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A practical step towards “hydrogen”: The conditions under which the existing natural gas system can be used for mixtures of hydrogen and natural gas (the NATURALHY -project)

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ABSTRACT

Hydrogen is foreseen as an important energy carrier and an essential element for global sustainable development. However, there are many significant challenges for implementing all the components of a complete energy system based on hydrogen. Despite these challenges, there is global interest in hydrogen. The transition towards the situation in which hydrogen is an important energy carrier will be lengthy (decades), costly and needs a significant effort for R&D. The development of a hydrogen system requires a practical strategy within the context of an existing, extensive natural gas system which has resulted from substantial capital investment over a long period of time.

The NATURALHY-project aims to define the conditions under which the existing natural gas system (transmission and distribution system, end user infrastructure and end user appliances) can be used for mixtures of natural gas and hydrogen. Innovative membranes will be developed to selectively withdraw hydrogen from a hydrogen/natural gas stream.

As the physical and chemical properties of mixtures of hydrogen and natural gas may differ significantly from “pure” natural gas, the NATURALHY -project addresses particularly the safety, durability and integrity issues related to the transmission, distribution and end use of such mixtures.

A European consortium of 39 partners (15 from gas industry) has been assembled, and guidance will be provided by a Strategic Advisory Committee consisting of representatives from relevant (inter)national organisations. The execution of the project started on 1st May 2004, and takes 5 years.

The European Commission has selected the NATURALHY -project for financial support within the Sixth Framework Programme.

INTRODUCTION

Hydrogen is foreseen to become an important energy carrier. However, the very significant technical, economic and institutional changes required to establish the full hydrogen economy will take several decades to implement. These changes will concern all individual elements of the energy system-production, delivery, storage, conversion and end-use applications. These elements are interrelated and interdependent, and, as a consequence of this, there is a “chicken and egg” dilemma regarding market segment development and how supply and demand will push or pull these activities.

In any transition scenario for the full hydrogen economy and in all variants of hydrogen economies, there must be a connection between the hydrogen production and the appliance powered by hydrogen. The distance between the hydrogen production and the appliance will range from several centimetres to several thousands of kilometres depending on production, whether centralised, decentralised or hybrid, and its use. For sure, pipelines will be an important part of this connection.

Given the strong political stress on the implementation of hydrogen as an important energy carrier, several companies united in the NATURALHY project whose core business is the transmission and distribution of gas, and who want to prepare themselves to the situation that hydrogen will actually be offered for transmission and distribution. An obvious and pragmatic first step is to examine the possibilities presented by the existing natural gas system for adaptation to new opportunities.

More over, it is important to assess the contribution of the existing assets because:

- Significant financial and economic benefits can arise from the use of the existing European infrastructure with its inherent economic value of several hundreds of billions of EUROs;
- Using the existing gas infrastructure for the change to the full hydrogen economy accelerates the transition rate and innovations in all relevant fields.

This vision is also supported by the United States Department of Energy as reported in the National Hydrogen Energy Roadmap (April 2-3, 2002): “*Vision of hydrogen delivery: A national hydrogen supply network will evolve from the existing fossil fuel-based infrastructure to accommodate both centralized and decentralized production facilities*”.

From previous preparatory experiments it is already known that the existing system will not be suitable for 100% hydrogen and that even 50% hydrogen added to natural gas will be too much to compromise safety and acceptable effects on pipeline durability. Nevertheless, in view of its enormous capacity, its extent, and its availability on the short term it is worth examining what the natural gas system offers to the implementation to hydrogen, especially during the transition period.

OBJECTIVES

For urgent progress towards developing hydrogen as a realistic energy option, a practical strategy must be adopted within the context of the existing, extensive natural gas system. In the view of the NATURALHY-partners, this is the only realistic solution to large-scale distribution of hydrogen in Europe in the next 30 to 50 years. Further to this vision, the NATURALHY-project aims to prepare stakeholders by identifying and solving the barriers for progressively introducing hydrogen to natural gas networks and to support the development of a roadmap towards the full hydrogen economy by Integrated Project HYWAYS (also funded by the European Commission within FP6). Gaining experience with testing key components of full hydrogen systems will speed up the transition process.

The NATURALHY-project will achieve these aims by means of the following set of coherent and complementary objectives:

- To define the technical conditions under which hydrogen can be accommodated in the existing natural gas system with acceptable risks, to avoid leakage and significant degradation of the system and consequences for the end users.
- To develop a Decision Support Tool for the assessment of the suitability of an existing natural gas system (transmission, storage, distribution, end user infra structure and end user appliance) for mixtures of hydrogen/natural gas and to develop models to determine the economic and environmental aspects of the whole chain from sustainable hydrogen production up to and including end user appliances.
- To analyse the socio-economic aspects of transitional natural gas/hydrogen systems and the full hydrogen system and compare these with current natural gas and related systems with particular reference to job creation and maintenance, capital investment and total economic costs.
- To carry out life cycle assessment as a means of comparing the major resource inputs and environmental outputs of current natural gas and related systems, transitional natural gas/hydrogen systems and the full hydrogen system including methods of hydrogen production.
- To develop innovative devices (membranes) to separate hydrogen from hydrogen/natural gas mixtures: these devices will enable an early establishment of full hydrogen growth centres that will advance a gradual transition to the full hydrogen economy.

- To motivate all stakeholders in the whole chain from production up to and including end use to “welcome hydrogen”. Such stakeholders consist of, among others, the public, end users, manufacturers of appliances, owners and operators of gas transmission grids, hydrogen producers, local, regional and national authorities, manufacturers of all kinds of equipment and components for gas, etc. This objective will be met in cooperation with Integrated Project HYWAYS and the Network of Excellence HYSAFE.
- To assess the current situation of standards and regulations regarding hydrogen/natural gas mixtures, to identify necessary modifications and to initiate required changes.

APPROACH

Figure 1 shows the field of activities of the NATURALHY-project:

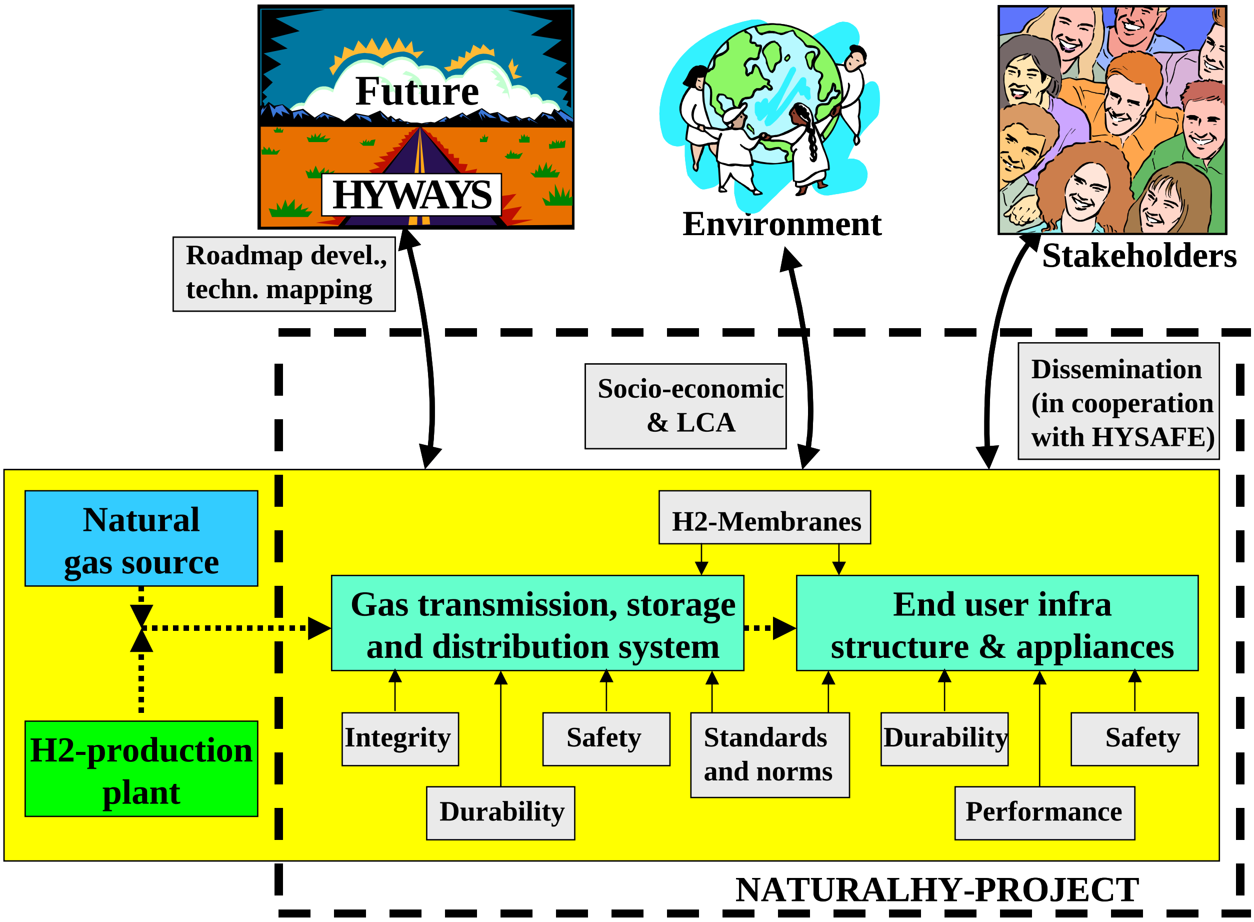

Figure 1: The approach of the NATURALHY-project

- The attention for safety, durability, integrity and performance (the <u>technical aspects</u>) in this project focuses at:

    - Gas transmission system;
    - Gas distribution system;
    - End-user infra structure and appliances, and membranes to selectively withdraw hydrogen from hydrogen/natural gas mixtures.
- And, for all <u>non-technical issues</u> (life cycle assessment, dissemination, and roadmapping as indicated in upper part of Figure 1), emphasis is on:
    - The whole chain including:
        - Various sustainable hydrogen production facilities and processes, and
        - Natural gas exploitation is taken into account.

The technical activities are focussed on <u>existing</u> situations/materials/constructions/ circumstances/equipment in relation to the specific physical and chemical properties of hydrogen/natural gas mixtures.

The chemical and physical properties of hydrogen differ significantly from those of natural gas and so the properties of mixtures will also differ from “pure” natural gas. In this respect, the main fields in which these changes are relevant are safety, durability, pipeline integrity and the performance of the end user appliances. For safety and appliance performance, it is important to realise that

- the explosion limits of hydrogen/air mixtures are much wider than for natural gas;
- the ignition energy for hydrogen is much less than for natural gas;
- the latent energy per unity of volume of natural gas is about 3 times of that of hydrogen;
- the flame velocity of hydrogen is much higher than for natural gas;
- the radiation of hydrogen flames is much less than from natural gas flames.

As a consequence of this, the impact on safety aspects by the addition of hydrogen to the transmission and distribution has to be assessed. Within the work programme on the safety aspects, it will be necessary to investigate to what extent mixtures of hydrogen/natural gas behave differently from “pure” natural gas: large scale experiments with different percentages hydrogen added to natural gas will be carried out (such experiments were previously carried out for the preparation of the natural gas safety models). The approach is to adapt these existing safety models for hydrogen/natural gas mixtures. For a more detailed description of the activities planned within the NATURALHY-project regarding “Safety”, the authors would like to refer to the paper presented by Professor Geoff Hankinson at this Conference.

It is well-known that the diffusion of hydrogen into the pipeline material can have a negative effect on the mechanical properties of the material (embrittlement of steel pipelines).

Consequently, activities have been defined within the NATURALHY-project regarding the acceptability of corrosion defects and sharp defects contained in these brittle zones, to update the associated assessment criteria and the maintenance procedures, repair techniques and equipment required to assess the integrity of pipelines in presence of hydrogen and natural gas mixtures.

The necessary sensitivity of monitoring equipment for defects for the hydrogen situation is higher than in the case of natural gas: a defect that is not of importance in a pipeline used for “pure” natural gas, might be of importance if the pipeline is used for hydrogen/natural gas mixtures. Additionally, questions on the permeation of hydrogen/natural gas mixtures through the wall of polymer pipelines are also considered in the NATURALHY-project.

The results of the technical tasks will be used in the development of the Decision Support Tool which is the main technical deliverable of the project: this expert systems enables the user to determine the technical conditions under which hydrogen can be injected into a defined existing natural gas system, with acceptable safety standards, acceleration of the aging processes, drawbacks for the end users involved and costs related to measures to overcome any unacceptable consequences. The Tool to be developed, comprises, among others aspects, of a set of guidelines, tests procedures, criteria, models, material data and is dedicated to predict and judge the consequences of adding hydrogen to natural gas regarding durability, safety, economic and life cycle assessment aspects of the transmission and distribution systems and the end user infrastructure and appliances. Figure 2 gives an impression of a feasible outcome of the Tool applied to a specific limited natural gas grid.

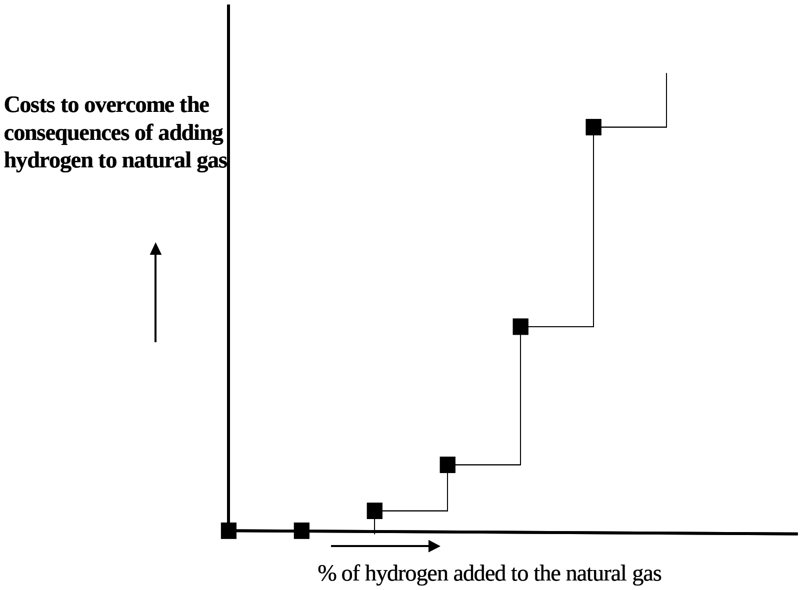

Figure 2: Costs as a function of the percentage of hydrogen added to natural gas

Socio-economic and life cycle assessment concerns the use of the existing gas system for hydrogen/natural gas mixtures and the full hydrogen situation with a new-dedicated hydrogen infrastructure. The existing situation will be the reference case.

No physical work is planned regarding hydrogen production: including hydrogen production would make the project too extensive for the Sixth Framework Programme. However, hydrogen production aspects are taken into account in the socio-economic and life cycle assessment. Hydrogen producers participate in the NATURALHY-project and several partners participate in projects dedicated to sustainable hydrogen production.

PROJECT ORGANISATION

A set of Work Packages (WPs), each on a well-defined issue or set of issues, are defined within the NATURALHY project to enable an efficient communication amongst the partners, and each WP has a specified leader . Although closely integrated, they have been defined in such way that they can mainly be executed independently from other WPs.

The following table summaries the distinct WPs in the NATURALHY-project as well as the leaders and organisations taking care of the technical coordination of these WPs.

Table 1: NATURALHY Work Packages

Number	**Work Package**	**Work package leader (person/organisation)**
WP1	Socio-economic and life cycle assessment	Prof. Nigel Mortimer / Warwick University
WP2	Safety	Prof. Geoff Hankinson / Loughborough University
WP3	Durability	Dr. Isabelle Alliat / Gaz de France
WP4	Integrity	Ir. Adriaan den Herder / Netherlands Organisation for Applied Scientific Research TNO)
WP5	End Use	Dr. Costa Komodromos / Warwick University
WP6	Decision Support Tool	Dr. Peter Bartlam / Instituto de Soldadura e Qualidade (ISQ)
WP7	Dissemination	Dr. George Vlondakis / EXERGIA, Energy and Environment Consultants S.a
WP8	Project management	Ir. Onno Florisson / N.V. Nederlandse Gasunie (Gasunie Research)

Getting the support of all stakeholders is crucial in the NATURALHY-project. Therefore, throughout the whole duration of the execution of the project, an extensive programme of engaging with the public, authorities and gas companies will be executed within the framework of the WP "Dissemination". Regarding the communication with the public and decision makers about safety aspects, there will be an arrangement with the Network of Excellence HYSAFE (see the Section on "Co-operation").

PARTICIPANTS

Table 2 shows the list of NATURALHY-partners.

Table 2: List of NATURALHY-partners

Partner Name	**Partner Short Name**	**Country**
N.V. Nederlandse Gasunie	GASUNIE	NL
Högskolan i Borås	UCB	SE
BP Gas Marketing Limited (BP)	BP	UK
Commissariat à l'énergie atomique (CEA)	CEA	F
Compagnie d'Etudes des Technologies de l' Hydrogène	CETH	F
Computational Mechanics International Ltd	CMI	UK
The European Association for the Promotion of Cogeneration	COGEN	B
Centro Sviluppo Materiali Spa	CSM	I
DBI Gas- und Umwelttechnik GmbH	DBI-GUT	D
Public gas corporation S.A.	DEPA	EL
Danish Gas Technology Centre	DGC	DK
Energy Research Centre of the Netherlands	ECN	NL
EXERGIA, Energy and Environment Consultants S.a	EXERGIA	EL
Technische Universität Berlin	TU BERLIN	D
Gaz de France	GDF	F
General Electric PII Ltd	GE PII	UK
EUROGAS – Groupe Européen de Recherches Gazières	GERG	B
The Health and Safety Executive	HSE (UK)	UK
Istanbul Gaz Dagitim Sanayi ve Ticaret A.S	IGDAS	TR
Institut Français du Pétrole	IFP	F
Instituto de Soldadura e Qualidade	ISQ	P
University of Leeds	UNIV LEEDS	UK
Loughborough University	LOUGH	UK

Tubitak Marmara Research Center Energy Systems and Environmental Research	MRC	TR
Naturgas Midt-Nord I/S	MIDT-NORD	DK
Netherlands Standardization Institute	NEN	NL
National Technical University of Athens	NTUA	EL
Norwegian University of Science and Technology	NTNU	NO
Planet - Planungsgruppe Energie und Technik Gbr	PLANET	D
Ecole Nationale d'ingénieur de Metz	ENIM	F
SAVIKO Consultants ApS (Saviko Roskilde ApS)	SAVIKO	DK
Shell Hydrogen B.V	SH	NL
STATOIL ASA	STATOIL	NO
SQS Portugal - Sistemas de Qualidade de Software, Lda	SQS	P
Total S.A	TOTAL	F
Netherlands Organisation for Applied Scientific Research	TNO	NL
X/ Open Company Limited	TOG	UK
Transco plc (part of National Grid Transco plc)	TRANSCO	UK
University of Warwick	WPTG	UK

PLANNING AND BUDGET

The actual execution of the NATURALHY-project started on 1st May 2004, and the duration of the project amounts to 5 years. The total project budget exceeds 17 M EURO, while the European Commission's contribution within the Sixth Framework Programme amounts to 11 M EURO.

CO-OPERATION

At the request of the European Commission, the NATURALHY-consortium will cooperate with Integrated Project HYWAYS regarding the development of roadmaps and timelines to the hydrogen economy and with Network of Excellence HYSAFE regarding the communication with the public and decision makers about safety aspects of the transmission, distribution and use of hydrogen/natural gas mixtures. Furthermore, there will be a connection with the Dutch project "Vergroening van Gas" financially supported within the EET-programme.

In order to establish a platform for dissemination, public awareness and understanding, a Strategic Advisory Committee has been defined that consists of leading global entities from politics, decision makers, regulators and normalisation and authorities active in the fields of environment, safety, energy, standardisation and policy. The International Energy Agency, International Gas Union, UK Health and Safety Executive, ministries of economic and environmental affairs, European Natural Gas Vehicle Association, the Carbon Trust, Bellona, the coordinators of the Integrated Project HYWAYS and Network of Excellence HYSAFE will participate in this Committee which is chaired by the chairman of CEN. Representatives of the “EU-Platform for hydrogen and fuel cells” and a regulator will be invited onto the Committee as well.

ACKNOWLEDGEMENT

The authors would like to express their gratitude to the European Commission for selecting this project for funding within the Sixth Framework Programme (Sustainable Energy Systems). Furthermore, the authors would like to emphasise that defining a project like this can only be completed successfully with the active support of all partners involved. The authors would like to kindly acknowledge the representatives of the partners and more in particular the persons mentioned in table 1 on the WPs for their efforts and enthusiasm which were essential in the development of this challenging project.

The NATURALHY-project: The potential of the existing natural gas system for hydrogen

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Abstract

The transition towards the hydrogen economy will be lengthy and costly. Therefore, a practical strategy has to be followed and the examination of the potential contribution of the existing assets (natural gas transmission and distribution grids) in this framework is a logical first step. By adding hydrogen to natural gas, the physical and chemical properties of the mixture will differ from "pure" natural gas and this may have a major effect on safety and durability issues related to the gas delivery and the performance of end use appliances. The NATURALHY-project aims to define the conditions under which hydrogen can be transmitted and distributed as a mix with natural gas by the existing natural gas system, and can be withdrawn afterwards from the mix by separation technologies. The socio-economic and life cycle consequences of this hydrogen delivery approach will be mapped out.

Keywords: hydrogen delivery, existing natural gas system, mixtures, membranes

Introduction

Hydrogen is assumed to play a major role in the future sustainable energy society (the so-called hydrogen economy). Hydrogen can be produced from various sustainable sources (including biomass and sustainable produced electricity) and can be converted to electricity in high efficient fuel cells without the emission of greenhouse gasses. The transition towards the hydrogen economy will be lengthy (decades), costly and requires a significant R&D effort. An important issue concerns the needed means to connect the hydrogen producers and the end users and to match the patterns of production and demand.

The existing natural gas system offers a unique opportunity for the widespread and cost-effective introduction of hydrogen into society in the relative short term; it will catalyse developments in hydrogen production and end-use. Using the existing natural gas system will also help to increase public acceptance of hydrogen and will give more time to define the future energy system and the necessary means in sufficient detail. In fact, it is a strategic element in the transition phase to the establishment of hydrogen as an important energy carrier.

As the physical and chemical properties of hydrogen differ significantly from natural gas, it is not at all possible to simply exchange natural gas by hydrogen in the existing natural gas system. However, using the existing system to transport mixtures of natural gas and hydrogen and then selectively removing hydrogen from the mixture near the end-user by means of membranes, will offer a unique opportunity to connect hydrogen producers and end users in the short term and at relatively low cost.

By adding hydrogen to natural gas, the physical and chemical properties of the mixture will differ from "pure" natural gas and this may have a major effect on safety and durability issues related to the gas delivery and the performance of end use appliances.

Objectives

The NATURALHY-project aims to define the conditions under which hydrogen can be mixed with natural gas for delivery by the existing natural gas system and later withdrawn selectively from the pipeline system by advanced separation technologies. The socio-economic and life cycle consequences of this hydrogen delivery approach will be mapped out.

Therefore, the main activities of the NATURALHY-project are focussed on:

- To define the conditions under which hydrogen can be added to natural gas in the existing natural gas system (transmission-distribution-end used infrastructure and appliances) with acceptable safety risks, impact on the integrity of the system and consequences of the end user. The main technical deliverable of the project concerns an expert system (the “Decision Support Tool”) which will determine the maximum percentage of hydrogen that can be added to natural gas supplied in a well defined area and pinpoint the elements that limit the percentage.
- To develop membranes to separate hydrogen from hydrogen/natural gas mixtures;
- To assess the socio-economic and Life Cycle aspects of the NATURALHY-approach.

The enclosed figure shows the main fields of interest in the project.

The main fields of activities

Safety: similar large scale fire and explosion tests will be performed as the experiments used for the development of the natural gas safety models (this work is coordinated by the University of Loughborough);
Durability: hydrogen might diffuse in pipeline materials and reduce its mechanical properties (hydrogen embrittlement). Further to this, small defects which are not relevant in case the pipeline is used for just natural gas, might be crucial in case the pipeline is used for hydrogen/natural gas mixtures (this work is coordinated by Gaz de France);
Pipeline integrity: examination whether the existing techniques for monitoring the condition of pipelines are adequate in case of mixtures (e.g. is the equipment sensitive enough to detect small defects) (this work is coordinated by Netherlands Organisation for Applied Scientific Research, TNO);
Performance: adding hydrogen to natural gas changes the combustion properties of the gas, and of course the performance of the end user appliances should be assured (this work is coordinated by University of Warwick).
Life cycle and socio-economic assessment of the NATURALHY-approach, taking a newly build hydrogen delivery system as a reference (this work is coordinated by University of Warwick).

The main technical deliverable of the project concerns an expert system that determines the maximum percentage of hydrogen that can be added to natural gas supplied in a well defined area and pin points the elements that limit the percentage (this work is coordinated by Instituto de Soldadura e Qualidade, ISQ). A significant dissemination programme has been defined, that is coordinated by Exergia.

Project characteristics

The NATURALHY- project has been selected by the European Commission for financial support within the sixth Framework Programme. The execution of the project started on 1st May 2004, and its duration will be 5 year. In this project 39 organisations participate, including 15 from the gas industry. The project budget is over 17 M EURO.

