recognising that larger releases are outside of scope).
- initial tests on ignited releases from these layouts
  - tests on location of igniter, impact of distance from the leakage point and supply pressure
- comparison tests to be undertaken with methane or natural gas
- focus on no impingement or secondary heating - photographic records and additional data gathered
- investigation of ignited releases adjacent to a number of surfaces to evaluate the impact on flame visualisation
  - Material types included blocks, bricks, terracotta block, metallic surface, painted surface, wooden surface, MDF/chipboard, and various coloured tiles
- presentation of results through photographic records with additional commentary on observations by eye. These results are supported by IR camera images to provide additional insight into the leak ignition and extent of the hydrogen flame.

---

[1] It is acknowledged that other pipe materials may be present, but the majority involves copper pipes of diameters typically from 15 mm up to 28 mm.

7.1 Influence of background material or colour on ignited hydrogen leaks

Small leaks of hydrogen have the potential to produce a flame if there is an ignition source present and the work undertaken, detailed below, identifies if they can be established and if they are visible.

It is known that hydrogen flames in a clean environment will emit a very small amount of visible light and in the past hydrogen flames have been described as ^invisible flames'" Although this is not a completely correct designation, as the flames do emit some visible light, it is evident that the intensity of the emission is low and this has been shown in Section 2.2: Existing hydrogen flames and burners.

This section investigates the influence of various backgrounds of different colours that would typically be found in a household environment on the perceived visibility of a hydrogen flame. The supply pressures for the tests ranged from 10-80 mbar, recognising that although domestic supplies are typically around 20 mbar there is potential got both higher and lower supply pressures.

Figure 17 shows the selection of background materials used for this investigation which are also identified in Table 7. Additionally, a plain black background was in order to enhance visualisation. Figure 26 also shows the experimental rig used. Note that the arrangement seen is for horizontal release which will be discussed later in this report.

ID Number	Material	ID Number	Material
1	Chipboard	9	Grey Brick
2	Brick	10	Red Tile
3	Blue Brick	11	Grey Tile
4	Clay	12	Grey Ceramic
5	White Tile (square)	13	White Ceramic
6	Dark Grey Tile (square)	14	Plain Wood Plank
7	Dark Wood Plank	15	Cardboard
8	White Kitchen Cupboard	16	Black Background

Table 7 - Selection of background materials

Figure 17 - Selection of background materials used for the flame visualisation studies

7.2 Preliminary test output using reverse pitot tube

For the purposes of this report, only the materials towards the extreme ranges of colours will be shown in this section. The materials chosen for this are the dark wood plank, white kitchen cupboard and a plain black background. A wide range of pressure from 10 – 80 mbar was tested and a selection of results is shown below.

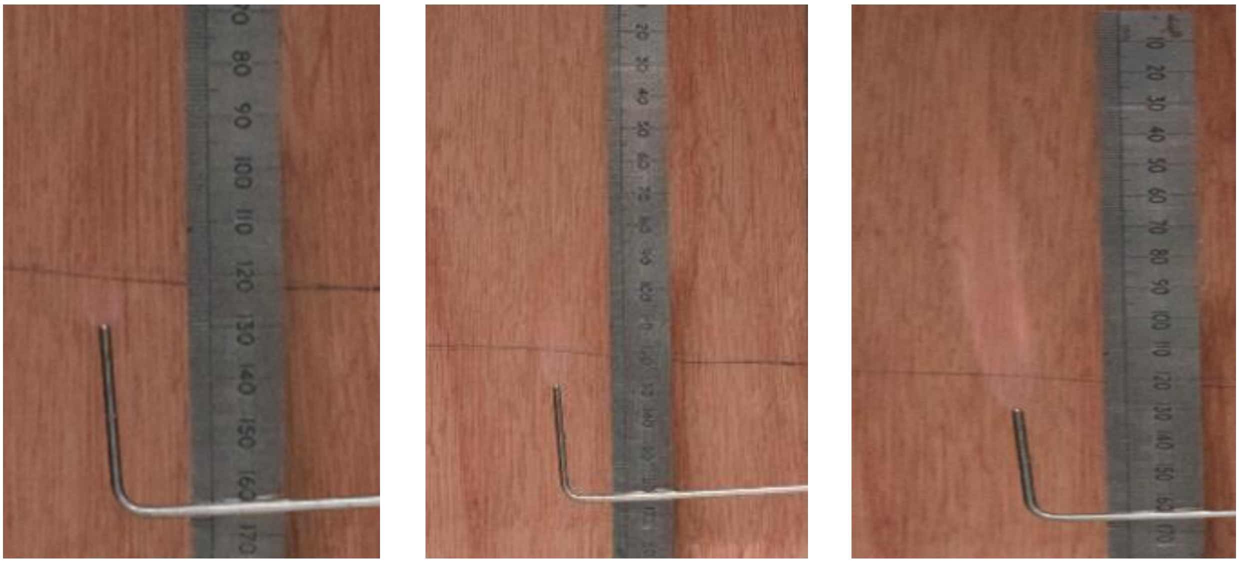


Figure 18 - Hydrogen flame with dark wood plank background at 10 mbar (left), 20 mbar (middle) and 80 mbar (right)

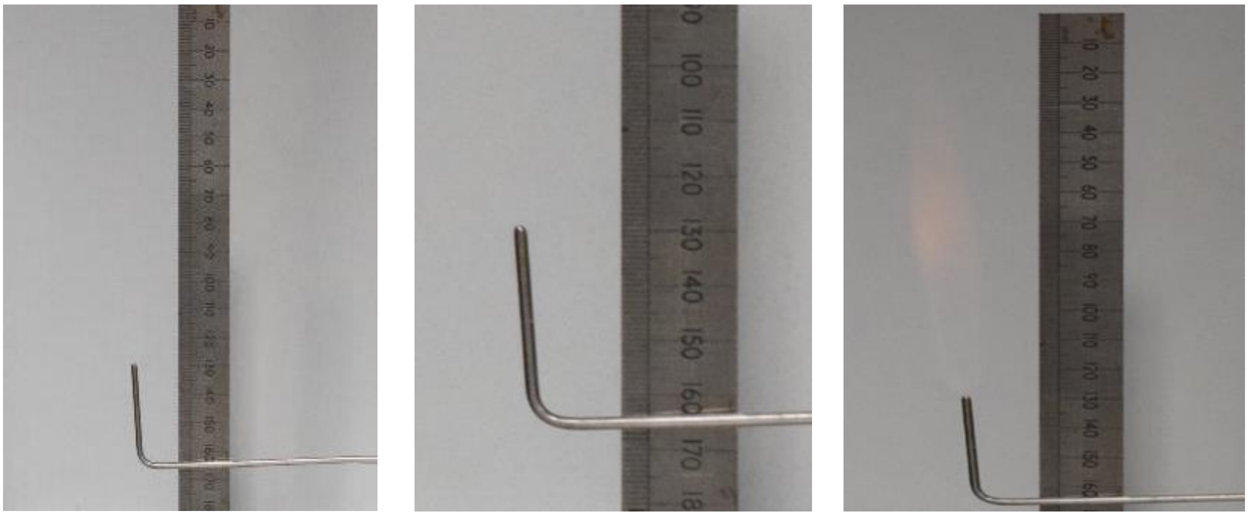


Figure 19 - Hydrogen flame with white kitchen cupboard background (left – 10 mbar, middle – 20 mbar; right 80 mbar)

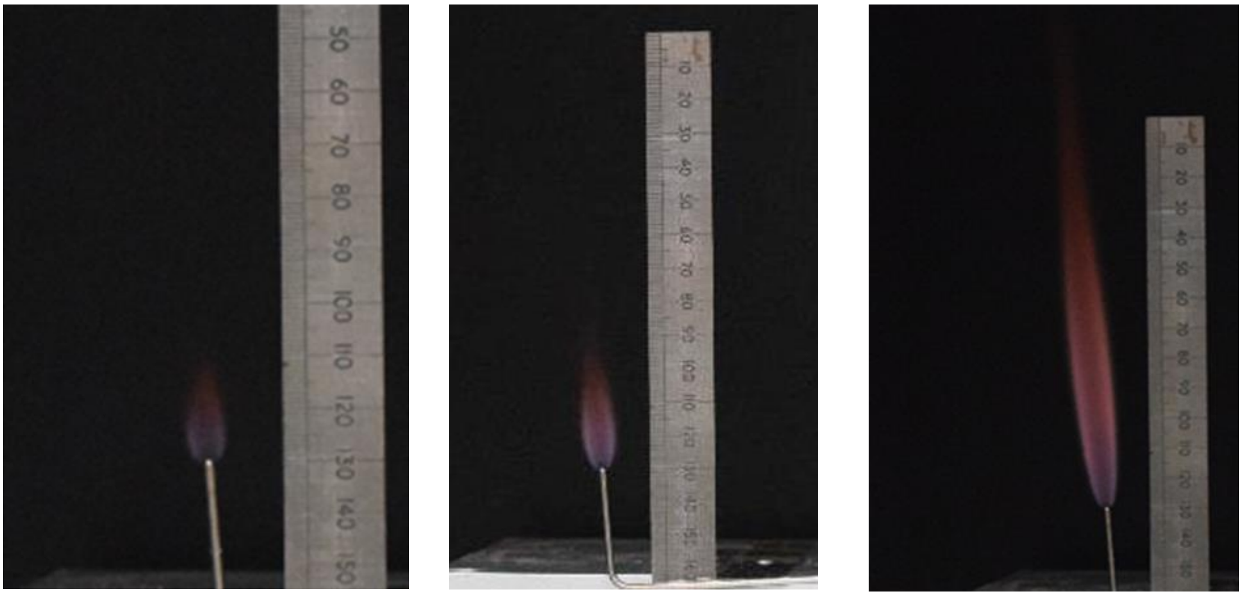


Figure 20 - Hydrogen flame with black background (left – 10 mbar, middle 20 mbar; right 80 mbar)

Figures 18 - 20 show the visibility of the hydrogen flame between 10 and 80 mbar using a 0.9mm reverse pitot tube against various background materials. From these figures it is clear that visibility of the flames is greatly enhanced when they are in front of a darker background. For the white and wood backgrounds, it is evident just how difficult it is to see the established flame especially at lower pressure (cf. the results at 10 and 80 mbar).

For comparison, methane flames are shown in figures 21 and 22. Methane flames established on the jet are much more visible, showing a characteristic blue region close to the tip of the nozzle and an intense yellow flame at the top as a result of soot formation within the flame.

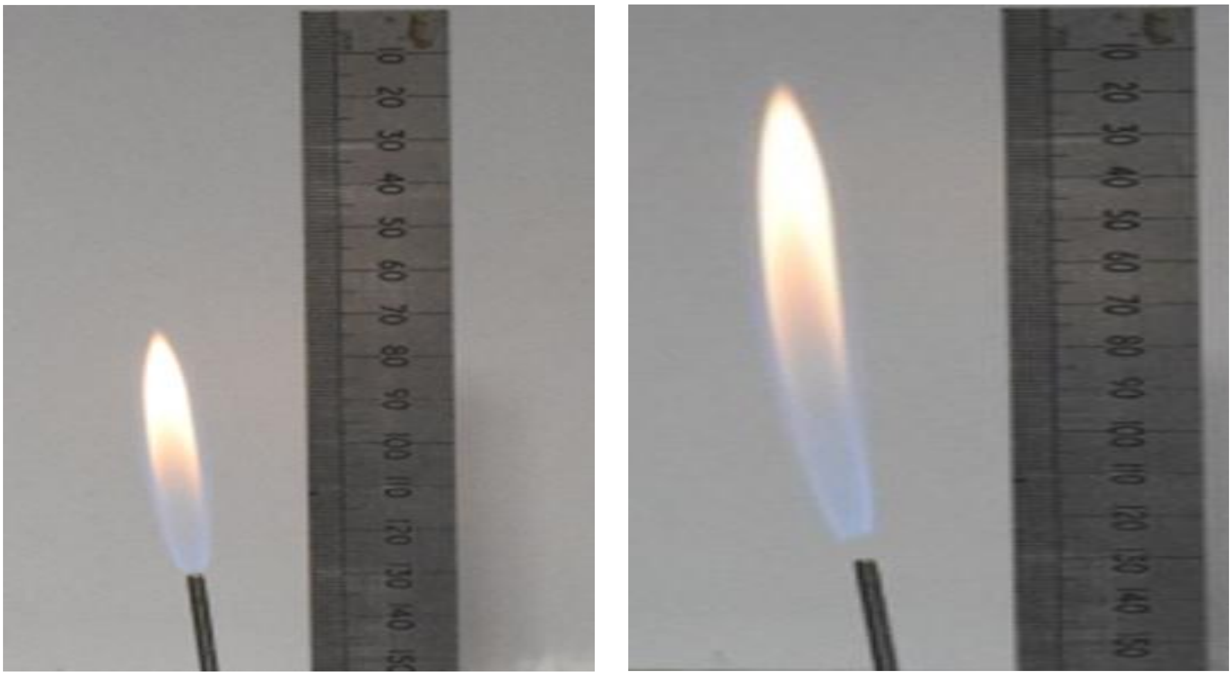


Figure 21 - Methane flame in front of a white kitchen cupboard background at 10 mbar (left) and 20 mbar (right)

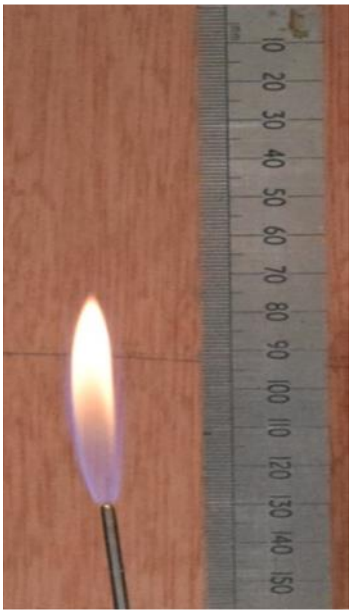


Figure 22 - Methane flame in front of a dark wood background at 10 mbar

For methane flames on the reverse pitot tube, no flame could be stabilised at a pressure greater 25 mbar unlike hydrogen which could be established easily at 80 mbar (the highest pressure used in these tests). This is due to the flame speeds of the fuels where methane has a much slower burning velocity than that of hydrogen. At higher test pressures, the flow velocity becomes too high for methane and exceeds the flame speed resulting in ‘blow-off’.

7.3 Ignited leaks from copper pipework

Building on the preliminary work undertaken with the reverse pitot tube, a series of experiments was undertaken to investigate leakage from a mimic of internal, domestic gas supply pipework , focusing on the impact of supply pressure, ignition point, flame establishment and flame visibility. Typical standard 15 mm copper pipe was used in all these cases and holes or connectors added to simulate different modes of leakage (see Table 8 and Figure 23).

Test Samples – to mimic internal domestic pipework leakage – 15 mm diameter copper pipe	
1.0mm drilled hole	Large hole to simulate damage from a nail or drill
0.5mm drilled hole	Medium sized hole to simulate minor damage to a pipe
0.3mm drilled hole	Small hole to simulate corrosion damage
End cap (unsoldered)	Unsoldered end cap to simulate a badly assembled joint or a damaged pipe connector
Push Fit End cap	New fitting to simulate incorrect assembly , as these connectors should not be used for gas service.

Table 8 – Test samples

Figure 23 - Copper pipe test pieces (from left to right) - unsoldered end cap, "push-fit" end cap, 0.3mm (left), 0.5mm (middle), 1.0mm (right)

The test pieces were installed in a test bay along with instruments to measure pressure and temperature (see Figure 24). The experimental set up was flexible to enable pressure control, interchange of test pieces and insertion of different background materials, and also had good access for digital photography and collection of infrared images.

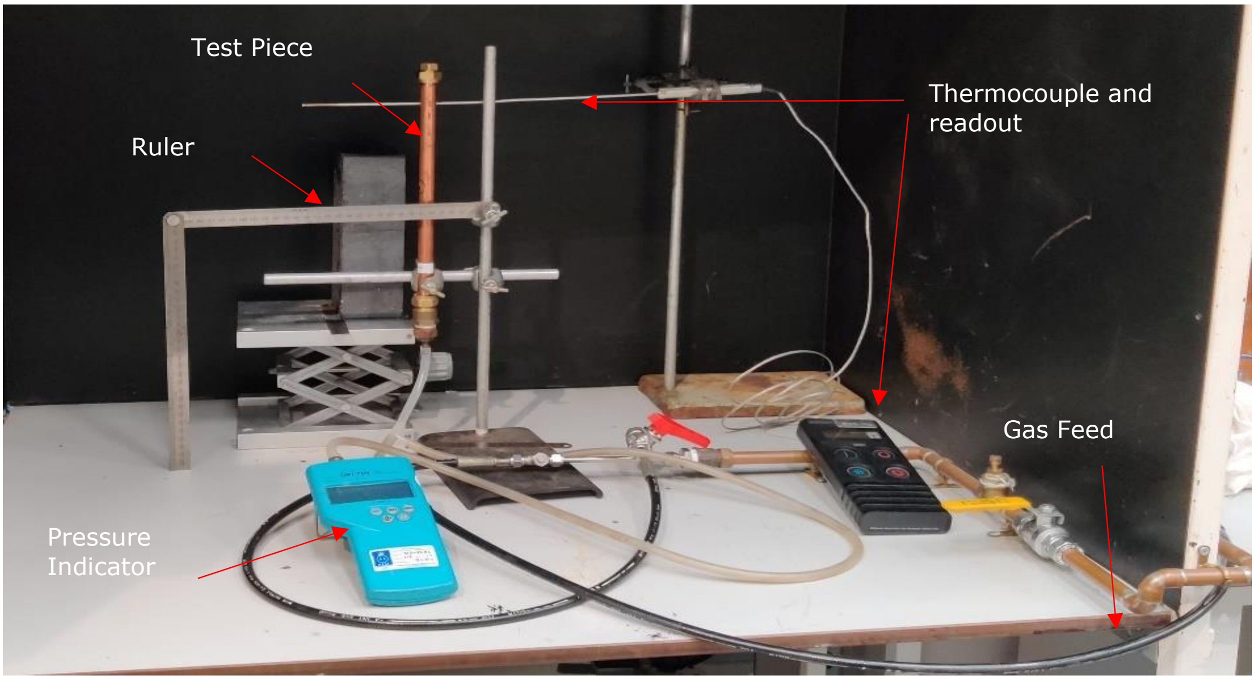


Figure 24 - Experimental rig (showing the test piece arranged for a horizontal release)

For all test pieces, comparison was made between hydrogen and methane flames and the range of background materials, with tests undertaken mainly with gas supply pressures between 10 and 80 mbar, but with additional measurements made at lower pressures to investigate the impact of lower flows.

[N.B. only images in front of a plain black background will be shown as it has already been demonstrated that hydrogen flames are difficult to see by eye or digital camera in front of a white and intermediate coloured backgrounds.]

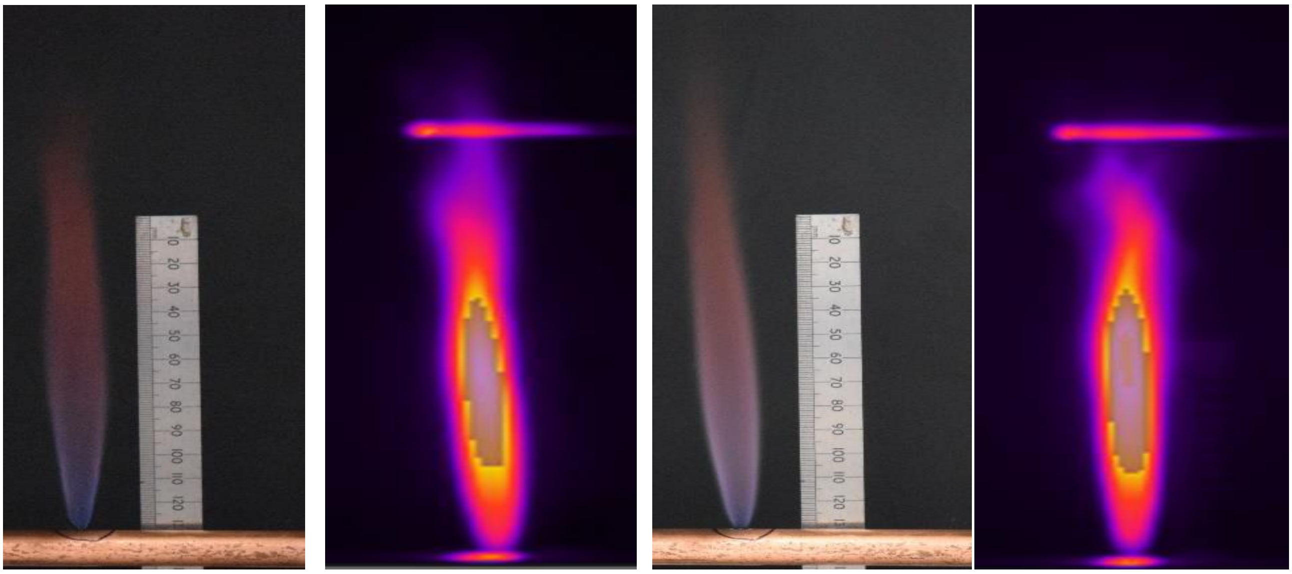


Figure 25 - 1.0 mm drilled hole in copper pipe at 10 mbar (left) and 20 mbar (right)

Figures 25 to 28 show the variation in flame length and luminosity as a function of the leakage hole diameter and the supply pressure. In each figure the infrared camera image is shown alongside the digital camera image. (The horizontal bar feature in the infrared images is due to the igniter.)

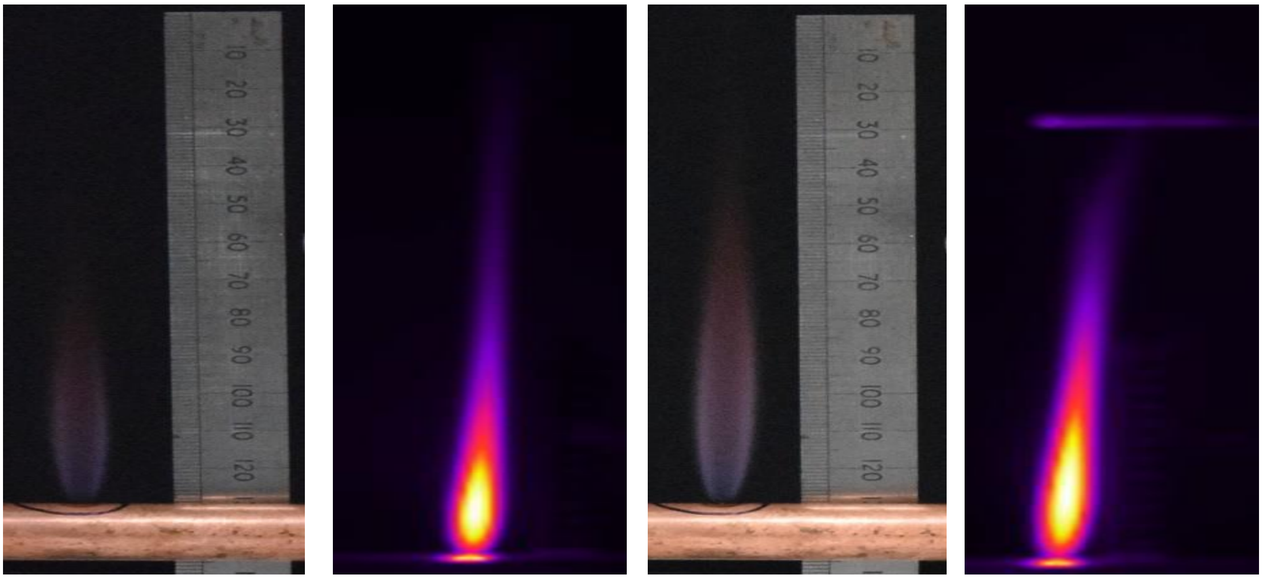


Figure 26 - 0.5mm drilled hole in copper pipe at 10 mbar (left) and 20 mbar (right)

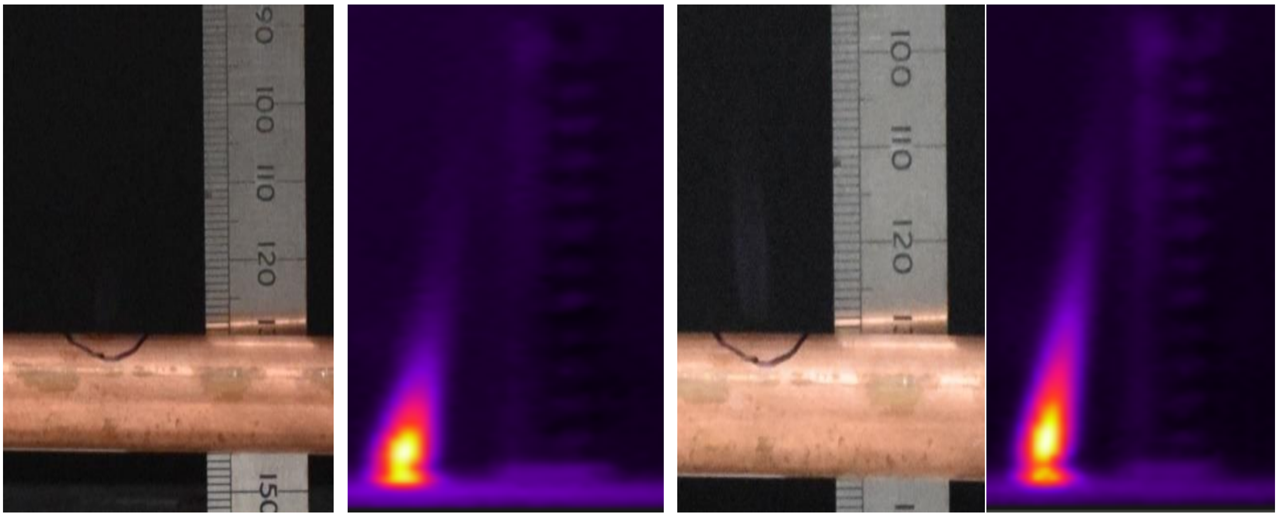


Figure 27 - 0.3 mm drilled hole in copper pipe at 10 mbar (left) and 20 mbar (right)

From these figures, it is clear that the hydrogen flame becomes more visible (noticeable) at higher pressures due to the extended flame length and overall flame volume. Additionally, there is a large difference in visibility of the flame as the hole diameter decreases as seen when comparing the results for the 0.5 mm and 0.3 mm drilled hole in copper pipes at 10 mbar. It should be noted that the enhanced visibility of the hydrogen flame could be due to leftover debris or dust particles present inside the pipe due to drilling of the hole as the particles can interact or react and influence the luminosity. Attention is drawn to the difference between the IR and digital images, in particular the flame tip as this is the region that is virtually invisible to the naked eye. In this region temperatures can still be high enough to cause harm or initiate a secondary fire if it impacts on combustible material although occupants may not be able to see the full extent of the flame.

An interesting result that was found during these tests is that a methane flame could not be established regardless of hole diameter, over the pressure range from 10 to 80 mbar.

To investigate further, the pressure was decreased to a value of 1 mbar but methane could still not be lit. However, hydrogen was still ignitable at this low pressure. The pressure was further reduced and still produced a positive result for hydrogen. This is shown by the infrared image in Figure 28 for the 1.0 mm drilled hole. The flame produced was estimated to be 41 mm in length, based on where the end of the flame tip (blue region) roughly ends in the IR background.

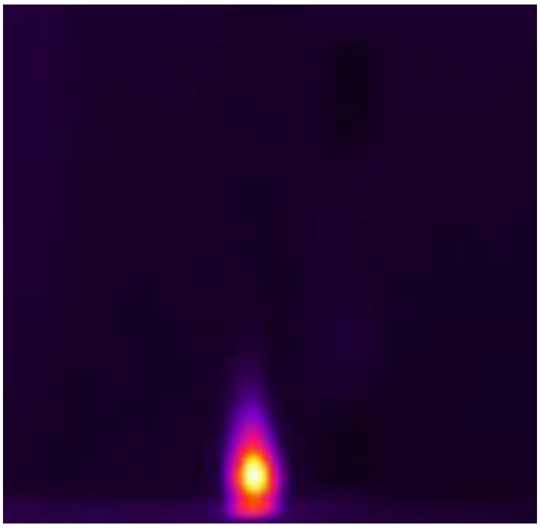


Figure 28 - IR image of flame established at 0.1 mbar for 1.0 mm drilled hole in copper pipe

As mentioned previously, two additional cases were investigated to provide simulations of different leakage in additional to the holes. These were an unsoldered end cap to represent a badly soldered joint and a push fit connector used commonly for water pipes, to represent a DIY assembled system rather than a professionally installed one. For the push fit connector, no leakage could be detected, and this was not investigated further.

For the unsoldered end-cap, a different leakage and flow orientation was observed with the hydrogen or methane issuing from the full circumference of the pipe in the annulus between the pipe and the connector (see Figure 29 for an example image).

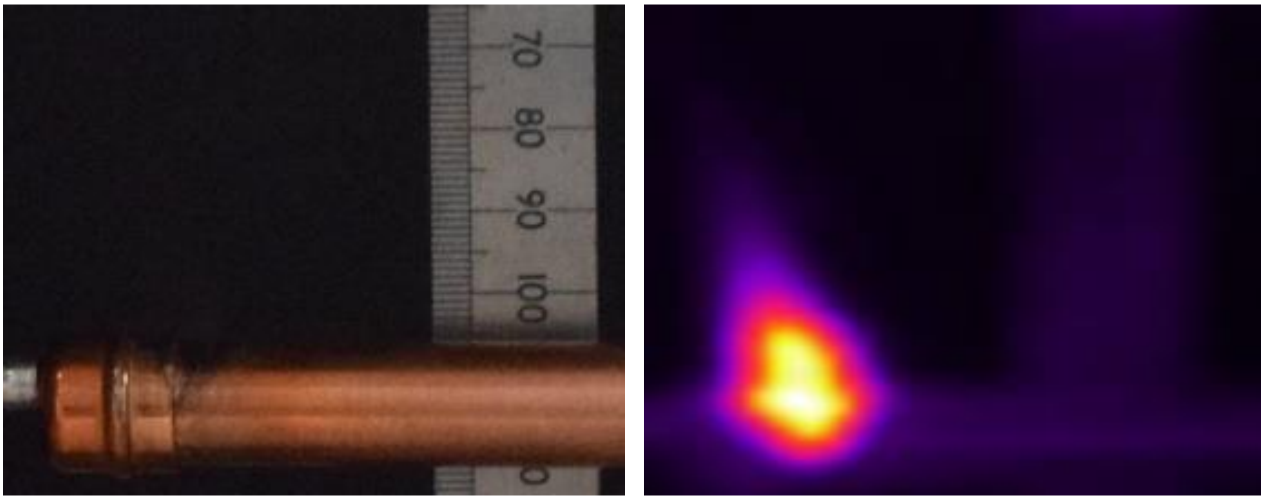


Figure 29 – Unsoldered end cap at 10 mbar (hydrogen)

For the drilled holes it was not possible to ignite methane from leaks from any of the drilled copper pipe samples. However, both methane and hydrogen flames could be established on the unsoldered end cap. The following figures show example results for both cases.

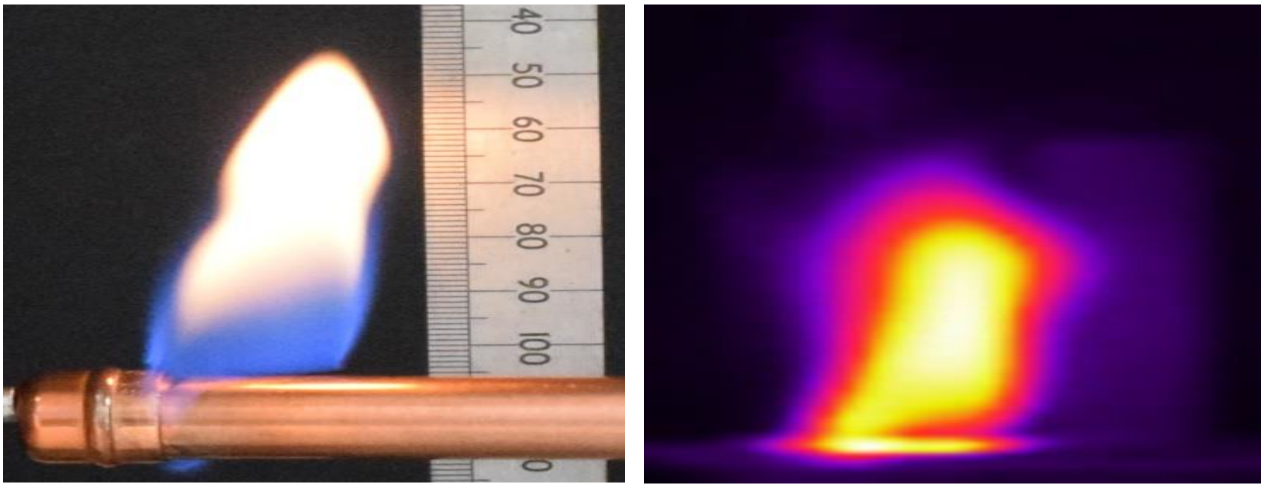


Figure 30 - unsoldered soldered joint at 20 mbar (methane)

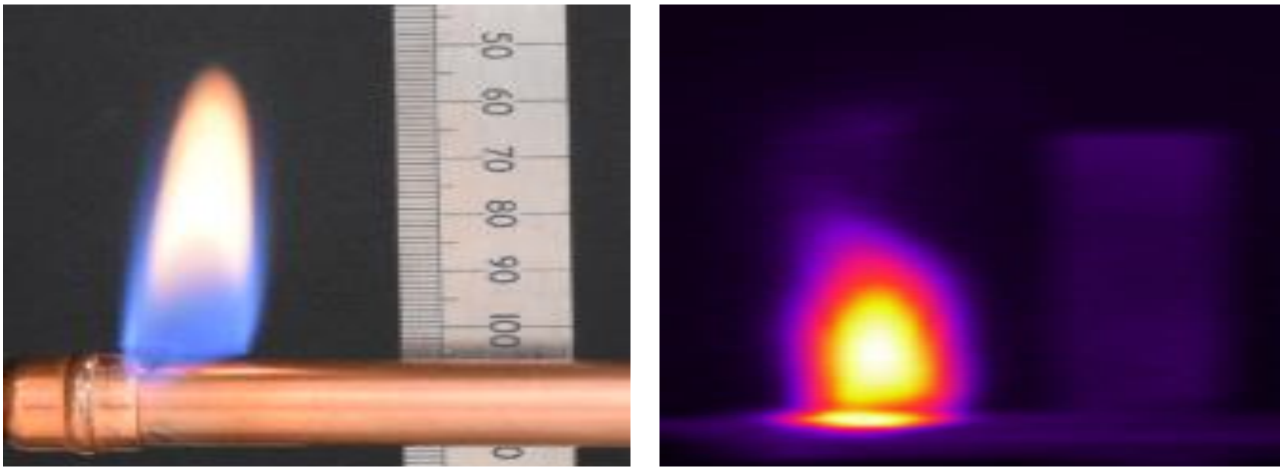


Figure 31 - Badly soldered joint at 10 mbar (methane)

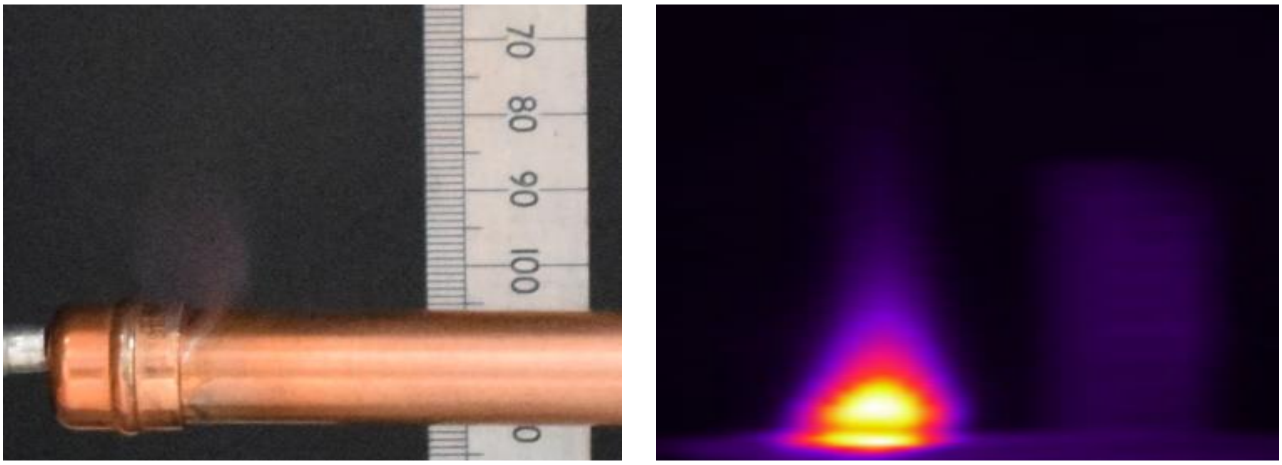


Figure 32 - Badly soldered joint at 20 mbar (hydrogen)

It is clear that the same conclusions regarding flame visibility and hydrogen can be made from the unsoldered joint as for the drilled hole leakage.

In the unsoldered joint there is a reduction in area through which gas can escape and this reduces the extent of the flame. Comparing the digital images of methane and hydrogen at 20 mbar, it is clear that methane is the thicker flame and it appears that the centreline of methane is further from the joint exit than hydrogen. This is most likely due to the fact that methane is a heavier gas and is not as buoyant as hydrogen.

Based on the information obtained from the use of different background materials and different test samples used, it has been shown that hydrogen flames are difficult to see by eye at all pressures even in the cases with a black background.

As the supply pressure increases, the visibility of the flame increases but will still be most clearly seen in a dark environment. Comparing with methane, regardless of background this flame is easily visible. Additionally, it has been found that hydrogen is much easier to ignite than methane due to its faster flame speed and can be stabilised even at significantly reduced pressures.

7.4 Audible sound levels from leaks

Gas leaks are most commonly noticed due to the odorant smell that is added to natural gas. It is anticipated that odorant will be used in hydrogen supplies also. An additional method for detection could be the production of audible sound from the leak. During the test work for leak ignition and flame production, audible sound checks were made. The results from the perception of sound during testing is presented in the following tables. It should be noted that sound levels were not recorded but are based on human hearing.

In the table, “Ignited” refers to the audible sound when the hydrogen jet has been ignited, and the “Unignited” from the hydrogen jet prior to ignition.

Pressure (mbar)	Test Sample			
	1.0 mm drilled hole in Copper Pipe			
	Ignited	Sound Description	Unignited	Sound Description
0.5	No		No	
1	No		No	
5	Yes	Extremely faint, only heard at close range	Yes	Noticeable hiss which occurs approximately at 3 mbar
10	Yes	Noticeable hiss (from 8.5 mbar)	Yes	Hiss increases
20	Yes	Whistling/Static radio noise	Yes	As above
30	Yes	Deep hiss similar to blowtorch	Yes	‘’
80	Yes	-	Yes	-

Table 9 - Sound descriptions for ignited and unignited regimes for 1.0 mm drilled hole

Pressure (mbar)	Test Sample			
	0.5 mm drilled hole in Copper Pipe			
	Ignited	Sound Description	Unignited	Sound Description
0.5	-	-	-	-
1	-	-	-	-
5	-	-	-	-
10	No		Yes	Faint
20	No		Yes	Relatively loud and sharp
30	No		Yes	Slightly quieter than 20 mbar
80	Yes	Loud	Yes	Slightly louder than 20 mbar

Table 10 - Sound descriptions for ignited and unignited regimes for 0.5mm drilled hole

Pressure (mbar)	Test Sample			
	0.3 mm drilled hole in Copper Pipe			
	Ignited	Sound Description	Unignited	Sound Description
0.5	-	-	-	-
1	-	-	-	-
5	-	-	-	-
10	No		No	
20	No		No	
30	No		No	
80	Yes	Noise becomes noticeable at 50 mbar	Yes	Very faint

Table 11 - Sound descriptions for ignited and unignited regimes for 0.3mm drilled hole

The initial conclusions from this study indicate that for typical gas supply pressures, it is possible to hear an ignited leak from a 0.5 or 1.0 mm hole but not from the 0.3 mm drilled hole. If the leak was unignited then only the 1.0 mm hole leak was detectable.

7.5 Flame length and extent

Flame lengths are an important aspect of stabilised flames. Valuable information is to be gained from measuring hydrogen flames in particular as the flame tip is practically invisible and will vary significantly as has been seen in the IR images in Section 7.3: Ignited leaks from copper pipework.

In this section, a series of graphs depicting the influence that the hole diameter has on the overall flame length is presented. The IR images show different false colour regions and these are termed different reaction zones to enable comparison and discussion.

The length of these reaction zones has been measured, and in some examples, the flame extent has been included, covering both the length and the width to give an indication of overall flame volume.

7.5.1 0.9 mm reverse pitot tube

In this section, flame length measurements have been estimated based on IR images. At higher supply pressures, turbulence affects the accuracy of the length estimations which are solely based on human eye perception of where the flame tip region finishes.