Project partners

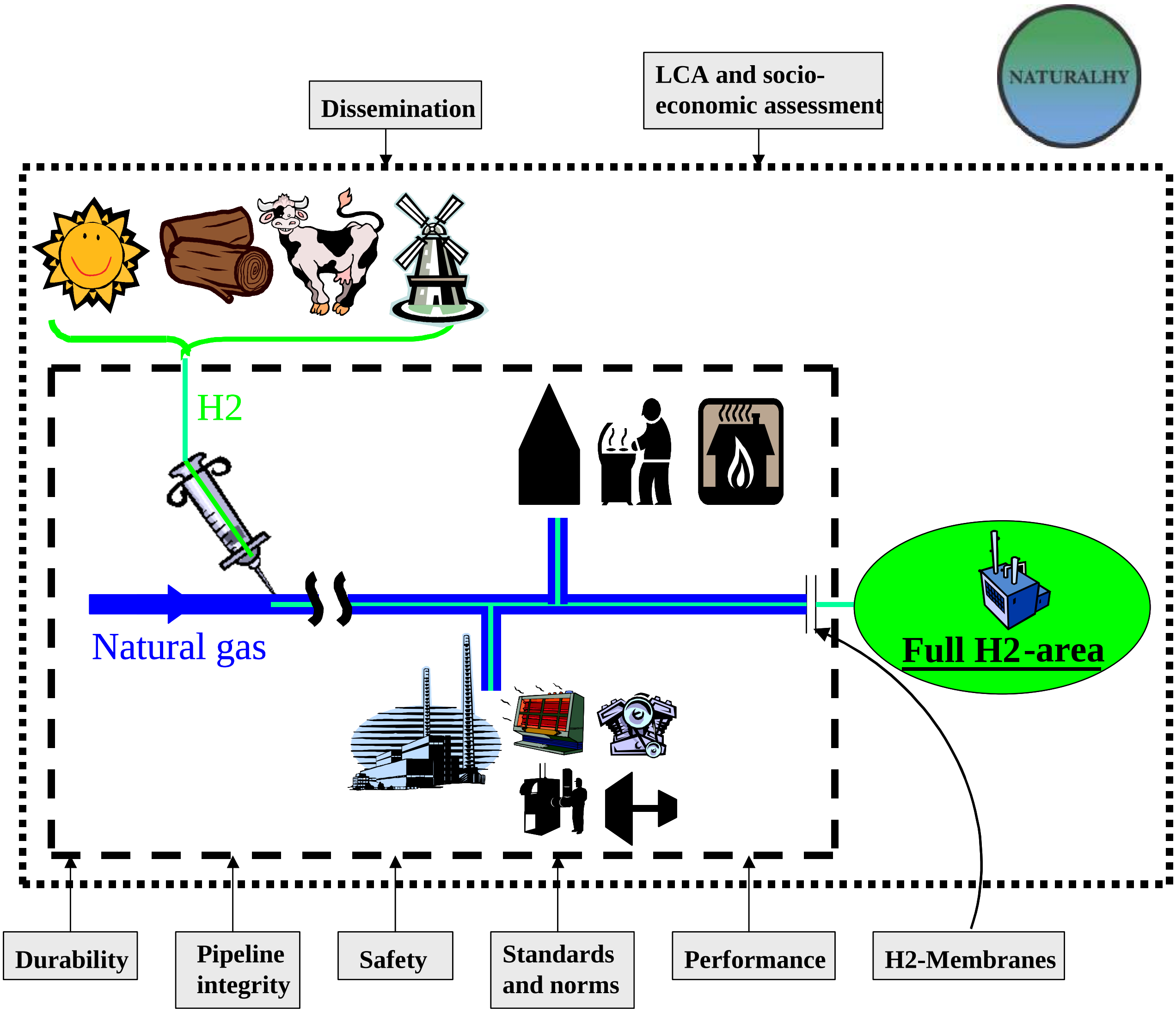
Strategic Advisory Committee

In order to ensure a good communication with stakeholders

Next to the organisations that are active in the execution of the project, the NATURALHY Strategic Advisory Committee has been established. This is the forum at which strategic issues are discussed with the stakeholders including governments, decision makers, regulators, NGO's active in the fields of hydrogen, energy, natural gas, safety or environment. The Strategic Advisory Committee contains members such as US Department of Energy, International Gas Union, International Energy Agency, International Association for Hydrogen Energy, European Commission, UK Health & Safety Executive and Bellona as well as the leading organizations of the NATURALHY-project being Gaz de France, Universities of Warwick and Loughborough, Instituto de Soldadura e Qualidade (ISQ), Exergia, GERG, Netherlands Organisation for Applied Scientific Research (TNO), and N.V. Nederlandse Gasunie (project coordinator).

Next to the consortium executing the programme, guidance will be provided by a Strategic Advisory Committee consisting of representatives from relevant (inter)national organisations such as International Gas Union, International Hydrogen Energy Association, the European Commission and Parliament, U.S. Department of Energy, UK Health and Safety Executive.

The execution of the project started on 1st May 2004, and takes 5 years. The European Commission has selected the NATURALHY -project for financial support within the Sixth Framework Programme.


NATURALHY
Dissemination
LCA and socio-economic assessment
H2
Natural gas
Full H2-area
Durability
Pipeline integrity
Safety
Standards and norms
Performance
H2-Membranes

EUROPEAN GAS
RESEARCH GROUP

GROUPE EUROPÉEN DE
RECHERCHES GAZIÈRES

Natural Gas R&D in Europe and the prospects for collaboration

David Pinchbeck, General Secretary

GERG – The European Gas Research Group

1. INTRODUCTION

GERG is strictly a research and development (R&D) organisation and this paper begins with a brief outline of its rôle in the European Gas Industry. It goes on to detail some of the current pressures on R&D activity and argues the case for collaborative R&D as a fairly obvious solution.

It illustrates the breadth of the very latest R&D activity within GERG with a range of examples of current or recently completed collaborative projects, of great importance to the gas industry, none of which would have been possible without a network of quality R&D practitioners.

2. GERG - THE EUROPEAN GAS RESEARCH GROUP

The History

GERG, the European Gas Research Group, was founded in 1961 to strengthen the gas industry within the European Community and it achieves this by promoting research and technological innovation in all aspects of the gas chain. Established initially as a network to enable exchange of information between a select group of specialist R&D centres to avoid duplication of effort, it has grown steadily to its current size.

GERG members have developed a large European reservoir of specialist knowledge, which currently represents a high quality research resource numbering in excess of 2000, many of whom are international leaders in their field. However, its priorities remain: networking; technical information exchange; and the promotion of collaborative R&D, as evidenced by its wide portfolio of projects carried out by dedicated, multi-disciplinary project teams.

Membership currently stands at 16 from 10 European countries, each actively involved in natural gas R&D, and these members serve a European gas industry which has the responsibility of supplying in excess of 80 million domestic, commercial, industrial and power station customers. It’s worth noting that despite, or maybe as a result of, the changes in the European natural gas landscape, GERG membership is growing steadily, with six new members in recent years.

Over the years, GERG has evolved, from the small, original group of gas industry R&D organisations to a considerably stronger, more professional organisation, located in Brussels to benefit from proximity to the institutions of the European Union (EU).

How does it work?

GERG operates at several levels, with a Board and Plenary responsible for strategic direction, operating within a structure designed to maximise high level networking. However, the success of GERG relies principally on the interactions within the Programme Committees, where groups of technical experts, drawn from the member organisations, meet on a regular basis. Their objectives are to exchange ideas, to explore the potential for collaboration and, most important, to establish GERG projects.

The whole activity is supported by a professional, full-time Secretariat based in Brussels, to underpin the activities of GERG and to maintain links with outside bodies, particularly the offices of the European Union and gas industry organisations world-wide.

Collaboration is the key to GERG, which operates as a project brokerage, based in the technical Programme Committees, and thrives on a steady flow of new project proposals. Members decide whether new proposals are of interest, whether they wish to support them and, in conjunction with the Secretariat, whether they could be eligible for external funding. Once projects have been initiated, they are run by dedicated Project Teams which can, and often do, include non-GERG members such as universities, manufacturers and, importantly, non-European natural gas organisations, in key roles.

GERG has four Programme Committees (PCs), covering the Gas Industry’s main areas of activity:

- PC General Studies;
- PC Transmission and Storage;
- PC Distribution;
- PC Utilisation;

- covering a very wide range of projects, some of which will be described later.

What does it do for the Gas Industry?

Probably the most important feature of GERG is that it facilitates participation in collaborative R&D projects with shared cost and shared risk. At times of reducing R&D expenditure and increasing short-term views, this single factor can enable R&D projects to take place when they otherwise may have failed to get off the ground.

3. THE EFFECT OF LIBERALISATION ON R&D

In recent years, liberalisation of the gas market has fundamentally changed the structure of the gas industry in Europe leading, in many cases, to the creation of distinct, new companies with specific responsibilities for network management or for gas sales. However, its implementation across Europe is very different and, in some countries, liberalisation has been a tougher exercise than in others. With regard to R&D, the changes have generated a variety of outcomes, ranging from business as usual to virtually no business at all, with several permutations in between… and the evolution continues.

Inevitably, liberalisation of the gas market has had a negative impact on the amount of gas-related R&D being conducted within Europe. This is certainly the case for GERG members, amongst whom there is clear evidence of reduced availability of funds; a concentration on shorter-term projects; reduction in R&D staff levels and a more critical appraisal of cost and benefits.

It’s easy to take the short-term view and to rest on one’s laurels but there is a widely shared view that companies without some investment in R&D could be out of business within 10 years. It’s clear then that an absence of R&D capability in the gas industry equates to a potential risk.

Of course, you would expect such views from a representative of an R&D organisation, but I would suggest that gas companies need to make a critical assessment of where they would like to be in 10 years - and in 20 years - and to follow this with a rigorous analysis of what needs to be done to achieve those ends.

Most important, they must recognise the key rôle that R&D has played in achieving the position we have today, the *status quo*, and that continued R&D will be essential in securing the future.

4. GERG PROJECTS

The Good News

It’s true that there is pressure on R&D budgets, but it is exactly in circumstances such as these when collaborative R&D becomes vitally important as it spreads the risk, enables leverage of R&D funding, and gives life to projects which otherwise would not have got off the ground.

GERG is increasingly seen as providing a viable option that enables R&D to continue in times when individual company funding is scarce.

The Projects

It's important in assessing the value of GERG to consider the breadth and depth of R&D activity in which it is involved, so the following provides a review of some recently completed GERG projects, all of which have been co-funded by the European Union:

- **MICROMAP: MINI AND µCHP – MARKET ASSESSMENT AND DEVELOPMENT PLAN**

  … was a paper exercise which considered the potential for mini- and micro-CHP systems in an enlarged Europe. It evaluated the technologies, the markets and the players and examined both grid connection issues and the possible take-up in European countries to 2020. It assessed the potential for cost savings, for energy and CO_2 emission reductions and proposed routes by which the new technology could be exploited.

- **PRESENSE - PIPELINE REMOTE SENSING FOR SAFETY AND THE ENVIRONMENT**

  …relied on images of the earth available from satellites that we are all so familiar with these days and, as we get better access to spin-offs from military developments, with their superior quality and resolution, we can see progressively more and more detail. With a little more R&D, it should be possible to derive images with sufficient resolution to pick out the locations of individual buried pipelines - as a means of detecting 3rd party interference; soil movement, such as landslip or subsidence, and even methane leakage.

  So, PRESENSE is a satellite-based remote sensing project for monitoring pipelines which, overall, should improve the safe and secure transmission of gas in the world's high pressure gas pipelines. A range of sensors, including Synthetic Aperture Radar, LIDAR, infra-red and optical surveillance technologies, has been assessed, both for their ability to 'see' in a variety of atmospheric conditions and for their contribution to a data-fusion approach to image processing and recognition.

- **VOGUE: VISUALISATION OF GAS FOR UTILITIES AND THE ENVIRONMENT**

  … has been developing sophisticated new tools to aid the processes of detecting and locating leaks from pipeline systems - on the street. Passive infra-red and active, laser-based, technologies are being developed so that dispersing natural gas clouds can be visualised as a means of pinpointing gas leaks from both high and low pressure gas pipelines.

- **GIGA: GROUND PENETRATING RADAR FOR HIGH PRECISION PIPE LOCATION**

  …was a research study to inform and enable the design and build of a new, dependable Ground Probing Radar (GPR). Its eventual objective - in a subsequent phase of the project - is a system specifically designed to provide the precision and high resolution required to enable no-dig installation of gas pipelines in association with Horizontal Directional Drilling. It is hoped that the second phase will begin early in 2006 to develop what we believe to be the next generation of GPR.

5. THE FUTURE?

The decade ahead will be a time of great change for the natural gas industry in Europe. The demand for natural gas is set to grow and the development of safe, well controlled, and reliable natural gas networks will be essential if optimum performance is to be achieved.

Historically, the requirement to deliver benefits to shareholders in newly privatised companies has implied short-term cost savings and, almost inevitably, this has meant reductions in R&D expenditure. However, at the same time, there will be an increasing requirement to address the problems associated with energy efficiency and emissions. Although natural gas is the preferred fossil fuel as it offers a clean and efficient energy source, there will still be a demand for high quality R&D if a continuing contribution is to be made.

Clearly, there are certain projects which can not or should not be taken on by individual companies, because of cost, and because of risk and a particular example is outlined below.

Hydrogen

Looking well ahead to what is a major plank in the European Union's 'bridge to security of energy supply' brings us to the 'Hydrogen Economy'. There is no doubt that hydrogen could become important, but there are barriers to be overcome associated with production, storage, distribution and, not least, perceptions of reduced safety. If serious progress is to be made towards the development of a European hydrogen system, a practical interim strategy must be adopted within the context of the existing natural gas system and this brings me to NATURALHY.

The European gas industry is working together with key players in a European Union-funded project to examine the barriers that exist to, and the advantages that might accrue from, the addition of hydrogen to the natural gas transmission and distribution system. Clearly, the environmental advantages could be significant with respect to the Kyoto targets - even if the distributed mixture contains no more than 20% hydrogen. However, this is not a trivial exercise and it will require both considerable R&D effort and significant external funding.

Inspired by Gasunie in the Netherlands and set up within the GERG framework, the NATURALHY project represents a large, integrated body of work that could lead to the widespread delivery of hydrogen in Europe within the next 20-30 years. It could make a significant contribution to Europe's environmental aspirations whilst, at the same time, providing a logical stepping stone to the hydrogen future in Europe. The slide is an illustration of the scope of the project which will examine aspects across the whole of the natural gas system. It is a 5 year project, which began in May 2004 with 39 partners spread across Europe; it is valued at €17 million, €11 million of which is provided by the European Union.

Without doubt, one of the most important aspects of the project will be changing the perception amongst the general public of reduced safety associated with hydrogen. As a consequence, a major part of NATURALHY will be associated with safety and dissemination of information in an attempt to dispel the common view of hydrogen which results primarily from memories and images of the Hindenberg disaster.

6. CONCLUSIONS

Given the key rôle of natural gas in both primary energy supply and in achieving our environmental objectives, it is vital to ensure that the gas industry's R&D capability is maintained so that the benefits of gas are fully exploited. The examples I have given, which are ambitious and expensive R&D projects - collaborative projects - have illustrated that there are gas companies which consider it essential to be involved in R&D that will deliver solutions that are important for their business and, crucially, for their future survival.

In Europe we are facing significant reductions in R&D funding and, in such times, many agree that it is essential to maintain involvement in organisations and events such as this that allow, even promote, collaboration in R&D - to ensure that mechanisms exist for shared cost and shared risk activities - in a period when short-term business thinking has become increasingly prevalent. It's quite evident that the GERG members, including many major European gas companies, appreciate the many obvious benefits of collaboration in R&D activities.

The members of GERG represent some of the most expert technical performers in the international natural gas R&D community, combining to contribute key skills and experience that would be impossible to resource at the purely national level. The combination makes for a very strong organisation, significantly stronger than its individual parts, which is well-equipped to undertake energy sector research and technological development.

GERG is always seeking new partners for collaborative R&D projects to enhance the gas business and CIGEC 2005 provides a strong impetus for collaboration between China and Europe. It is hoped that it will initiate the development of strong and lasting links so that, between us, we can develop new technologies that will serve to strengthen the position of the gas industry worldwide.

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ASSESSING THE DURABILITY AND INTEGRITY OF NATURAL GAS INFRASTRUCTURES FOR TRANSPORTING AND DISTRIBUTING MIXTURES OF HYDROGEN AND NATURAL GAS

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ABSTRACT

Extensive infrastructure exists for the transport of natural gas and it is an obvious step to assess its use for the movement of hydrogen. The Naturalhy project's objective is to prepare the European natural gas industry for the introduction of hydrogen by assessing the capability of the natural gas infrastructure to accept mixtures of hydrogen and natural gas. This paper presents the ongoing work within both Durability and Integrity Work Packages of the Naturalhy project. This work covers a gap in knowledge on risk assessment required for delivering H2+natural gas blends by means of the existing natural gas grids in safe operation.

Experiments involving several parts of the existing infrastructure will be described that are being carried out to re-examine the major risks previously studied for natural gas, including: effect of H2 on failure behaviour and corrosion of transmission pipes and their burst resistance (link to the Work Package Safety), on permeability and ageing of distribution pipes, on reliability and ageing of domestic gas meters, tightness to H2 of domestic appliances and their connexions. The information will be integrated into existing Durability assessment methodologies, originally developed for natural gas.

An Integrity Management Tool will be developed taking account of the effect of hydrogen on the materials properties. The tool should enable a cost effective selection of appropriate measures to control the structural integrity and maintaining equipment. The main measures considered are monitoring, non destructive examination (pigging and non pigging) and repair strategies. The tool will cover a number of parameters, e.g.: percentage of hydrogen in the gas mixture, material of construction, operating conditions and condition of cathodic protection. Thus, the Integrity Management Tool will yield an inspection and maintenance plan based on the specific circumstances.

1 INTRODUCTION

Extensive infrastructure exists for the transport of natural gas and it is an obvious step to assess its use for the movement of hydrogen. The Naturalhy project is a major "Integrated Project" which has been selected for funding by the European Commission within the Sixth Framework Programme (started in May 2004). The objective is to prepare the European natural gas industry for the introduction of hydrogen by assessing the capability of the natural gas infrastructure to accept mixtures of hydrogen and natural gas. Many aspects of compatibility with existing natural gas infrastructure need to be considered, including safety.

This paper presents the ongoing work within both Durability and Integrity Work Packages of the Naturalhy project. This work covers a gap in knowledge on risk assessment required for delivering H2+natural gas blends by means of the existing natural gas grids in safe operation. The strategy adopted for the Durability and Integrity work within Naturalhy is to gain an understanding of the changes induced by injecting H2 in the natural gas on the Durability of the existing infrastructures and associated risk assessment and to update the Tools for Integrity Management. An extensive literature survey [1] was carried on for fitting the work programme to the most relevant experimental and numerical studies.

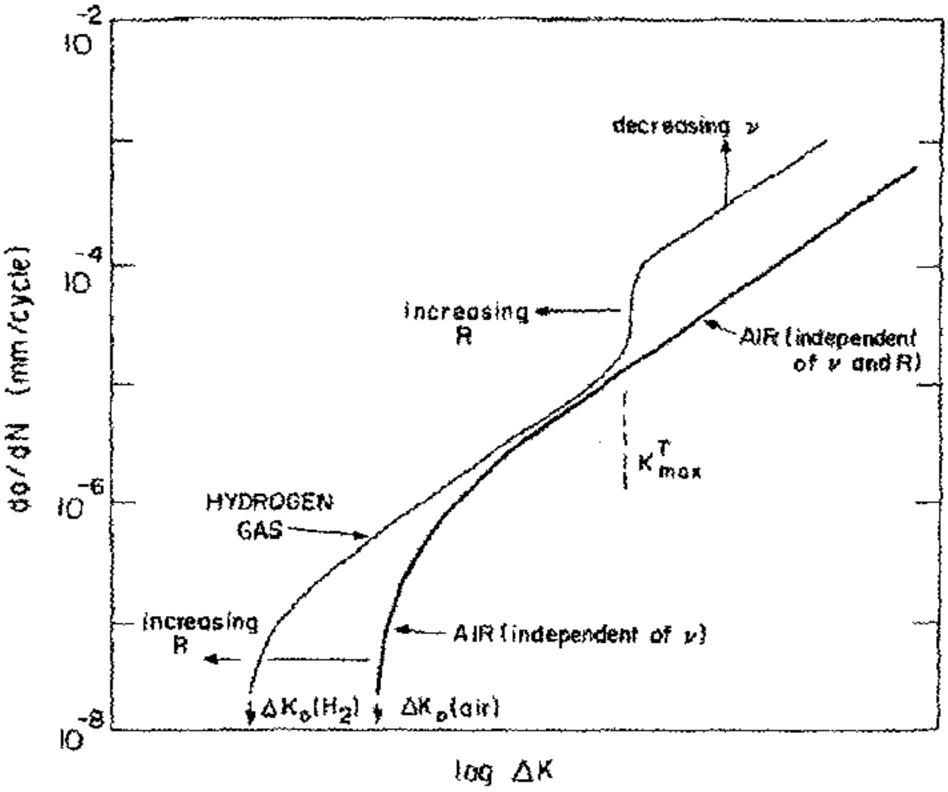
2 DURABILITY OF THE EXISTING NATURAL GAS GRIDS FOR H2 DELIVERY

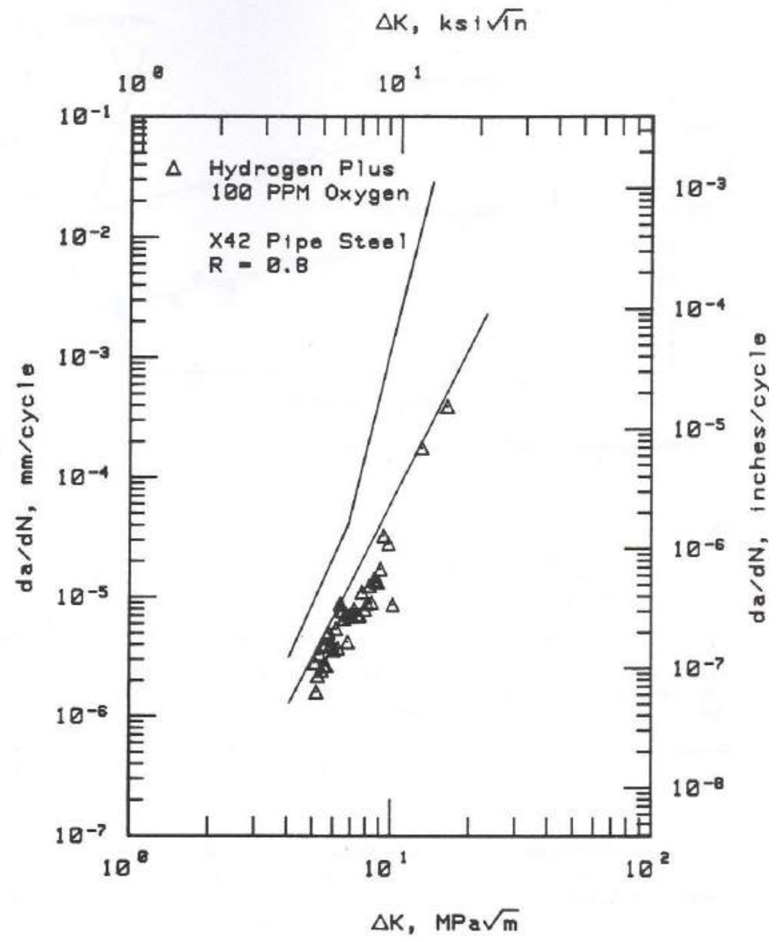
The existing natural gas system has been designed for natural gas. The physical properties of hydrogen differ from natural gas and consequently the impact of hydrogen added to natural gas on the durability of the materials of the grids should be studied. According to the type of the materials of the pipes and therefore their interaction with hydrogen, several approaches for up-dating the major risks previously managed with only natural gas are followed.

2.1 Durability of steel for transmission pipes with H2

Transmission pipes in the existing natural gas grids operates under high pressures for example from 40 bar up to 100 bar. The steels (low carbon steels) used for building the transmission grids have been developed with higher and higher mechanical strength; the steel X42 is one of the oldest, used in the 60's and today operators start to use the X80. But higher is the yield strength, lower is the resistance to crack growth. This risk is well managed for natural gas, and should be assessed for hydrogen. Although the interaction of hydrogen with steels has been largely studied, the aim of using the steel grids designed for natural gas for transport of H2 requires extended studies about the effect of hydrogen on the properties of these steels and understanding of the mechanisms.

Hydrogen embrittlement and its effect on toughness and fatigue behaviour (figure 1); it is well known that hydrogen might initiate brittleness of steel pipes, which affects the failure resistance of the pipe and has consequences for the safety and the lifetime of the pipeline. The degradation mechanism of a pipeline by hydrogen is a very complex matter: for instance, preliminary experiments showed that the sensitivity of a pipeline for degradation by hydrogen is effected by amongst others the operational history of the pipeline. It was proven that a pipeline that has been operated under fluctuating pressures is more sensitive to degradation than a pipeline of the same material that has been operated under a more or less constant pressure.





Solid lines represent hydrogen (upper line)
and nitrogen (lower line) data.

Figure 1. Effect of gaseous hydrogen on resistance of pipe steel to crack growth in fatigue loading [2, 3].

- Tests will be executed on laboratory specimens as well as a few tests on real structures containing defects, to quantify the effect of hydrogen on structures with typical in-service damage; measurement of fracture toughness and fatigue crack growth on steels with defects (welds, gouges, cracks, corrosion pitting) and without defects.

- Moreover the effect of addition of H2 on the evolution of the defects existing in the pipes will be investigated, and the existing defect assessment criteria will be adapted to take into account an increasing percentage of H2 in the natural gas.

- Some demonstrative tests will be carried on at full-scale under H2 pressure; fatigue tests and burst tests on parts of pipes with well-controlled defects. The results will be exchanged with the Work Package on Safety).

- The special case of the rapid propagation of crack, following the opening of the gas pipe, will be studied by numerical modelling. It is expected that due to their different thermo-dynamical properties, the crack arrest will happen sooner in case where hydrogen is present in the gas pipe.

2.2 Durability of polymer for distribution pipes with H2

The poly-ethylene (PE) is the mostly used material for local distribution of natural gas at low pressures, from 16 bar down to few mbar. The main concern about pipes made in polymer like the poly-ethylene (PE) is its permeability to H2 which may induce leakage of gaseous H2 and therefore a dangerous situation. Measurements were done on PE80 material samples in various conditions of pressure, H2 content and temperature. Results showed that H2 diffuses quicker than CH4 and with larger quantity (figure 2). Results will be used for calculating the potential leakages on distribution network and these data will be exchanged with the Work Package on Safety.