As previously stated, a methane flame was unable to be ignited at pressures greater than 25 mbar. Therefore, only 2 pressure points have been measured and included in the figures. These can be used for comparison with hydrogen.

From Figure 33 it is seen that for the comparable pressures, methane has a longer flame length compared to hydrogen. There appears to be a similar trend for both gases as the supply pressure increases, in that the flame length increases.

For the hydrogen test at 80 mbar supply pressure the flame length increases as at a reduced rate. This is due to the generation of turbulence.

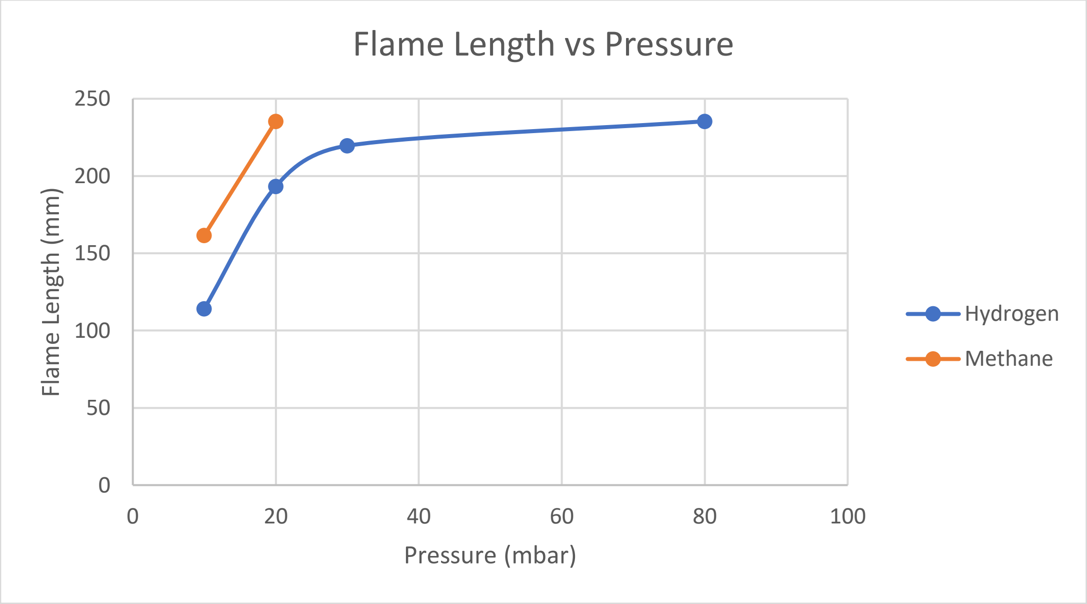


Figure 33 – Comparison of hydrogen and methane flame lengths for 0.9 mm reverse pitot tube

Figure 34 compares the reaction zone lengths produced within methane and hydrogen flames. This graph indicates the distance from the pipe exit (i.e. the leakage point) to the end of each zone. The lengths of each reaction zone can then be found by subtracting the values from the two consecutive zones. From the graph it can be seen that methane has longer reaction zones than hydrogen and hence will have a longer flame length. Again, there is an increasing trend as the pressure increases

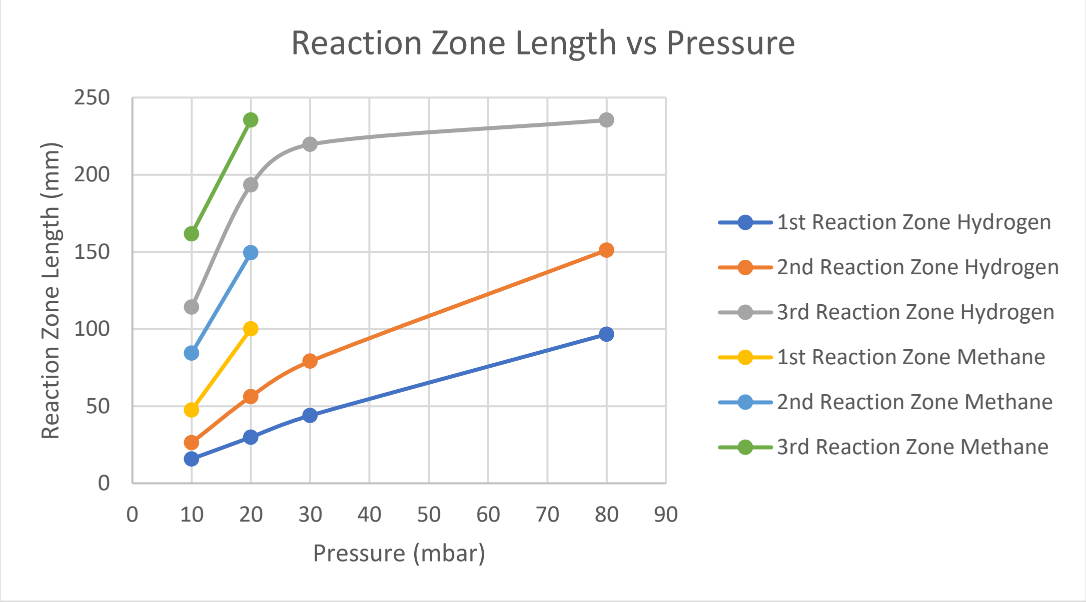


Figure 34 – Comparison of hydrogen and methane reaction zone lengths for 0.9mm pitot tube

Finally, comparing the thickness or width of both flames, it can be seen that methane is the thicker of the two (see Figure 35). The flame width follows a similar trend to flame length, as it increases as the pressure increases. The flame thickness for hydrogen at methane at the same pressure differs by approximately 5 mm.

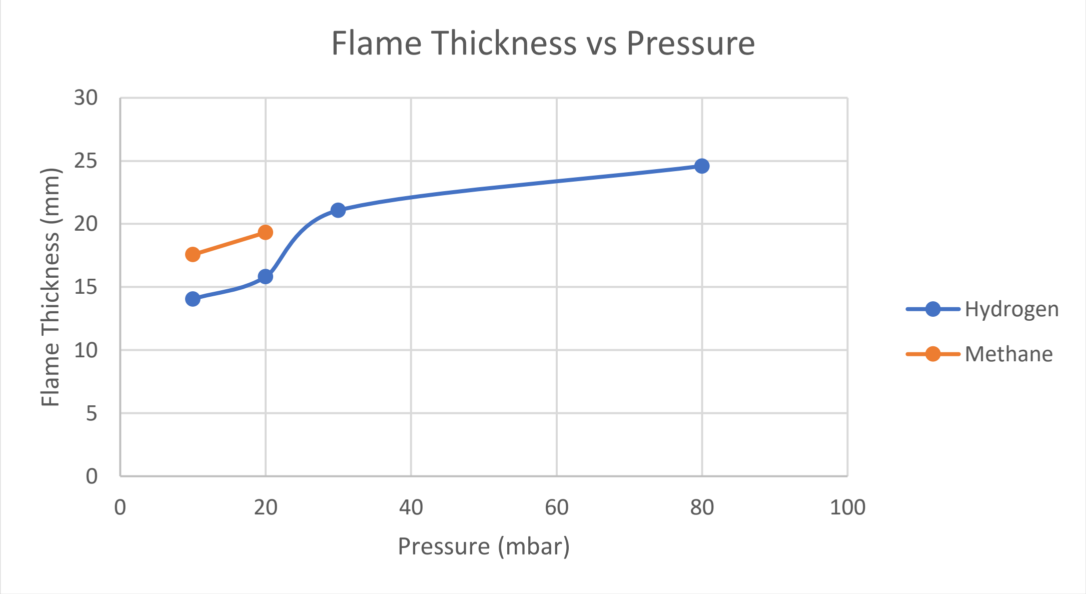


Figure 35 – Comparison of hydrogen and methane flame thickness for 0.9 mm reverse pitot tube

7.5.2 1.0 mm drilled hole in Copper Pipe

As previously mentioned, methane could not be established on the copper pipes so hydrogen alone will be analysed in the following sections.

Figure 36 shows estimated flame lengths over a wide range of pressures from 0.1 mbar to 30 mbar with a general increasing trend. After reaching 20 mbar, the flame length appears to level off before reducing slightly at the highest pressure. This is an indication of increased flow turbulence.

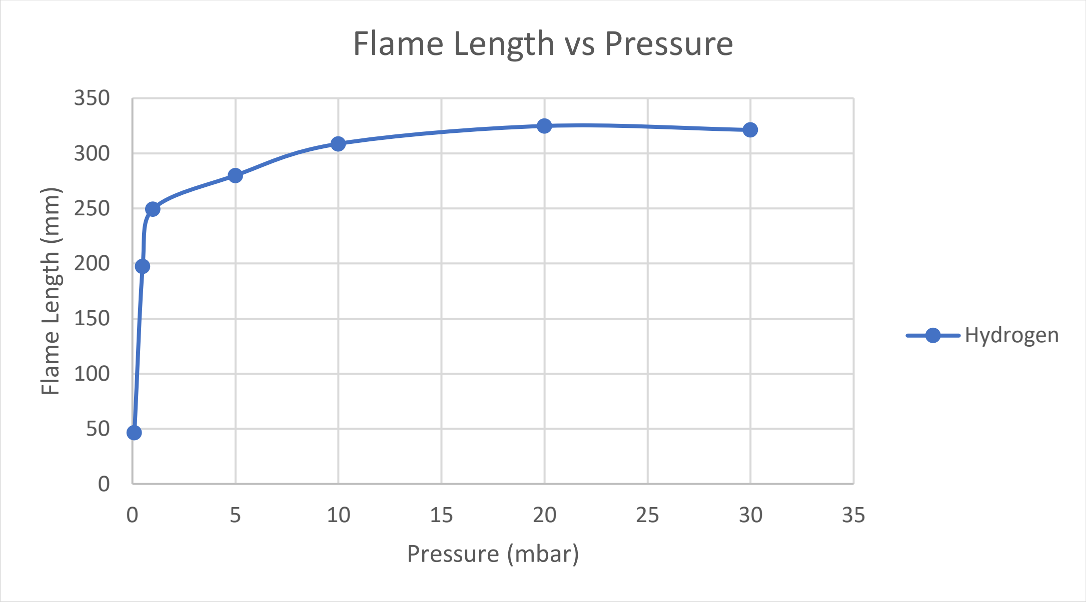


Figure 36 – Comparison of hydrogen flame length with pressure for 1.0 mm drilled hole in copper pipe

Figure 37 shows a similar trend found above in which the length of each reaction zone will increases and reach a peak roughly at 20 mbar before reducing.

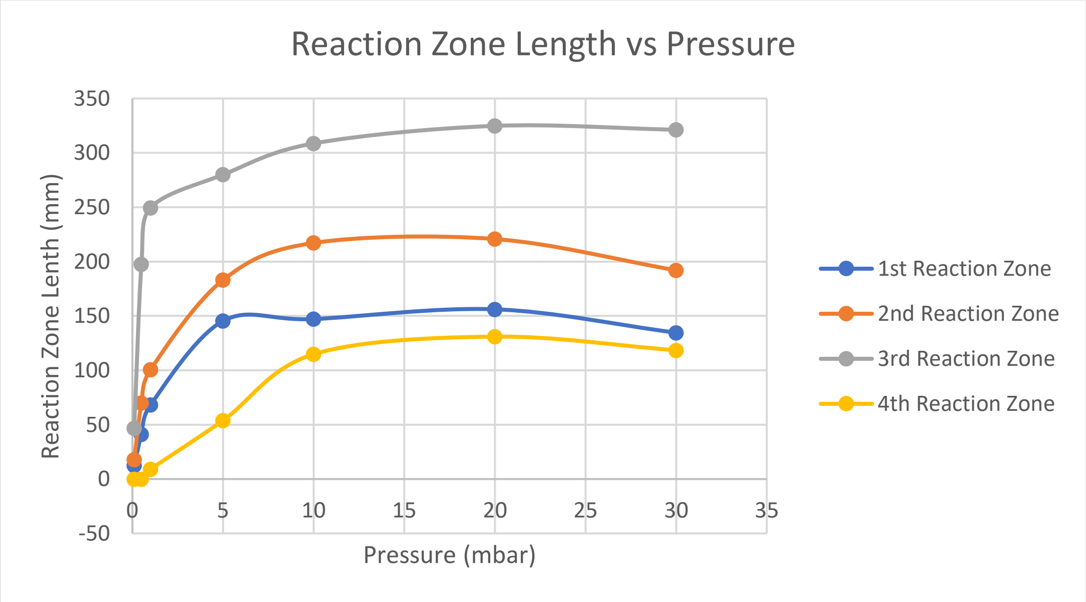


Figure 37 – Comparison of hydrogen reaction zone lengths with pressure for 1.0 mm drilled hole in copper pipe

7.5.3 0.5 mm drilled hole in copper pipe

For this test sample, the flame lengths were measure for both vertical and horizontal release orientations, and the results are shown in the following figures.

From Figure 38, it is clear that the flame length increases slightly until 20 mbar before reducing indicating a small amount of turbulence is present. This is shown by the decrease in the 3rd reaction zone of Figure 41.

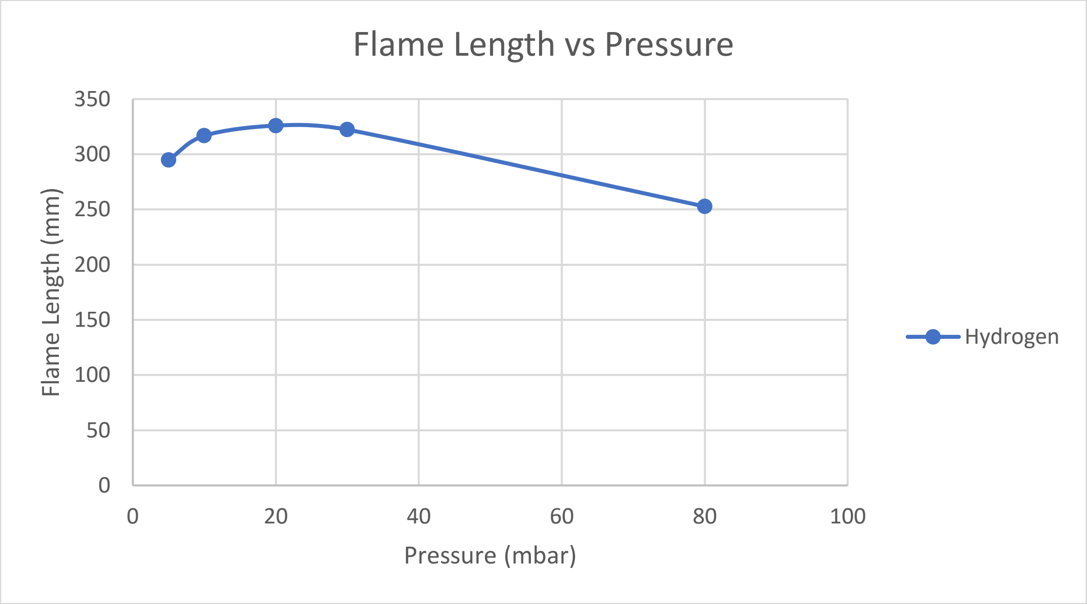


Figure 38 – Comparison of hydrogen flame length with pressure for 0.5 mm drilled hole in copper pipe

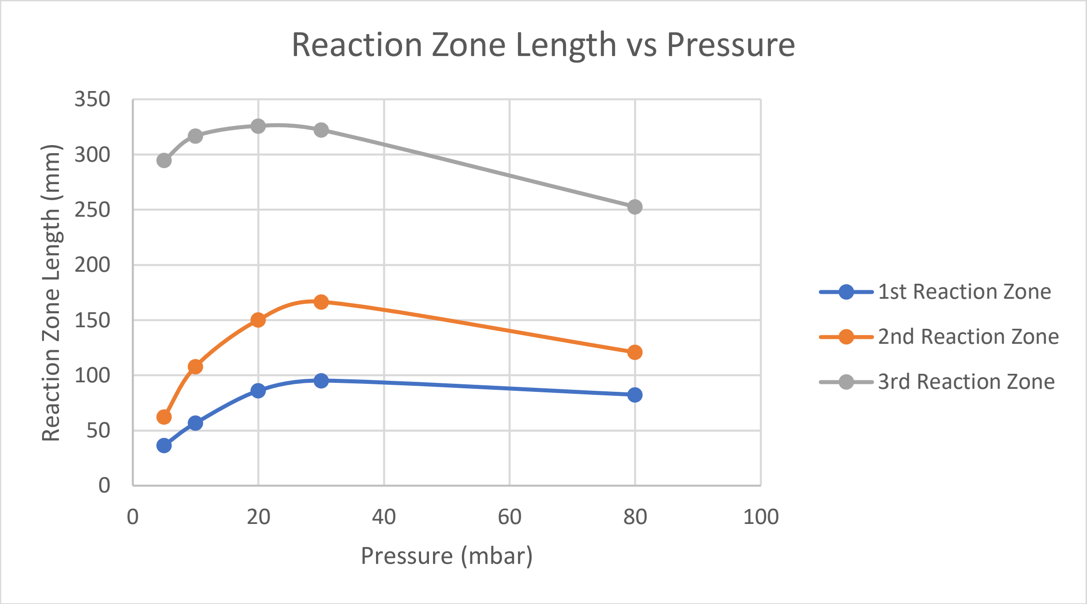


Figure 39 – Comparison of hydrogen reaction zone lengths with pressure for 0.5 mm drilled hole in copper pipe

Relating to the flame thickness, the pressure was found to have no influence for this hole diameter as shown in Figure 40. This was also the case for tests using the 0.3 mm copper pipe.

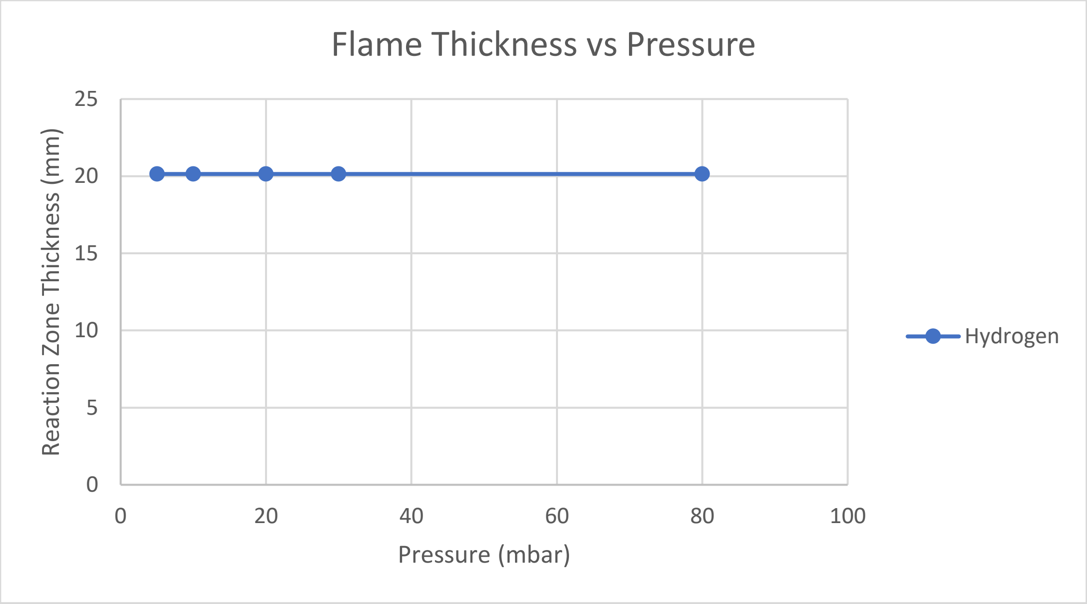


Figure 40 – Comparison of hydrogen flame thickness with pressure for 0.5 mm drilled hole in copper pipe

Figures 41 and 42 show IR images of the flames produced for horizontal releases.

From Figure 41, it can be seen that there a ‘bulge’ is present in the upper surface of the flame. Another aspect seen in this image is towards the end of the flame where the tip starts to curve upwards. Both of these are due to the buoyancy effects of hydrogen gas. In this scenario, the jet is said to be buoyancy-dominated. This differs to the flame in Figure 44. In this image the flame shows no ‘bulge’ or tendency for the flame to curve upwards. In this scenario, the jet is said to be momentum-dominated.

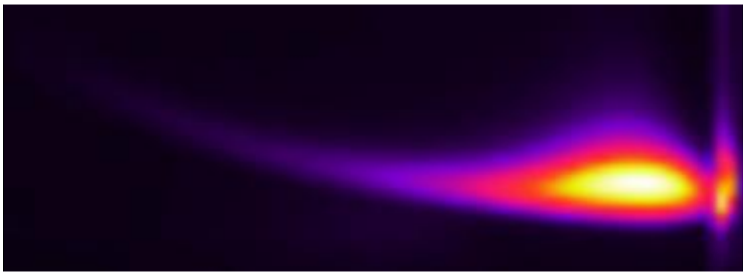


Figure 41 – Horizontal release for 0.5 mm drilled hole in copper pipe at 10 mbar

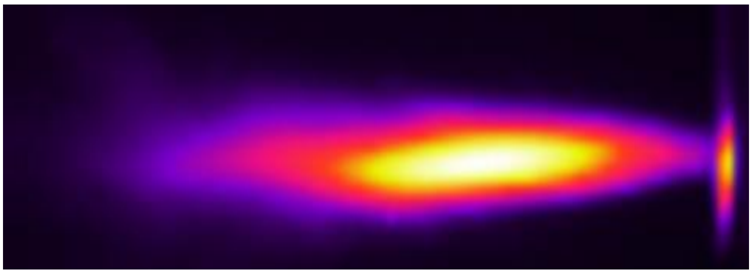


Figure 42 – Horizontal release for 0.5 mm drilled hole copper pipe at 80 mbar

Figure 43 shows the flame lengths for horizontal releases. Comparing with the vertical orientation, the flame length is reduced which is mostly like due to buoyancy effects. Also, the same trend is observed for the reaction zone lengths shown in Figure 46.

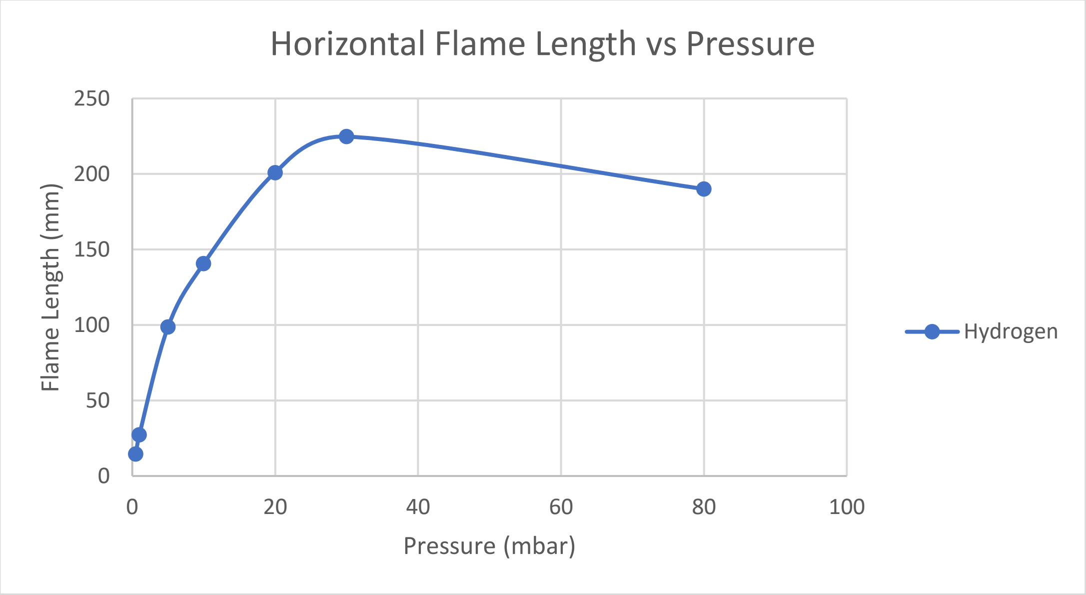


Figure 43 – Comparison of hydrogen flame thickness with pressure for 0.5 mm drilled hole in copper pipe (horizontal release)

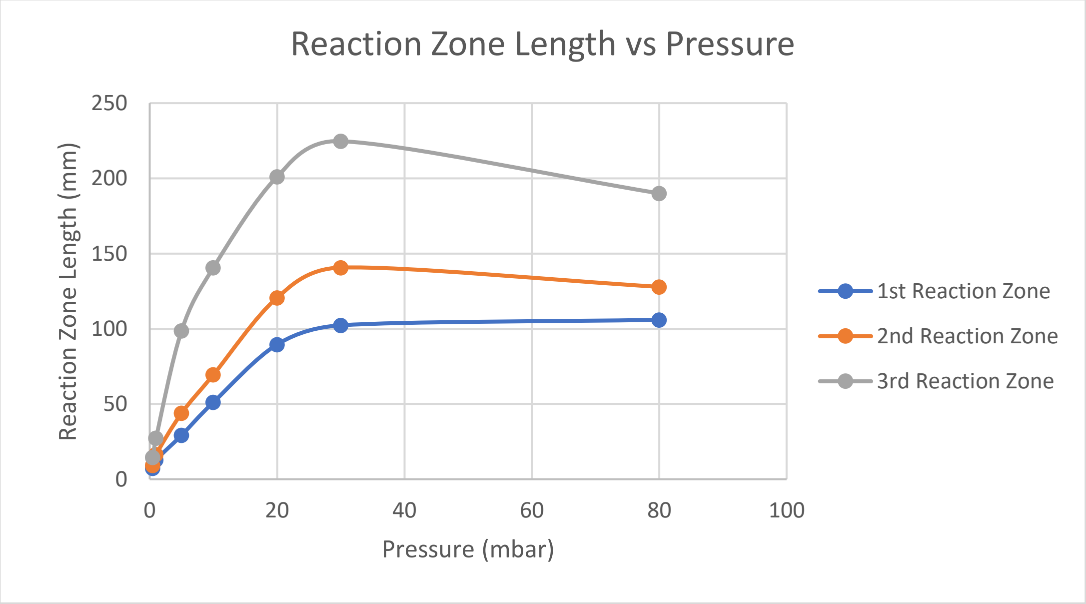


Figure 44 – Comparison of hydrogen reaction zone lengths with pressure for 0.5 mm drilled hole in copper pipe (horizontal release)

Comparing the flame thickness for both orientations and referring to the IR images above, due to the buoyancy effects the flame appears to be thicker. From Figure 45, it is estimated that the flame is approximately 10 mm thicker on average than a vertically released jet.

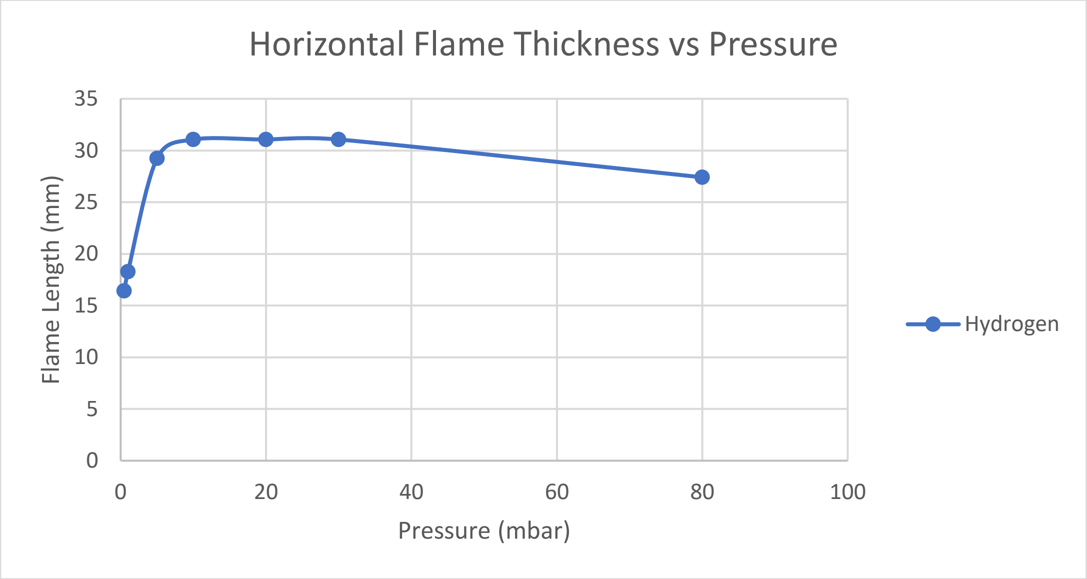


Figure 45 – Comparison of hydrogen flame thickness with pressure for 0.5 mm drilled hile in opper pipe (horizontal release)

7.5.4 0.3 mm drilled hole in copper pipe

Similar to previous sections, this test shows similar trends of an increasing flame length with pressure. However, one comment to make on this sample is that the position of the established flame appears to be angled and will affect the overall length of the flame. This is shown by the IR images in Figure 46. This angle may be a consequence of the hole drilling. With regards to the reaction zones, the 1st and 2nd reaction zones increase slightly before maintaining a stable length as the pressure increases (Figure 47 and Figure 48).

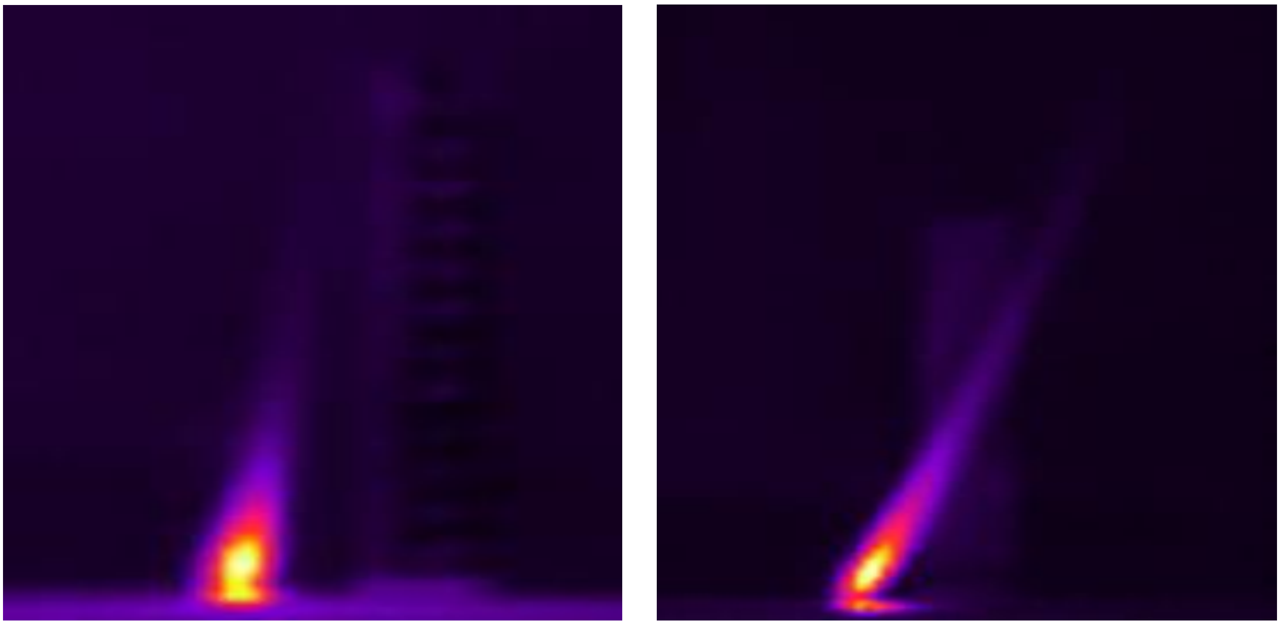


Figure 46 - IR images for angled flame of 0.3 mm drilled hole in copper pipe at 10 mbar (left) and 80 mbar (right)

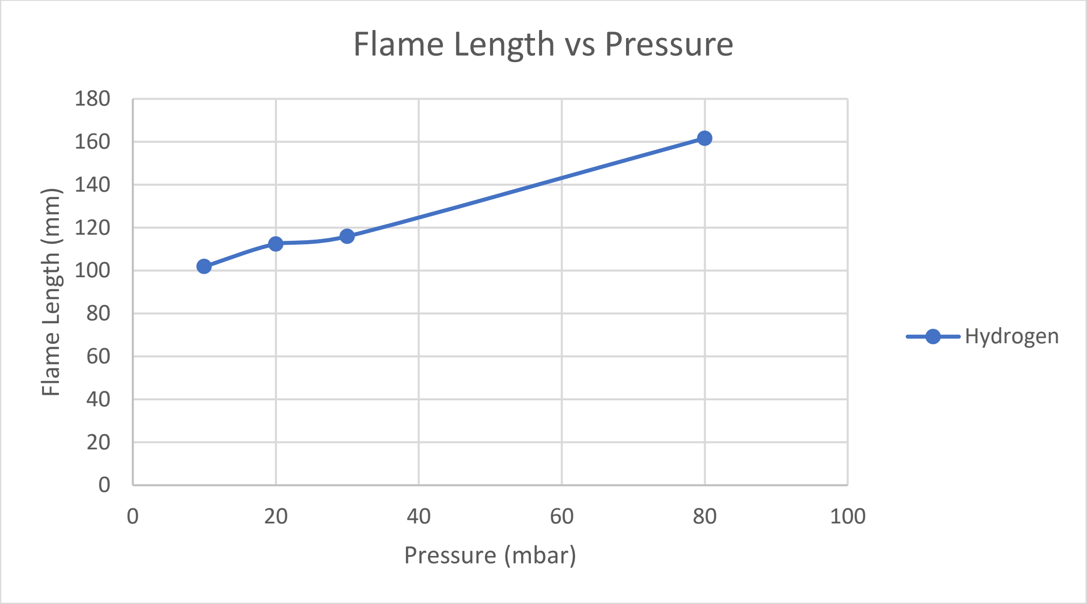


Figure 47– Comparison of hydrogen flame length with pressure for 0.3 mm drilled hole in copper pipe

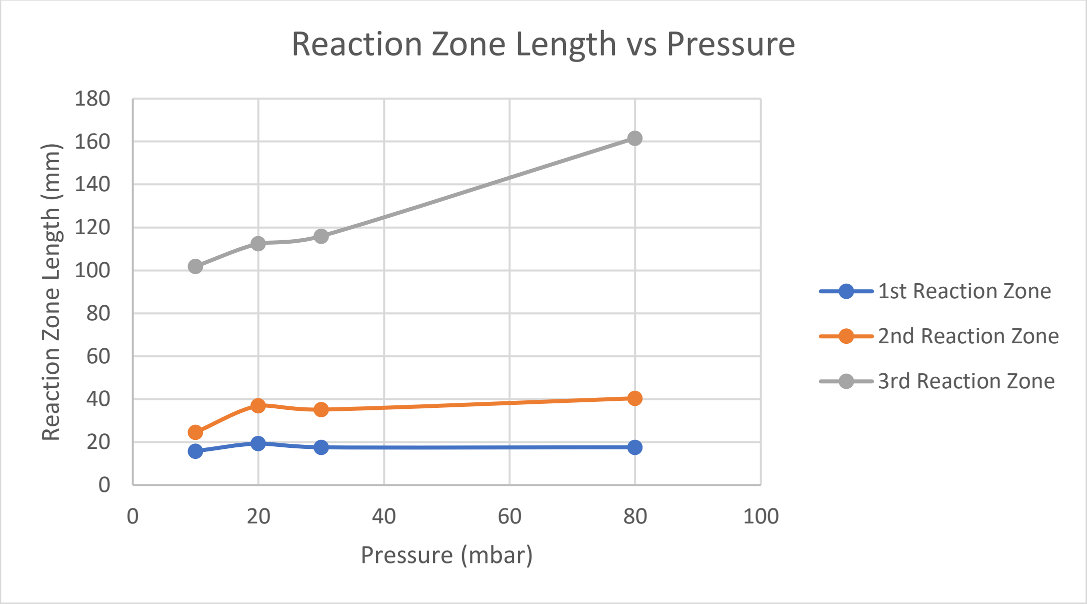


Figure 48 – Comparison of hydrogen reaction zone lengths with pressure for 0.3 mm drilled hole in copper pipe

7.5.5 Unsoldered joint

Similar trends were obtained for this set of experiments. Looking at the flame length, methane is much greater than hydrogen – approximately 80 mm longer than hydrogen at all pressures. Referring back to the reverse pitot tube, which was the only other experimental set up which could establish a methane flame, the difference in flame length was lower than this at approximately 50 mm. As would be expected, the reaction zone lengths of methane are greater than hydrogen as shown in Figure 49 and Figure 50.

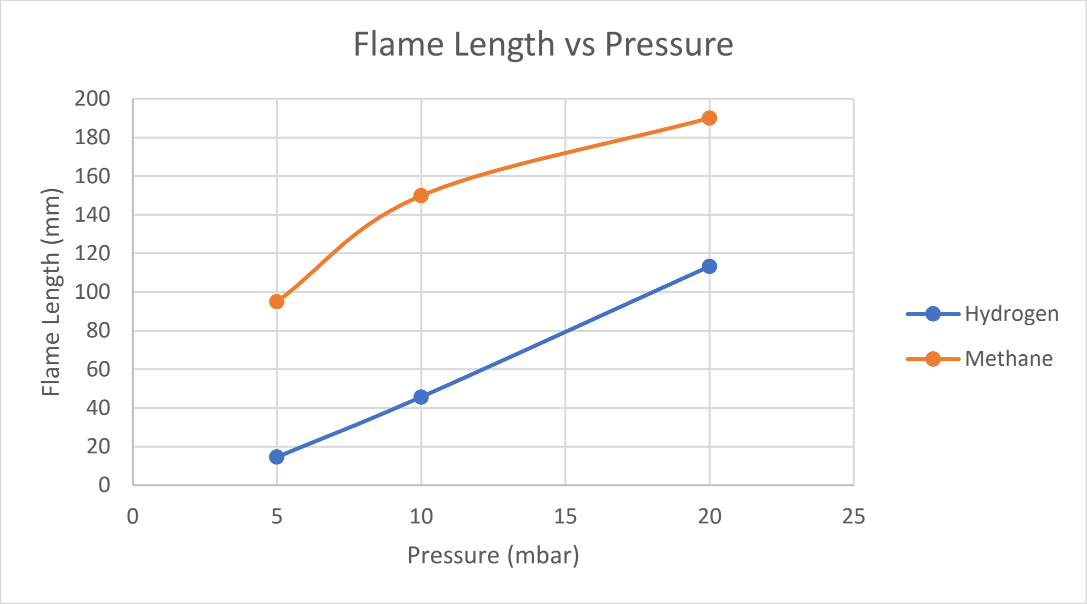


Figure 49 - Comparison of hydrogen and methane flame lengths for unsoldered joint

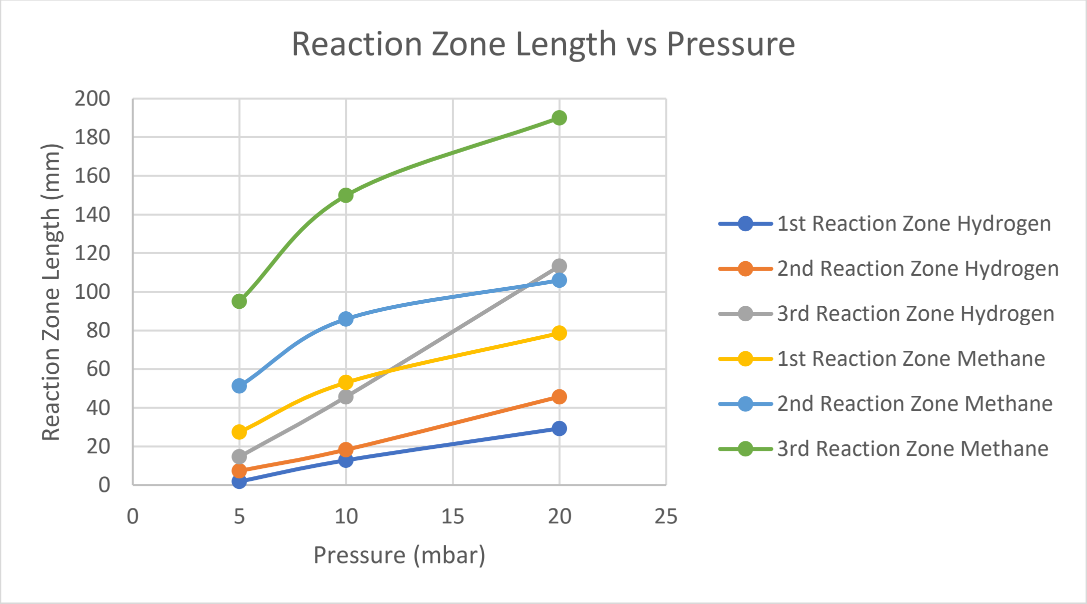


Figure 50 - Comparison of hydrogen and methane reaction zone lengths for unsoldered joint

Referring back to the digital images presented in Figure 31 to Figure 34, another difference that can be seen between the two flames for this set up is the distance from the exit of joint that the flame is positioned at. From the images, methane is seen to travel a greater distance from the exit than hydrogen. Measurements were made to the centreline and edge of the flames and results are shown below in Figure 51.