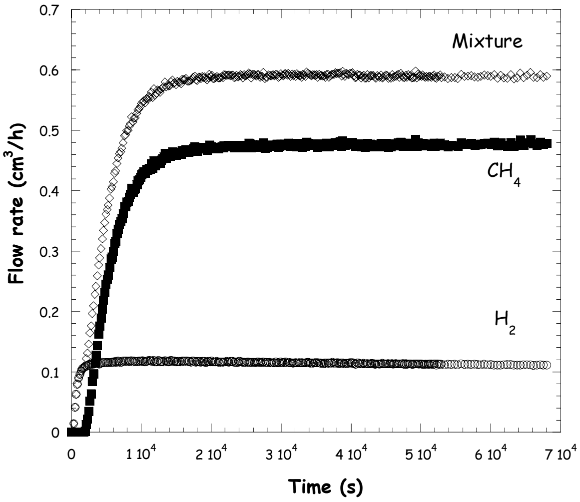


Figure 2. Permeation of PE80 to hydrogen, methane and their mixture (90%CH4-10%H2)
(at 80°C and 21 bar).

Literature survey is quite fine on ageing of PE in H2 gas atmosphere. This subject will be studied under H2 pressure (up to 100 bar) with different H2 content in CH4 (up to 100%). The ageing tests will be accelerated by means of temperature increases (up to 60°C). Tests at 10°C will simulate the actual thermal conditions. Mechanical and physical-chemical techniques will be used for investigating the evolution of the PE properties and micro-structure with ageing conditions.

2.3 Durability of domestic gas meters

The most common domestic gas meters are membranes meters, made with a polymeric membrane which is sensitive to H2 permeation. Several potential effects of H2 are expected;

- Potential influence on metering accuracy; the fact that hydrogen particles are smaller than natural gas ones may cause leakages through the membrane. In such a case, the measuring accuracy would be impaired,

- Potential influence on safety; the dimensions of hydrogen particles may lead to a leakage into the atmosphere through connection sealing,

- Potential influence on durability; Hydrogen physicals characteristics may damage the internal parts of the meter.

Then, the meters will be tested regarding their reliability for H2 metering and ageing behaviour of the membrane in presence of hydrogen.

2.4 Durability assessment tool

All results obtained within the Work Package on Durability will be used for providing the lifetime estimation for the different parts of the gas networks (transmission, distribution and inner grids) and for adjusting the existing lifetime models for pipelines designed for natural gas. The results will be synthesized with the aim to develop sufficient knowledge in order to produce the assessment tool; new software tool for predicting damage impact on pipeline strength, verification of software simulation, and user guidelines.

It will be useful for simulating the most risky situations (severe defects, weak material pieces or joints, H2 release, etc.), so that the safety resulting from the handling of mixtures of hydrogen and natural gas can be determined.

Furthermore, the results are an essential input for the Work Package on Integrity.

3 INTEGRITY MANAGEMENT

3.1 Integrity management of existing pipelines

The most common integrity problems in the existing transmission pipelines include external corrosion and mechanical damage. Internal corrosion has not been a significant issue in most instances due to a strict control of moisture content in the natural gas to meet consumer specifications. Similarly, manufacturing and construction defects are not normally a problem as the quality control during construction and a hydrostatic test ensure that no critical defects are present after construction.

Generally speaking, crack like defects or mechanical gouges are treated by grinding to remove the possibility of crack propagation. Once the defect is removed, the remaining strength of the pipe is assessed using one of the recognised techniques for calculating the effects of a metal loss defect on the strength of the pipe.

If a metal loss defect (non-leaking) is deemed to be critical and in need of repair, the normal methods to apply are for instance a non-welded pipe sleeve or a clock-spring type repair. Both methods are based on a localised mechanical reinforcement of the pipe to compensate for metal loss while avoiding interference with the cathodic protection system or changing the properties of the pipe metal. Fundamental in any repair is that the corrosion process be stopped with a good coating to ensure that the defect in question does not grow.

3.2 Defect criticality

With regard to the foreseen application of hydrogen to natural gas, one of the most interesting issues is the so-called defect criticality. The current practice for determining whether a defect is critical and needs to be repaired are based on defect geometry, material properties and to a certain extent service use. However, if the hydrogen or hydrogen mixture within the pipeline acts to change the pipe material properties, in particular with respect to crack propagation, these criteria may need to be revised. Therefore, the critical issue to be investigated is related to the question which type of defects and up to which size can be judged to be acceptable. Within the population of the current acceptable defects, there may be a certain group that become critical under hydrogen service.

Another aspect which will be of interest, will be the potential for acceleration of fatigue - type failures. Typically in a natural gas transmission system, the number of pressure cycles is so small that defects surviving the hydrostatic test after construction will not fail from fatigue during the life of the pipeline. Thus a number of pipe material or weld defects may exist in today's pipeline networks that are non-injurious and essentially undetectable with the inspection technology in use. If it can be shown that these types of defects may grow more rapidly in the presence of hydrogen, a new inspection technique may have to be adopted to detect and eliminate these defects in a timely fashion.

The various effects from hydrogen on the materials behaviour are depicted in figure 3.

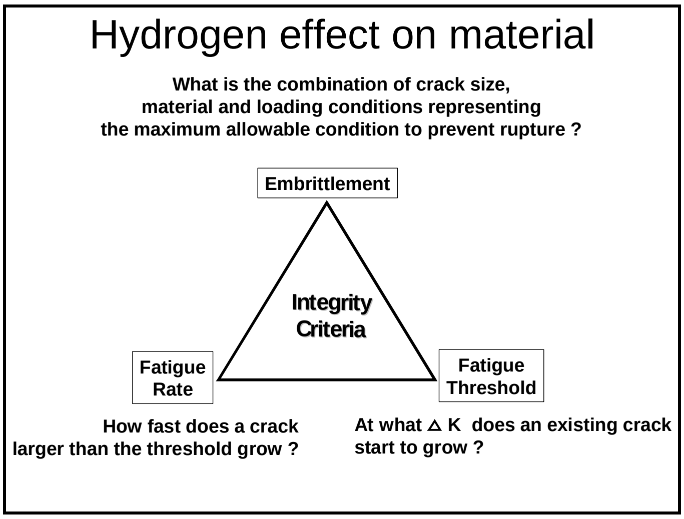


Figure 3. The influence of hydrogen on the material behaviour.

3.3 Development of inspection effectiveness

It is expected that hydrogen addition will have a certain effect on the materials behaviour although no results are currently available to support this expectation. Especially, the fatigue threshold value is expected to decrease. Therefore, it will be important to verify whether the existing inspection tools (for pigging e.g. Magnetic Flux Leakage) will be capable of detecting the smaller defect sizes. Possibly, improvements on the detection capability of existing inspection techniques are needed to meet the more stringent detection requirement. The inspection methods can be split in inspection method for piggable pipelines and non-piggable pipelines. A large testing and validation programme is foreseen to demonstrate the capability of existing techniques.

3.4 Development of repair strategies

Certain non-acceptable defects can be repaired by different kinds of techniques like grinding, weld deposit, metallic sleeves, composite sleeves to save money comparing to the cost of cut and replacement of pipe defective sections.

Due to mechanical steel properties affected by hydrogen around the defects, the current repair criteria for gas pipelines should be changed. For example, the steel toughness affected by hydrogen could modify the weld deposit conditions, the maximum acceptable sizes of grinding, and the maximum acceptable sizes of defects to repair by sleeves.

In addition, it will be interesting to consider the possibility of crack formation under a mechanical reinforcement repair. These repairs generally accept a certain degree of plastic deformation around the metal loss defect as the pipe expands and transfers the excess stress to the mechanical reinforcement. The amount of plastic deformation depends on the type of reinforcement and the quality of the installation process. In considering a hydrogen mixture, it should be verified that the pipe will continue to support these small plastic deformations without cracking. A crack, if it forms under the mechanical reinforcement, could propagate along the pipe and away from the area being reinforced.

3.5 Integrity Management Tool

At present asset owners make use of Integrity Management Tools to support the process of decision-making and selection of cost effective, appropriate measures to control the structural integrity. Possible measures are monitoring, non destructive examination (pigging and non pigging), excavations and various repair strategies. The Integrity Management Tool should integrate all the available data and models to enable risk management. The tool can be used to demonstrate the effect of influencing factors on integrity, i.e. the probability of failure of a certain pipeline system, see figure 4.

In the project a tool will be developed consisting of models and data in order to take account of the presence of natural gas containing hydrogen. The tool will cover a number of parameters, e.g.: percentage of hydrogen gas mixture, material of construction, operating conditions and condition of cathodic protection. Eventually, the Integrity Management Tool will yield an inspection and maintenance plan based on the specific circumstances.

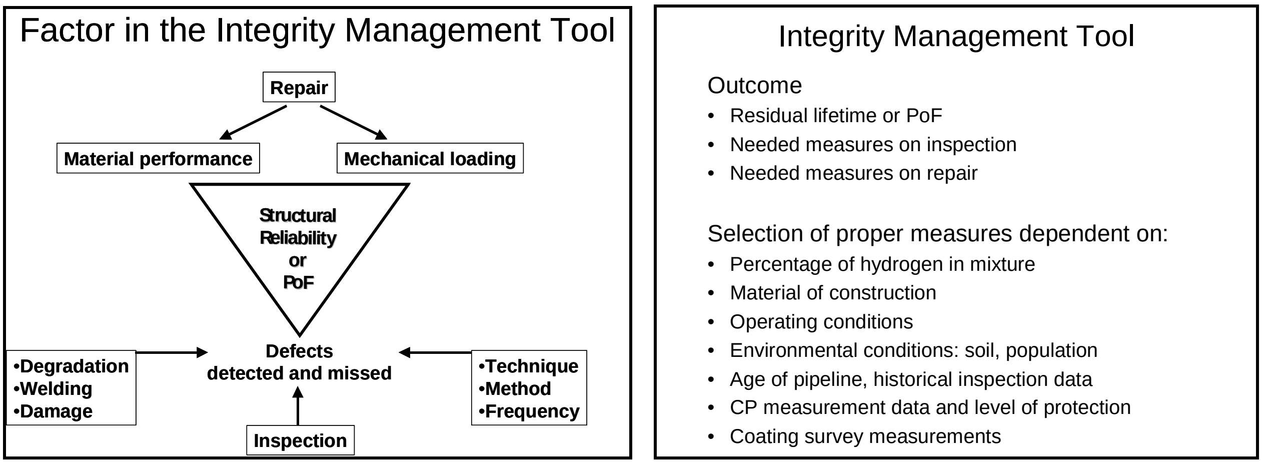


Figure 4. The Integrity Management Tool.

4. CONCLUSION

The addition of hydrogen in pipes and appliances originally designed for natural gas induces large campaigns of testing for determining the characteristics and performance of the materials used since the 60’s or younger in new conditions, and then for determining their lifetime in case of delivery of H2-natural gas mixtures in safe conditions. Understanding of the mechanisms of interaction with H2 is an other important point. Data will be used also for up-grading the existing assessment tools, and guidelines.

The presence of hydrogen in natural gas can decrease in certain cases the mechanical integrity of steel pipelines by local embrittlement in high plastically strained zones, e.g. near defects. The updated defect assessment criteria determined will be more severe than for the existing natural gas situation. So, the acceptable sizes of certain defects will diminish.

Inspection techniques and methods will have to be improved towards a better reliability and more precise detection to maintain a high level of safety and to enable monitoring the degradation for transmission pipelines containing hydrogen – natural gas mixtures,. In addition, repair methods and integrity management will be adapted. The new knowledge will be implemented in an Integrity Management Tool for resource management.

5. ACKNOWLEDGMENTS

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The Work Package on Durability is coordinated by GAZ DE FRANCE (F). The partners involved are; BP Gas Marketing Ltd (UK), Commissariat à l’Energie Atomique (F), Computational Mechanics International (UK), DBI-GUT (D), DEPA (EL), Gasunie (NL), GE PII (UK), Institut Français du Pétrole (F), Instituto de

Soldadura e Qualidade (P), National Technical University of Athens (EL), TOTAL (F), STATOIL (NO), TNO (NL), Ecole Nationale d'Ingénieur de Metz (F), IGDAS (TR), TUBITAK (TR).

The Work Package on Integrity is coordinated by TNO (NL). The partners involved are; Computational Mechanics International (UK), DBI-GUT (D), GAZ DE FRANCE (F), Gasunie (NL), GE PII (UK), Instituto de Soldadura e Qualidade (P), TOTAL (F), STATOIL (NO), IGDAS (TR), TUBITAK (TR).

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THE SAFE USE OF THE EXISTING NATURAL GAS SYSTEM FOR HYDROGEN (OVERVIEW OF THE NATURALHY-PROJECT)

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ABSTRACT

The transition towards the situation in which hydrogen is an important energy carrier will be lengthy (decades), costly (for Europe, hundreds of billion EUROs) and will require significant R&D. The availability of a safe, economic, widespread and high capacity hydrogen delivery system is a key, strategic issue. A practical development strategy is needed for the infrastructure and an examination of the potential of the existing, extensive natural gas system is a important, logical step.

As the physical and chemical properties of mixtures of hydrogen and natural gas may differ significantly from “pure” natural gas, NATURALHY addresses, in particular, the safety issues related to the transmission, distribution and use of hydrogen/natural gas mixtures in the existing natural gas system, including the transmission and distribution grids, the end-user infrastructure and end-use appliances. Additional safety related issues, such as pipeline durability and integrity, are also addressed. The economic, social and environmental costs and benefits of the approach including hydrogen production technologies will be evaluated and compared with existing systems. In preparation for hydrogen-specific appliances, membranes will be developed to enable the separation of hydrogen from distributed mixtures.

A European consortium of 39 partners (including 15 from the gas industry) has been assembled, involving major network operators, hydrogen producers, specialist practitioners and academic researchers in all relevant fields. In this project, set up under the auspices of GERG, The European Gas Research Group, there are leading roles for N.V. Nederlandse Gasunie (NL), Gaz de France (F), TNO (NL), ISQ (P), the Universities of Loughborough and Warwick (UK) and Exergia (GR). In addition to the management team, guidance will be provided by a Strategic Advisory Committee consisting of representatives from relevant (inter)national organizations.

The project started on 1st May 2004 and will run for 5 years. The European Commission has selected the Integrated Project NATURALHY for financial support within the Sixth Framework Programme.

1.0 INTRODUCTION

Hydrogen is foreseen as an important energy carrier. However, the very significant technical, economic and institutional changes required to establish the full hydrogen economy will take several decades to implement. These changes will concern all individual elements of the energy system: production, delivery, storage, conversion and end-use applications. These elements are interrelated and interdependent and, as a consequence of this, there is a “chicken and egg” dilemma regarding market segment development and how supply and demand will push or pull these activities.

In any transition scenario for the full hydrogen economy and in all variants of hydrogen economies, there must be a connection between the hydrogen production and the appliances powered by hydrogen. The distance between the hydrogen production and the appliances will range from several centimeters to several thousands of kilometers depending on production, whether centralized, decentralized or hybrid, and its use. For many situations, pipelines are favorable to, for instance, delivery by trucks. For economic and safety reasons, pipelines will have an important role in connecting hydrogen production facilities and consumers and also in matching the patterns of hydrogen production and demand.

Transmission and distribution of gas is the core business of several partners of the NATURALHY-Project. Hence, they have made a preliminary examination of the possibilities of using their existing gas systems as the connection between hydrogen production and appliances powered by hydrogen. In fact, it is an obvious and pragmatic step to assess the existing situation for adaptation to new opportunities, and in this way to break the "chicken and egg" dilemma.

The NATURALHY-project, prepared by all stakeholders involved and, crucially, including the main gas industry aims to investigate comprehensively the practical means of transition from the existing natural gas infrastructure to the hydrogen economy.

The basic principle investigated in the NATURALHY-Project concerns the addition of hydrogen to natural gas within the existing natural gas system including the high and medium pressure transmission systems, the distribution system, the end-user infrastructures and end-user appliances. The mixture should be suitable for direct use in the existing end-user appliances. Membranes to be developed within the project will enable the extraction of hydrogen from the mixture so that it can be used for hydrogen appliances and for supplying hydrogen to fuel stations for road transport applications. This approach is explained in Fig.1.

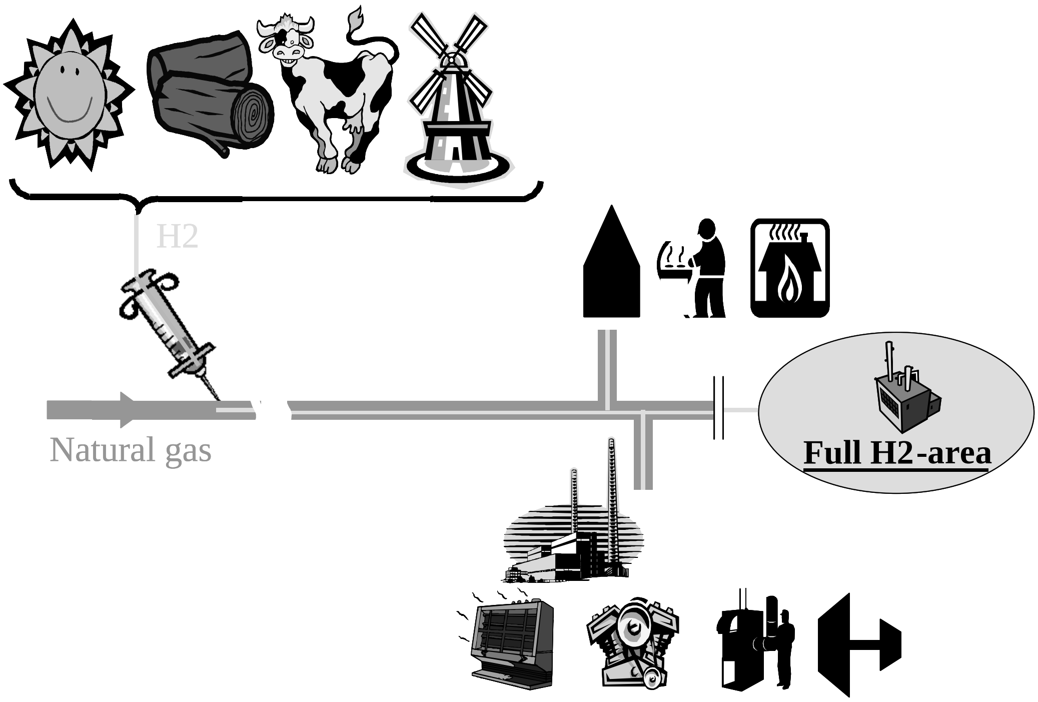

Figure 1. The NATURALHY approach: addition of hydrogen to natural gas in the existing natural gas system, and use of the mixture as well as separation of hydrogen by membranes

The addition of hydrogen to natural gas in the existing natural gas system may result in different chemical and physical properties compared to "pure" natural gas. The impact of added hydrogen on the combustion properties necessitates appropriate actions to mitigate the consequences for, *inter alia*, the performance of end-user appliances, with regard to aspects such as flashback, unintended gas release, efficiency and lifetime; and safety related to all aspects of the supply chain from production up to an including consumption. In addition, hydrogen might also affect the material properties of pipeline systems, which could have an effect on safety.

This paper presents an overview of the project. The paper presented at this conference by Mrs. I. Allait and Mr. J. Heerings gives further details on the NATURALHY programme concerning pipeline durability and integrity, while the paper presented by Professor G. Hankinson explains the safety programme included in NATURALHY.

2.0 PROJECT OBJECTIVES

If urgent progress is to be made towards developing hydrogen as a realistic energy option, a practical strategy must be adopted within the context of the existing, extensive natural gas system. Advantage should be taken from the extensive experience of the natural gas industry, particularly with regard to its excellent safety record. The NATURALHY approach is the only realistic solution to large-scale distribution of hydrogen in Europe in the next 30 to 50 years. The main basis of this view is that:

- Significant financial and economic benefits can arise from the use of the existing European infrastructure with its inherent economic value of several hundreds of billions of EUROs.
- Using the existing gas infrastructure for the change to the full hydrogen economy will accelerate the transition rate and the innovation in all relevant fields.

Further to this vision, the NATURALHY project aims to identify and solve the barriers for progressively introducing hydrogen into natural gas networks and to support the development of a roadmap towards the full hydrogen economy by the EU-funded Integrated Project HYWAYS. Gaining experience with testing key components of full hydrogen systems will speed up the transition process.

Safety is the key issue in the NATURALHY project, and is represented by the following set of objectives:

- To define the technical conditions under which hydrogen can be accommodated in the existing natural gas system with acceptable risks, to avoid leakage and significant degradation of the system and consequences for the end-users.
- To assess the current situation of standards and regulations regarding hydrogen/natural gas mixtures and to identify necessary modifications and to initiate required changes.
- To develop a Decision Support Tool for the assessment of the suitability of an existing natural gas system (transmission, storage, distribution, end-user infrastructure and end-user appliance) for mixtures of hydrogen/natural gas and to develop models to determine the economic and environmental aspects of the whole chain from sustainable hydrogen production up to and including end-user appliance.
- To motivate all stakeholders in the whole chain, from production up to and including end-use, to welcome hydrogen. Such stakeholders consist of, among others, the public, end-users, manufacturers of appliances, owners and operators of gas transmission grids, hydrogen producers, local, regional and national authorities, manufacturers of all kinds of equipment and components for gas, etc. This objective will be met in cooperation with IP HYWAYS and the NoE HYSAFE.

In addition, the following coherent and complementary objectives have been defined:

- To analyse the socio-economic aspects of transitional natural gas/hydrogen systems and the full hydrogen system and compare these with current natural gas and related systems, with particular reference to job creation and maintenance, capital investment and total economic costs.
- To carry out life-cycle assessment as a means of comparing the major resource inputs and environmental outputs of current natural gas and related systems, transitional natural

gas/hydrogen systems and the full hydrogen system, including methods of hydrogen production.

- To develop innovative devices (membranes) to separate hydrogen from hydrogen/natural gas mixtures. These devices will enable an early establishment of full hydrogen growth centres that will help to advance a gradual transition to the full hydrogen economy.

3.0 PARTICIPANTS

Table 1. List of organizations participating in the NATURALHY-project

Participant name	**Part. short name**	**Country**
N.V. Nederlandse Gasunie	GASUNIE	NL
Högskolan i Borås	UCB	SE
BP Gas Marketing Limited (BP)	BP	UK
Commissariat à l'énergie atomique (CEA)	CEA	F
Compagnie d'Etudes des Technologies de l' Hydrogène	CETH	F
Computational Mechanics International Ltd	CMI	UK
The European Association for the Promotion of Cogeneration	COGEN	B
Centro Sviluppo Materiali Spa	CSM	I
DBI Gas- und Umwelttechnik GmbH	DBI-GUT	D
Public gas corporation S.A.	DEPA	EL
Danish Gas Technology Centre	DGC	DK
Energy Research Centre of the Netherlands	ECN	NL
EXERGIA, Energy and Environment Consultants S.a	EXERGIA	EL
Technische Universität Berlin	TU BERLIN	D
Gaz de France	GDF	F
General Electric PII Ltd	GE PII	UK
GERG - The European Gas Research Group	GERG	B
The Health and Safety Executive	HSE (UK)	UK
Istanbul Gaz Dagitim Sanayi ve Ticaret A.S	IGDAS	TR
Institut Français du Pétrole	IFP	F
Instituto de Soldadura e Qualidade	ISQ	P
University of Leeds		UK
Loughborough University		UK
Tubitak Marmara Research Center Energy Systems and Environmental Research	MRC	TR
Naturgas Midt-Nord I/S	MIDT-NORD	DK
Netherlands Standardization Institute	NEN	NL
National Technical University of Athens	NTUA	EL
Norwegian University of Science and Technology	NTNU	NO
Planet - Planungsgruppe Energie und Technik Gbr	PLANET	D
Ecole Nationale d'ingénieur de Metz	ENIM	F
SAVIKO Consultants ApS (Saviko Roskilde ApS)	SAVIKO	DK
Shell Hydrogen B.V		NL
STATOIL ASA	STATOIL	NO
SQS Portugal - Sistemas de Qualidade de Software, Lda	SQS	P
Total S.A	TOTAL	F
Netherlands Organisation for Applied Scientific Research	TNO	NL
X/ Open Company Limited	TOG	UK
Transco plc (part of National Grid Transco plc)	TRANSCO	UK

University of Warwick	WPTG	UK

4.0 PROJECT APPROACH

A set of Work Packages (WP), each covering a well-defined issue or set of issues, has been established within the NATURALHY project. Although closely integrated, they have been defined in such way that they can mainly be executed independently from the other Work Packages.

Technical activities are focussed on existing situations/materials/constructions/circumstances /equipment in relation to the specific physical properties of hydrogen/natural gas mixtures. In fact, the bigger part of these activities is dedicated directly to "safety" and to pipeline durability and integrity aspects, which are strongly related to safety.

With regard to technical aspects, the main focal points of the projects are:

- the high and medium pressure natural gas transmission system;
- the natural gas distribution system;
- the end-user infra structure and appliances;
- membranes for the selective withdrawal of hydrogen from hydrogen/natural gas mixtures.

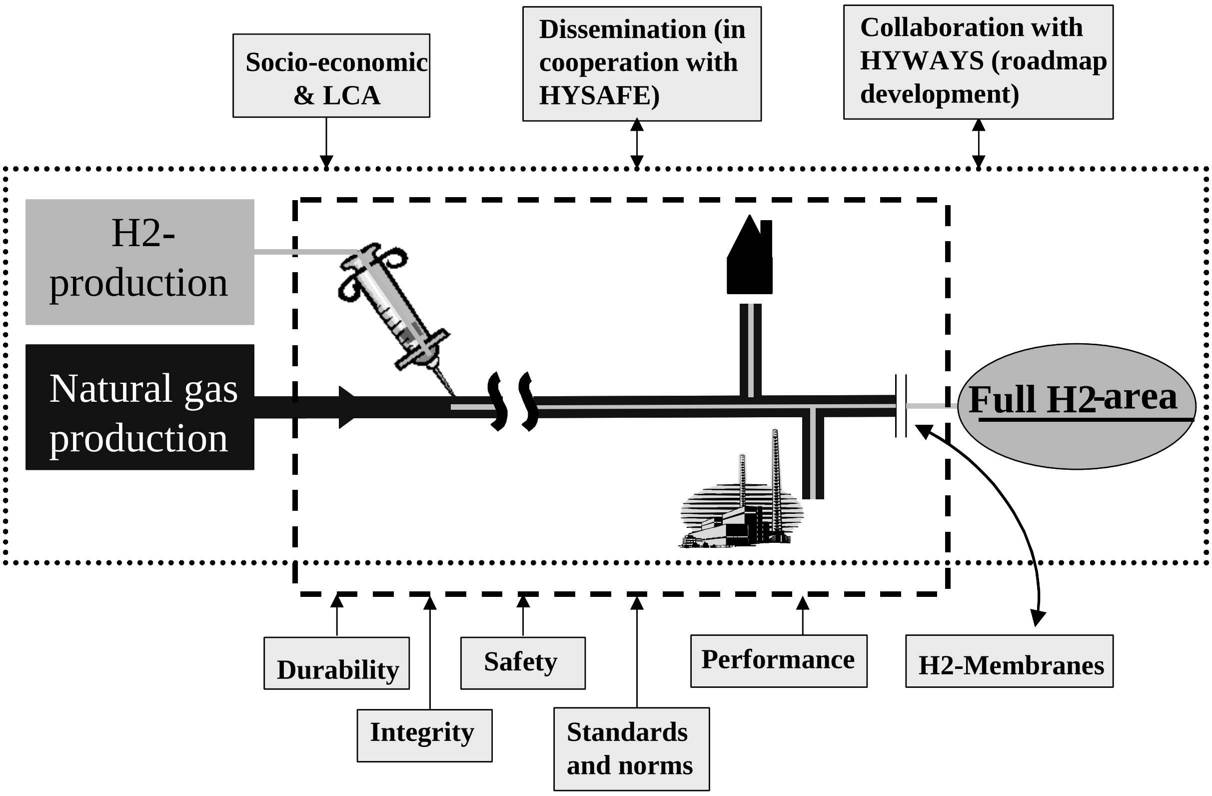

Figure 2. The approach of the NATURALHY-project

And, for all non-technical issues (upper part of figure 2):

The whole chain is taken into account, from production down to and including end-use, covering

- various sustainable hydrogen production facilities and processes, and
- natural gas exploitation.

The Life-cycle and Economic Analyses concern the use of the existing gas system for hydrogen/natural gas mixtures and the full hydrogen situation with a new, dedicated hydrogen infrastructure. The existing situation will be the reference case.

The potentials of the existing natural gas system during the transition towards the full hydrogen economy will be mapped out. In addition, the means (including membranes) for local full hydrogen areas (growth centres) will be developed, based on the separation of hydrogen from hydrogen/natural gas mixtures at/near the location of the end-user.

Table 2 details the distinct Work Packages in the NATURALHY-Project and the organizations coordinating the activities within these packages.

Table 2: NATURALHY Work Packages

Number	**Work Package (Work package leader)**
WP1	Socio-economic and Life Cycle Analysis (Warwick University)
WP2	Safety (Loughborough University)
WP3	Durability (Gaz de France)
WP4	Integrity (TNO)
WP5	End Use (Warwick University)
WP6	Decision Support Tool (ISQ)
WP7	Dissemination (Exergia)
WP8	Project management (Gasunie Engineering & Technology)

The technical Work Packages 2, 3, 4, 5 and 6 originate from the impact of hydrogen on safety, because the properties of hydrogen differ significantly from natural gas.

Within the framework of Work Package Safety, large-scale experiments are foreseen related to domestic and industrial utilization (confined & vented explosions), transmission and distribution (pipeline rupture fires), transmission, distribution and operational sites (jet fires and vapour cloud explosions). In fact, experiments are planned which are similar to the experiments on which the current safety models for natural gas are based, but with different concentrations of hydrogen added to the natural gas.

In addition to differences in the combustion properties already mentioned, the diffusion of hydrogen into pipeline materials can have a negative effect on the mechanical properties of the material (embrittlement of steel pipelines). Consequently, activities have been defined regarding the acceptability of corrosion defects and sharp defects contained in these brittle zones, to update the associated assessment criteria (WP3) and the maintenance procedures, repair techniques and equipment to assess the integrity of pipelines in presence of hydrogen and natural gas mixtures (WP4).

The sensitivity required of monitoring equipment used to find defects for the case when hydrogen is added to natural gas is higher than in the case of “pure” natural gas and the smallest defect might be critical in the situation of hydrogen/natural gas. Additionally, the question of permeation of hydrogen/natural gas mixtures through the wall of polymer pipelines is also considered in the NATURALHY project.

During approximately the first half of the project, attention will be dedicated to acquiring the basic information concerning safety, durability, pipeline integrity, and the performance of end-user appliances. This information will be used for the development of the “Decision Support Tool” (the main technical Deliverable). The “Decision Support Tool” will comprise, *inter alia,* a set of guidelines, tests procedures, criteria, models and material data; this will be necessary to predict and judge the consequences of adding hydrogen to natural gas regarding durability, safety, economic and life cycle assessment aspects of the transmission and distribution systems and end-user infrastructure and appliances. The Decision Support Tool will enable any given gas system to be assessed for its suitability for carrying hydrogen/natural gas mixtures.

Getting the support of all stakeholders is crucial in this project. So, over the whole length of the project, the Work Package “Dissemination" will concentrate on attracting the attention of public, authorities and gas companies to the projects aims, objectives and results. Regarding the communication with the public and decision makers about safety aspects, there will be an arrangement with NoE HYSAFE (see the paragraph “Co-operation”).

5.0 PLANNING AND BUDGET

The execution of the NATURALHY project actually started on 1st May 2004, and will run for 5 years. The total project budget exceeds 17 M EURO, while the European Commission’s contribution within the Sixth Framework Programme amounts to 11 M EURO.

6.0 CO-OPERATION

In order to establish a platform for dissemination and to encourage public awareness and understanding, a strategic advisory board has been defined consisting of global leading entities from politics, decision makers, regulators, normalisation and authorities active in the said fields, such as International Energy Agency, International Gas Union, UK Health and Safety Executive, Dutch ministry of economic affairs, European Natural Gas Vehicle Association, US Department of Energy, International Hydrogen Energy Association, the Wuppertal Institute, NUON, European Commission, the Carbon Trust, Bellona and HYWAYS and HYSAFE and is chaired by the former chairman of CEN.

The NATURALHY consortium cooperates with IP HYWAYS regarding the development of roadmaps and timelines to the hydrogen economy and with NoE HYSAFE regarding the communication towards the public and decision makers about safety aspects of the transmission, distribution and use of hydrogen/natural gas mixtures. Furthermore, there will be a connection with the Dutch project “Vergroening van Gas” financially supported within the EET-programme.

7. ACKNOWLEDGEMENT

The authors would like to express their gratitude to the European Commission for selecting this project for funding within the Sixth Framework Programme. Furthermore, the authors would like to show their gratitude to the representatives of the participants listed for their efforts and enthusiasm which were essential to raise and execute successfully this challenging project.

23rd World Gas Conference, Amsterdam 2006

THE VALUE OF THE EXISTING NATURAL GAS SYSTEM FOR HYDROGEN, THE SUSTAINABLE FUTURE ENERGY CARRIER (PROGRESS OBTAINED IN THE NATURALHY-PROJECT)

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ABSTRACT

Hydrogen is foreseen as an important energy carrier in the future sustainable energy society. The transition towards the situation in which hydrogen becomes an important energy carrier will be lengthy (decades), costly and needs a significant effort for R&D. In view of this, an examination of the potential of using the existing natural gas pipeline system for the transmission and distribution of hydrogen is a logical first step.

The NATURALHY-project investigates the conditions under which hydrogen can be added to natural gas with acceptable consequences for safety, durability of the system, gas quality management and performance of the end-user appliances. Membranes will be developed to subtract hydrogen from a hydrogen/natural gas mixture for use by hydrogen powered equipment.

The NATURALHY-project is the main European project on hydrogen delivery, in which 39 partners participate. The project is financially funded by the European Commission, and is recognised by the International Partnership for the Hydrogen Economy.

The existing natural gas system has been designed for natural gas. The physical properties of hydrogen differ from natural gas and consequently the impact of hydrogen added to natural gas on the durability of the materials of the grids should be studied in order to up-date the tools of integrity management previously assessed with only natural gas. Therefore the following subjects will be assessed: effect of H2 on failure behaviour and corrosion of transmission pipes and their burst resistance, permeability and ageing of distribution pipes, reliability and ageing of domestic gas meters, tightness to H2 of domestic appliances and their connections.

In terms of safety, the addition of hydrogen to the natural gas within the pipeline has the potential to change (increase) the level of risk presented to the public, because of the different physical and chemical properties of this gas. In particular, hydrogen could increase the likelihood of failures occurring and might increase the severity of the consequences due to the increased reactivity of hydrogen. Therefore, within the NATURALHY project, the risks presented to the public by operating a natural gas network conveying a mixture of natural gas and hydrogen must be examined. A major part of this work will be to assess the fire and explosion hazards presented by accidental releases of natural gas/hydrogen mixtures for comparison with natural gas alone. This will be achieved by conducting large scale experiments and developing improved mathematical models.

By combining new information on failure frequency with a revised assessment of the consequences, the risks presented to the public by the proposed introduction of hydrogen can be re-assessed. In particular, by varying the level of hydrogen, it may be possible to identify the maximum ‘safe’ level which could be introduced whilst maintaining an acceptable risk to the public.

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1. INTRODUCTION

Hydrogen is foreseen as an important energy carrier in the future sustainable energy society. Hydrogen can be produced in many sustainable ways (electrolysis using wind energy, gasification of biomass), and can be used for highly efficient electricity production in fuel cells for domestic, industrial and transportation applications. However, the very significant technical, economic and institutional changes required to establish the "hydrogen economy" will take several decades to implement. These changes will concern all individual elements of the energy system-production, delivery, storage, conversion and end-use applications. These elements are interrelated and interdependent, and, as a consequence of this, there is a "chicken and egg" dilemma regarding market segment development and how supply and demand will push or pull these activities.

In any transition scenario for the full hydrogen economy and in all variants of hydrogen economies, there must be a connection (pipeline) between the hydrogen production and the appliance powered by hydrogen. The distance between the hydrogen production and the appliance will range from several centimetres to several thousands of kilometres depending on the nature of the production, whether centralised, decentralised or hybrid, and its use (e.g. possible hydrogen production in Norway and transmission to Central Europe).

The transition towards the situation in which hydrogen is an important energy carrier will be lengthy (decades), costly (as an illustration, at today's prices, the cost to build from scratch the European natural gas system would be several times 10^{11} Euro) and needs a significant effort for R&D. Transmission and distribution of natural gas is the core business of several partners of the NATURALHY project. In order to prepare themselves for a role in "hydrogen", they have made a preliminary examination of the possibilities of using their existing natural gas systems as the connection between hydrogen production and appliances powered by hydrogen. In fact, it is an obvious and pragmatic step to assess the existing situation for adaptation to new opportunities, and in this way to break the "chicken and egg" dilemma.

Moreover, the preparation is important because hydrogen might offer interesting future business opportunities for natural gas transporters but is also necessary as the EU Directive 2003/55/EC states that "… *taking into account the necessary quality requirements, biogas and gas from biomass or other types of gas are granted non-discriminatory access to the gas-system, provided such access is permanently compatible with the relevant technical rules and safety standards. These rules and standards should ensure, that these gases can technically and safely be delivered into, and transported, through the natural gas system and should also address the chemical characteristics of these gases…*". Although not explicitly stated in this Directive, it also applies to biogas that contain hydrogen. In addition, it can be argued that "or other types of gas" include hydrogen produced as for instance a by-product of a chemical process.

The NATURALHY-project, prepared by all stakeholders involved and crucially including the main gas industry, aims to investigate comprehensively the practical means of using the existing natural gas infrastructure for hydrogen accommodation and delivery.

2. OVERVIEW OF THE NATURALHY-PROJECT

As the physical and chemical properties of hydrogen differ significantly from natural gas, it is generally speaking not possible to simply replace the natural gas completely by hydrogen in the existing natural gas system. However, using the existing system for mixtures of natural gas and hydrogen will offer the possibility to accommodate significant volumes of hydrogen and a unique opportunity to connect hydrogen producers and end users on the short term and at relatively low cost.

These mixtures can be used as such in the existing natural gas appliances (and thereby potentially offer reduced CO_2 emissions) but also in combination with membranes to split the gas stream near the end user, the mixtures can be used to supply high purity hydrogen to hydrogen end users, At least during the transition phase leading to the situation when hydrogen becomes an important energy carrier, this option is interesting and will promote public acceptance of hydrogen, due to the excellent safety record of the natural gas industry. It will also catalyse developments in hydrogen production and end use, and will give more time to define the future energy system and the requirements in sufficient detail. In this respect, the competition of hydrogen with other sustainable energy carriers including large volumes of mainly methane containing biogas will be of particularly importance.

By adding hydrogen to natural gas, the physical and chemical properties of the mixture will differ from “pure” natural gas and this may have a major effect on:

- The safety aspects related to the transmission, distribution and end-use of the gas;
- The durability of the transmission and distribution pipeline systems and the end user infrastructure (hydrogen may diffuse into materials and change the mechanical properties):
- The gas quality management issues related to the gas delivery;
- The performance of end use appliances.

In this paper we will further highlight the work included in the NATURALHY-programme focussing on the impact of hydrogen added to natural gas on the durability aspects of existing natural gas delivery system and on the safety aspects related to the transmission, distribution and use of hydrogen/natural gas mixtures.

The NATURALHY-approach and the main field of activities are indicated in Figure 1.

The main objectives of the NATURALHY-project are:

- To define the conditions under which hydrogen can be added to natural gas in the existing natural gas system (transmission-distribution-end use infrastructure and appliances) with acceptable safety risks, impact on the integrity of the system and consequences for gas quality management and to the end user. The main technical deliverable of the project concerns an expert system (called the “Decision Support Tool”) that determines the maximum percentage of hydrogen that can be added to natural gas supplied in a given section of a natural gas pipeline system and identifies the factors that limit the percentage.
- To develop techniques (membranes) to separate hydrogen from hydrogen/natural gas mixtures;
- To assess the socio-economic and Life Cycle aspects of the NATURALHY-approach.

The following work packages consisting of several coherent tasks have been defined (between brackets the work package leader):

- Socio-economic and Life Cycle Analysis (Warwick University)
- Safety (Loughborough University)
- Pipeline durability (Gaz de France)
- Pipeline Integrity (TNO)
- End Use and membranes (Warwick University)
- Decision Support Tool (ISQ)
- Dissemination (Exergia)
- Project management (Gasunie Engineering and Technology)

In addition, GERG has an important advising role in the management of the project.

Besides the organizations mentioned above the following organizations participate which are particularly active in the gas business: BP Gas Marketing Limited, DBI Gas- und Umwelttechnik GmbH, DEPA, DGC, GE PII, IGDAS, IFP, Naturgas Midt-Nord I/S, Shell Hydrogen, Statoil ASA, Total S.A. and TRANSCO (part of National Grid Transco plc).

Apart from the consortium of partners actually executing the research program, the NATURALHY Strategic Advisory Committee has been established. This Committee addresses the strategic aspects of the project and establishes a platform for dissemination and for promoting public understanding and acceptance, and consists of the stakeholders including governments, decision makers, regulators, NGO’s active in the fields of hydrogen, energy, natural gas, safety or environment. At the moment of preparing this paper the Committee includes amongst others the following organisations: IGU (link Dr. B. Harris), IEA, Ruhrgas, ENItecnology, GERG, DVGW, IAHE, NaturCorp, CONTINUON, UK Health Safety Executive, HYSAFE, HYWAYS, EU-Commission, NL Ministry of Economics, EU-Parliament (Link Mr. G. Adam), US Department of Energy, CEN (link Dr. C.

Beckervordersandforth). Discussions with several hydrogen producers about participation are ongoing.
Very recently, the NATURALHY-project has been recognised in the framework of the International Partnership for the Hydrogen Economy (IPHE, a world wide initiative to coordinate hydrogen research). This recognition opens the way to further international collaborations with organisations and projects active in the fields relevant to the NATURALHY-project.

The NATURALHY-project started on 1st May 2004, and its duration is 5 years. The total project budget amounts to 17.3 MEURO and is financially funded by the European Commission within the 6th Framework Programme for Research, Technological Development and Demonstration.

3. THE EFFECTS OF INJECTING HYDROGEN ON THE DURABILITY AND INTEGRITY OF THE EXISTING NATURAL GAS INFRASTRUCTURES

The existing natural gas system has been designed for natural gas. The physical properties of hydrogen differ from natural gas and consequently the impact of hydrogen added to natural gas on the durability of the materials of the grids should be studied in order to up-date the tools of integrity management previously assessed with only natural gas.

3.1 Durability of Steel for Transmission Pipes with H2

Transmission pipes in the existing natural gas grids operates under high pressures for example from 40 bar up to 100 bar. The steels (low carbon steels) used for building the transmission grids have been developed with higher and higher mechanical strength; the steel X42 is one of the oldest, used in the 60’s and today operators start to use the X80. But higher is the yield strength, lower is the resistance to crack growth. This risk is well managed for natural gas, and should be assessed for hydrogen. It is well known that hydrogen might initiate brittleness of steel pipes, which affects the failure resistance of the pipe and has consequences for the safety and the lifetime of the pipeline [1, 2]. The degradation mechanism of a pipeline by hydrogen is a very complex matter: for instance, preliminary experiments showed that the sensitivity of a pipeline for degradation by hydrogen is effected by amongst others the history of the pipeline.
Therefore, the aim of using the steel grids designed for natural gas for transport of H2 requires extended studies about the effect of hydrogen on the properties of these steels and understanding of the mechanisms;

- Tests will be executed on laboratory specimens as well as a few tests on real structures containing defects, to quantify the effect of hydrogen on structures with typical in-service damage; measurement of fracture toughness and fatigue crack growth on steels with defects (welds, gouges, cracks, corrosion pitting) and without defects.
- Moreover the effect of addition of H2 on the evolution of the defects existing in the pipes will be investigated, and the existing defect assessment criteria will be adapted to take into account an increasing percentage of H2 in the natural gas.
- Some demonstrative tests will be carried on at full-scale under H2 pressure; fatigue tests and burst tests on parts of pipes with well-controlled defects. The results will be exchanged with the Work Package on Safety (see §4)).
- The special case of the rapid propagation of crack, following the opening of the gas pipe, will be studied by numerical modelling. It is expected that due to their different thermo-dynamical properties, the crack arrest will happen sooner in case where hydrogen is present in the gas pipe.

3.2 Durability of Polymer for Distribution Pipes with H2

The poly-ethylene (PE) is the mostly used material for local distribution of natural gas at low pressures, from 16 bar down to few mbar. The main concern about pipes made in polymer like the poly-ethylene (PE) is its permeability to H2 which may induce leakage of gaseous H2 and therefore a dangerous situation. Measurements were done on PE80 material samples in various conditions of pressure, H2 content and temperature. Results showed that H2 diffuses quicker than CH4 and with larger quantity (Figure 2). Results will be used for calculating the potential leakages on distribution network and these data will be useful for assessing the risks (see §4).

Literature survey is quite fine on ageing of PE in H2 gas atmosphere. This subject will be studied under H2 pressure (up to 100 bar) with different H2 content in CH4 (up to 100%). The ageing tests will be accelerated by means of temperature increases (up to 60°C). Tests at 10°C will simulate the actual thermal conditions. Mechanical and physical-chemical techniques will be used for investigating the evolution of the PE properties and micro-structure with ageing conditions.

3.3 Durability of Domestic Gas Meters

The most common domestic gas meters are membranes meters, made with a polymeric membrane which is sensitive to H2 permeation. Several potential effects of H2 are expected;

- Potential influence on metering accuracy; the fact that hydrogen particles are smaller than natural gas ones may cause leakages through the membrane. In such a case, the measuring accuracy would be impaired,
- Potential influence on safety; the dimensions of hydrogen particles may lead to a leakage into the atmosphere through connection sealing,
- Potential influence on durability; hydrogen may damage the internal parts of the meter.

Then, the meters will be tested regarding their reliability for H2 metering and ageing behaviour of the membrane in presence of hydrogen.

3.4 Integrity Management; Updating for Natural-gas+H2 Mixtures Delivery

All results obtained on Durability will be used for providing the lifetime estimation for the different parts of the gas networks (transmission, distribution and inner grids) and for adjusting the existing tools used for integrity management of the pipelines designed for natural gas.
The most common integrity problems in the existing transmission pipelines include external corrosion and mechanical damage.

3.4.1 Defect Criticality

With regard to the foreseen application of hydrogen to natural gas, one of the most interesting issues is the so-called defect criticality. The current practice for determining whether a defect is critical and needs to be repaired are based on defect geometry, material properties and to a certain extent service use. However, if the hydrogen or hydrogen mixture within the pipeline acts to change the pipe material properties, in particular with respect to crack propagation, these criteria may need to be revised. Therefore, the critical issue to be investigated is related to the question which type of defects and up to which size can be judged to be acceptable. Within the population of the current acceptable defects, there may be a certain group that become critical under hydrogen service.
Another aspect which will be of interest, will be the potential for acceleration of fatigue - type failures. Typically in a natural gas transmission system, the number of pressure cycles is so small that defects surviving the hydrostatic test after construction will not fail from fatigue during the life of the pipeline. Thus a number of pipe material or weld defects may exist in today's pipeline networks that are non-injurious and essentially undetectable with the inspection technology in use. If it can be shown that these types of defects may grow more rapidly in the presence of hydrogen, a new inspection technique may have to be adopted to detect and eliminate these defects in a timely fashion.

3.4.2 Development of Inspection Effectiveness

It will be important to verify whether the existing inspection tools (for pigging e.g. Magnetic Flux Leakage) are capable of detecting the smaller defect sizes. Possibly, improvements on the detection capability of existing inspection techniques are needed to meet the more stringent detection requirement. A large testing and validation programme is foreseen to demonstrate the capability of existing techniques.

3.4.3 Development of Repair Strategies

Certain non-acceptable defects can be repaired by different kinds of techniques like grinding, weld deposit, metallic sleeves, composite sleeves to save money comparing to the cost of cut and replacement of pipe defective sections.

Due to mechanical steel properties affected by hydrogen around the defects, the current repair criteria for gas pipelines should be changed. For example, the steel toughness affected by hydrogen could modify the weld deposit conditions, the maximum acceptable sizes of grinding, and the maximum acceptable sizes of defects to repair by sleeves.

In addition, it will be interesting to consider the possibility of crack formation under a mechanical reinforcement repair. A crack, if it forms under the mechanical reinforcement, could propagate along the pipe and away from the area being reinforced.

3.5 Integrity Management Tool

At present asset owners make use of Integrity Management Tools to support the process of decision-making and selection of cost effective, appropriate measures to control the structural integrity. Possible measures are monitoring, non destructive examination (pigging and non pigging), excavations and various repair strategies. The Integrity Management Tool should integrate all the available data and models to enable risk management (Figure 3).

In the project a tool will be developed consisting of models and data in order to take account of the presence of natural gas containing hydrogen. The tool will cover a number of parameters, e.g.: percentage of hydrogen gas mixture, material of construction, operating conditions and condition of cathodic protection. Eventually, the Integrity Management Tool will yield an inspection and maintenance plan based on the specific circumstances.

4. THE RISKS TO THE PUBLIC ASSOCIATED WITH INTRODUCING HYDROGEN INTO A NATURAL GAS PIPELINE SYSTEM

As a result of many years experience, the hazards associated with operating natural gas pipeline systems are well understood. Within Europe, a risk based approach is taken in relation to most hazardous industries installations, such as gas pipeline operations, whereby the risk to the public is assessed by considering both the likelihood of a failure occurring and the consequences that failure may have on a member of the public. To determine the overall risk, a wide range of potential failure scenarios (such as third party damage, corrosion and mechanical failure) and failure sizes (from small leaks to total pipeline rupture) would be considered and the consequences on an individual located in the vicinity of the pipeline assessed. Criteria for what is deemed an ‘acceptable risk’ to present to the public as a result of operating the pipeline system have been agreed with regulatory bodies and pipeline operators endeavour to ensure that their operations do not exceed this risk level.

The addition of hydrogen to the natural gas within the pipeline has the potential to change (increase) the level of risk presented to the public, because of the different physical and chemical properties of this gas. The main two contributors which could result in an increased risk are:

- Increased likelihood of failure occurring due to an adverse affect of hydrogen on pipeline materials (such as corrosion, degradation, permeation)
- Increased consequences following failure due to the increased reactivity of hydrogen compared to natural gas (such as increased severity of explosions).

The first item is considered in more detail within the Durability Work Package of the NaturalHY Project as discussed in Section 3 above. The results of this work will allow estimation of the failure probability of potential failure mechanisms for a system conveying natural gas/hydrogen mixtures. The second item is studied in more detail within the Safety Work Package. The Safety Work Package will then reassess the risks presented to the public by combining new information on failure frequency with a revised assessment of the consequences. In this way, it is the intention to assess any unacceptable change in the risk presented to the public by the proposed introduction of hydrogen into a natural gas pipeline system. In particular, by varying the level of hydrogen considered, it may be possible to identify the maximum ‘safe’ level.

4.1 Scope of the Safety Studies

As mentioned above, the Safety Work Package will reassess the risks presented to the public by combining new information on failure frequency with a revised assessment of the consequences. To this end, a large part of the Safety Work Package is aimed at understanding the hazards which may arise following an accidental release of hydrogen/natural gas from a pipeline system and assessing how this differs (if at all) from natural gas.

Failures from the high pressure pipeline system are most likely to give rise to large jet fires in the open air. For natural gas pipelines, the hazard distances in this situation are dominated by the thermal radiation hazard, as any overpressure developed as a result of ignition has been shown to be insignificant. However, due to the increased reactivity (burning velocity) of hydrogen, it is possible that the overpressure hazard may need to be reconsidered and its contribution to the risk presented to an individual assessed.

Large failures in process areas or where significant levels of congestion (obstacles) might be present can give rise to a large gas/air cloud which, if ignited, can produce a Vapour Cloud Explosion (VCE) generating damaging overpressures. For natural gas/air mixtures, research has shown that whilst damaging overpressures can be produced, the risk of deflagration to detonation transition (DDT) occurring (whereby a step change in the explosion severity results) is remote, and furthermore, any flame passing out of a congested region into an uncongested region will decelerate. However, it is known that hydrogen/air mixtures can undergo DDT and consequently, it will be crucial to identify the maximum percentage of hydrogen that can be introduced into the natural gas without the probability of DDT being unacceptably high.