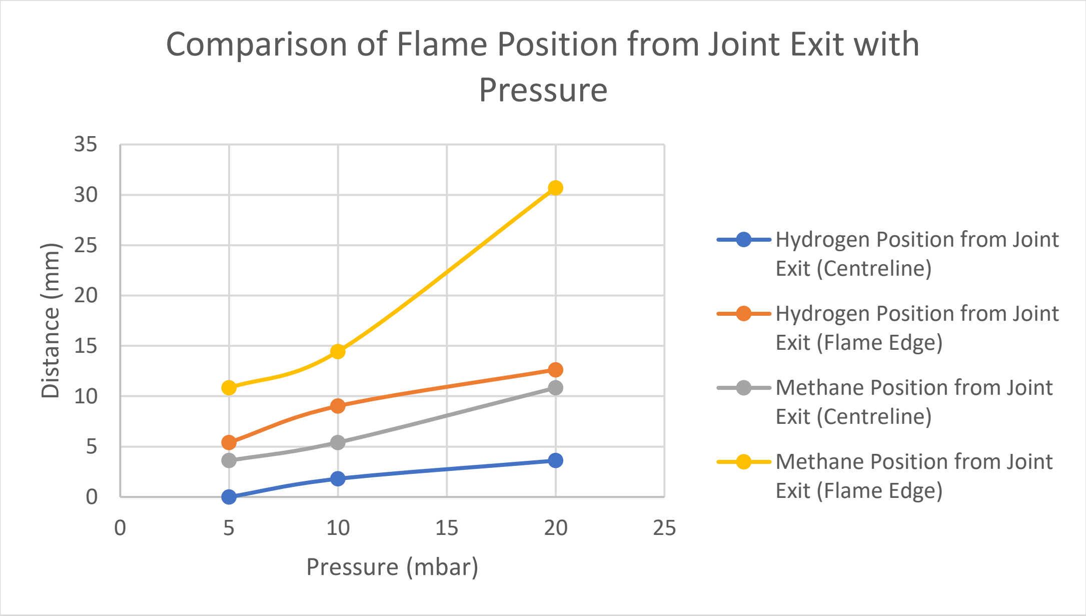


Figure 51 - Horizontal distance travelled by hydrogen and methane flames for unsoldered joint

From the results discussed, it should be realised that the flame length increases with pressure until turbulence is generated. Additionally, the hole size will affect the flame length due to the mass flow exiting the pipe. Generally, the flame length will decrease as hole diameter decreases. Figure 52 compares the flame lengths for each test for direct comparison.

Comparing the 0.5 mm and 1.0 mm drilled holes, the latter has a shorter flame due to the onset of turbulence at a low pressure of 5 mbar. Table 12 summarises the flame length results.

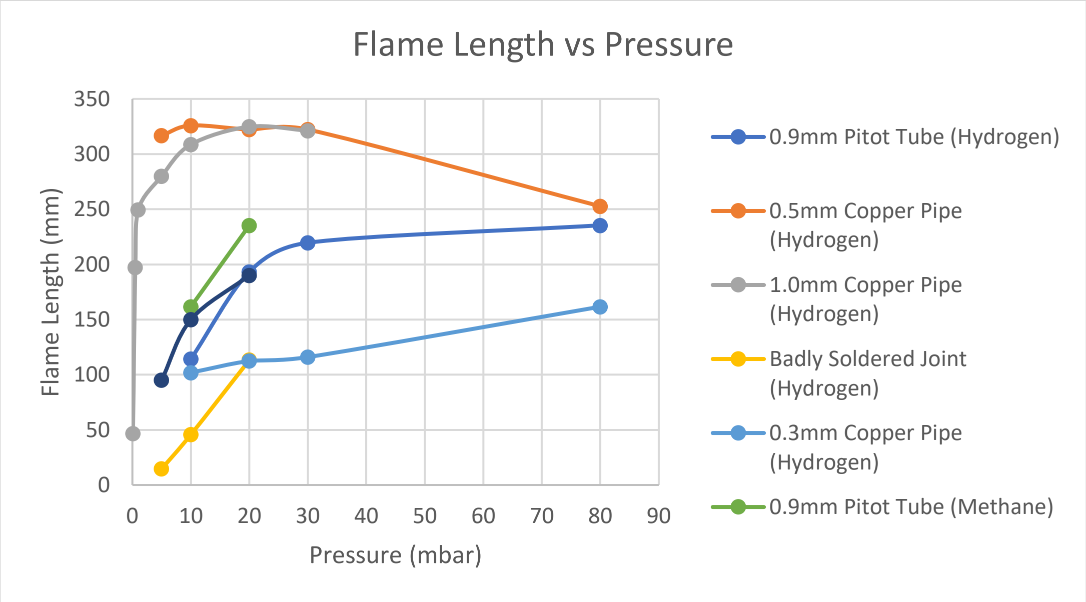


Figure 52 - Comparison of flame lengths for all test samples

Table 12 provides a comparison of flame lengths for all test samples.

Pressure (mbar)	Test Sample				
	0.9 mm Reverse Pitot Tube (Methane / Hydrogen)	Copper Pipe Test Pieces			
		1.0 mm	0.5 mm	0.3 mm	Unsoldered Joint (Methane / Hydrogen)
	Flame Length (mm)				
0.1	-	46.66	-	-	-
0.5	-	197.40	-	-	-
1	-	249.44	-	-	-
5	-	279.94	316.76	-	95.03 / 14.62
10	161.62 / 114.19	308.66	325.91	101.89	149.86 / 45.69
20	235.40 / 193.24	324.81	322.25	112.43	190.07 / 113.31
30	- / 219.59	321.22	322.25	115.94	-
80	- / 235.40	-	252.68	161.62	-

Table 12 - Comparison of flame lengths for all test samples

7.6 Ignition height and ignition distance

An important factor to investigate is the minimum ignition height required for an ignition source to lead to formation of a stabilised flame. This could be useful to provide data to determine a safe distance that appliances should be positioned from any potential ignition sources, such as plugs where the spark would be able to cause ignition.

To carry out these tests, a piezo igniter was used and set at different distances above the pipe exit. The spark from the igniter did not necessarily occur at the same place within the piezo igniter and it is not possible to state a true ignition height but the results are indicative of the trends. During the tests, in some cases, it was found that a flame would form on top of the igniter but was unable to propagate towards the source of fuel. This is most likely due to the structure of the igniter interfering with the reaction process and highlights the complex interplay between flow, reaction and structures. An example of this effect is shown by the IR image in Figure 53.

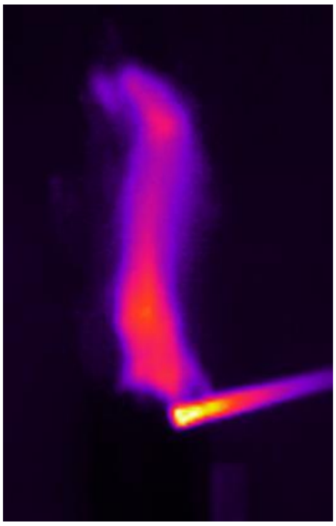


Figure 53 - IR image of flame position on top of igniter during ignition height tests for 1.0 mm drilled hole in copper pipe

Additionally, horizontal ignition distances were determined during the horizontal release regime. In these tests it is slightly more difficult to determine an accurate distance due to the buoyancy effects as already mentioned above.

As shown in Figure 54, the ignition height generally increases with pressure but as only a limited number of tests were performed, the result should be viewed as indicative at this stage. Generally, the larger hole diameters lead to higher ignition heights. This is due to a greater mass flow and greater concentration of reactants available in the flow, enabling the reaction to propagate from the spark backwards to the hole exit.

For the unsoldered joint, ignition distances are greater for methane than for hydrogen which would be expected since methane has a greater flame extent. At 20 mbar it should be noted that only one test proved positive for methane so further investigation is required.

For horizontal ignition, only the 0.5 mm copper pipe was selected so no measurements have been made for methane in this orientation. From Figure 55, the horizontal ignition distance between 10-30 mbar is lower than that of the ignition height. A surprising result is that the mixture can be ignited at a greater distance for the lower pressure of 5 mbar.

Overall, it has been determined that methane is unable to be ignited for drilled holes in copper pipe test pieces. It could be ignited for some conditions in the initial set-up study of the reverse pitot tube and for the unsoldered joint.

Hydrogen leakage ignition is possible for all leak sizes and flows studied here, and the ignition point can be reasonably distant from the leak point.

Additional work is required for investigation into determining an accurate ignition distance.

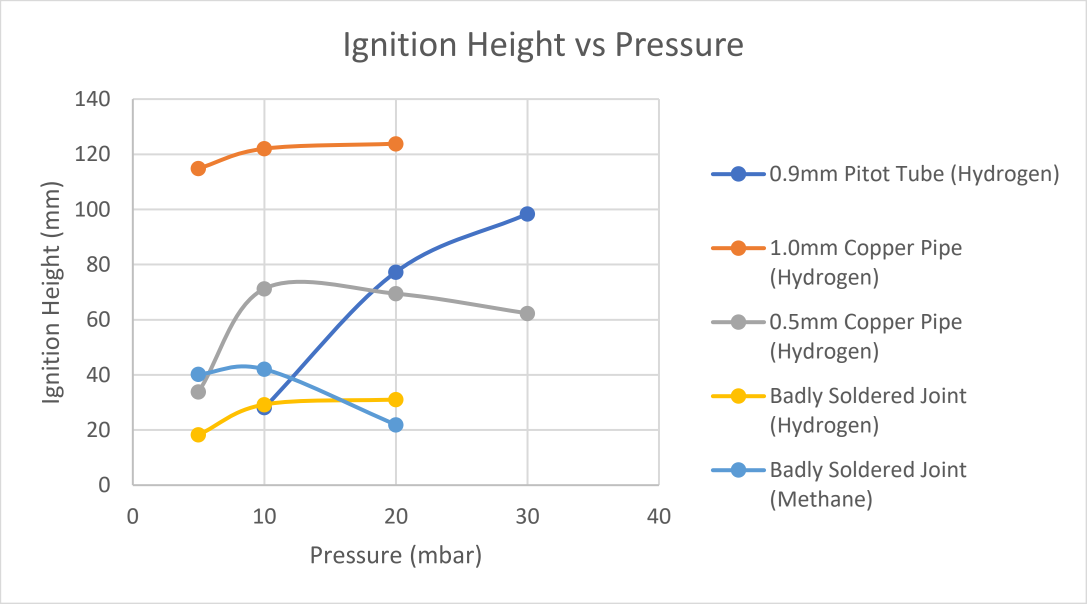


Figure 54 - Comparison of ignition heights for different test samples

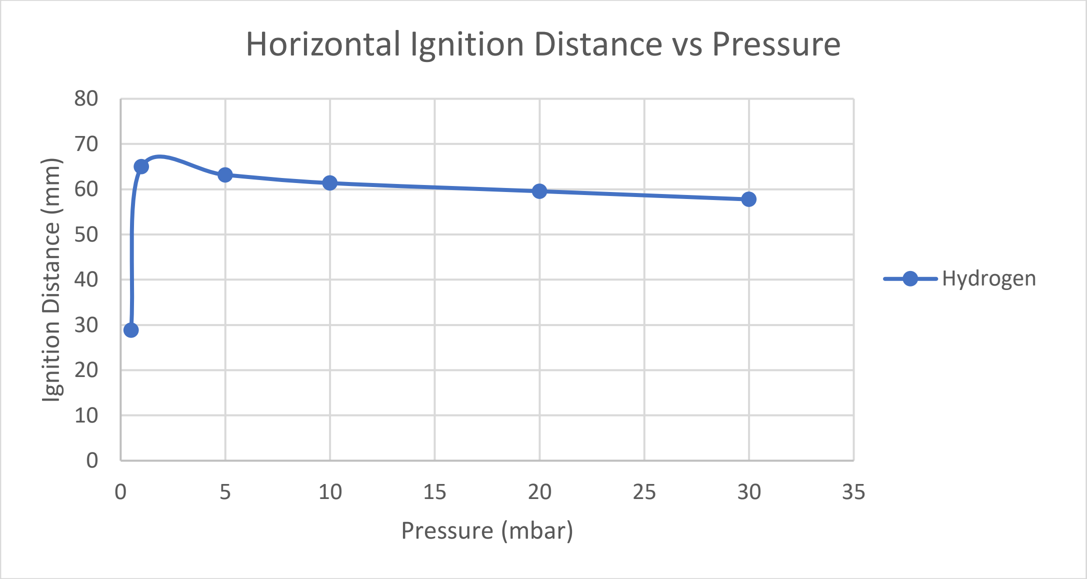


Figure 55 - Horizontal ignition distance for 0.5 mm drilled hole in copper pipe

7.7 Analysis of pipes pre- and post-ignition studies

High magnification optical images were taken of the holes drilled in the copper tubes before and after the ignition and flame tests.

Figure 56 shows the drilled holes before the start of the ignition and combustion tests. It can be seen that the 0.3 mm hole is less "neat" than the 0.5 mm and 1.0 mm holes reflecting the difficulty in machining these holes.

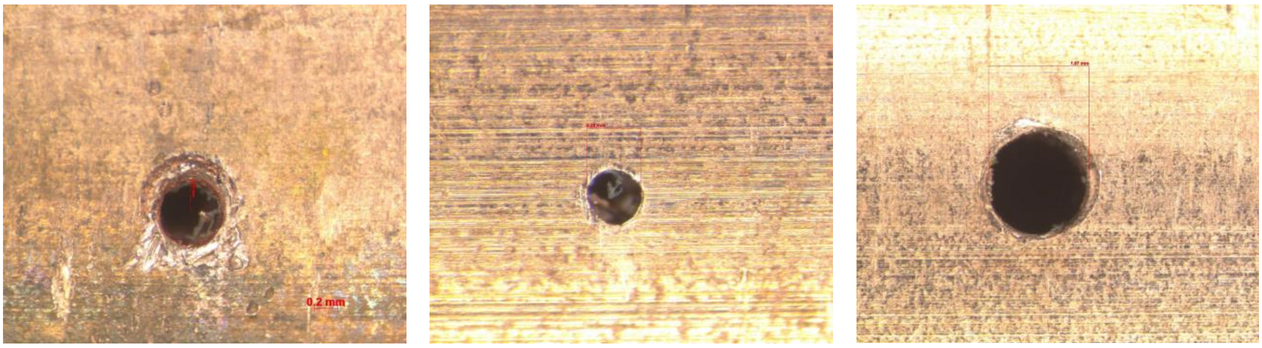


Figure 56 - Optical images of 0.3 mm (left), 0.5 mm (middle) and 1.0 mm (right) drilled holed in the copper pipes, before the ignition and flame tests

After the tests had been completed, the pipes were again analysed under an optical microscope to investigate the amount of corrosion or impact that the tests had caused. Images of the pipe holes after operation are shown in Figure 57.

From the images, it can be seen the damage caused by the flames.

There is clear scorching of the pipes near the holes as a consequence of the heat from the flames. As the hydrogen flames seem to "attach" to the pipe surface, there is darkening and oxidation caused by the elevated surface temperatures

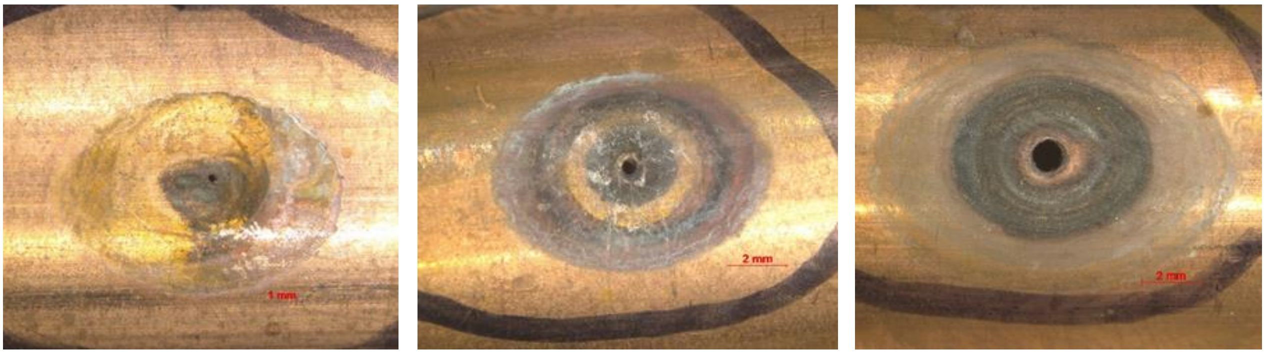


Figure 57 - Optical images of 0.3 mm (left), 0.5 mm (middle) and 1.0 mm (right) drilled holed in the copper pipes, after the ignition and flame tests

Further studies are required to investigate if degradation of the copper surface affects the overall integrity of the pipework infrastructure.

7.8 Outline options for hydrogen flame detection - thermal, ultraviolet and infrared detection

Thermal detectors should be placed directly above the site of the flame. However, if a leak occurs, a flame can develop in a different position which is not detected by the instrument. Another thermal device that can be used is a thermocouple for the detecting the presence of heat. Thermochromic materials can be used for thermal detection of flames. These materials contain a pigment which when exposed to heat, will cause a colour change on the surface of the material [19]. UV and IR radiation detectors are an alternative method of flame detection. Since hydrogen flames emit UV radiation, photo-electrons are emitted which create an electrical impulse [20]. Infrared detectors use IR sensor filters to enable visualisation of the flame but need to be designed to detect the low levels of infrared emitted [20].

7.9 Recommendations for future testing

In order to mitigate the risks and hazards identified in Section 7: colourant leakage testing (from a household pipe), the following additional leakage testing programme is recommended. This could include:

- Extended study on leakage from different hole sizes and the potential to establish hydrogen flames to include:
    - Other pipework types and failures (including connection hoses to cookers)
    - Extracts from installed domestic copper carcass to extend the study from idealised holes to ones that may be present in the wider population
- Combined studies on leak rate, ignition and gas tightness testing to increase the level of understanding on existing approaches for leak detection in particular with establishing a maximum permissible leak rate (MPLR) for hydrogen in the same manner as that for natural gas. (This will combine aspects from Hy4Heat Work Packages 2 and 7, and support the development of the Quantitative Risk Assessments (QRAs).
- Impact of ignition energy and ignition location on the potential to form a stable hydrogen flame on leaks from domestic pipework

  - Extend the current work to provide supporting information on flame development as a function of distance from the leak point and the ignition energy.(Again, with the aim of providing data for the QRAs).

8 CONCLUSIONS

The overall conclusion of this work is that a colourant is not required at all as it does not offer any additional benefit in relation to safety when compared to natural gas. Adding a colourant would incur additional costs, may have negative impacts on appliances and network operations, and may lead to potential health impacts.

More detail is given as follows:

8.1.1 The addition of a colourant into the network

- **High pressure flames** - High pressure hydrogen flames (typically > 2bar) can have increased luminosity if they entrain dust, solid particles or humidified air. This tends to result in an orange flicker and glow.
- **Network Operations** - Network operators have highlighted that addition of any colourant material to the hydrogen gas could result in network operational issues and could impact on some end users . These effects may include drop-out of liquid or solid, material integrity impacts and may possibly lead to detrimental effects on flow measurement, pressure control and other network operations.
- **Risk vs. benefit** - The technical and logistic problems with introducing a colourant into a network may introduce additional risk without significant benefit. Here, the nature of the colourant was considered with solids eliminated and water too from the viewpoint of network integrity. Volatile liquids could be added but the quantities required could result in liquid collection in the pipelines.

Our conclusion is that a colourant should not be added into the network:

  - High pressure flames from ignited releases from the pipeline network (> 2bar) will be visible due to the entrainment of dust or other material so a colourant is not required.
  - Network operators do not want to add colorant due to increased operational activities, potential increased risk to operatives working on the network and potential reduced performance on network equipment.
  - Adding colourant could add risk due to the additional process plant required, handling or processing of colourant to add, and potential failure modes of any colourant injection equipment.

8.1.2 The addition of a colourant into internal pipework or at the appliance

- **Flame visibility -** The ability of the eye to detect low luminosity hydrogen flames is influenced by the background surrounding to a far greater extent than for natural gas. Natural gas flames and burners can be surrounded by stainless steel, white enamel painted surfaces or other coloured material and are nearly always visible even if the burner is operating at a low (turn-down) rate.

  This is not the case for hydrogen in that white or light coloured backgrounds can render the flames nearly invisible. Even against black backgrounds it is sometimes difficult to distinguish hydrogen flames, especially if there is a bright, surrounding light level. Appliance manufacturers may need to address issues regarding flame visibility to ensure compliance with the Gas Appliance Regulations.

Where the flame is in an area which can be seen, there is therefore an increased risk when using hydrogen. However, where a flame is produced behind a kitchen cabinet or in a void where it cannot easily be seen, adding a colourant will not decrease the risk.

- **Supply pressure** - Flame visibility is also dependent on the supply pressure. A higher supply pressure produced a larger flame, and this increased flame "volume" assisted with visual detection. Although the guidance from the Hy4Heat team is that the preferred network and delivery pressures for hydrogen will be similar to those for the natural gas system, the lower calorific value of hydrogen may necessitate a slightly higher supply pressure. Slight increases on pressure will not significantly impact the flame luminosity
- **Coloured flame desirability** - If a colourant is required or desired for the indication of a flame at a cooker or decorative fire then there is a wide range of materials for the appliance manufacturers to choose from (from a practicality, ease of delivery and user operability perspective, an aqueous salt solution may be a suitable candidate).

  Thermochromic materials can also be used for thermal detection of flames. These materials contain a pigment which when exposed to heat, will cause a colour change on the surface of the material. This option could provide manufacturers with a desired flame colour for fires and cookers.
- **Appliance risks** - Alongside the practicality of adding colourant at the appliance, we have also considered the main risks (deposition on metal surfaces, enhanced corrosion rates and potential production of particulates in the combustion products).
- **Flame detection** - Thermal flame detectors can be used to detect a hydrogen flame but must be placed directly above the site of the flame. However, if a leak occurs, a flame can develop in a different position which is not detected by the instrument. This is an increased risk which must be considered fully by the appliance manufacturers.

  UV and IR radiation detectors can also be used as alternative methods of flame detection. Since hydrogen flames emit UV radiation, photo-electrons are emitted which create an electrical impulse. Infrared detectors use IR sensor filters to enable visualisation of the flame but need to be designed to detect the low levels of infrared emitted. As for thermal flame detectors, this is an increased risk which must be considered fully by the appliance manufacturers.

Our conclusion is that a colourant should not be added into the internal pipework or at the appliance:

- A colourant cannot help to detect a flame that cannot be seen (i.e. produced behind a kitchen cabinet or in a void).
- A colourant may impact on the performance and safety of an end-use appliance.
- A colourant may impact on the potential use of the hydrogen in fuel cell systems.
- A colourant will only be required for decorative fires and cookers (not for boilers). Where a coloured flame is desired, this can easily be provided by the manufacturer through use of additives or inserts.
- Flames detection methods are readily available to appliance manufacturers to detect hydrogen flames, and UV sensors may provide the most appropriate approach.

Addition of colourant into the domestic pipework does not appear to produce a reduction in risk for unignited or ignited releases. Any addition of colourant has the potential to add additional risk factors including material handling problems and failures in the addition process.

As colourant may be required only for exposed flame burners (cookers, hobs or fires) it is proposed that methods to add colour at the point of use are considered to be the best option.

8.1.3 Alternative methods to create a coloured flame or provide a flame indication at the appliance should be considered where desirable

Where a coloured flame is desirable at the end use appliance (for a fire or cooker), there are a number of ways this can be achieved safely, and these are being investigated by appliance manufacturers

- Use of temperature sensors and indicators, possibly LED systems, especially for cooker hobs as there are parallels with current hot surface indication for ceramic/electric hobs.
- Consideration of a coating on decorative coals for use in fires. This could take up some of the information on flame colouration using metal salts, recognising that the flue products will be discharged external to the home.
- Consideration of flame inserts that could radiate when hot or provide additional flame colour.

8.1.4 Additional Risks have been identified through leakage testing

- **Ease of ignition** - A key finding from the leakage test work undertaken was the ease of ignition of small hydrogen leaks from holes in domestic copper gas supply pipework. Pin holes in the pipe give rise to gas leakage and hydrogen can be ignited easily to form a flame that attaches to the pipe at the point of release whereas natural gas did not form a stable flame. Also, hydrogen could be ignited at a significant distance from the pin hole.

  These different characteristics of hydrogen and natural gas highlight that further comparative studies are required to evaluate the potential change to the evaluation of risk.

  This will also need to consider the impact on the frequency or probability of a leak resulting in an ignition which could then give rise to a secondary fire, if the flame impinges on a combustible surface.

- **Ignition distances** - Ignition of the flames could occur at a significant distance from the hole, dependent on the pressure and the hole diameter. For example, for a 1 mm hole diameter with a hydrogen supply pressure of 20 mbar, a flame can be established with a spark ignition from a piezo igniter held at around 12 cm above the pipe.

  This example highlights that a risk evaluation is required to understand the probability that a hydrogen leak could develop into a flame and cause a secondary fire if it impacts on combustible material. This phenomenon is not observed for natural gas flames which would not ignite or produce a stable flame.

- **Flame retention** - Leakage testing from holes in the copper pipework all produced stable hydrogen flames when the leak was ignited and these flames were attached to the pipe at the leak point. This was not the case for methane flames. The relative risks of a hydrogen leak producing a hydrogen flame vs. a methane leak not producing a flame needs to be considered.

- The unsoldered joint leak test demonstrated that both hydrogen and natural gas can be ignited and retained around a badly assembled joint. The natural gas leak produced a visible yellow flame around the joint whereas the hydrogen flame was not very luminous.

Our conclusion is that there are additional risks that need to be further investigated:

- Hydrogen can be ignited more easily than natural gas to form a flame. Further comparative studies should be undertaken to evaluate the potential change to the evaluation of risk.
- Ignition of a hydrogen flame could occur at a significant distance from the point of leakage. A risk evaluation is required to understand the probability that a hydrogen leak could develop into a flame and cause a secondary fire if it impacts on combustible material
- Hydrogen forms a stable flame that attaches to the pipe at the point of release whereas natural gas does not form a stable flame. The relative risks of a hydrogen leak producing a hydrogen flame vs. a methane leak not producing a flame needs to be investigated.

APPENDIX A: STAKEHOLDER QUESTIONNAIRE TEMPLATE

Questionnaire on options for colourants for hydrogen flames

Please help us by completing this short survey

We are contacting industry colleagues to gather views and opinions on the requirement for colourant for hydrogen gas. Hydrogen flames are not as luminous as natural gas flames and we would welcome suggestions on options for making the flames more visible.

This survey only takes a few minutes to complete so we'd be grateful if you could help us with our research. Information received will be treated confidentially but we hope to be able to summarise all the information through the Hy4Heat programme.

Background

The Hy4Heat programme is a feasibility study into the use of hydrogen for heat in UK homes and businesses aimed at establishing whether it is technically possible, safe and convenient to replace methane with hydrogen in residential and commercial applications.

The Department for Business, Energy and Industrial Strategy (BEIS) has appointed Arup+ as the programme management contractor for the Hy4Heat programme to manage and co-ordinate the various work packages within the programme, including Work Package 2 which will look specifically at hydrogen purity and flame colourisation.

DNV GL has been appointed to deliver Work Package 2, alongside The Health and Safety Executive Laboratory (HSL), The National Physical Laboratory (NPL), Element Energy and Loughborough University.

This work package comprises two distinct phases:

Phase 1 will evaluate the varying hydrogen purity levels available in the UK and the potential impacts and cost effectiveness of introducing hydrogen at these quality levels into the wider distribution network and to recommend a purity level for use by the Hy4Heat programme.

Phase 2 will determine if there is a requirement for adding a colourant to hydrogen to ensure safe burning and user acceptance is achieved, and to investigate the optimum solution if a colourant is required.

Hydrogen Gas Flame Characteristics

Hydrogen flames are not as luminous as natural gas flames and may be difficult for the homeowner to see in some instances. The flame luminosity is dependent on burner type and aeration

Q1. Do you believe that the majority of people in your organisation are aware of the low luminosity of hydrogen gas flames?

A. Yes / No / Don't Know

Q1a. Can you let us know why you've answered in this way?

Q1b. Has your organisation (or staff) seen hydrogen burning?

It is possible to increase the luminosity of flames by introducing a colourant compound.

Q2. Do you think a Colourant will be required if hydrogen replaces methane in the gas network?

A. Yes / No / Don't Know

Q2a. Can you let us know why you've answered this way?

Q2b. If you answered "YES", which type of appliances might require coloured flames?

Q2c. Do you think such colorant might be deleterious to some appliances? Which ones?(see also Q7)

Q2d. What risks might colorant addition bring?

Options for Colourant Addition

The colourant could be added as a gas, liquid or solid. All aspects of the colourant will need to be considered including potential detrimental impacts on pipework (or pipelines), control systems, burners emissions and heat transfer surfaces.

Q3. Do you think a Colourant should have a particular physical characteristic?

A. Yes / No / Don't Know

Q3a. For example, do you think a gas, liquid or solid Colourant should be selected? Or if another method should be used to highlight the presence of flame?

Q3b. Please indicate if you have a particular recommendation - Gas, liquid, solid, other method?

Q3c. Can you tell us why you have this preferred approach?

The location for colourant addition may impact on the options available for colourant selection. It could be introduced into the pipeline network and distributed to all end users (although some may not need it), or it could be added locally into specific appliances.

Q4. What location do you think would be best for the Colourant to be added to the hydrogen gas?

A. Pipeline / appliance / don't Know

Q4a. Please say why you've answered this way

Management of the Colourant Addition

If the colourant is injected into the pipeline then this will impact on all downstream use, and the colourant must not impact on the safe distribution and use of the hydrogen. If it is added at the appliance, then systems must be in place to manage the colourant addition and checks made to ensure that it is present as and when needed. Also, the colourant addition must be able to scale with the controls and the addition rate must turn down in line with the burner setting.

Q5. What processes or systems are needed to manage colourant addition?

Q5a. Please provide information on your preferred method or approach?

Q5b. Is the description offered above flawed? Would you adopt a fundamentally different approach to the issue of flame visibility in appliances? If so, can you share this with us?

If the colourant is added at the appliance, then who will be required to do maintenance and replacement of colourant when it runs out during normal operation. The consumer could replace this or is a GasSafe engineer required to make the change.

Q6. If the Colourant could be added at the appliance, do you think the public could add / replace it, provided the process was in accord with the GS(I&U)R i.e. without tools?

A. Yes / No / Don't Know

Q6a. Can you let us know why you've answered this way?

Safety considerations of the colourant

If the colourant is injected into the pipeline, then this will impact on all downstream use in all appliances. If it is added at the appliance, then it will only impact on that appliance.

Safe operation of the appliances and equipment is of prime importance.

Q7. Do you think the Colourant will impact on the safe operation of the burners or appliance?

A. Yes / No / Don't Know

Q7a. Additional Information (please provide additional comments to support your views):

Q8. Do you think the Colourant will impact on consumers?

A. Yes / No / Don't Know

Q8a. Additional Information (please provide additional comments to support your views):

Q8b. Let us know if there's anything else that you think we should be considering regarding the use of Colourant with hydrogen gas?

APPENDIX B QUESTIONNAIRE RESPONSES

The questionnaire was sent to a number of senior engineers and/or managers from leading manufacturers, consultancies, testing organisations, and also trade associations for distribution to their members.

Questionnaire responses were received from 11 companies / organisations – names of the companies/organisations have been removed for the purposes of this report.

Hydrogen Flame Characteristics

Q. Do you believe that the majority of people at your organisation are aware of the low luminosity of hydrogen gas flames?

Manufacturer

NO - Nobody needs to be aware of the low luminosity of hydrogen flames unless it's a vital safety issue.

Burner manufacturer

Yes -We have been investigating Hydrogen for 2-3 years now as an alternative to methane gas.

Tester

The majority of people in my organisation are not combustion experts and probably have little or no knowledge of hydrogen combustion

Manufacturer

No - Personnel involved in product development are aware. Attended Hydrogen introduction meetings

Q. Has your organisation (or staff) seen hydrogen burning

Manufacturer

No

Manufacturer

We have undertaken extensive test work on hydrogen combustion. A normally aspirated flame is visible (only just) with a slight yellow tinge. A premixed flame is invisible to the naked eye.

Tester

Not all of them – but quite a few of us, yes

Manufacturer

Yes

Q. Do you think a colourant will be required if hydrogen replaces methane in the gas network?

Manufacturer

Yes and No - I've answered yes and no, because some sort of indication for customers of a flame will be necessary for some products like 'gas-hobs'. In other products like those with a case a colourant will not be needed. But indication of a flame doesn't have to be a colourant in the gas itself, and hence also the partial 'No' answer.

Manufacturer

Don't know - While I can understand that colourant would be a great help to gas cooking hobs and gas fires, I am not sure that the size of these markets warrants the technical challenges of adding a colourant. I do understand the H&S implications, but it may be easier to resolve the visibility issue at the appliance. Particularly with gas fires it depends on the primary function of the appliance, provide a heat source or look nice?

Tester

Yes - The safety case for quite a few appliance types depends (or is influenced) by the visibility of the flame…

Manufacturer

Yes - Safe operation of some appliances is fundamentally dependent upon the flames being visible for instance open burners on cooking products and flame effect space heating appliances where accidental burns or ignition of clothing etc. could be an issue. EN30-1-1 requires burner flames to be visible to the user during operation.

Adjustment of burner flames is often by eye and not by looking at the burner control.

If burners have been incorrectly assembled the flame picture is often the clearest indication that this is the case.

Q. Which type of appliances might require coloured flames?

Manufacturer

Gas hobs. Gas fires.

Manufacturer

Gas Hobbs, Gas Fires

Tester

Those where the flame is accessible, and visibility is part of the protection strategy to avoid accidental contact, burns etc (whether this is conscious or not…). So gas cookers, fires, some catering products… etc.

Manufacturer

Cooking and some space heating appliances where open flames are present

Q. Do you think such colorant might be deleterious to some appliances? Which ones?

Manufacturer

Potentially Fuel Cells, although it depends on the nature of the colourant.

Manufacturer

This depends on the colourant and how it reacts to water, heat and the surrounding components. This is true of all appliances a colourant in the gas may have an adverse effect on boilers, though boilers do not need colourant.

Tester

No idea – will depend on the method and specific colourant to be added

Manufacturer

Don’t know, depends upon the substance or method used. The correct colourant selection is required that does not impact on supply and product systems

Q. What risks might colorant addition bring?

Manufacturer

Burning chemicals in a hot flame can produce some unexpected chemical by-products. Colourant should be chosen for simple decomposition pathways and low levels of inherent toxicity.

Manufacturer

Corrosion, Staining, Smell, Hazardous Fumes, Burner port issues

Tester

Clearly using the wrong type of chemical to provide a colourant could have an impact on the combustion process (potentially producing unwanted emissions) or potentially adversely affecting the safety and reliability of gas appliances (e.g.: affecting the seals of gas valves, causing corrosion etc…)

Manufacturer

May have a detrimental effect on the combustion of the Hydrogen depending upon material selection. May affect appliance materials

Options for Colourant Addition

Q. Do you think a colourant should have a particular physical characteristic?

Manufacturer

Yes

Manufacturer

Don’t know

Tester

No

Manufacturer

Yes

Q. For example, do you think a gas, liquid or solid colourant should be selected? Or if another method should be used to highlight the presence of flame?

Manufacturer

Yes – Gas

Manufacturer

Yes – Gas and other method

Q. Please indicate if you have a particular recommendation Gas, liquid, solid, other method?

Manufacturer

I am a bit surprised by this question. I would assume the colourant inside a gas flow would itself be made of gas molecules.

Manufacturer

Good Luck keeping the colourant in the gas?

Manufacturer

Gas, preferably with similar properties to Hydrogen needs to be homogeneous

Q. Can you tell us why you have this preferred approach?

Manufacturer

How would you stop a liquid from congealing inside an apparatus and how would a solid colourant get to the end consumer?

Manufacturer

Can be added upstream and managed in a more controllable manner and not reliant on end consumer.

Alternative method may be via system such as IR flame detection and visible indicator light system although this is not fool proof and would require each burner to have indicator on the appliance adjacent to the control if a flame presence is detected. Another option would be for flame impingement on a material to produce a visible flame within the burner design

Q. What location do you think would be best for the colourant to be added to the hydrogen gas? Please say why you've answered this way

Manufacturer

Appliance - I actually don't think you should add a colourant to the gas itself. Most devices don't require customers to know there is a naked flame, and in my opinion the future is fuel cells so there won't be a naked flame for most devices anyway(fuel cells don't burn hydrogen in the traditional sense). For those devices where a customer is required to monitor the flame you could detect either heat or UV light coming off a hydrogen flame and this then triggers a signal indicator that the customer can see.

If you must have some sort of colourant injected into the gas, then this could be an option in gas hobs or gas heaters at the time of ignition, probably by injecting some liquid along with the igniting spark. Even a liquid as simple as ethanol will burn nicely and cleanly and it is already a consumer facing product (as in the non-drinking type). There would be a safety issues in having a flammable liquid alongside a source of ignition, but it's OK for cigarette lighters so I guess it's not technically difficult.

Manufacturer

Don't know

Tester

There is no "right answer" here – there are pros and cons for each and a lot more analysis would be needed to reach a meaningful decision. Adding for all users will deal with the visibility risks from all appliances (but may be a burden on some appliance types) but adding locally brings huge challenges to ensure the visibility remains for the life of the product.

Manufacturer

Pipeline - Consistency of approach that does not require regular replenishment. Unless the colourant method is an integral part of the product design i.e. flame impingement on a metal component of the burner to produce a visible flame. Must NOT be reliant on end user.

Management of the Colourant Addition

Q. What processes or systems are needed to manage colourant addition. Please provide information on your preferred method or approach?

Manufacturer

Don’t know

Tester

No preferred solution – this is an economic choice once all the risks have been addressed.

Manufacturer

Preferred approach is for gas supplier to add to pipeline and control

Q. Is the description offered above flawed? Would you adopt a fundamentally different approach to the issue of flame visibility in appliances? If so can you share this with us?

Manufacturer

Just in case, obviously the colourant has to luminesce in a hot flame (either natural fluorescence/phosphorescence or as part of decomposition) to give it a colour. The gas itself doesn’t have to be coloured at room temperature as that would be difficult and no-one would expect that. Anyway, there is not a lot of light in dark kitchens in Winter, so some people wouldn’t see a coloured gas due to poor lighting. For gas leaks of unburning hydrogen an odorant should be used.

My preferred approach would be to use Inorganic Fluorescence Pigments

It would be an interesting design challenge for gas flame products to come up with different designs of fluorescent pigments to attract customers. More than just a safety feature, it could become a design feature a unique product offering. For instance, green glowing rings on hobs when there is a hydrogen flame? Gas flame heaters with dancing rainbow colours on the glass panel?

Manufacturer

The flame visibility is not an issue with boilers. The fundamental question is, does the flame need to be visible in other appliances? Will some kind of radiant indicator suffice?

Tester

If the chemical risk is found to be high, I would personally adopt an approach that prohibited accessible naked flames, which would remove the visibility issue as a significant risk.

Manufacturer

If above approach is not possible then permanent material within appliance is required to produce luminous flame or indicator light system within product. It is fundamental that the end consumer is not required to add a colourant.

Q. If the colourant could be added at the appliance, do you think the public could add / replace it, provided the process was in accord with the GS(I&U)R i.e. without tools? Can you let us know why you’ve answered this way?

Manufacturer

Yes - You let the public use cigarette lighters even though that is inherently dangerous, and they could hurt themselves. You let the public wear perfume and smoke even though that perfume aerosol is (20%?) ethanol. I don’t see that refilling a colourant liquid needs to be any more dangerous than this. Also, it’s an interesting design challenge for engineers.

If the colourant injection doesn’t happen into the gas line, but into the flame or onto a nearby object, a gas-safe engineer would not be needed. For those who need support any professional handy-person should also be able to run maintenance as they are not modifying the gas line itself. Q7a. Do you think the colourant will impact on the safe operation of the burners or appliance?

Manufacturer

Any potential for a hydrogen leak should be avoided. It follows that a colourant vessel that can be replaced or refilled could possibly leak at the interface. Unless the design is fail safe then this should be avoided.

Tester

No - Extremely unlikely that this could be made fool proof, as this would require interfering with gas circuits, whether or not this require tools. System would have to ensure appliances remained safe if users forgot (or didn’t bother) to replace colourant too.

Manufacturer

No - Reliance on the user adds another risk element to human interaction with the product. Appliances with the highest human interaction for instance cooking appliances already have the highest inherent risks associated that rely on correct use. Needs to be a fool proofed method and NOT reliant upon the public and must NOT impact of safe use of the appliance

Safety Considerations of the Colourant

Q. Do you think the colourant will impact on the safe operation of the burners or appliance?

Manufacturer

That is a question for appliance makers and depends on colourant method and chemical composition.

Manufacturer

Dependant on colourant could block burner ports over time. An easily visible flame will clearly be safer than a near invisible one.

Manufacturer

No - Colourant needs to be inert in terms of impact on combustion and also on materials used within the gas systems

Q. Do you think the colourant will impact on consumers?

Manufacturer

Yes - I assume a colourant will be needed. I forget my gas hob is on all the time, but at least I can see it when I walk past.