Failures from the low pressure distribution system can give rise to gas/air mixtures forming within buildings served by the gas supply system, such as domestic properties and commercial or industrial buildings. In such cases, there is a potential for a confined explosion to occur resulting in a hazard to persons within the building either directly (burns or overpressure injury) or indirectly (crush injuries as a result of building collapse). The introduction of hydrogen may change the characteristics of the formation of a flammable accumulation within a building and may also change the severity of the explosion, for example, it may increase the likelihood of building collapse.

As fire and explosion phenomena are strongly scale dependent, it is extremely difficult to study such hazards in the laboratory. Hence, all the above aspects are to be studied by undertaking large scale experimental studies which will provide data for the development and validation of improved mathematical models of the fire and explosion hazard arising following the introduction of hydrogen into a natural gas pipeline system. These large scale studies will be supported by a detailed examination in a laboratory facility of the laminar and turbulent burning velocity of hydrogen/natural gas mixtures as these parameters are crucial for understanding and predicting large scale explosion behaviour, especially in relation to the potential for a detonation to occur. Using the data from all the experimental work, mathematical models previously developed by the natural gas industry for assessing gas accumulation, fire and explosion hazards will be extended to allow their use for assessing natural gas/hydrogen mixtures. In addition, a computational fluid dynamic CFD model developed by the nuclear industry for hydrogen accumulation will also be applied to natural gas/hydrogen mixtures.

To date, work has commenced primarily on two topic areas: large scale experiments to study gas accumulation and explosions in a confined region; and the experimental assessment in a laboratory facility of the laminar and turbulent burning velocities.

4.2 Determining Laminar and Turbulent Burning Velocities

A 380mm diameter, fan-stirred explosion bomb is being used for these experiments, located at the University of Leeds in the UK (Figure 4). A large number of experiments are to be performed enabling a comprehensive study of methane and hydrogen/methane mixtures containing up to 50% hydrogen to be completed with Equivalence Ratios (ER) from 0.5 to 1.3. (Equivalence Ratio is defined as r x (*mass of fuel/mass of air)* where *r* is the air:fuel ratio required for stoichiometric combustion). The turbulence level has also been varied. For laminar flames, the results have been compared with other experimental data from the literature for methane and methane/hydrogen mixtures, and with the predictions of a detailed chemical kinetic model [3]. The experiments have confirmed that for methane the laminar burning velocity varies with Equivalence Ratio, with the peak occurring at ERs of between 1 and 1.1. For 50% hydrogen in methane, the peak laminar burning velocity occurred between an ER of about 1.1 and 1.2. Adding hydrogen to the methane also resulted in increased laminar burning velocities compared to methane (Figure 5). This Figure also demonstrates good agreement between the experimental data and predictions made using the detailed kinetic scheme. Little burning velocity data exists for turbulent methane/hydrogen mixtures, so the comprehensive measurements being gathered at present will represent of unique database for use by the project.

4.3 Large Scale Experiments to Study Gas Accumulation and Explosions in a Domestic Property

A series of 10 experiments have been conducted in which gas (methane and hydrogen/methane mixtures) has been released into a test rig representing a typical domestic room. The test rig was constructed from steel and was 3m by 3m by 2.3m high and the experiments were conducted at the Advantica Test Site in Cumbria, UK. To simulate the circumstances typical of a domestic environment, the gas release was at a low pressure (30 or 20mbar) representing the typical pressure upstream and downstream of a domestic gas meter. Leak sizes from 2 to 10mm diameter were studied representing a leaking joint and complete failure of an internal gas pipe. An accumulation of gas above the lower flammability limit is more likely to be produced if the released gas occupies only part of the room. For this reason and since the gas is a buoyant gas, the test conditions selected were those most likely to give rise to a gas layer being formed in the upper half of the room. Consequently, the gas was released vertically upwards and the ventilation regime used was an upward crossflow, whereby air entered through a low level vent on one wall and gas mixture left through a high level vent on the opposite wall. A typical domestic door was fitted in one wall. During the experiments, the gas concentration was measured with time at 20 locations throughout the enclosure using oxygen depletion cells. The experiments confirmed that the gas concentrations were uniform in the horizontal plane and varied only with height. Figure 6 shows typical gas concentrations against height at various time intervals, measured at the instrument locations during a test in which methane was released vertically upwards from a 5mm diameter hole positioned 1.1m above the floor for a period of about 1000 seconds. This figure shows that the gas accumulation formed as a layer above the height of the release point. In some experiments, where a flammable accumulation was produced, the gas/air mixture was ignited using an electric spark. The door provided a low failure pressure vent. Explosion overpressures were measured both within the enclosure and outside.

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Acknowledgments

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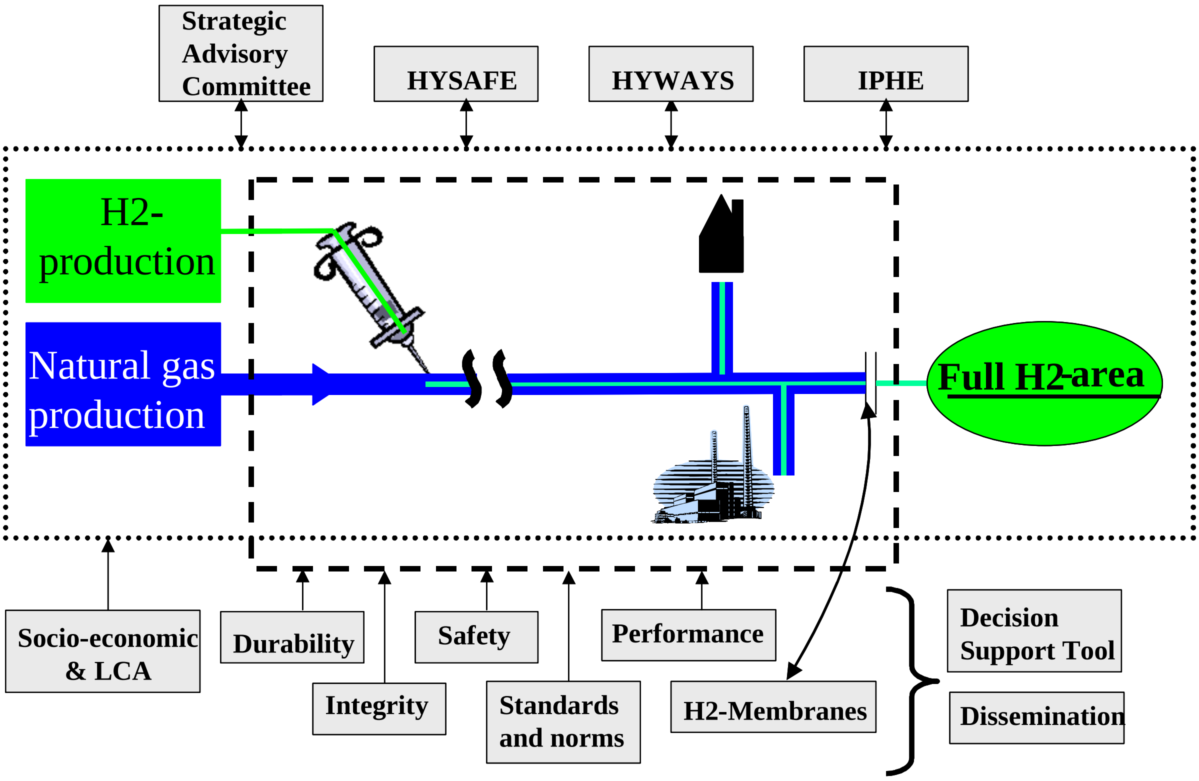
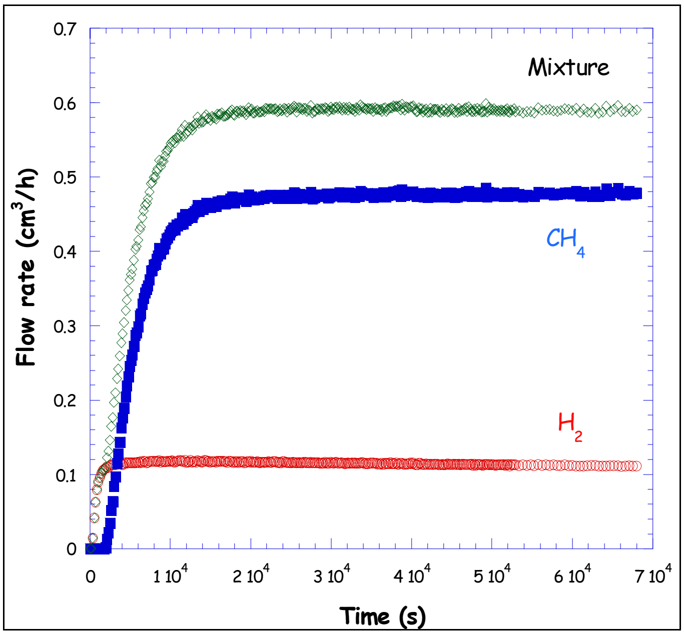


Figure 1: The NATURALHY-approach and the main fields of activities of the project



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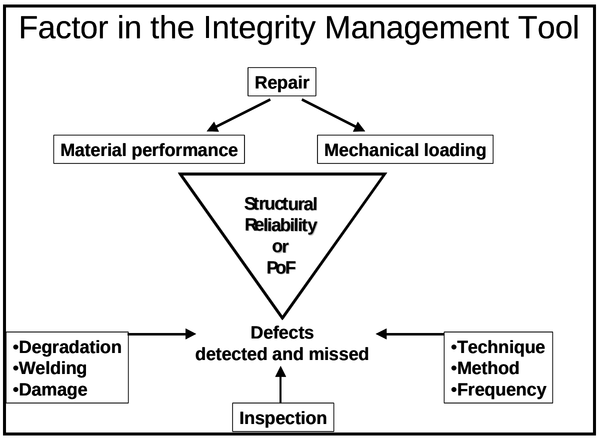

Integrity Management Tool

Outcome

- Residual lifetime or PoF
- Needed measures on inspection
- Needed measures on repair

Selection of proper measures dependent on:

- Percentage of hydrogen in mixture
- Material of construction
- Operating conditions
- Environmental conditions: soil, population
- Age of pipeline, historical inspection data
- CP measurement data and level of protection
- Coating survey measurements

Figure 3. The Integrity Management Tool

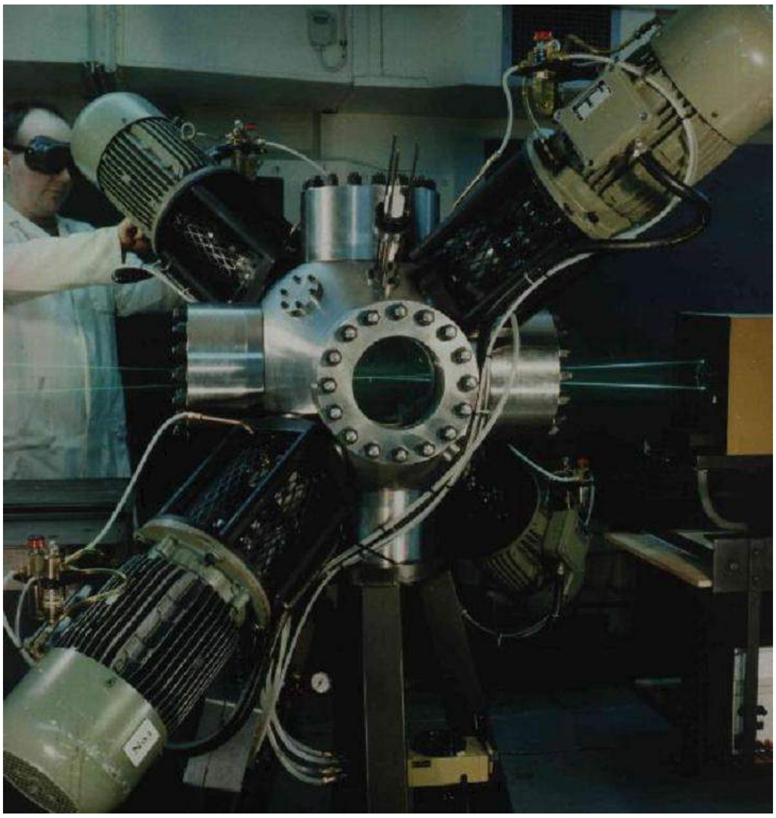

Figure 4: Fan stirred explosion bomb at Leeds University

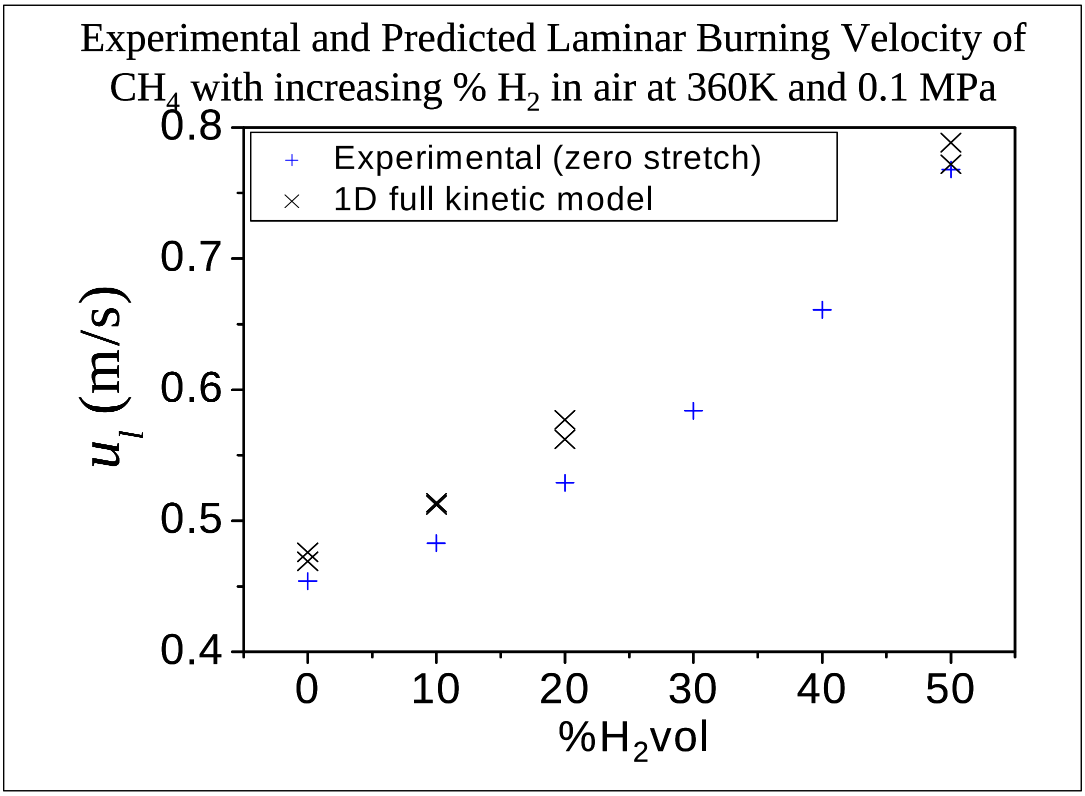

Figure 5: Laminar Burning Velocity of hydrogen/methane mixtures

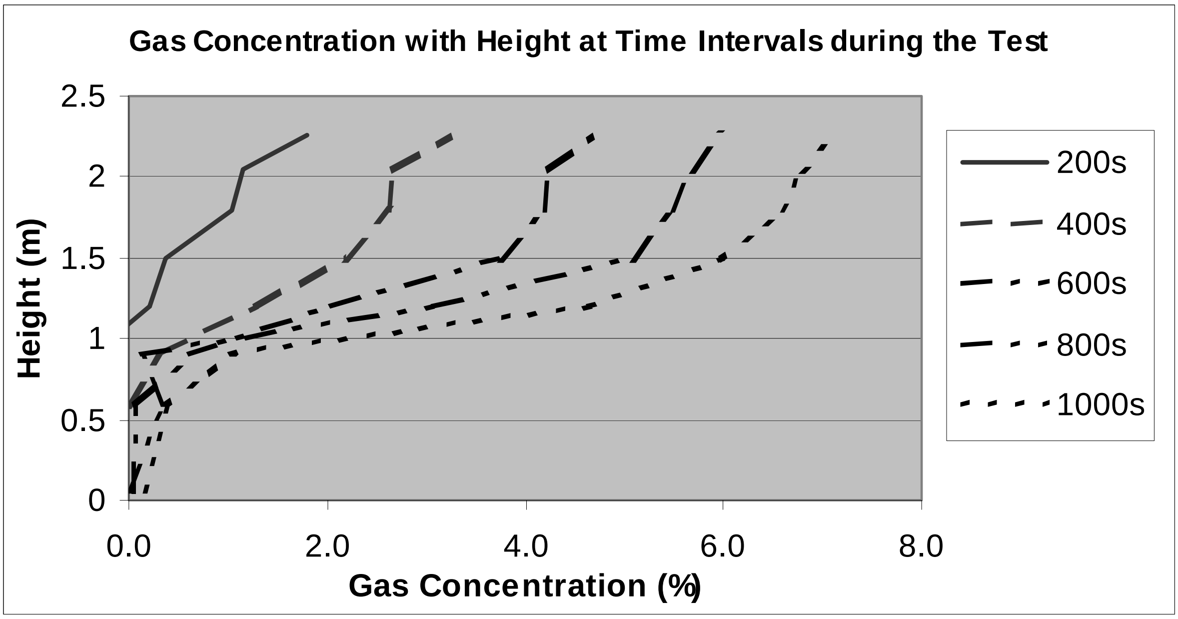

Figure 6: Gas Concentration with Height above the Floor within the Room at Various Time Intervals during a test (methane from a 5mm hole located 1.1m above the floor)

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Carbon membranes from cellulose: Synthesis, performance and regeneration

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Abstract

Cellulose hydrolysis with trifluoroacetic acid (TFA), that is gentle enough to preserve the monosaccharides, provided an anticipative route to carbon membrane formation. Increasing the hydrolysis time, resulted in reduced weight loss during carbonization, and better separation performance for selected gas pairs. The permeability of N_2, H_2, CH_4, O_2, and CO_2 is reported for carbon membranes obtained from wood pulp hydrolyzed to different extents, as well as for carbon membranes obtained from different heating protocols (single gas tests at 30 °C and 2 bar).

A simple, energy effective and rapid regeneration method for membranes that are conductors or semi-conductors has been developed: when a low voltage, direct current was applied on an iron-doped carbon, enhanced permeation rates were immediately observed. The permeability increase depends on several factors, including gas critical temperature and current size. Electrothermal regeneration may also be applied on-stream, avoiding process interruption or an extra set of membranes. The method can be used for a continuous process, and not only for batchwise regeneration (e.g. activated carbon).

Keywords: Carbon; Cellulose; Trifluoroacetic acid; Metal additive; Electrothermal regeneration

1. Introduction

Koresh and Soffer [1] produced molecular sieve carbon membranes for a continuous gas separation process by simple thermochemical treatment two decades ago. In 1995, Soffer et al. [2] had developed a protocol suitable for cellulose carbonization. It is well known that depolymerization to monosaccharides (mainly levoglucosan) occurs during carbonization, see e.g. Kawamoto et al. [3]. Monosaccharides then form condensed, aromatic structures, releasing gases containing non-carbon atoms (O, H). Cellulose treatment with an acid that is gentle enough to preserve the monosaccharides, will provide an anticipative route to carbon formation. Only a limited number of solvents exist for cellulose.

Trifluoroacetic acid (TFA) is an example of this kind of acid, and is widely used in fractionation of plant materials. Depolymerization to oligo- or monosaccharides is expected to occur. The 1,4-β-linkage in cellulose is hydrolyzed with subsequent decrease in molecular weight. Morrison and Stewart [4] evaluated the stability of oat straw in 99% TFA at 37 °C. Their findings did not indicate any major depolymerization of the cellulose molecules during the first 8 days, but after 12–16 days some depolymerization seemed to have occurred. Glucose was one of the major hydrolysis products. TFA is gentle towards monosaccharides compared to sulfuric acid. But extensive TFA treatment converts the monosaccharides to furan derivatives (caramel-like) through dehydration [5]. Hemicellulose is more susceptible to decomposition because of its more amorphous structure compared to cellulose. Carbonization of glucose produces more furans (five-membered rings), but less levoglucosan compared to carbonization of cellulose. The higher yield of furans is due to the kinetic preference to form five-membered rings over six-membered rings when both are possible (as here). In addition, furans are particularly thermally stable because of their aromatic nature. This was also documented by Sanders et al. [6]. Furans are more volatile than the six-membered rings, hence degradation will take place at a higher temperature—this is favorable for the formation of microporous carbon.

A carbon membrane may be modified by adding metals to the precursor solution. Adding metals to the carbon matrix has a three-sided motivation in the current work:

1. Increasing the micropore volume in the membrane (a spacer effect).

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2. Stimulating interactions with the preferred penetrant by stronger adsorption and possible selective surface flow (condensation on metal oxide clusters).
3. Increasing the electric conductivity of the matrix, for regeneration purposes.

Membrane performance is often evaluated by a type of Robeson plot [7]. In order to better evaluate membrane performance, a time dimension should be added to this kind of performance plot. A specified membrane permeability could be very misguiding if it changes rapidly over time. To achieve an attractive membrane lifetime, the membrane should have a long-time stable permeance (i.e. no significant aging). A stable permeance may be achieved by regeneration, and several techniques exist. The regeneration efficiency (RE) is often defined as

$$\mathrm{RE} = \frac{P_\mathrm{r}}{P_\mathrm{v}} \times 100\% \tag{1}$$

where P_r is the permeance of the regenerated carbon membrane and P_v is the permeance of the virgin carbon.

Traditionally, *thermal regeneration* has been applied to carbon membranes. The method usually has limited regeneration efficiency, see e.g. Menendez and Fuertes [8]. Thermal regeneration also suffers from other drawbacks such as the high temperature requirement (200–500 °C) with possible burnout of the carbon.

Chemical regeneration requires an additional chemical (if a regenerating gas/vapor is not part of the stream), followed by removal of that chemical. Jones and Koros [9] tested air feeds saturated with different organics on carbon membranes made from aromatic polyimides carbonized at 500 or 550 °C. They managed to completely remove sorbed hexane and isopropyl alcohol from carbon membranes by purging with pure propylene at about 10 bar. Membrane function was restored to varying degrees when exposed to some other organics. For example, the regeneration efficiency for O_2 permeance was about 65% after exposure to toluene.

Electrothermal regeneration of carbon membranes is especially suitable in non-oxidizing atmospheres. The continuous medium of graphene sheets makes the CMS membranes electrically conductive. The conductivity may be enhanced by adding metals to the carbon matrix. An adsorbed gas, such as CO_2, may be quickly and efficiently desorbed by the passage of a direct current (DC), thereby allowing for a low-energy, electric swing separation system with operational simplicity [10]. The van der Waals forces between the carbon skeleton and the CO_2 are disrupted or perhaps reversed by the electric current. This interaction most likely results from the quadrupole moment and the free electrons of CO_2. As a result, adsorbed CO_2 is released or repulsed from the micropore surface and desorption occurs. The same effect may apply to other adsorbed gases. Electrothermal desorption is a process where the heat is generated *inside* the adsorbent. Hence, the heat and mass flux directions are the same, i.e. from the solid to the fluid, as opposed to traditional thermal regeneration. Petkovska and Mitrovic [11] showed that electrothermal desorption is more energy efficient than conventional desorption because the fluid temperature can be substantially lower than the adsorbent temperature determining the adsorption equilibrium. They also showed that the same direction of heat and mass fluxes results in better desorption kinetics. Electrothermal regenerating of carbon membranes is especially suitable for separation in non-oxidizing atmospheres, like separation of CO_2 from CH_4. The risk of burning (oxidative degradation) is reduced. If the carbon burns, it will crack and render useless. The current can be applied when the membrane is in operation, without reducing the CO_2 flux. The method also has the possibility of high heating rates. Narbaitz and Cen [12] used electrothermal regeneration applying 50 mA for 5 h to desorb phenol from activated carbon. They reached a regeneration efficiency of 74–90%.

The aim for the reported research has been to make a suitable, cheap carbon membrane for CO_2 recovery from various gas mixtures, with special focus on upgrading biogas to fuel quality. In addition, a simple, online regeneration method was sought, since interruption of a process or having an extra set of membranes (regeneration in parallel with the process) would result in added cost.

2. Experimental

2.1. Materials

Wood pulp (also called kraft pulp) from a mixture of spruce and pine was supplied from Södra Cell Tofte, Norway. It is composed of cellulose and hemicellulose.

Trifluoroacetic acid (TFA, 99%) was supplied from Aldrich, Belgium. $Fe(NO_3)_3{\cdot}9H_2O$ (M_w 404.1) was delivered from Fluka, Switzerland. Gases for permeation tests were supplied from AGA, Norway, with a purity of 99.9% or higher.

2.2. Film formation

The pulp was dissolved in TFA to a concentration of about 1 wt.%. The TFA exposure time may have an effect on the separation performance. In this paper, the *hydrolysis time* is defined as the time from dissolving the cellulose in TFA until the film is dried in the vacuum oven. One pulp sample was exposed for 6 days, and another one for 74 days. For the rest of the films, the exposure time was 2–5 weeks for practical reasons (to limit time consumption).

Iron nitrate was added in various concentrations to some of the solutions to improve the separation performance of the resulting membranes and increase their ability to be regenerated. Other metal nitrates such as silver nitrate may also be used, but is more expensive. The solution was stirred overnight and then ultrasonicated with a VibraCell 130 (Sonics & Materials Inc., CT, USA) 6 mm rod for 2 min at amplitude 80 μm. Then a film was cast on a Teflon$^\mathrm{TM}$ dish at room temperature. The film was covered to protect it from dust and to saturate the atmosphere above the film surface in order to slow down the evaporation rate, thereby increasing the homogeneity of the resulting film. Casting at room temperature was chosen, because 75 and 50 °C resulted in inhomogeneous films with bubble formations. The cast film precursor was left at room temperature

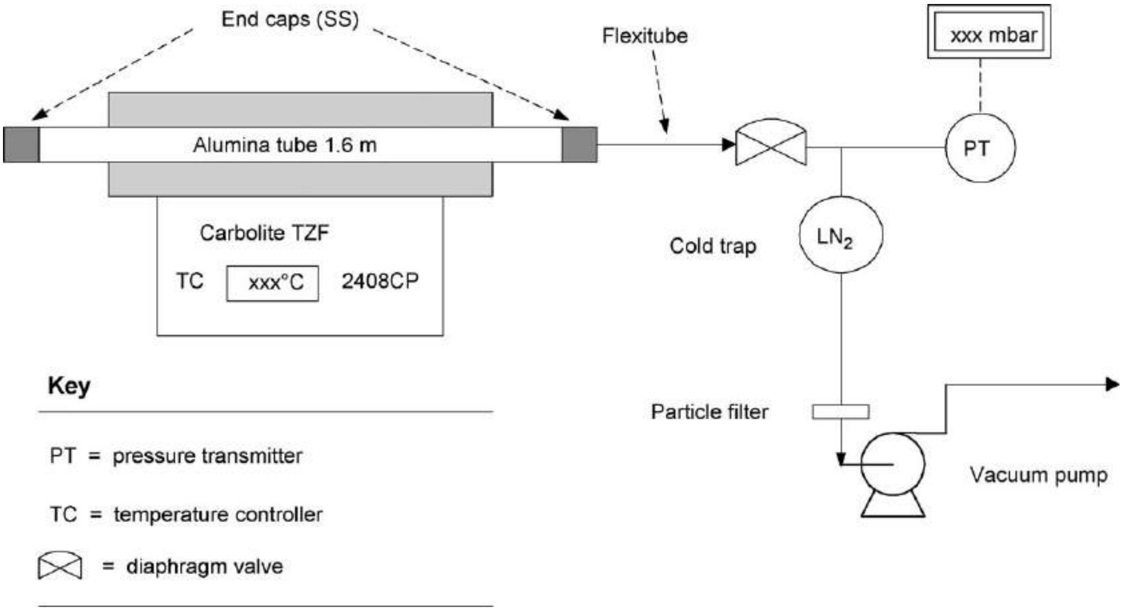

Fig. 1. Constructed set-up for carbonization (SS = stainless steel, LN_2 = liquid N_2 trap).

and after 4 days finally dried in a vacuum oven at 105 °C for about 18 h.

2.3. Carbonization procedure

Films were carbonized under mild vacuum (0.5 mbar) in a tubular furnace (Carbolite® TZF 12/100/900), using a working tube of alumina and a stainless steel grid as support for the films, see Fig. 1.

The basic protocol had a final temperature of 550 °C, kept for 2 h, a heating rate of 1 °C/min and several dwells. The protocol is pictured in Fig. 2, and is based on the protocol developed by Soffer et al. [2] for a cellulosic precursor. Their protocol was optimized with respect to mechanical properties of the carbon and its separation properties. The first two dwells are important in order to remove traces of water and solvent in the precursor. The other dwells are important in order to allow the carbon matrix to rearrange and form micropores in between turbostratically arranged layers of graphene sheets. In addition, different final temperatures in the range 500–850 °C (no soak) were tested, in order to optimize the protocol for pure carbon. After the final temperature was reached the system was allowed to cool naturally to a temperature less than 50 °C, before the furnace was purged with ambient air and the films removed.

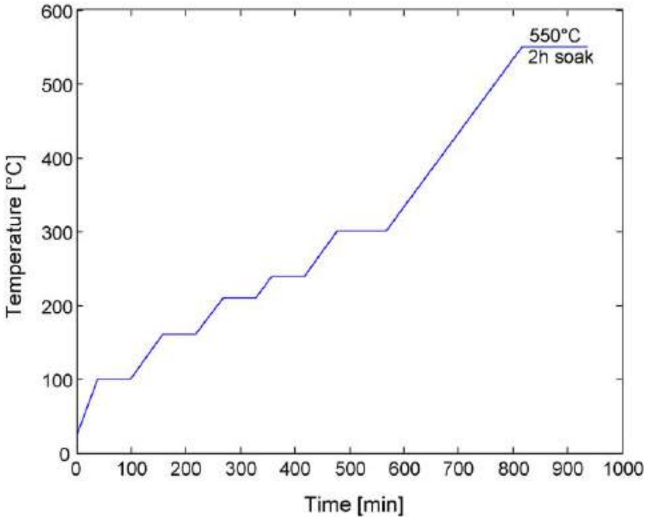

Fig. 2. Basic carbonization protocol (based on [2]).

Thermogravimetric analysis (Q500, TA Instruments, New Castle, DE, USA) was performed on selected samples, with 100 ml N_2 (99.999%) per min and the samples in an open platinum pan. Each sample was dried in vacuum at 105 °C for 18 h prior to analysis.

Metal oxides are known to be stable at high temperatures, whereas, metal nitrates probably decompose to MeO and NO_x. For example, copper nitrate seems to form CuO with evaporation of the remaining nitrate groups, according to Silverstein et al. [13]. The following reaction may take place during carbonization of iron nitrate in a carbon matrix (R–C):

$$2\text{R–C(s)} + \text{Fe(NO}_3)_3\text{(s)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + \text{R–CO(s)} + \text{NO}_x\text{(g)} + \text{CO}_2\text{(g)} \qquad (2)$$

The release of gases should make the iron nitrate-containing membranes more open-structured and permeable than membranes without additives. The released gases may to a large extent contribute to the formation of micropores and rearrangement of the cellulosic carbon. Thus the nitrates may be regarded as porogens.

2.4. Permeation tests

The circular carbon films were masked using an impermeable aluminum tape, leaving open a defined permeation area. Epoxy was then applied along the interface of the tape and the carbon. A sintered metal disc covered with a filter paper was used as support for the film in the test cell. Single gases were tested at 30 °C and a feed pressure of 2 bar (permeate side evacuated) in a standard pressure-rise setup (MKS Baratron® pressure transducer, 0–100 mbar range) with LabView® data logging. The experimental method and setup is described elsewhere [14,15]. The order of testing was always N_2, H_2, CH_4, O_2, CO_2, SF_6, and finally N_2 again to measure any degree of aging (productivity loss). This test order prevents the strongly adsorbing gases from disturbing the performance of the more ideal or non-interacting gases in carbon. The tests were run for several hours or days, to ensure that the transient phase of diffusion was passed and steady state obtained (linear pressure versus time correlation). For CH_4 and SF_6 1 or 2 days of permeation were typically needed, while for H_2 a linear regression curve was obtained after a couple of hours. The permeation system was evacuated overnight in between each gas test. In this paper, selectivity is defined as the ratio of the single gas permeabilities. Permeability is often expressed in Barrer, which is converted to SI-units (kmol m m^{-2} s^{-1} kPa^{-1}) by dividing by 2.99×10^{15}.

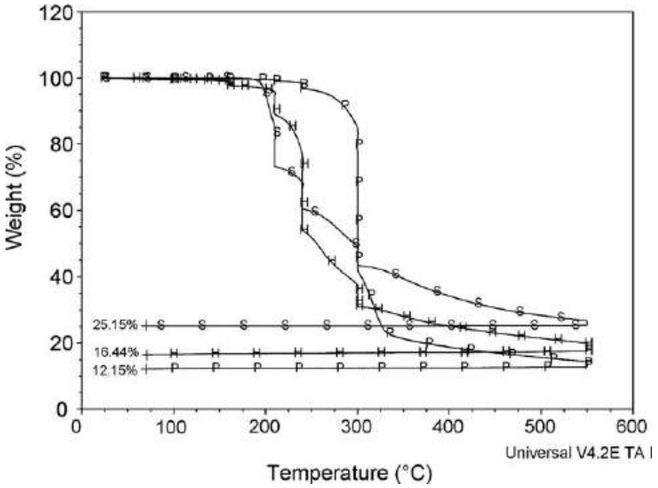

Fig. 3. Thermogravimetric analysis of kraft pulp (P), pulp hydrolyzed for 14 days (H) and sucrose (S) in N_2 atmosphere with the heating procedure identical to the membrane carbonization procedure (550 °C, 2 h soak).

2.5. Regeneration procedure

Electrothermal regeneration was used. First, soldering was tested as a way of attaching single-core cables to the membrane. A soldering paste was used to increase the wettability of the tin solder on carbon, but poor adhesion remained a problem. Hence, a two-component conductive epoxy (ITW Chemtronics® CW2400) was used. An increasing current was applied on a test membrane (not masked), and at about 100 mA current the carbon started to burn. Initial tests showed that when burning occurs, the electric circuit is disrupted or the carbon membrane is cracked. The amount of current used in this work was therefore set well below this failure limit. A carbon membrane was then masked. After the ordinary epoxy had dried, and the membrane was found to function, the single-core cables were connected with conductive glue at opposite regions at the membrane feed side and then cured at 65–70 °C for 10 min.

The permeation tests were run in the same manner as described in the previous section. When steady state was reached, the current was turned on and monitored by a 30 V power supply (Mascot 719) and a multimeter in series.

3. Results and discussion

3.1. Effect of hydrolysis time on performance of carbons from pulp without metal additives

Depolymerization and formation of furan and its derivatives (see Section 1) may explain the increased carbon yield when increasing the TFA exposure time, Table 1. The weight loss is based on the amount of total material. According to Kawamoto et al. [3], the path to solid carbon formation from cellulosic materials includes a depolymerization step followed by ring-opening polymerization. Carbon films from 5 days exposed pulp were also made, but were too porous and brittle to test. Using a light table it was observed that those films had pinholes and were non-isotropic.

Fig. 3 shows an overlay of curves from thermogravimetric analysis of sucrose (a disaccharide), kraft pulp (polysaccharide) and hydrolyzed pulp (oligosaccharide). The heating procedure is identical to the membrane carbonization protocol, except for the atmosphere being pure nitrogen (vacuum was not possible with the TGA). From the figure it is clear that the hydrolyzed pulp has a track that resembles that of sucrose: the onset of thermal decomposition is found at a lower temperature and the carbon yield is increased compared to the original pulp. This supports the idea that the pulp is transformed to a saccharide with short chain fragments when exposed to TFA.

Permeation test results for several gases are given in Table 2 and Fig. 4 for CO_2/CH_4. The wide range of film thicknesses was due to thickness variations within each precursor film. One of the reasons for this is most likely the variation in surface tension between the Teflon™ dish and the different casting solutions. TFA exposure for only 6 days resulted in films showing non-selective diffusion. After 2 weeks a critical threshold in the hydrolysis process has been reached, and the CO_2/CH_4 separation performance seems to increase with time. All the films used

Table 1
Descriptions of carbons from pure pulp exposed to TFA for different times (carbonized at 550 °C, 2 h soak)

Sample ID	Exposure time (days)	Precursor appearance	Carbon appearance	Weight loss of carbon batch (%)	Diameter shrinkage (%)
C-6	6	Flexible, rough	Black/grey, dull, rough	84.4–84.5	42–46
C-14	14	Black, brittle, smooth	Black, shiny, smooth	80.6–81.2	–
C-74	74	Black, brittle, smooth	Black, shiny, smooth	71.9–72.6	31

Table 2
Results for carbons (550 °C, 2 h soak) from pure pulp exposed to TFA for 6, 14 and 74 days, respectively (single gases, 2 bar, 30 °C)

Film	Thickness (μm) ± 2S.D.	P_{N_2} (Barrer)	P_{H_2} (Barrer)	P_{CH_4} (Barrer)	P_{O_2} (Barrer)	P_{CO_2} (Barrer)	P_{SF_6} (Barrer)	Aging (% change in N_2 permeability)
C-6	86 ± 7	29×10^3	55×10^3	32×10^3	17×10^3	28×10^3	21×10^3	−18
C-14	40 ± 4	4.2	9.4×10^2	4.6	54	1.9×10^2	0.63	+14
C-74	46 ± 9	5.7	8.6×10^2	1.3	48	1.5×10^2	–	−24

For conversion of Barrer to kmol m m^{-2} s^{-1} kPa^{-1}, divide by 2.99×10^{15}.

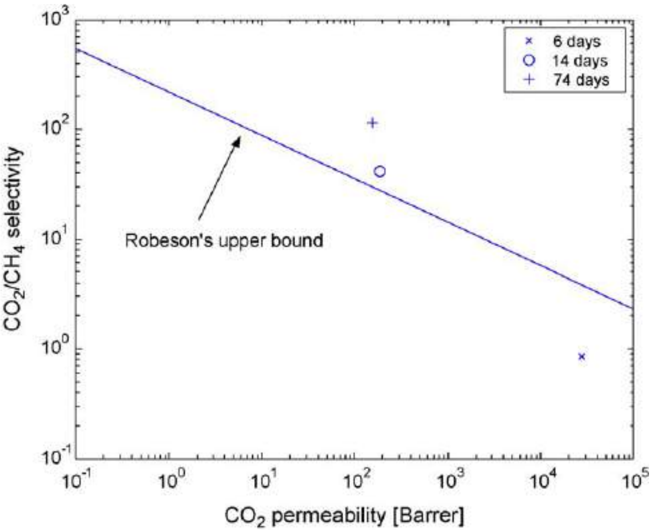

Fig. 4. Separation performance for carbons (550 °C, 2 h soak) from different precursor exposure times in TFA (single gases at 30 °C, 2 bar). Robeson's upper bound was derived from measurements of polymers, mostly at 35 °C [7].

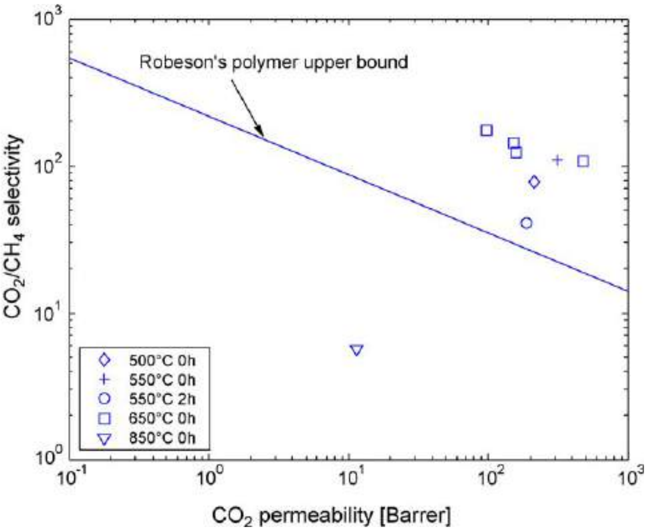

Fig. 5. CO_2/CH_4 separation performance of pure carbon films from different protocols (same heating rate), single gases at 30 °C and 2 bar. The samples were exposed to TFA for 2–5 weeks. Robeson's upper bound was derived from measurements of polymers, mostly at 35 °C [7].

in the other experiments, i.e. for making carbons with metal additives and for testing different carbonization protocols, had a TFA exposure time of 2–5 weeks, for practical reasons. This variation in exposure time could influence the selectivity, but has minor influence on CO_2 permeability, according to Fig. 4. Increased exposure time probably causes a change in the carbon matrix, where the average pore width is shifted towards the sieving diameter of CO_2 (3.3 Å). This pore narrowing excludes methane to a larger extent.

As can be seen from Table 2, the permeabilities generally decrease with exposure time—this is according to what is to be expected. The value reported for nitrogen, however, after 14 days is most likely influenced by an experimental error (improper conditioning), and should be neglected.

The results indicate that furans are a key intermediate in forming microporosity with high separation performance. It is probably favorable that this intermediate also is formed *prior to* carbonization (through TFA treatment), and not only during the carbonization process.

3.2. Effect of final carbonization temperature and soak

In order to optimize the carbonization protocol, different final temperatures were tested, Table 3. From the carbon batch made at 650 °C, four films were tested, but only the results from the first tested film is given in the table. Results for all four films are shown in Figs. 5 and 6.

Table 3
Permeation results from pure pulp carbonization (single gases, 2 bar, 30 °C)

Protocol	Thickness (μm) ± 2S.D.	P_{N_2} (Barrer)	P_{H_2} (Barrer)	P_{CH_4} (Barrer)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	P_{SF_6} (Barrer)	Aging (% N_2 permeability change)
500 °C, no soak	23 ± 6	6.6	4.6×10^2	2.8	2.2×10^2	49	0.050	−0.76
550 °C, no soak	52 ± 7	8.6	11×10^2	2.8	3.1×10^2	90	0.23	−1.0
550 °C, 2 h soak	40 ± 4	4.2	9.4×10^2	4.6	1.9×10^2	54	0.63	+14
650 °C, no soak	66 ± 5	15	13×10^2	4.4	4.8×10^2	1.3×10^2	0.61	−6.1
850 °C, no soak	33 ± 7	3.7	55	2.0	11	5.8	–	−48

For conversion of Barrer to kmol m m^{-2} s^{-1} kPa^{-1}, divide by 2.99×10^{15}.

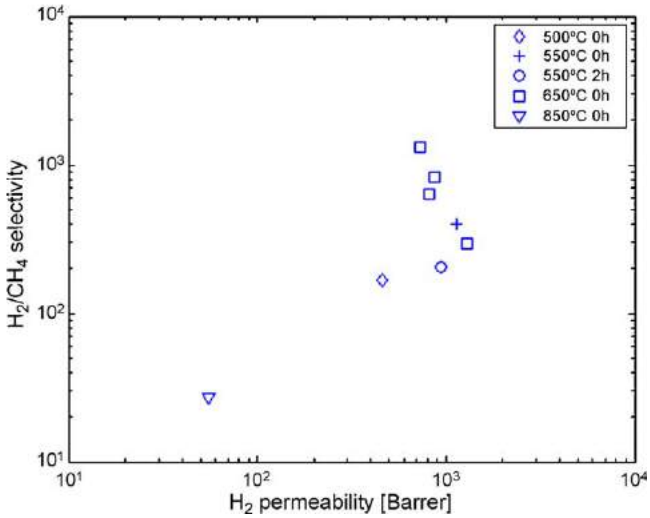

Fig. 6. H_2/CH_4 separation performance of pure carbon films from different protocols (same heating rate), single gases at 30 °C and 2 bar. The samples were exposed to TFA for 2–5 weeks.

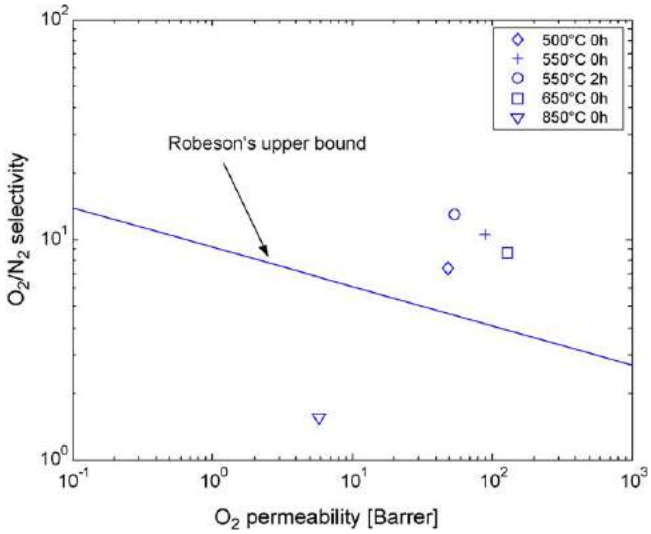

Fig. 7. O_2/N_2 separation performance of pure carbon films from different protocols (same heating rate), single gases at 30 °C and 2 bar. The samples were exposed to TFA for 2–5 weeks. Robeson's upper bound was derived from measurements of polymers, mostly at 35 °C [7].

The performance for CO_2/CH_4 separation as a function of carbonization temperature (Table 3) is plotted in Fig. 5. The increase in permeability as the final carbonization temperature is brought up to 650 °C is in agreement with a gradual pore opening. At 850 °C, the permeability of all gases is reduced, in accordance with a sintering of the carbon matrix. At 850 °C, the volumetric loss (film diameter and thickness change) was found to be larger than the weight loss, whereas, at 650 °C, the losses were equal. Below 650 °C, the weight loss was slightly larger than the volumetric loss. The low selectivity of the carbon made at 850 °C is somewhat unexpected. However, the H_2/N_2 selectivity is higher than at 650 °C and the strong aging (Table 3) suggests that large penetrants (N_2 and CH_4) are still sorbed in some of the pore network and hinder O_2 and CO_2 permeation.

For the separation of CO_2 from CH_4 a soak at 550 °C has a negative impact on performance. The increase in CH_4 permeability when adding a soak is difficult to explain, and could be caused by measurement errors. From the 650 °C batch, four different films were tested to check the scattering in performance data of the films produced. From Fig. 5, a significant scattering can be seen. However, the repeats seem to line up on a line parallel to the trade-off line. Hence, it is possible to distinguish at least the results at 550 °C with soak and those at 850 °C, from the results at 650 °C. Still the exact optimum carbon formation temperature is difficult to tell.

The repeated tests for the gas pair H_2/CH_4 are shown in Fig. 6. Again the repeats at 650 °C are lined up, and it is possible to distinguish them from 500 and 850 °C.

For the gas pair O_2/N_2, Fig. 7 (from data in Table 3), the situation is different. The soak is not a drawback, and can easily be explained by a sintering mechanism.

From the permeation results presented, it is clear that other final temperatures need to be tested to identify the exact optimum for carbonization, as well as repeats to measure the repeatability. Most of the presented carbons have however a better separation performance than the upper bound [7] for polymers.

3.3. Electrothermal regeneration

To make the carbons more conductive, iron nitrate (FeN) was added to the precursor solution. On the other hand, too high metal loading resulted in carbons that were too brittle to test. Hence, a trade-off between mechanical properties and electric conductivity exists. The metal nitrate content of the precursor (crystal water subtracted) was 1.8 wt.% for one batch and 4.4 wt.% for another batch. Membranes were carbonized at 550 °C, with a 2 h soak. Membrane data and single gas permeabilities are given in Table 4.

Higher percentage of Fe in carbon results in lower carbon yield probably due to catalytic oxidation (Fe as the catalytic metal and nitrate as the oxidiser). The carbon with 4.4 wt.%

Table 4
Results from carbonization (550 °C, 2 h soak) of metal nitrate containing wood pulp (single gases, 2 bar at feed side, 30 °C)

Film	Weight-loss (%) ± 2S.D.	Thickness (μm) ± 2S.D.	P_{H_2} (Barrer)	P_{CH_4} (Barrer)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	P_{N_2} (Barrer)
C–FeN 1.8	69.0 ± 0.8	75 ± 8	10×10^2	2.1	3.1×10^2	86	8.2
C–FeN 4.4	83.14 ± 0.04	41 ± 9	3.3×10^2	5.5	30	14	6.0

For conversion of Barrer to kmol m m^{-2} s^{-1} kPa^{-1}, divide by 2.99×10^{15}.

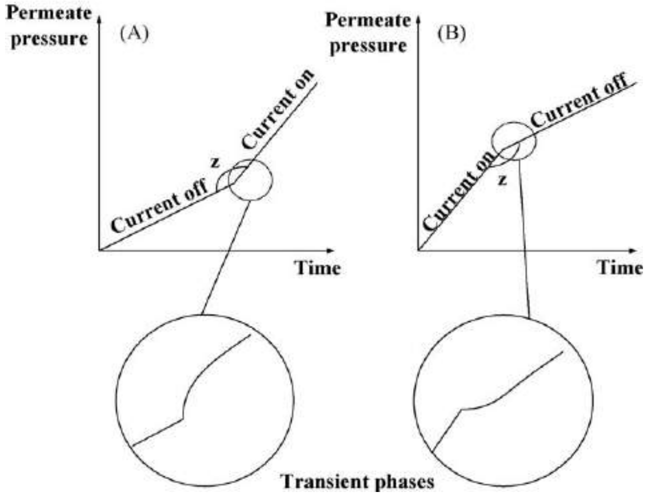

Fig. 8. Procedure for permeation test, and shapes of the transient phases.

FeN was chosen for regeneration experiments, because of its higher conductivity. Hence, the chance of detecting any effect of electric current should increase.

When a low voltage direct current (17.5 V, 10 mA) is applied to the metal-doped carbon during a permeation test, the permeability increases instantaneously and remains stable, see Fig. 8.

The relative permeability increase depends among other factors on the gas type and on the amount of current applied. Oxygen permeation tests showed that the effect (or the knee angle z) was the same, whether the current was applied during the first half of the experiment (Fig. 8B), or during the second half (Fig. 8A). The *absolute* permeabilities had a small change between the experiments, indicating history dependence (amount of preadsorbed gas in the carbon, etc.), while the *relative* permeabilities (the angles) seem to depend on the physics of the process. Fig. 9 shows the relative permeabilities for gases tested according to Fig. 8A. In this work, relative permeability is defined as the ratio of the permeability with current applied and the permeability without any current.

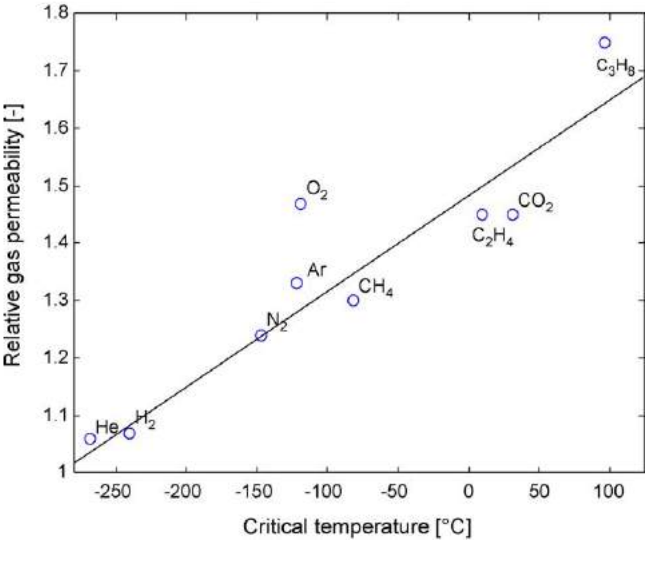

Fig. 9. Relative gas permeability as a function of gas critical temperature (10 mA, 30 °C, 2 bar feed).