Manufacturer

Don’t know - Depends on the appliance design, and even then, there will be some aesthetic differences that may impact the consumers (especially with fires)

Manufacturer

No - If the flame is as visible as the current natural gas/LPG flames then no issue

Q. Let us know if there's anything else that you think we should be considering regarding the use of colourant with hydrogen gas?

Manufacturer

Not to do with hydrogen gas but a general safety feature – I am surprised that gas hobs and gas fires don't have a solenoid shut valve that is working on a timer to naturally turn off gas supply after a certain period (say 1 hour). The customer should then have to press a switch to re-open the solenoid valve. It's a pain for the customer to press a switch but if they aren't in front of the flame anyway then maybe it's a good idea to turn it off for them. It's also an interesting challenge for engineers how to get customers attention to the product they are using.

Obviously, this is not for gas boilers as they need a constant supply of gas and run autonomously or for gas-hobs in professional kitchens as it is a workplace. However, for domestic consumers it could be handy.

APPENDIX C: CLASSIFICATION OF COLOURANT OPTIONS

Item	Compound name	CAS Number	Harmonised classification		SDS Classification	
			Harmonised (Yes/No)	Classification	SDS Company	Classification
1	Carbon Dioxide	124-38-9	No	N/A 10 ECHA submissions for H332 - Acute toxicity inhalation, category 4	BOC	H280 - Gas under pressure, liquefied gas
					Matheson	Gas under pressure, compressed gas STOT-SE 3 (central nervous system)
1A	Carbon Dioxide (5%)	-	No	N/A	-	N/A
2	Methane	74-82-8	Yes	Gas under pressure H280 - Gas under pressure, compressed gas	BOC	H220 - Flammable gas, category 1 H280 - Gas under pressure, compressed gas
2A	Methane (10%)	-	No	N/A	-	N/A
3	Propane	74-98-6	Yes	Gas under pressure H280 - Gas under pressure, compressed gas	BOC	H220 - Flammable gas, category 1 H280 - Gas under pressure, liquefied gas
3A	Propane (10%)	-	No	N/A	-	N/A
4	Nitrous Oxide	10024-97-2	No	N/A 4 ECHA submissions for H330 - Acute toxicity inhalation, category 2	BOC	H270 - Oxidising gas, category 1 H280 - Gas under pressure, liquefied gas

Item	**Compound name**	**CAS Number**	**Harmonised classification**		**SDS Classification**	
			Harmonised (Yes/No)	**Classification**	**SDS Company**	**Classification**
4A	Nitrous Oxide (1%)	-	No	N/A	-	N/A
5	Water	7732-18-5	No	N/A	Sigma-Aldrich	-
6	Ammonia	7664-41-7	Yes	Gas under pressure H221 - Flammable gas, category 2 H331 - Acute toxicity inhalation, category 3 H314 - Skin corrosion, category 1B H400 - Acute aquatic toxicity, category 1	Sigma-Aldrich	H221 - Flammable gas, category 2 H280 - Gas under pressure, compressed gas H331 - Acute toxicity inhalation, category 3 H314 - Skin corrosion, category 1B H400 - Acute aquatic toxicity, category 1 H410 - Chronic aquatic toxicity, category 1
7	Ethanol	64-17-5	Yes	H225 - Flammable liquid, category 2	Sigma-Aldrich	H225 - Flammable liquid, category 2 H302 - Acute toxicity oral, category 4 H319 - Eye irritation, category 2 H371 - STOT-SE 2
8	Methanol	67-56-1	Yes	H225 - Flammable liquid, category 2 H301 - Acute toxicity oral, category 3 H311 - Acute toxicity dermal, category 3 H331 - Acute toxicity inhalation, category 3 H370 - STOT-SE 1	Sigma-Aldrich	H225 - Flammable liquid, category 2 H301 - Acute toxicity oral, category 3 H311 - Acute toxicity dermal, category 3 H331 - Acute toxicity inhalation, category 3 H370 - STOT-SE 1 (eyes)
9	Propanone	67-64-1	Yes	H225 - Flammable liquid, category 2 H319 - Eye irritation, category 2 H336 - STOT-SE 3	Sigma-Aldrich	H225 - Flammable liquid, category 2 H319 - Eye irritation, category 2 H336 - STOT-SE 3 (central nervous system)

Item	Compound name	CAS Number	Harmonised classification		SDS Classification	
			Harmonised (Yes/No)	**Classification**	**SDS Company**	**Classification**
10	Butanone	78-93-3	Yes	H225 - Flammable liquid, category 2 H319 - Eye irritation, category 2 H336 - STOT-SE 3	Sigma-Aldrich	H225 - Flammable liquid, category 2 H319 - Eye irritation, category 2 H336 - STOT-SE 3 (central nervous system)
11	Tetrachloromethane	56-23-5	Yes	H301 - Acute toxicity oral, category 3 H311 - Acute toxicity dermal, category 3 H331 - Acute toxicity inhalation, category 3 H351 - Carcinogenicity, category 2 H372 - STOT-RE, category 1 H412 - Chronic aquatic toxicity, category 3 H420 - Hazardous to the ozone layer, category 1	Sigma-Aldrich	H301 - Acute toxicity oral, category 3 H311 - Acute toxicity dermal, category 3 H331 - Acute toxicity inhalation, category 3 H317 - Skin sensitisation, category 1B H351 - Carcinogenicity, category 2 H372 - STOT-RE, category 1 H412 - Chronic aquatic toxicity, category 3 H420 - Hazardous to the ozone layer, category 1
12	Chloroform	67-66-3	Yes	H302 - Acute toxicity oral, category 4 H331 - Acute toxicity inhalation, category 3 H315 - Skin irritation, category 2 H319 - Eye irritation, category 2 H351 - Carcinogenicity, category 2 H361d - Reproductive toxicity, category 2 H372 - STOT-RE, category 1	Sigma-Aldrich	H302 - Acute toxicity oral, category 4 H331 - Acute toxicity inhalation, category 3 H315 - Skin irritation, category 2 H319 - Eye irritation, category 2 H351 - Carcinogenicity, category 2 H361d - Reproductive toxicity, category 2 H336 - STOT-SE, category 3 (central nervous system) H372 - STOT-RE, category 1
13	Tribromofluoromethane	353-54-8	No	N/A No ECHA submissions for acute toxicity	Sigma-Aldrich	H315 - Skin irritation, category 2 H319 - Eye irritation, category 2 H335 - STOT-SE, category 3 (respiratory system)

Item	**Compound name**	**CAS Number**	**Harmonised classification**		**SDS Classification**	
			Harmonised (Yes/No)	**Classification**	**SDS Company**	**Classification**
14	Ferrocene	102-54-5	No	N/A Over 400 ECHA submissions for H302 - Acute toxicity oral, category 4 4 ECHA submissions for H332 - Acute toxicity inhalation, category 4	Sigma-Aldrich	H228 - Flammable solids, category 1 H302 - Acute toxicity oral, category 4 H332 - Acute toxicity inhalation, category 4 H361 - Reproductive toxicity, category 2 H373 - STOT-RE, inhalation category 2 (liver) H410 - Chronic aquatic toxicity, category 1
15	Butyryl Ferrocene	1271-94-9	No	N/A 10 ECHA submissions for H302 - Acute toxicity oral, category 4, H312 - Acute toxicity dermal, category 4 and H332 - Acute toxicity inhalation, category 4	Thermo Fisher	H302 - Acute oral toxicity, category 4 H315 - Skin Corrosion/irritation, category 2 H319 - Serious Eye Damage/Eye Irritation, category 2 H335 - STOT-SE, category 3
16	Chromium Hexacarbonyl	13007-92-6	No	N/A 23 ECHA submissions for H301 - Acute toxicity oral, category 3 3 ECHA submissions for H331 - Acute toxicity inhalation, category 3	Sigma-Aldrich	H301 - Acute toxicity oral, category 3
17	Molybdenum Hexacarbonyl	13939-06-5	No	N/A 42 ECHA submissions for H300 - Acute toxicity oral, category 2, H310 - Acute toxicity dermal, category 2 and H330 - Acute toxicity inhalation, category 1	Sigma-Aldrich	H300 - Acute toxicity oral, category 2 H310 - Acute toxicity dermal, category 2 H330 - Acute toxicity inhalation, category 1

Item	Compound name	CAS Number	Harmonised classification		SDS Classification	
			Harmonised (Yes/No)	Classification	SDS Company	Classification
18	Ammonium Molybdate	12054-85-2	No	N/A Over 100 ECHA submissions as Not Hazardous 8 ECHA submissions for H302 - Acute toxicity oral, category 4	Sigma-Aldrich	-
19	Potassium Chloride	7447-40-7	No	N/A Over 500 ECHA submissions as Not Hazardous	Sigma-Aldrich	-
20	Rubidium Chloride	7791-11-9	No	N/A 87 ECHA submissions as Not Hazardous	Sigma-Aldrich	-
21	Sodium Chloride	7647-14-5	No	N/A Over 1300 ECHA submissions as Not Hazardous	Sigma-Aldrich	-
22	Calcium Nitrate	13477-34-4	No	N/A Over 200 ECHA submissions for H302 - Acute toxicity oral, category 4	Sigma-Aldrich	H302 - Acute toxicity oral, category 4 H318 - Serious eye damage, category 1

Item	**Compound name**	**CAS Number**	**Harmonised classification**		**SDS Classification**	
			Harmonised (Yes/No)	**Classification**	**SDS Company**	**Classification**
23	Decaborane	17702-41-9	No	N/A 24 ECHA submissions for H301 - Acute toxicity oral, category 3, H311 - Acute toxicity dermal, category 3 and H330 - Acute toxicity inhalation, category 2	Sigma-Aldrich	H228 - Flammable solids, category 1 H301 - Acute toxicity oral, category 3 H311 - Acute toxicity dermal, category 3 H330 - Acute toxicity inhalation, category 2 H315 - Skin irritation, category 2 H319 - Eye irritation, category 2 H335 - STOT-SE, category 3
24	Borax	1330-43-4	No	N/A No ECHA submissions for acute toxicity	Sigma-Aldrich	H319 - Eye irritation, category 2 H360 - Reproductive toxicity, category 1B
25	Barium Chloride	10326-27-9	Yes	H301 - Acute toxicity oral category 3 H332 - Acute toxicity inhalation, category 4	Merck	H301 - Acute toxicity oral category 3 H332 - Acute toxicity inhalation, category 4
26	Lithium Chloride	7447-41-8	No	N/A Over 400 ECHA submissions for H302 - Acute toxicity oral, category 4 54 ECHA submissions for H312 - Acute toxicity dermal, category 4 31 ECHA submissions for H332 - Acute toxicity inhalation, category 4	Sigma-Aldrich	H302 - Acute toxicity oral, category 4 H315 - Skin irritation, category 2 H319 - Eye irritation, category 2
27	Strontium nitrate	10042-76-9	No	N/A 68 ECHA submissions as Not Hazardous 28 ECHA submissions for H302 - Acute toxicity oral, category 4	Sigma-Aldrich	H272 - Oxidizing solids, category 3 H302 - Acute toxicity oral category 4 H318 - Serious eye damage, category 1

Item	Compound name	CAS Number	Harmonised classification		SDS Classification	
			Harmonised (Yes/No)	Classification	SDS Company	Classification
28	Copper Sulfate	7758-99-8	No	N/A 6 ECHA submissions for H302 - Acute toxicity oral, category 4	Sigma-Aldrich	H302 - Acute toxicity oral, category 4 H315 - Skin irritation, category 2 H319 - Eye irritation, category 2 H400 - Acute aquatic toxicity, category 1 H410 - Chronic aquatic toxicity, category 1
29	Selenium Oxide	7446-08-4	No	N/A Over 100 ECHA submissions for H301 - Acute toxicity oral, category 3 and H331 - Acute toxicity inhalation, category 3	Sigma-Aldrich	H301 - Acute toxicity oral category 3 H331 - Acute toxicity inhalation, category 3 H373 - STOT-RE, category 2 H400 - Acute aquatic toxicity, category 1 H410 - Chronic aquatic toxicity, category 1
30	Cerium Chloride	18618-55-8	No	N/A No ECHA submissions for acute toxicity	Sigma-Aldrich	H314 - Skin corrosion, category 1C
31	Bismuth Chloride	7787-60-2	No	N/A Over 200 ECHA submissions as Not Hazardous	Sigma-Aldrich	H315 - Skin irritation, category 2 H319 - Eye irritation, category 2

APPENDIX D: COLOURANT TOXICITY EVALUATION (ORAL)

item	Compound name	Acute toxicity values				
		Oral				
		Value LD50 rat	Data source	Category	Reference	Comments
1	Carbon Dioxide	-	-	-	-	-
1A	Carbon dioxide (5%)	-	-	-	-	-
2	Methane	-	-	-	-	-
2A	Methane (10%)	-	-	-	-	-
3	Propane	-	-	-	-	-
3A	Propane (10%)	-	-	-	-	-
4	Nitrous Oxide	-	-	-	-	-
4A	Nitrous oxide (1%)	-	-	-	-	-
5	Water	-	-	-	-	-
6	Ammonia	-	ECHA registration dossier	-	-	A waiver is proposed as the substance is a gas. However data are available (Smyth et al, 1941) which report an oral LD50 value of 350 mg/kg bw in the rat for ammonium hydroxide (aqueous ammonia), which is an aqueous solution of the substance
7	Ethanol	10470 mg/kg	ECHA registration dossier	Not classified	-	Reliability 1 (reliable without restriction) OECD Guideline 401
8	Methanol	1187 mg/kg	ECHA registration dossier	4	-	Reliability 2 (reliable with restrictions) OECD Guideline 401

item	Compound name	Acute toxicity values				
		Oral				
		Value LD50 rat	Data source	Category	Reference	Comments
9	Propanone	5800 mg/kg	ECHA registration dossier	Not classified	Acetone potentiation of acute acetonitrile toxicity, Freeman JJ, Hayes EP, 1985, J Toxicol Environ Health 15: 609-621	Reliability 2 (reliable with restrictions)
10	Butanone	2193 mg/kg	ECHA registration dossier	Not classified	-	Value read across secondary butyl alcohol. Further data from secondary sources (MAK documentation of the Deutsche Forschungsgemeinschaft-DFG); OECD SIDS) reported oral LD50 values in mice and rats between 2000 and 6000 mg/kg bw
11	Tetrachloromethane	2500 mg/kg	ECHA registration dossier	Not classified	A new approach to practical acute toxicity testing, Lorke D., 1983, Arch Toxicol., vol. 54, no. 4, p. 275-87	Reliability 2 (reliable with restrictions) OECD Guideline 401
12	Chloroform	908 mg/kg	ECHA registration dossier	4	The acute toxicity of four trihalomethanes in male and female rats, Chu I, Secours V, Marino I, Villeneuve D, 1980, Toxicology and Applied Pharmacology 52, 351-353	Reliability 2 (reliable with restrictions) OECD Guideline 401
13	Tribromofluoromethane	-	-	-	-	-
14	Ferrocene	1320 mg/kg	ECHA registration dossier	4	Bingham, E.; Cohrssen, B.; Powell, C.H., 2001, Patty's Toxicology Volumes 1-9 5th ed. John Wiley & Sons. New York, N.Y.	Reliability 2 (reliable with restrictions) OECD Guideline 401
15	Butyryl Ferrocene	-	-	-	-	-
16	Chromium Hexacarbonyl	230 mg/kg	US Toxnet	3	Gigiena Truda i Professional'nye Zabolevaniya. Labor Hygiene and Occupational Diseases. Vol. 20(2), Pg. 38, 1976	-
17	Molybdenum Hexacarbonyl	-	-	-	-	-
18	Ammonium Molybdate	333 mg/kg	ECHA registration dossier	4	Acute oral toxicity test on rat, David C. Ayres, Desmond G. Hellier, 1999, Dictionary of Environmentally Important Chemicals, 29 page	Reliability 2 (reliable with restrictions)

item	Compound name	Acute toxicity values				
		Oral				
		Value LD50 rat	Data source	Category	Reference	Comments
19	Potassium Chloride	3020 mg/kg	ECHA registration dossier	Not classified	-	Reliability 2 (reliable with restrictions)
20	Rubidium Chloride	4440 mg/kg	US Toxnet	Not classified	Gigiena i Sanitariya. For English translation, see HYSAAV. Vol. 53(5), Pg. 76, 1988	-
21	Sodium Chloride	3550 mg/kg	ECHA registration dossier	Not classified	-	Reliability 2 (reliable with restrictions) Sodium chloride administered as 25% water solution
22	Calcium Nitrate	3900 mg/kg	US Toxnet	Not classified	"Sbornik Vysledku Toxixologickeho Vysetreni Latek A Pripravku," Marhold, J.V., Institut Pro Vychovu Vedoucicn Pracovniku Chemickeho Prumyclu Praha, Czechoslovakia, 1972Vol. -, Pg. 9, 1972	-
23	Decaborane	64 mg/kg	US Toxnet	3	Lewis, R.J. Sax's Dangerous Properties of Industrial Materials. 9th ed. Volumes 1-3. New York, NY: Van Nostrand Reinhold, 1996., p. 990 **PEER REVIEWED**	-
24	Borax	2660 mg/kg	US Toxnet	Not classified	European Chemicals Bureau; IUCLID Dataset, Sodium Tetraborate (1330-43-4) (2000 CD-ROM edition). Available from, as of May 17, 2005: http://esis.jrc.ec.europa.eu/ **PEER REVIEWED**	-
25	Barium Chloride	118 mg/kg	US Toxnet	3	Lewis, R.J. Sr. (ed) Sax's Dangerous Properties of Industrial Materials. 11th Edition. Wiley-Interscience, Wiley & Sons, Inc. Hoboken, NJ. 2004., p. 340 **PEER REVIEWED** WHO; Environ Health Criteria 107: Barium (1990). Available from, as of August 3, 2010: http://www.inchem.org/pages/ehc.html **PEER REVIEWED**	-

item	Compound name	Acute toxicity values				
		Oral				
		Value LD50 rat	Data source	Category	Reference	Comments
26	Lithium Chloride	526 mg/kg	ECHA registration dossier	4	Lithium Chloride, 1980, Acta Pharmacologica et Toxicologica 47, 351, 1980 (APTOA6); via RTECS	Reliability 2 (reliable with restrictions)
27	Strontium nitrate	2750 mg/kg	US Toxnet	Not classified	Tarasenko NY, Zyuzyukin YV; Gig Sanit (5): 28-32 (1976) **PEER REVIEWED**	-
28	Copper Sulfate	960 mg/kg	US Toxnet	4	WHO; Environ Health Criteria 200: Copper p.101 (1998) **PEER REVIEWED**	-
29	Selenium Oxide	68.1 mg/kg	ECHA registration dossier	3	Behavioral and toxic profile of some essential trace metal salts in mice and rats, Singh PP, Junnarkar AY, 1991, Indian Journal of Pharmacology 23(3):153-159	Reliability 2 (reliable with restrictions)
30	Cerium Chloride	-	-	-	-	-
31	Bismuth Chloride	3334 mg/kg	US Toxnet	Not classified	Gigiena Truda i Professional'nye Zabolevaniya. Labor Hygiene and Occupational Diseases. Vol. 30(6), Pg. 16, 1986	-