Several factors may cause enhanced permeability when a direct current is applied: traditionally, carbon is used as resistors, and ohmic heating of the carbon may increase the desorption rate of the gas through the membrane. If desorption is the rate-limiting step for gas transport, the effect of heating should be pronounced. Since the heat is generated in the inner parts of the carbon, and not by an external fluid (i.e. the direction of heat and mass transfer are the same), this kind of regeneration will be very energy efficient. The shapes of the transient phases during permeation (Fig. 8) and the correlation between gas critical temperature and relative permeability (Fig. 9) also indicate that desorption enhancement is involved. Secondly, the magnetic field generated by the electric current may cause orientation of the diffusing polar molecules, and hence less degree of rotation. This entropy reduction *prior to* entering the pores thus increases the chance of overcoming the pore entrance barrier.

Thirdly, when a magnetic field is applied to a ferromagnetic solid like iron oxide, the iron oxide clusters are oriented parallel to the magnetic field, causing a mechanical change in the carbon matrix. This phenomenon is called magnetostriction, and may cause a reduction in tortuosity. However, application of current to a metal-free carbon and a copper-containing carbon also showed permeability increase. Hence, magnetostriction is not a significant factor. Another possibility is that application of current may displace or further carbonize the structure. However, this should result in permanent changes in permeability, which is not observed.

By focusing on the first two explanations a simple pore model, like that given in Fig. 10, may be useful to illustrate the observed phenomenon. Spherical molecules, e.g. Ar, are also affected by the current, though less than a linear molecule like O_2, having about the same critical temperature. Hence, ohmic heating stands as a general explanation to the phenomenon. By electroheating the effective pore entrance is increased due to gas desorption from low energy sites of the pore entrance, and thus higher permeability is achieved. This may also be viewed as an increase in the gas hopping rate along the pore walls in the direction of diffusion.

When it comes to terminology, *permeability* is a material property and is not a quite correct expression in this case. The system (membrane + electrical field) property *flux* is a better

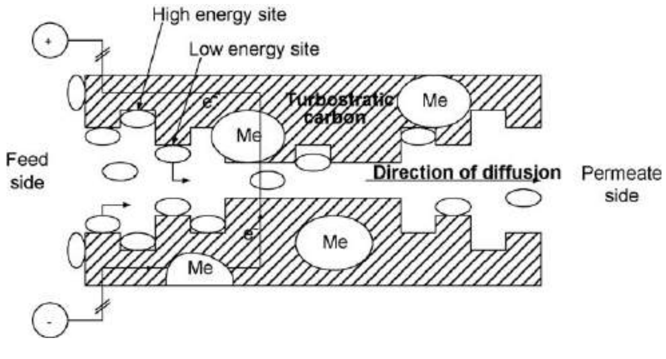

Fig. 10. Simplified pore model in a wired carbon membrane (Me = metal, e = electron).

term, but since the gas fluxes are obtained with a standard permeability measurement setup and normalized by trans-membrane pressure and thickness, yet the term permeability is used in this work.

When it comes to the long-term effect of electrothermal regeneration, the same carbon film was used for hydrogen and methane permeation tests (30–50 °C and 0.5–2.0 bar) for 2 weeks. Current (5–15 mA) was applied for 2 h in average each day. After the test series, the hydrogen permeability (with the current off) was increased by 14%, i.e. a regeneration efficiency of 114% (Eq. (1)). The overall increase in methane permeability was 7%, which gives an overall increase in H_2/CH_4 selectivity of 7%.

Electric current can be used not only as a periodic regeneration method, but also in a continuous way, facilitating the transport of some gases, but blocking others. In this way, both permeability and selectivity may be increased. The benefit of this approach depends on the power consumption (regeneration costs).

Deconvolution of any field effects and heating effects on permeation is a challenging task. Mixed gas tests will probably provide more insight to this problem and the mechanisms that are active, and have the highest priority in the further research, together with electrothermal treatment of other metal containing carbon membranes. Extended long-term tests with two membranes in parallel, one wired and one non-wired, should also be performed to obtain the actual benefit of the regeneration method.

4. Conclusions

An alternative path to carbons from cellulosic materials by hydrolysis of the cellulose prior to carbonization has been tested out in the current work. Increasing the hydrolysis time, resulted in reduced weight loss during carbonization, and better separation performance for the gas pair CO_2/CH_4.

The effect of changing the final carbonization temperature was evaluated for H_2, CO_2, CH_4, O_2 and N_2. Most of the presented carbons possess a better separation performance than the upper bound [7] for polymers.

A simple, energy effective and rapid regeneration method for membranes that are conductors or semi-conductors has been developed: when a low voltage, direct current is applied on an iron-doped carbon, enhanced permeation rates are achieved. This probably results from enhanced desorption rate and hopping rate of the gases in the carbon due to ohmic heating. The relative increase depends a.o. on gas critical temperature and current size. Electrothermal regeneration may be applied on-stream, hence avoiding process interruption or an extra set of membranes. The method is able to fully restore the initial permeability of the carbon membrane. The method can also be used in a continuous way, and not only for batchwise regeneration.

Acknowledgements

The authors want to thank research fellow David Vaaler and Assoc. Prof. Størker Moe at the Paper and Fibre Research Institute (PFI) in Trondheim, for supplying cellulose materials and for useful discussions on cellulosic materials. Dr. Arne Lindbråthen in our research group is also acknowledged for useful discussions and comments on electrothermal regeneration.

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Carbon membranes from metal loaded cellulose, and the application of an external field for improved performance

Authors: Jon Arvid Lie, May-Britt Hägg

During the last two decades, microporous carbon membranes have been promising candidates for separation units in selected industrial gas streams, including upgrading of biogas to fuel quality and the application as a CO2 capture device in a strategy for cutting carbon emissions to the atmosphere. In the petrochemical industry, carbon membranes may become an efficient technique for the separation of an alkane from its corresponding alkene, and recovery of hydrogen. A major obstacle for a breakthrough for carbon membranes has been the loss of permeability when exposed to strongly adsorbing gases. This paper addresses a possible solution to this aging issue. The paper presents the separation performance of cellulosic carbon, both in its pure form and loaded with different metals.

The presence of a metal in the carbon matrix may promote interactions with selected permeating gases. Different metal nitrates, i.a. iron nitrate, were added to disturb the packing of carbon graphene sheets, i.e. to increase the micropore volume, and to increase the electric conductivity of the carbon matrix, for regeneration purposes. The metal nitrate is most likely transferred to a metal oxide during carbonization.

The resulting membranes, obtained from vacuum carbonization, are characterized by permeation of different probe gases, e.g. H2, He, N2, O2, CO2, CH4 and C3H8. Gas permeation results are visualized in Robeson plots for selected gas pairs. The separation performance of cellulosic carbon is at the same level as carbons derived from specialty polymers like polyimides. The advantage of cellulose is its abundance and low cost. No catalyst is used during the carbonization. When a low voltage direct current is applied to the metal doped carbon during a permeation test, the permeability increases instantaneously and remains stable. The relative permeability increase depends among other factors on the gas type and on the amount of current applied. A great advantage of this regeneration technique is the on-stream operation, avoiding shutdown or switching to an extra set of membranes.

At least three effects may cause enhanced permeability when a direct current is applied: Traditionally, carbon is used as resistors, and ohmic heating of the carbon may increase the desorption rate of the gas through the membrane. If desorption is the rate-limiting step for gas transport, the effect of heating should be pronounced. Since the heat is generated in the inner parts of the carbon, and not by an external fluid (i.e. the direction of heat and mass transfer are the same), this kind of regeneration will be very energy efficient.
Secondly, the magnetic field generated by the electric current may cause orientation of the diffusing polar molecules, and hence less degree of rotation. This entropy reduction *prior to* entering the pores thus increases the chance of overcoming the pore entrance barrier.

Thirdly, when a magnetic field is applied to a ferromagnetic solid like iron oxide, the iron oxide clusters are oriented parallel to the magnetic field, causing a mechanical change in the carbon matrix. This phenomenon is called magnetostriction, and may cause a reduction in tortuosity.

Abstract for NAMS 2007

Injection of hydrogen into the European gas network - and recovering the same from the gas mix by use of CMS-membranes at the end user.

Within the 6th European frame work program a large integrated project (NaturalHy) with 39 partners from academia and industry are investigating the possibility of using the existing natural gas network for transport of hydrogen (up to 30%) in mixture with natural gas (NG). The hydrogen will be injected into the gas net where it is being produced, and by the end user it will be separated out again from the gas mix. One option for this separation is by using membranes, and the focus for the research reported here, is carbon molecular sieve membranes with high H_2/CH_4 selectivity. The research group, Memfo at NTNU in Norway, is a partner in the NaturalHy-project and is tailoring CMS membranes for performing H_2-CH_4 separation.

In the main distribution net, the gas pressure will be high (~40 bar), while where the separation is to take place at the end user, the gas feed pressure to the membrane will be 6-8 bar.

The performance of the membrane investigated so far is done for single and mixed gas (mix of NG – H_2 in a range with 5 – 30vol% H_2), with feed pressure 2 - 6 bar and temperature 25° – 90°C. The H_2 permeability documented is in the range of 600 - 1000 Barrer, and with a selectivity $H_2/CH_4 > 1000$ for the mixed gas. The effect of aging and regeneration has also been investigated. The precursor used for the preparation of the CMS-membrane is cellulose derived from wood pulp with metal salts added – the best results were obtained with copper(II)nitrate and silver nitrate.

The concept of the project, as well as obtained results for membrane separation, will be discussed in the presentation.

Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Application of carbon molecular sieve membranes in a mixed hydrogen-natural gas distribution network

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1. Summary

Carbon membranes have been identified as a promising technology for separation of hydrogen from natural gas. These are produced by carbonization of cellulose in vacuum or in an inert gas atmosphere. Mixed gas tests show a hydrogen selectivity over methane greater than 1000 and a pressure-normalised flux greater than 0.2 m^3(STP)/m^2.bar.h. Carbon membranes may experience a loss of permeability when exposed to strongly adsorbing gases at ambient to moderate temperatures. Electrothermal treatment is presented as a possible solution to this aging issue. A procedure for making hollow carbon fibres is also presented.

Keywords: H_2, membranes, carbon, natural, gas

2. Extended Abstract

The transition to a full hydrogen distribution system may be a lengthy and costly exercise; hence a transitional approach using existing natural gas (NG) networks to transmit mixtures of hydrogen and NG is being investigated. NaturalHy, a 6th Framework Programme EU project, in which the NTNU is a participant, aims to test all critical components in a mixed network by adding hydrogen to existing natural gas networks.

Membranes have been identified as a promising technology for recovering hydrogen for end-use. One promising membrane material, under development at the Membrane Research Group (MEMFO) at NTNU, is the carbon molecular sieve. This is produced by the carbonisation of cellulose at temperatures of 550-750°C to produce a nanoporous carbon film, capable of discriminating between the smaller hydrogen molecules and the remaining molecules in a NG stream. The starting material, cellulose, is also cheap and abundant.

Carbon membranes at MEMFO are at the bench scale testing stage. Performance has been shown to depend on the temperature, pressure and composition of the feed. Mixed gas feed tests show that carbon membranes can achieve a hydrogen selectivity over methane greater than 1000 and a pressure-normalised flux greater than 0.2 m^3(STP)/m^2.bar.h.

An obstacle for a breakthrough of carbon membranes has been the loss of permeability when exposed to strongly adsorbing gases at ambient to moderate temperatures. This paper addresses a possible solution to this aging issue. When a low voltage direct current is applied to the metal doped carbon during a permeation test, the permeability increases instantaneously and remains stable. The relative permeability increase depends among other factors on the gas type and on the amount of current applied. Carbon membranes containing different metals will be compared with respect to the effect of electrothermal treatment. Possible explanations of the phenomenon will also be given. A great advantage of this regeneration technique is the on-stream operation, avoiding shutdown or switching to an extra set of membranes.

To be commercially attractive, the packing of the membrane inside a module has to be efficient. Hollow fibres provide a configuration with a packing density up to 30 000 m^2 membrane per m^3 module. A procedure for making such fibres from cellulosic materials will be presented.

Membranes placed at various end-user sites on the distribution network must cope with varying hydrogen concentrations in, and pressures of, the feed. However, process simulations show that 80% of the hydrogen can be recovered from the pipeline or a slipstream thereof at a purity greater than 90 vol%, in a single separation stage. The volume and footprint of these membranes would be small and they could conveniently be placed at commercial and residential sites.

The Laminar Burning Properties of Premixed Methane-Hydrogen Flames Determined Using a Novel Analysis Method

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Abstract

Laminar burning velocities, u_l, and Markstein lengths, L_b, have been obtained from spherically expanding flame experiments. A novel method, using least squares, of calculating u_l and L_b from the radius time record is presented. This avoids the amplification of noise in the experimental results when the radius time record is differentiated. Measurements were made for methane and methane/hydrogen mixtures (up to 50 % by volume hydrogen) with air at 0.1 MPa and 360 K. The addition of hydrogen resulted in increases in u_l, decreases in L_b (for constant equivalence ratio ϕ) and a widening of the ignition limits. Laminar burning velocities were also computed with a one dimensional solver for two published kinetic mechanisms.

Introduction

Hydrogen could be an important future energy carrier, offering CO_2 free emissions at the point of combustion. It has been proposed that existing natural gas pipelines could be employed for hydrogen transmission, with hydrogen mixed with natural gas. The mixture could then be used directly, or the hydrogen separated at the point of application (e.g. by differential diffusion using a suitable membrane) for use, for example, in engines or fuel cells. In the currently reported study experiments have been performed to determine burning rates to help quantify the risk resulting from accidental releases of natural gas-hydrogen mixtures

In these experiments pure methane was used to represent natural gas. A new and comprehensive data base on the burning velocity of hydrogen-methane mixtures has been generated. Data for premixed laminar flames at atmospheric pressure (0.1 MPa) for an initial temperature of 360 K are reported here (corresponding turbulent burning data are reported elsewhere [1]). Mixtures with air of pure methane (CH_4), 10, 20, and 50 % hydrogen in methane mixtures (referred to as 10 % H_2, 20 % H_2, 50 % hydrogen, respectively) were considered, with equivalence ratios ranging from lean ($\phi \leq 0.5$) to the rich ($\phi \geq 1.7$) ignition limits.

One-dimensional kinetic modelling of the laminar flames has also been performed, employing two published chemical kinetic models; GRI-Mech 3.0 [2] and Konnov [3]. Resultant laminar burning velocities are compared with experimentally derived data, and differences discussed below.

The laminar burning velocity of premixed fuel/air mixtures is now routinely obtained from spherically expanding flames captured using shadowgraphy or schlieren imaging [4, 5]. The flame radius may then be found by processing the resulting flame images and the radius obtained directly from measurement of the flame area. In this way the unstretched flame speed, S_s, (and ultimately unstretched laminar burning velocity, u_l) and a Markstein length can be obtained [4]. The total stretch rate acting across the surface of a spherically expanding flame can be shown to be:

$$\alpha = \frac{2}{r_u}\frac{dr_u}{dt} = \frac{2}{r_u}S_n \tag{1}$$

where r_u is the flame radius. The burned gas Markstein length, L_b, is a proportionality coefficient between the local values of the observed stretched flame speed, S_n, and the stretch rate:

$$S_n = S_s - L_b\alpha \tag{2}$$

To derive L_b and S_s using Eq. (2) the radius-time record requires numerical differentiation. Such a procedure amplifies any noise, which is present when the radius is experimentally determined from the schlieren images.

After substitution of Eq. (1) into Eq. (2), re-arrangement and integration with respect to time gives:

$$r_u(t) - r_u(t_0) + 2L_b \ln\left(\frac{r_u(t)}{r_u(t_0)}\right) = S_n(t - t_0). \tag{3}$$

Equation (3) is implicit for r_u but explicit for t. The resulting least squares function is:

$$\psi(L_b, S_n) = \sum_{i=1}^{N}\left(t_i - t_0 - \frac{r_i - r_0}{S_n} - 2\frac{L_b}{S_n}\ln\frac{r_i}{r_0}\right)^2$$

and the conditions of its minimum

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Proceedings of the European Combustion Meeting 2007

$$\frac{\partial \psi}{\partial S_n} = \frac{\partial \psi}{\partial L_b} = 0 .$$

This results in

$$\sum_{i=1}^{N} \left(S_n \left(t_i - t_0 \right) - \left(r_i - r_0 \right) - 2 L_b \ln \frac{r_i}{r_0} \right) \times \left(r_i - r_0 + 2 L_b \ln \frac{r_i}{r_0} \right) = 0$$

$$\sum_{i=1}^{N} \left(S_n \left(t_i - t_0 \right) - \left(r_i - r_0 \right) - 2 L_b \ln \frac{r_i}{r_0} \right) \ln \frac{r_i}{r_0} = 0$$

These two equations can be solved by multiplying by L_b and subtraction, giving:

$$S_n = \frac{c_1 b_{22} - c_2 b_{12}}{b_{11} b_{22} - b_{21} b_{12}}$$

$$L_b = \frac{c_2 b_{11} - c_1 b_{21}}{b_{11} b_{22} - b_{21} b_{12}}$$

where the coefficients are:

$$b_{11} = \sum \left(t_i - t_0 \right)\left(r_i - r_0 \right)$$

$$b_{12} = -2 \sum \left(r_i - r_0 \right) \ln \frac{r_i}{r_0}$$

$$b_{21} = \sum \left(t_i - t_0 \right) \ln \frac{r_i}{r_0}$$

$$b_{22} = -2 \sum \ln^2 \frac{r_i}{r_0}$$

$$c_1 = \sum \left(r_i - r_0 \right)^2$$

$$c_2 = \sum \left(r_i - r_0 \right) \ln \frac{r_i}{r_0}$$

In this way S_s and L_b can be solved without differentiating the radius-time measurements. Care must be taken with the selection of t_0 and r_0. Simplistically one might assume that the flame has zero radius at time zero. However, the flame is initiated with a spark; resulting in more rapid growth in the early stages than might be the case if the growth rate was solely governed by Eq. (2). The influence of the spark on the initial flame growth was investigated in an earlier study [6] and found to be present up to a radius of 8 mm (for this ignition unit). Therefore determination of S_s and L_b was initiated from this point, with t_0 and r_0 adjusted accordingly.

Experimental

A 30 litre spherical stainless steel vessel was employed in the experiments. Three pairs of orthogonal quartz windows of diameter 150 mm provided excellent optical access. Turbulence was generated in the bomb by four identical eight bladed fans, arranged in a tetrahedral configuration. In the 'laminar' experiments reported here the fans were stationary.

Mixture temperature was measured using a K type thermocouple, situated inside the chamber. The entire vessel was preheated by an internal 2 kW heater. A piezoresistive pressure transducer was employed to measure the pressure during mixture preparation. This transducer was situated outside the vessel and was isolated just prior to ignition.

Mixtures were prepared in the vessel, with gas concentrations set on the basis of partial pressures. After an experiment, the vessel was flushed with compressed air and then evacuated. Dry cylinder air was used in preparation of the combustible mixture. Fuel was supplied from high pressure cylinders containing set premixed hydrogen/methane mixtures (BOC). The fans were run during charge preparation to ensure full mixing and to maintain uniform heating of the vessel from the heater. The fans were switched off after the mixture was prepared, and the mixture left, for at least 60 seconds before ignition, allowing the mixture to become quiescent. An initial charge temperature of 360 K was adopted in all experiments, for convenience and compatibility with turbulent tests (not reported here). When the fans are run at high speed, kinetic heating would require vessel cooling for burning mixtures at room temperature. Estimated precision in the equivalence ratio setting was $\phi \pm 0.04$, a function of temperature variation during vessel filling and the accuracy of the pressure transducers.

Ignition was initiated from a purpose built stainless steel/ceramic sparkplug, with a gap of 1 mm, mounted in the centre of the vessel. A Lucas 12 V transistorised automotive ignition coil system was connected to the spark electrode assembly. The average spark energy was measured to be 23 mJ [7].

The flames were imaged using schlieren photography, employing of a 20 W tungsten element lamp, 1000 mm focal length lenses and a pinhole. The schlieren images were captured using a Photosonics Phantom 9 camera framing at 2000 fps. The resulting images were either hand traced or processed using Adobe PhotoShop 6.0. By subtracting the background (pre-explosion) image from the subsequent images and applying a threshold a binary image was produced for each frame where the burned area was white and the remainder black. The spark plug was manually removed. Flame areas were then measured by counting the number of pixels behind the flame front. Flame radii were computed as those of a circle of area equal to that of the imaged flame.

Flames ignited at the centre of the combustion vessel grew outward as essentially spherical flame balls. Typically, the flame surface were smooth, however, under certain circumstances, they spontaneously wrinkle and become 'cellular'. Cellular flames were not observed in this study.

In the parallel modelling study, both chemical kinetic mechanisms examined were solved using

CHEMKIN PREMIX [8]. The GRI-Mech 3.0 consisted of 53 species, including NOx chemistry [2]. The Konnov mechanism had 93 species, with NOx chemistry removed [3], and generally took longer to compute a solution. The computations were run up to either a maximum of 200 grid points or GRAD and CURV to 0.1, which ever was achieved first.

Results and Discussion

Shown in Fig. 1 are flame radii plotted against time for three 50 % H_2 flames, at fuel-lean, stoichiometric and rich equivalence ratios. These flames were chosen as they should exhibit different responses to flame stretch, and hence have different Markstein lengths [4]. All three flames had very similar initial radii as the initial stages controlled by the same spark process. After ~ 2 ms, flame chemistry became dominant and differences between the three flames were immediately apparent. The rich flame slowed, and then started to accelerate again 10 ms after ignition. The lean and stoichiometric flames were faster than the rich flame, but their radii diverged as time increased due to a slight de-acceleration in the rich flame and acceleration in the stoichiometric flame.

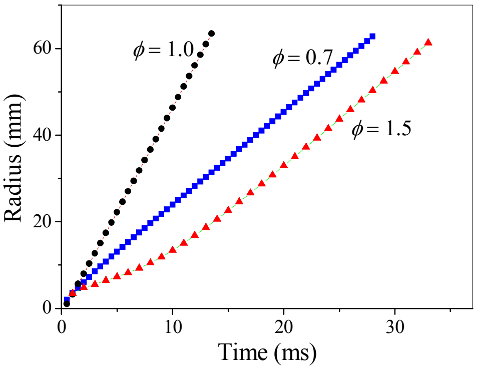

Fig. 1. Flame radius against time from ignition for 50% hydrogen flames at three equivalence ratios.

To demonstrate the determination of the laminar burning velocity and associated Markstein number, spherically expanding flames have been plotted on flame speed versus stretch graphs. These are shown for the three equivalence ratios in Figs. 2 – 4. The measured radii needed to be differentiated with respect to time to obtain the flame speed, this was performed using a three point central difference formula. Also shown are a fits obtained using Eq. (2). The flames were processed in two ways: for Method 1 the least squares of the radius time data was adopted as detailed above; in Method 2 a linear least squares fit was performed on the differentiated flame speed / stretch curve [6]. For both methods only data from 8 mm onwards was included in the fit to ensure spark effects were removed.

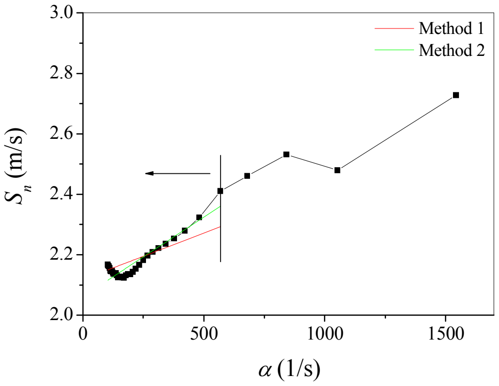

Fig. 2. Flame speed against stretch for a $\phi = 0.7$, 50% hydrogen/50% methane.

Data for the leanest mixture ($\phi = 0.7$) is shown in Fig. 2. The flame grows from right to left as flame stretch is inversely proportion to flame radius. The vertical line gives the assumed end of spark effects and the arrow shows the direction of increasing radius. As the flame grew its flame speed decreased by roughly 25%. Overall the experimental results are reasonably approximated by Eq. (2), despite a slight rise in the flame speed at large radii. The two methods give different fits resulting in different flame speeds and Markstein lengths, and these are given in Table 1. The cause in the rise in S_n at large radii is not known; simultaneous pressure measurements showed no significant increase, and no surface wrinkling was observed. Other flames did not show similar behaviour. Previous measurements of spherically expanding flames have had oscillations in the flame speed [6] and this could produce the observed rise, or it has also been shown that at low stretch rates the response of the flame speed can different to that observed at higher stretch rates [9].

Shown in Fig. 3 are the results for a $\phi = 1.0$ flame. Here flame speed increases as stretch decreased, although by less than 5 %. The higher flame speeds encountered resulted in measurements being performed over a much wider range of stretch rates compared with the $\phi = 0.7$ flame. The results for a rich flame ($\phi = 1.5$) are shown in Fig. 4, the flame responded very strongly to the decrease in the stretch rate, its flame speed doubling between 250 to 200 (1/s). The experimental data is poorly represented by Eq. (2). This more complicated behaviour, compared with the lean and stoichiometric flames, might be better fitted using a higher order equation requiring the adoption of at least 2 Markstein numbers [10].

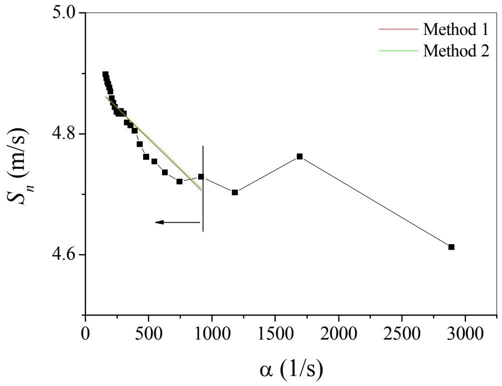

Fig. 3. Flame speed against stretch for a $\phi = 1.0$, 50% hydrogen/50% methane mixture.