APPENDIX E: COLOURANT TOXICITY EVALUATION (DERMAL)

item	Compound name	Acute toxicity values				
		Dermal				
		Value LD50 rat / LD50 rabbit	Data source	Category	Reference	Comments
1	Carbon Dioxide	-	-	-	-	-
1A	Carbon dioxide (5%)	-	-	-	-	-
2	Methane	-	-	-	-	-
2A	Methane (10%)	-	-	-	-	-
3	Propane	-	-	-	-	-
3A	Propane (10%)	-	-	-	-	-
4	Nitrous Oxide	-	-	-	-	-
4A	Nitrous oxide (1%)	-	-	-	-	-
5	Water	-	-	-	-	-
6	Ammonia	-	ECHA registration dossier	-	-	No data are available. A waiver is proposed as the substance is classified as corrosive. Dermal exposure to anhydrous ammonia will be dominated by local effects at the site of contact and significant systemic toxicity is unlikely
7	Ethanol	-	-	-	-	Dermal study was deemed not relevant
8	Methanol	15840 mg/kg	US Toxnet	Not classified	National Research Council; Prudent Practices in the Laboratory. Handling and Management of Chemical Hazards. the National Academies Press, Washington, D.C. 2011, p. CD **PEER REVIEWED**	LD50 rabbit

item	Compound name	Acute toxicity values				
		Dermal				
		Value LD50 rat / LD50 rabbit	Data source	Category	Reference	Comments
9	Propanone	> 7400 mg/kg	ECHA registration dossier	Not classified	Comparative acute effects of some chemicals on the skin of rabbits and guinea pigs, Roudabush RL, Terhaar CJ, Fassett DW, Dziuba SP, 1965, Toxicol Appl Pharmacol 7: 559-565	Reliability 2 (reliable with restrictions)
10	Butanone	6400 mg/kg	ECHA registration dossier	Not classified	-	According to the data provided in the REACH dossier, butanone is considered to be virtually non-toxic after single skin contact. Rabbit dermal: LD50 > 10 ml/kg bw. Further data from secondary source (OECD SIDS) reported dermal LD50 values in rabbits from 6.4 to 8 g/kg bw
11	Tetrachloromethane	5070 mg/kg	US Toxnet	Not classified	Lewis, R.J. Sr. (ed) Sax's Dangerous Properties of Industrial Materials. 11th Edition. Wiley-Interscience, Wiley & Sons, Inc. Hoboken, NJ. 2004., p. 709 **PEER REVIEWED**	LD50 rat
12	Chloroform	> 20000 mg/kg	US Toxnet	Not classified	National Technical Information Service. Vol. AD-A062-138	-
13	Tribromofluoromethane	-	-	-	-	-
14	Ferrocene	>3000 mg/kg	ECHA registration dossier	Not classified	-	LD50 rat Reliability 2 (reliable with restrictions) OECD Guideline 402
15	Butyryl Ferrocene	-	-	-	-	-
16	Chromium Hexacarbonyl	-	-	-	-	-
17	Molybdenum Hexacarbonyl	-	-	-	-	-
18	Ammonium Molybdate	-	-	-	-	-

item	Compound name	Acute toxicity values				
		Dermal				
		Value LD50 rat / LD50 rabbit	Data source	Category	Reference	Comments
19	Potassium Chloride	-	ECHA registration dossier	-	-	There is no data available on acute dermal toxicity for potassium chloride. Due to the low vapour pressure (5.73 hPa) and the low calculated octanol-water partition coefficient (Log POW: -0.46) of the substance, the potential for dermal absorption is low [UNEP 2003]
20	Rubidium Chloride	-	-	-	-	-
21	Sodium Chloride	> 10000 mg/kg	ECHA registration dossier	Not classified	-	LD50 rabbit Reliability 2 (reliable with restrictions)
22	Calcium Nitrate	-	-	-	-	-
23	Decaborane	71 mg/kg	US Toxnet	2	Lewis, R.J. Sax's Dangerous Properties of Industrial Materials. 9th ed. Volumes 1-3. New York, NY: Van Nostrand Reinhold, 1996., p. 991 **PEER REVIEWED**	LD50 rabbit
24	Borax	> 1055 mg/kg	US Toxnet	4 (or less hazardous)	European Chemicals Bureau; IUCLID Dataset, Sodium Tetraborate (1330-43-4) (2000 CD-ROM edition). Available from, as of May 17, 2005: http://esis.jrc.ec.europa.eu/ **PEER REVIEWED**	-
25	Barium Chloride	-	-	-	-	-
26	Lithium Chloride	> 2000 mg/kg	ECHA registration dossier	Not classified	-	LD50 rat Reliability 1 (reliable without restriction)
27	Strontium nitrate	-	-	-	-	-

item	Compound name	Acute toxicity values				
		Dermal				
		Value LD50 rat / LD50 rabbit	Data source	Category	Reference	Comments
28	Copper Sulfate	> 2000 mg/kg	US Toxnet	Not classified	Nippon Noyaku Gakkaishi. Journal of the Pesticide Science Society of Japan. Vol. 18, Pg. S161, 1993	LD50 rat
29	Selenium Oxide	-	-	-	-	-
30	Cerium Chloride	-	-	-	-	-
31	Bismuth Chloride	-	-	-	-	-

APPENDIX F: COLOURANT TOXICITY EVALUATION (INHALATION GAS)

item	Compound name	Acute toxicity values				
		Inhalation Gas				
		Value LC50 rat (4 h)	Data source	Category	Reference	Comments
1	Carbon Dioxide	-	-	-	-	-
1A	Carbon dioxide (5%)	-	-	-	-	-
2	Methane	-	-	-	-	-
2A	Methane (10%)	-	-	-	-	-
3	Propane	-	-	-	-	-
3A	Propane (10%)	-	-	-	-	-
4	Nitrous Oxide	-	-	-	-	-
4A	Nitrous oxide (1%)	-	-	-	-	-
5	Water	-	-	-	-	-
6	Ammonia	-	-	-	-	-
7	Ethanol	-	-	-	-	-
8	Methanol	-	-	-	-	-
9	Propanone	-	-	-	-	-
10	Butanone	-	-	-	-	-
11	Tetrachloromethane	-	-	-	-	-
12	Chloroform	-	-	-	-	-
13	Tribromofluoromethane	-	-	-	-	-
14	Ferrocene	-	-	-	-	-
15	Butyryl Ferrocene	-	-	-	-	-

item	Compound name	Acute toxicity values				
		Inhalation Gas				
		Value LC50 rat (4 h)	Data source	Category	Reference	Comments
16	Chromium Hexacarbonyl	-	-	-	-	-
17	Molybdenum Hexacarbonyl	-	-	-	-	-
18	Ammonium Molybdate	-	-	-	-	-
19	Potassium Chloride	-	-	-	-	-
20	Rubidium Chloride	-	-	-	-	-
21	Sodium Chloride	-	-	-	-	-
22	Calcium Nitrate	-	-	-	-	-
23	Decaborane	-	-	-	-	-
24	Borax	-	-	-	-	-
25	Barium Chloride	-	-	-	-	-
26	Lithium Chloride	-	-	-	-	-
27	Strontium nitrate	-	-	-	-	-
28	Copper Sulfate	-	-	-	-	-
29	Selenium Oxide	-	-	-	-	-
30	Cerium Chloride	-	-	-	-	-
31	Bismuth Chloride	-	-	-	-	-

APPENDIX G: COLOURANT TOXICITY EVALUATION (INHALATION VAPOUR)

item	Compound name	Acute toxicity values				
		Inhalation Vapour				
		Value LC50 rat (4 h)	Data source	Category	Reference	Comments
1	Carbon Dioxide	-	-	-	-	-
1A	Carbon dioxide (5%)	-	-	-	-	-
2	Methane	-	-	-	-	-
2A	Methane (10%)	-	-	-	-	-
3	Propane	-	-	-	-	-
3A	Propane (10%)	-	-	-	-	-
4	Nitrous Oxide	-	-	-	-	-
4A	Nitrous oxide (1%)	-	-	-	-	-
5	Water	-	-	-	-	-
6	Ammonia	-	-	-	-	-
7	Ethanol	124.7 mg/L	ECHA registration dossier	Not classified	-	Reliability 2 (reliable with restrictions) OECD Guideline 403
8	Methanol	-	-	-	-	-
9	Propanone	90 mg/L	ECHA registration dossier	Not classified	Evaluation of toluene and acetone inhalant abuse. I. Pharmacology and pharmacodynamics, Bruckner JV, Peterson RG, 1981, Toxicol Appl Pharmacol 61: 27-38	LC50 (3h) = 120 mg/L Reliability 2 (reliable with restrictions)
10	Butanone	-	-	-	-	-

item	Compound name	Acute toxicity values				
		Inhalation Vapour				
		Value LC50 rat (4 h)	Data source	Category	Reference	Comments
11	Tetrachloromethane	69.30 mg/L	ECHA registration dossier	Not classified	Determination of the median lethal concentration of the main chlorinated aliphatic hydrocarbons in the rat., Bonnet, P.; Francin, J.-M.; Gradinski, D.; Raoult, G.; Zissu, D., 1980, Arch Mal Prof Med Trav, vol. 41, No. 6 -7, s. 317-321	Reliability 2 (reliable with restrictions) OECD Guideline 403 The LC50 in rat was found to be 7228 ppm (= 46.260 mg/m3 air) after single exposure to CTC for 6 h
12	Chloroform	-	-	-	-	-
13	Tribromofluoromethane	-	-	-	-	-
14	Ferrocene	-	-	-	-	-
15	Butyryl Ferrocene	-	-	-	-	-
16	Chromium Hexacarbonyl	-	-	-	-	-
17	Molybdenum Hexacarbonyl	-	-	-	-	-
18	Ammonium Molybdate	-	-	-	-	-
19	Potassium Chloride	-	-	-	-	-
20	Rubidium Chloride	-	-	-	-	-
21	Sodium Chloride	-	-	-	-	-
22	Calcium Nitrate	-	-	-	-	-
23	Decaborane	-	-	-	-	-
24	Borax	-	-	-	-	-
25	Barium Chloride	-	-	-	-	-
26	Lithium Chloride	-	-	-	-	-
27	Strontium nitrate	-	-	-	-	-
28	Copper Sulfate	-	-	-	-	-
29	Selenium Oxide	-	-	-	-	-
30	Cerium Chloride	-	-	-	-	-

item	Compound name	Acute toxicity values				
		Inhalation Vapour				
		Value LC50 rat (4 h)	Data source	Category	Reference	Comments
31	Bismuth Chloride	-	-	-	-	-

APPENDIX H: COLOURANT TOXICITY EVALUATION (INHALATION AEROSOL)

item	Compound name	Acute toxicity values				
		Inhalation Aerosol				
		Value LC50 rat (4 h)	Data source	Category	Reference	Comments
1	Carbon Dioxide	-	-	-	-	-
1A	Carbon dioxide (5%)	-	-	-	-	-
2	Methane	-	-	-	-	-
2A	Methane (10%)	-	-	-	-	-
3	Propane	-	-	-	-	-
3A	Propane (10%)	-	-	-	-	-
4	Nitrous Oxide	-	-	-	-	-
4A	Nitrous oxide (1%)	-	-	-	-	-
5	Water	-	-	-	-	-
6	Ammonia	-	-	-	-	-
7	Ethanol	-	-	-	-	-
8	Methanol	-	-	-	-	-
9	Propanone	-	-	-	-	-
10	Butanone	-	-	-	-	-
11	Tetrachloromethane	-	-	-	-	-
12	Chloroform	-	-	-	-	-
13	Tribromofluoromethane	-	-	-	-	-
14	Ferrocene	-	-	-	-	-
15	Butyryl Ferrocene	-	-	-	-	-
16	Chromium Hexacarbonyl	-	-	-	-	-
17	Molybdenum Hexacarbonyl	-	-	-	-	-

item	Compound name	Acute toxicity values				
		Inhalation Aerosol				
		Value LC50 rat (4 h)	Data source	Category	Reference	Comments
18	Ammonium Molybdate	-	-	-	-	-
19	Potassium Chloride	-	-	-	-	-
20	Rubidium Chloride	-	-	-	-	-
21	Sodium Chloride	> 10.5 mg/L	ECHA registration dossier	Not classified	-	Reliability 2 (reliable with restrictions) An acute inhalation toxicity study was conducted at a dose of 42 mg/l administered as an aerosol of a 20% aqueous solution to male rats and the results of the study indicated that the LC50 of sodium chloride was greater than 42 mg/l and hence not classified. LC50-1h > 42mg/L
22	Calcium Nitrate	-	-	-	-	-
23	Decaborane	-	-	-	-	-
24	Borax	-	-	-	-	-
25	Barium Chloride	> 1.1 mg/L	ECHA registration dossier	4	-	Reliability 1 (reliable without restriction) OECD Guideline 403
26	Lithium Chloride	> 5.57 mg/L	-	Not classified	-	Reliability 1 (reliable without restriction) OECD Guideline 403 and EU method B.2.
27	Strontium nitrate	> 4.5 mg/L	ECHA registration dossier	4 (or less hazardous)	-	Reliability 1 (reliable without restriction) OECD Guideline 403
28	Copper Sulfate	-	-	-	-	-
29	Selenium Oxide	> 0.052 and ≤ 0.51 mg/L	ECHA registration dossier	2	-	Reliability 2 (reliable with restrictions)
30	Cerium Chloride	-	-	-	-	-
31	Bismuth Chloride	-	-	-	-	-

APPENDIX I: COLOURANT TOXICITY EVALUATION (OTHER NOTES)

item	Compound name	Other notes
1	Carbon Dioxide	No acute toxicity information found for carbon dioxide
1A	Carbon Dioxide (5%)	No acute toxicity information found for carbon dioxide
2	Methane	ECHA registration dossier: Oral and dermal studies not feasible. Methane is practically non-toxic but acts as a simple asphyxiant at very high concentrations. In both human and animal studies Petroleum Gases are of low acute toxicity by the inhalation route with LC50 values far exceeding the dose levels which would warrant classification under DSD or CLP
2A	Methane (10%)	If compound is not toxic, the diluted compound won't be acutely toxic either
3	Propane	ECHA registration dossier: In 1982 Clark et al demonstrated the acute inhalation LC50 following 15 minute exposure to rats exceeds 800000 ppm. Much of the acute inhalation data on propane are from pre-guideline studies. Nevertheless, Cavender (1994) concluded that the gas shows low toxicity in several species. No quantitative acute oral or dermal data were identified. In both human and animal studies Petroleum Gases are of low acute toxicity by the inhalation route with LC50 values far exceeding the dose levels which would warrant classification under DSD or CLP
3A	Propane (10%)	If compound is not toxic, the diluted compound won't be acutely toxic either
4	Nitrous Oxide	ECHA registration dossier: Nitrous oxide is not very toxic after single or repeated exposures concentrations of 300000 ml/m^3 and more have analgetic effects and 800000 ml/m^3 and more anaesthetic effects. (MAK evaluation 1993)
4A	Nitrous Oxide (1%)	If compound is not toxic, the diluted compound won't be acutely toxic either
5	Water	-

item	Compound name	Other notes
6	Ammonia	ECHA registration dossier. The acute inhalation toxicity of ammonia was assessed by exposing groups of male and female Wistar rats were to atmospheric ammonia for 10, 20, 40 or 60 minutes. The 60 minute LC50 in male rats was 9850 mg/m³ air. The 60 minute LC50 in female rats was 13770 mg/m³ air (Appelman et al, 1982). The acute inhalation toxicity of ammonia gas to rats was determined during single exposure times of 5, 15, 30 or 60 minutes. The LC50 during exposures of 5 and 15 minutes were 18693 mg/m³ and 12160 mg/m³, respectively, while for 30 and 60 minute exposures the values were 7035 mg/m³ and 7939 mg/m³ (Prokop'eva et al, 1973). No indication of the physical state it was tested as. Reliability 2 (reliable with restrictions). Reference: Acute inhalation toxicity study of ammonia in rats with variable exposure periods, Appelman, L.M., Ten Berge, W.F. and Reuzel, P.G.J., 1982, Am. Ind. Hyg. Assoc. J; 43(9), 1982, 662-665
7	Ethanol	-
8	Methanol	-
9	Propanone	-
10	Butanone	In accordance with column 2 of REACH Annex VIII, the acute toxicity by inhalation study (required in section 8.5.2) does not need to be conducted as acute toxicity studies are available for the oral and dermal routes of exposure
11	Tetrachloromethane	ECHA registration dossier: The substance is listed in Annex VI of EU Directive 67/548/EE and in Annex I of CLP Regulation for acute oral, dermal and inhalation toxicity, probably because of the cases of human poisoning following exposure to CTC
12	Chloroform	According to EU directive 67/548/EEC, the substance is harmful by inhalation (R20) and harmful if swallowed (R22). However, during the revision of the classification of chloroform on September 2007, the TC C&L agreed to classify chloroform Category 3 "toxic if inhaled". In addition, the TC considered that the narcotic effects that would be covered by Xn/R20 would trigger classification STOT single 3 under the CLP regulation. As chloroform exhibits rather low acute toxicity and based on acute toxicity data, the proposed GHS classification for chloroform is Category 4, "Harmful", with the hazard statements: harmful if swallowed and harmful if inhaled and

item	Compound name	Other notes
		STOT SE 3 with the hazard statement: may cause drowsiness and dizziness
13	Tribromofluoromethane	-
14	Ferrocene	Data is available for oral and dermal routes and in the interest of animal welfare this study is waived. However as the material is harmful by repeat exposure it is advisable to classify as harmful by inhalation for acute exposure too
15	Butyryl Ferrocene	-
16	Chromium Hexacarbonyl	-
17	Molybdenum Hexacarbonyl	-
18	Ammonium Molybdate	-
19	Potassium Chloride	There are no data available on acute inhalation toxicity for potassium chloride. Potassium chloride is a solid white odourless crystalline substance with low vapor pressure and high melting points (770 °C). Due to this physico-chemical property of potassium chloride the potential for generation of aerosols, particles or droplets in inhalable size is low. Therefore, exposure of humans via inhalation is unlikely to occur.
20	Rubidium Chloride	-
21	Sodium Chloride	
22	Calcium Nitrate	-
23	Decaborane	Dermal LD50 rat value 740 mg/kg (category 3). Reference: Lewis, R.J. Sax's Dangerous Properties of Industrial Materials. 9th ed. Volumes 1-3. New York, NY: Van Nostrand Reinhold, 1996., p. 991 **PEER REVIEWED**
24	Borax	-

item	Compound name	Other notes
25	Barium Chloride	Inhalation study. Exposure to 1.1 mg/L of barium chloride di-hydrate resulted in significant signs of toxicity (mortality of one male, severe and persisting clinical signs) indicating that significant mortality could be expected at the next higher exposure level of 5 mg/L. In consultation with the sponsor, it was therefore decided not to expose animals to a higher concentration
26	Lithium Chloride	-
27	Strontium nitrate	Inhalation study. The inhalatory LC50, 4h value of strontium nitrate in Wistar rats was considered to be 4.5 +/- 0.6 mg/l. *Based on these results Strontium Nitrate does not have to be classified*
28	Copper Sulfate	-
29	Selenium Oxide	Inhalation study. The LC50 combined for sodium selenate is considered to be > 0.052 and ≤ 0.51 mg/L
30	Cerium Chloride	-
31	Bismuth Chloride	-

APPENDIX J: REFERENCES

[1] H.R.N.Jones. Domestic Gas Burner Design. 1989
[2] unknown
[3] Safeflame website)
[4] Angeli Mehta. “Hydrogen: still the fuel of the future?” Chemistry World. 30 July 2018).
[5] Toyota Motor Corporation. Press Release November 8, 2018)
[6] Ding et al
[7] Chemiluminescence based operating point control of domestic gas boilers with variable natural gas composition. Yi Ding, D. Durox, N. Darabiha and T. Schuller. Applied Thermal Engineering 149 (2019), pp.1052-1060
[8] R.W. Schefer ⁎, W.D. Kulatilaka, B.D. Patterson, T.B. Settersten Visible emission of hydrogen flames. Combustion and Flame 156 (2009) 1234–1241
[9] Almaas Technologies
[10] Kiwa report DECC “Desk study on the development of a hydrogen-fired appliance supply chain” Report Number: 30686 Date: July 2016
[11] Frazer-Nash Consultancy “Appraisal of Domestic Hydrogen Appliances”. Prepared for the Department of Business, Energy & Industrial Strategy. February 2018. FNC 55089/46433R Issue 1
[12] Frazer-Nash report “Logistics of Domestic Hydrogen Conversion” Prepared for the Department of Business, Energy & Industrial Strategy. October 2018. FNC 57239/47448R Issue 1
[13] B. Fumey, S. Stoller, R. Fricker, R. Weber, V. Dorer and U.F. Vogt. “Development of a novel cooking stove based on catalytic hydrogen combustion”. International Journal of hydrogen energy 41 (2016), pp.7494-7499.
[14] W. F. Barrett, “On Certain Phenomena Associated with a Hydrogen Flame,” Nature, vol. 5, no. 129, pp. 482–484, Apr. 1872
[15] A. G. Gaydon, The Spectroscopy of Flames, Second. London: John Wiley & Sons, 1974.
[16] E. L. Nichols and D. T. Wilber, “Flame excitation of luminescence,” 1921
[17] R. W. Schefer, W. D. Kulatilaka, B. D. Patterson, and T. B. Settersten, “Visible emission of hydrogen flames,” Combust. Flame, vol. 156, no. 6, pp. 1234–1241, Jun. 2009.
[18] US 2012/0003593 A1 . W.E. Conrad “Method and apparatus for producing a visible hydrogen flame (2012)”
[19] Y. Shibarashi, “Thermochromic materials,” 1984.
[20] C. Anderson, “Detecting Hydrogen & Gas Fires: Seeing the unseen,” 2008.

APPENDIX K: LIST OF TABLES

APPENDIX L: LIST OF FIGURES

DNV GL is a global quality assurance and risk management company. Driven by our purpose of safeguarding life, property and the environment, we enable our customers to advance the safety and sustainability of their business. We provide classification, technical assurance, software and independent expert advisory services to the maritime, oil & gas, power and renewables industries. We also provide certification, supply chain and data management services to customers across a wide range of industries. Operating in more than 100 countries, our experts are dedicated to helping customers make the world safer, smarter and greener

Hy4Heat

www.Hy4Heat.info

@hy4heat