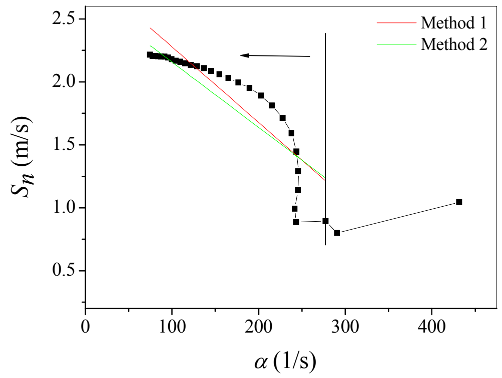

Fig. 4. Flame speed against stretch for a $\phi = 1.5$, 50% hydrogen/50% methane mixture.

ϕ	S_s (m/s)		L_b (mm)	
Method	1	2	1	2
0.7	2.12	2.06	-0.31	-0.52
1.0	4.89	4.89	0.20	0.20
1.5	2.88	2.68	6.01	5.20

Table 1. Unstretched flame speeds and Markstein Lengths.

Laminar burning velocities for all the fuels tested are shown in Fig. 5. The laminar burning velocity was obtained using the expression

$$u_l = \frac{\rho_b}{\rho_u} S_s \tag{4}$$

Where ρ_u and ρ_b are the unburned and burned gas densities. The addition of hydrogen generally increases u_l. For pure methane, flames could not be ignited beyond ϕ = 1.2. However, the ignition limit was extended to ϕ = 1.4 with the addition of only 10 % H_2, and the rich ignition limit was extended to 1.6 for 50 % hydrogen. The addition of hydrogen did not have such a dramatic effect on the lean ignition limit, where the limit decreased from 0.6 to 0.5 (from pure methane to 10 % hydrogen), but did not change further as more H_2 was added. There was a noticeable shift in the peak burning velocity to richer ϕ with increasing hydrogen content. Although with 50% addition the peak which is around ϕ = 1.15 is still significantly leaner than the peak for pure hydrogen which occurs at $\phi = 1.8$ [11].

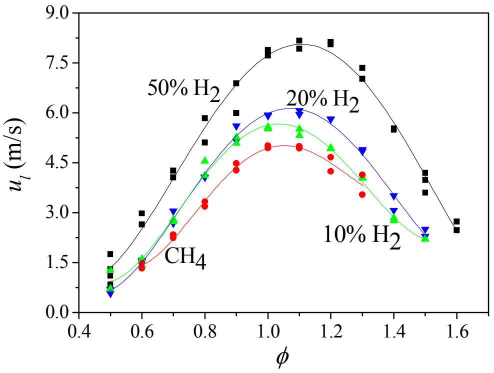

Fig. 5. Experimentally measured values of u_l against ϕ for all fuels, obtained using Method 2.

Values of L_b are shown in Fig. 6. All the fuels demonstrated a similar trend, an increase in L_b as ϕ increases. For each ϕ, methane had the highest L_b, which then dropped as hydrogen was added to the fuel. The 50 % H_2 could be approximated by $L_b \sim 0$ for $0.8 \leq \phi \leq 1.1$. For leaner (richer) mixtures L_b drops (rises) sharply. It has been shown that mixtures with lower Markstein lengths are likely to burn faster in turbulent flows especially at lean ϕ [12]. Therefore the 50 % H_2 fuel will burn faster in turbulent flows due to its higher laminar burning velocity and L_b.

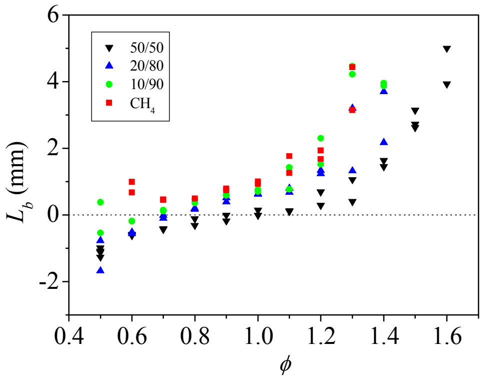

Fig. 6. Experimentally measured values of L_b against ϕ for all fuels, obtained using Method 2.

Comparisons between the experimentally derived values of u_l and those computed are shown in Fig. 7 for methane. Values determined using the GRI Mech proved consistently higher than those of Konnov. This is likely to reflect the experimental data used to 'calibrate' the mechanism, as GRI used data primarily from counterflow burners [13]. This experimental configuration tends to give consistently (slightly) higher u_l's those obtained using spherically expanding flames [14]. The Konnov mechanism, compiled slightly later (when more experimentally determined laminar burning velocities were available) yielded slightly lower values of u_l. The experimental results sit between the two, except at the extremes in ϕ. For lean mixtures the Konnov mechanism matches the experiments closely. At rich ϕ the assumption of a single L_b has been demonstrated to be questionable. That the experimental u_l were higher than both the modelled results might support fitting at lower values of α (larger radii).

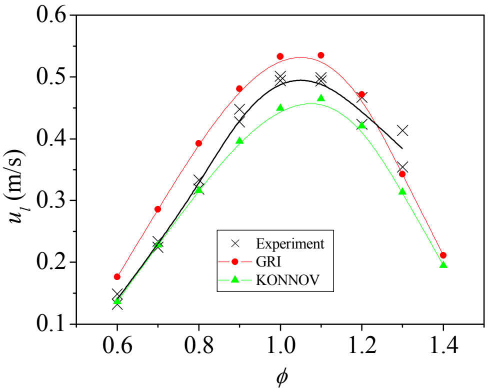

Fig. 7. Comparison of experimental and modelled values of u_l for CH_4.

Model and experimentally determined u_l's are compared in Fig. 8 for 50 % H_2. Here, the agreement between the experiments and the Konnov mechanism can be seen to be very close, with those yielded by GRI Mech again consistently higher than the data.

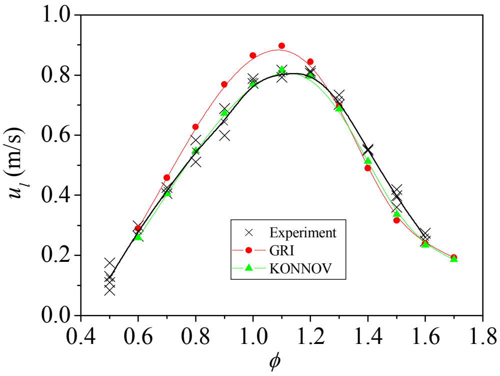

Fig. 8. Comparison of experimental and modelled values of u_l for 50 % H_2.

Conclusions

A method, using least squares, of calculating the laminar burning velocity and Markstein length from the radius time record of a spherically expanding laminar flame has been presented.

The influence of processing methods has been compared and the differences found to depend on the equivalence ratio (or stretch response) of the flame.

The addition of hydrogen to methane resulted in an increase in measured laminar burning velocity and decrease in Markstein length. It also increased the ignition limits, particularly at fuel-rich equivalence ratios.

Comparisons were made between experimental data and one-dimensional kinetic computations for u_l, using two full chemistry mechanisms, with reasonable agreement with data found. Overall the more recently constructed scheme by Konnov performed best, although this is likely to be a result of the more extensive experimental database used for its validation.

Acknowledgements

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GAS BUILD-UP IN A DOMESTIC PROPERTY FOLLOWING RELEASES OF METHANE/HYDROGEN MIXTURES

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ABSTRACT

The EC funded Naturalhy project is investigating the possibility of promoting the swift introduction of hydrogen as a fuel, by mixing hydrogen with natural gas and transporting this mixture by means of the existing natural gas pipeline system to end-users. Hydrogen may then be extracted for use in hydrogen fuel cell applications or the mixture may be used directly in conventional gas-fired equipment. This means that domestic customers would receive a natural gas (methane)/hydrogen mixture delivered to the home. As the characteristics of hydrogen are different from natural gas, there may be an increased risk to end-users in the event of an accidental release of gas from internal pipe work or appliances. Consequently, part of the Naturalhy project is aimed at assessing the potential implications on the safety of the public, which includes end-users in their homes. In order to understand the nature of any gas accumulation which may form and identify the controlling parameters, a series of large scale experiments have been performed to study gas accumulations within a 3 m by 3 m by 2.3 m ventilated enclosure representing a domestic room. Gas was released vertically upwards at a pressure typical of that experienced in a domestic environment from hole sizes representative of leaks and breaks in pipe work. The released gas composition was varied and included methane and a range of methane/hydrogen mixtures containing up to 50% hydrogen. During the experiments gas concentrations throughout the enclosure and the external wind conditions were monitored with time. The experimental data is presented. Analysis of the data and predictions using a model developed to interpret the experimental data show that both buoyancy and wind driven ventilation are important.

1.0 BACKGROUND

Hydrogen is seen as an important energy carrier for the future which offers carbon free emissions at the point of use. However, transition to the hydrogen economy is likely to be lengthy and will take considerable investment with major changes to the technologies required for the manufacture, transport and use of hydrogen. In order to facilitate the transition to the hydrogen economy, the EC funded project Naturalhy is studying the potential for the existing natural gas pipeline networks to transport hydrogen from manufacturing sites to hydrogen users. The hydrogen, introduced into the pipeline network, would mix with the natural gas. This mixture could then be used directly by consumers as a fuel within existing gas powered equipment, with the benefit of lower carbon emissions. In addition, hydrogen could be extracted from the mixture for use in hydrogen powered engines or for hydrogen fuel cell applications. Using the existing pipeline network to convey hydrogen in this way, would enable hydrogen production and hydrogen fuelled applications to become established prior to the development of a dedicated hydrogen transportation system, which would require considerable capital investment and time for construction.

However, the existing gas pipeline networks are designed, constructed and operated based on the premise that natural gas is the material to be conveyed. Hydrogen has different chemical and physical properties which may adversely affect the integrity or durability of the pipeline network, or which may increase the risk presented to the public. For these reasons, the Naturalhy project has been initiated to assess the feasibility and impact of introducing hydrogen into a natural gas pipeline system. Determining any change in risk to the public is a major part of this project. For example, although rare, escapes of gas from faulty appliances or joints in internal pipe work do occur and sometimes result in the formation of a flammable accumulation. Each year, a small number of such escapes result in an explosion with the potential to harm the occupants and cause damage to the building. The introduction of hydrogen into the supplied gas may increase the risk of such explosions due to the change in way in which the gas accumulation forms and/or due to the increased reactivity of hydrogen. In order to understand the nature of any accumulation of natural gas/hydrogen which may form and to identify the controlling parameters, a series of large scale experiments have been undertaken in which methane/hydrogen mixtures were released within a room-sized enclosure under conditions which are typical of a domestic environment. Assessment of the data enabled identification of the controlling parameters and aided the development and validation of a mathematical model.

2.0 INTRODUCTION

The concentration and extent of the flammable accumulation will affect the severity of the resulting explosion and hence it is important to understand the controlling parameters of gas build-up behaviour. For natural gas, the characteristics of gas escapes in the home are well understood. For example, gas accumulations will tend to form a layer of uniform concentration in that part of the room above the height of the release point. Factors which contribute to this behaviour are: the low momentum of gas release (due to the typical gas pressure being 20-30 mbar); the density of natural gas being less than that of air; and the generally low velocity of airflow (ventilation) within domestic buildings.

However, natural gas/hydrogen mixtures have a lower density than natural gas and this may give rise to different gas accumulation behaviour. Also, for a given supply pressure and leak size, the volume flow rate of natural gas/hydrogen will be greater than the equivalent leak involving methane. Hence, it might be expected that the resulting gas concentration will be higher. Furthermore, due to the wide flammability limits of the mixture, a larger flammable volume may result. In order to assess any change in gas accumulation behaviour, the large scale experiments reported here studied gas releases at pressures typical of that found in a domestic building from leak sizes typical of those that may occur, involving methane (representing natural gas) and methane/hydrogen mixtures. As a flammable concentration will be reached more readily if the escape results in an accumulation in only part of the room (a ‘layer’) this represents the more hazardous situation. Hence, the experimental programme was designed such that most tests involved a gas release which was vertically upwards from a location at half-height. Furthermore, the ventilation regime was such that air would enter the room at low level and gas mixture leave the room at high level. This situation promoted the formation of a ‘layer’ in the upper part of the room.

3.0 EXPERIMENTAL DETAILS

3.1 Experimental Arrangement

The experiments were conducted at the Advantica Limited test site at Spadeadam in the north of England. The test rig was designed to represent a typical domestic room and consequently measured 3 m by 3 m by 2.3 m high. Figure 1 shows a schematic of the test arrangement. In one wall of the test rig (front wall) a lightweight door (typical of that used inside a domestic property) was installed measuring 0.9 m by 2 m high. This was located within a typical door frame and a door jamb nailed to the doorframe to hold the door in place. The arrangement was therefore characteristic of the situation where the door opens into the room. The two side walls, each adjacent to the front wall, incorporated ventilation openings which could be adjusted in size and could provide a well-defined ventilation pattern to the enclosure. The upwind side wall (facing the wind) had an opening at low level, located 200 mm above the floor. The downwind side had an opening the same size at high level, 200mm below the ceiling. Each ventilation opening measured 1 m in the horizontal direction and was adjusted in size in the vertical direction. The back wall, floor and ceiling were plain and incorporated no fittings.

The gas used for the experiments was supplied in high pressure (200 bar) cylinders. Four different gases were used, methane and three mixtures of hydrogen and methane which contained nominally 10%, 20% and 50% by volume hydrogen respectively. Hereafter, these mixtures will be referred to as 90:10, 80:20 and 50:50 respectively. The pressure was reduced in stages and controlled to provide a fixed gauge pressure at the release point of either 20 or 30 mbar.

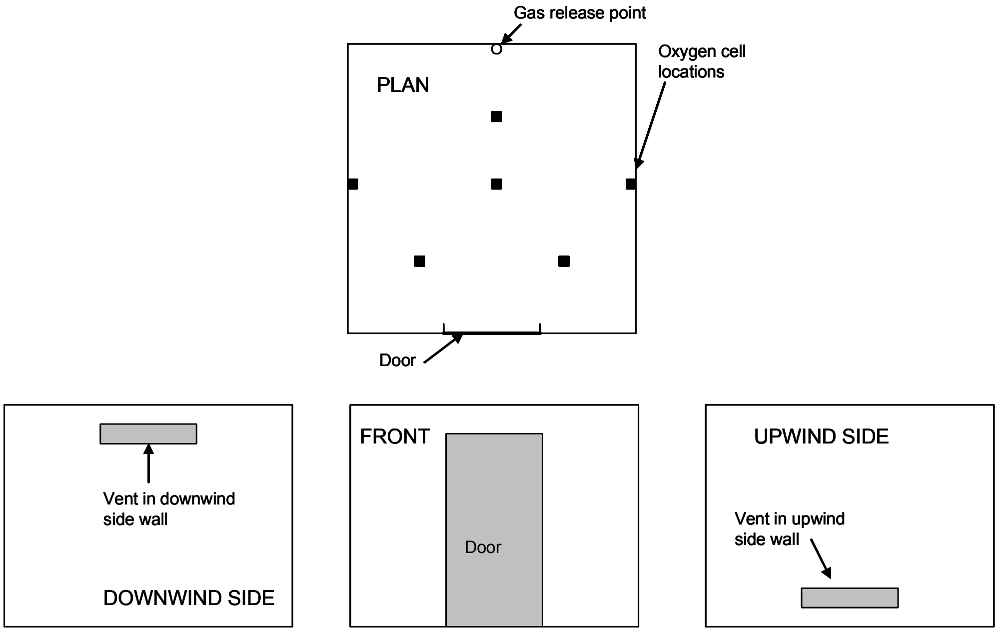

Figure 1. Schematic of the test arrangement.

The leak was simulated by a hole of a pre-determined size (5 or 10 mm diameter) drilled into a fitting at the end of the gas supply pipe work. The release point was positioned close to the back wall of the test rig, in the centre of wall (horizontally). For most of the tests, the release point was positioned at a height of 1.1 m above the floor, but for 2 tests, it was located close to the floor. In all cases, the release was directed vertically upwards.

3.2 Scientific Measurements

The gas release pressure and temperature were measured close to the release point. The gas release rate was then calculated using:

$$\dot{m} \quad = \quad B\,A\sqrt{(200\,\rho P)} \tag{1}$$

where $\dot{m}$ - mass release rate, kg s^{-1}; B - coefficient of discharge; A - area of release, m^2; ρ - density of gas, kg m^{-3}; P - gauge pressure immediately upstream of release, mbar.

The gas concentration was measured during each experiment using twenty A02 CiTicel detectors which measure the oxygen content of the atmosphere from which the gas concentration was determined. At the beginning of each test, prior to activation of the gas release, the output signals of the oxygen cells were recorded (nominally 10 mV) and taken to be representative of the oxygen concentration in the atmosphere corresponding to 0% gas. During the gas release, the signal decreased, being linearly related to the concentration of gas. The error analysis concluded that the gas concentrations could be measured with an accuracy of ±0.1%. The oxygen cells were located throughout the enclosure at different horizontal and vertical positions to determine the nature of the gas/air mixtures formed during the tests.

The prevailing wind speed and direction was measured at a location approximately 60 m from the test rig. The wind speed was measured at heights above the ground of 3, 4.85, 8.4 and 10.75 m.

4.0 TEST PROGRAMME

Table 1 summarises the test conditions for 8 tests. As can be seen, six tests considered a 10 mm diameter leak at nominally 30 mbar representing a break of typical internal pipe work. Two tests studied a 5 mm diameter leak at nominally 20 mbar representing smaller failures, such as, a leak from a joint or a faulty appliance.

Table 1. Summary of Experimental Conditions

Test	1	2	3	4	5	6	7	8
Gas composition	CH_4	50:50	CH_4	90:10	80:20	50:50	80:20	50:50
Release diameter (mm)	5	5	10	10	10	10	10	10
Release height (m)	1.1	1.1	1.1	1.1	1.1	1.1	0.1	0.1
Release gauge pressure (mbar)	20.5	20.7	30.3	30.4	30.5	30.2	31.1	29.7
Height of vent opening (mm)	10	15	50	15	10	50	20	15

5.0 EXPERIMENTAL RESULTS

In all cases, it was found that the gas concentrations measured at different locations within the enclosure but at the same height were the same, indicating that the gas accumulation was uniform in the horizontal plane and only varied with height above the floor. Consequently, in the results presented here, only the height of the sensor (oxygen cell) above the floor is given.

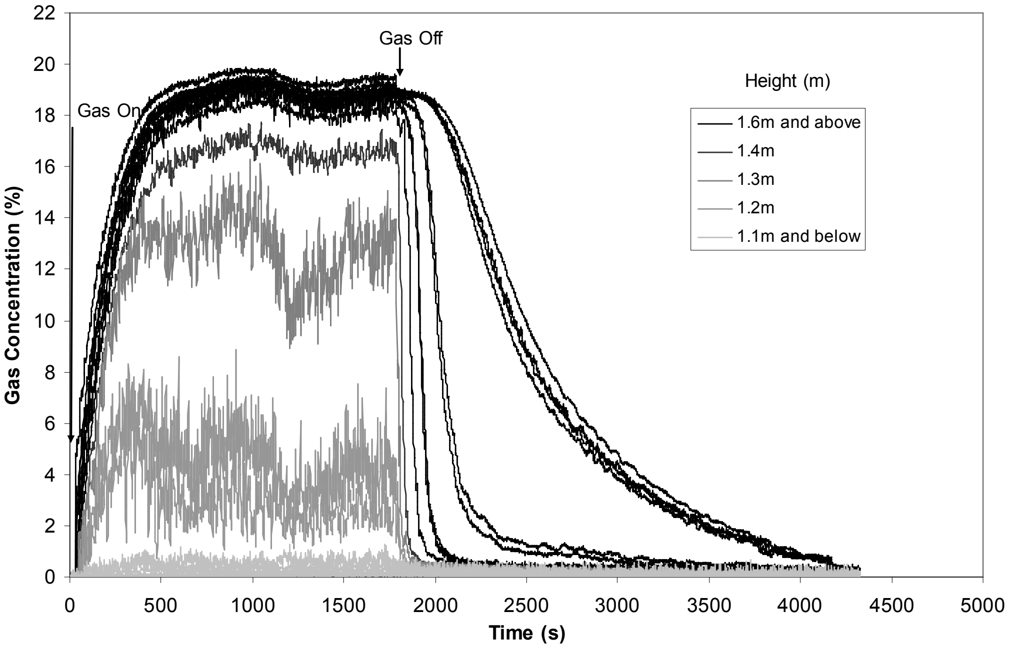

Figure 2. Gas concentration with time during Test 6.

Figure 2 shows the results of the measurements of gas concentration made using the 20 oxygen cells located within the room during Test 6. The time at which the gas release was initiated and terminated is shown. As can be seen, the gas concentrations increased with time until a steady state concentration was reached and prevailed until the gas release was terminated. It can also be seen that the gas concentrations were very low (less than 1%) for all sensors located 1.1 m or lower above the floor. Similarly, all sensors located 1.6 m or higher gave similar results, indicating an accumulation between 1.6 m and the ceiling which had a uniform concentration throughout. In the zone between these two regions the concentration varied significantly with height.

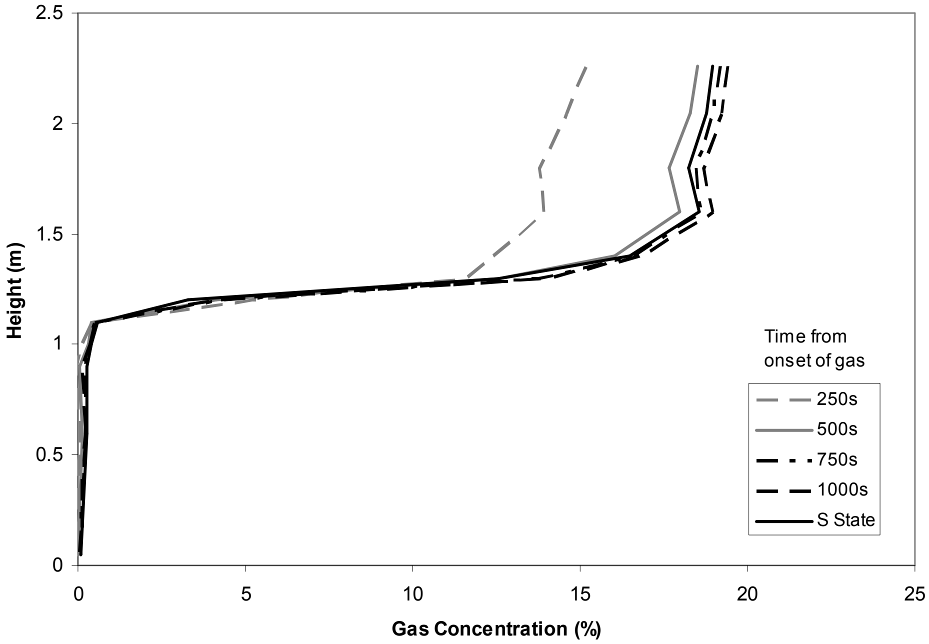

Figure 3. Gas layer formation within the room during Test 6.

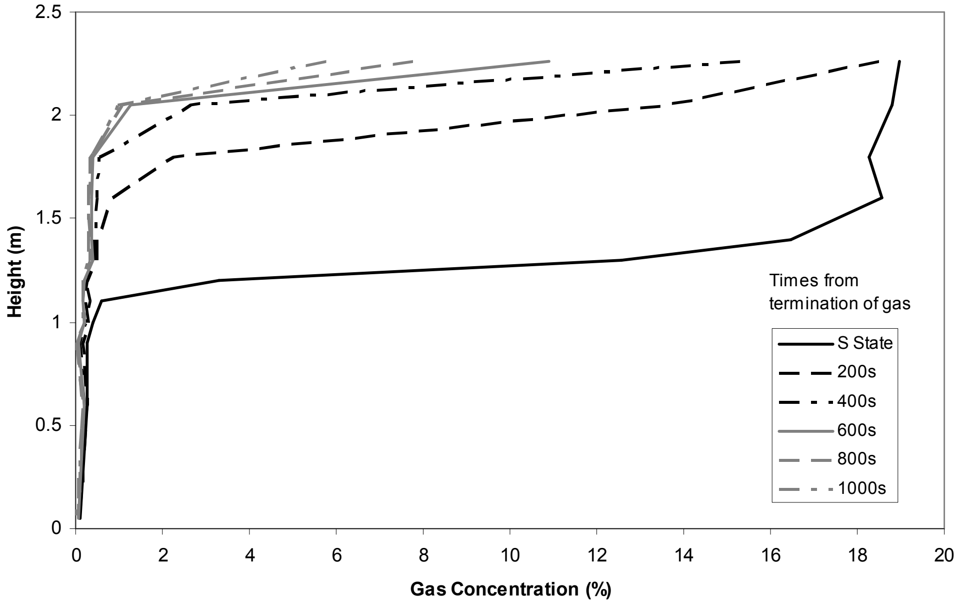

Figure 4. Gas layer dispersal during Test 6.

Figure 3 shows the results of the same test presented as gas concentration with height within the room. To produce this plot, for selected times after the onset of the gas release, the measurements made at sensors at the same height within the enclosure were averaged. This clearly shows that the formation of a layer of essentially uniform concentration occurs at an early stage after onset of the gas release, and that thereafter, the gas concentration in this layer increases until the steady state concentration is reached. For this test, the selected steady state period was 1300-1750 s and the steady state gas concentration in the layer was 18.6 %.

After the gas release was terminated, the gas accumulation dispersed. Figure 4 shows the dispersal phase for Test 6 and was produced in a similar manner to Figure 3. It can be seen that, following termination of the gas release, the layer of uniform concentration was not maintained. High gas concentrations persisted for some time close to the ceiling but at lower heights, the concentrations were significantly lower and gas accumulation was quickly dispersed.

The formation of a layer of essentially uniform concentration and the absence of gas below the height of the release was observed in all of Tests 1 to 6 where the release was from a height of 1.1 m above the floor, although the level of gas concentration achieved at steady state and the rate of change of gas concentration during the build-up phase differed from test to test due to the different release conditions and prevailing wind conditions.

Figures 5 and 6 show the formation and dispersal of the gas accumulation during Test 8, where the gas was released from close to the floor. In this Test, and in Test 7, the layer of uniform concentration extended almost down to the floor.

Table 2 summarises the height of the bottom of the layer (the interface) and the average gas concentration at steady state for all the tests. Also shown in the table are the calculated gas release rates, the measured wind speeds at 10.75 m above ground and the angle of incidence of the wind onto the inlet vent (all during the steady state period for each test).

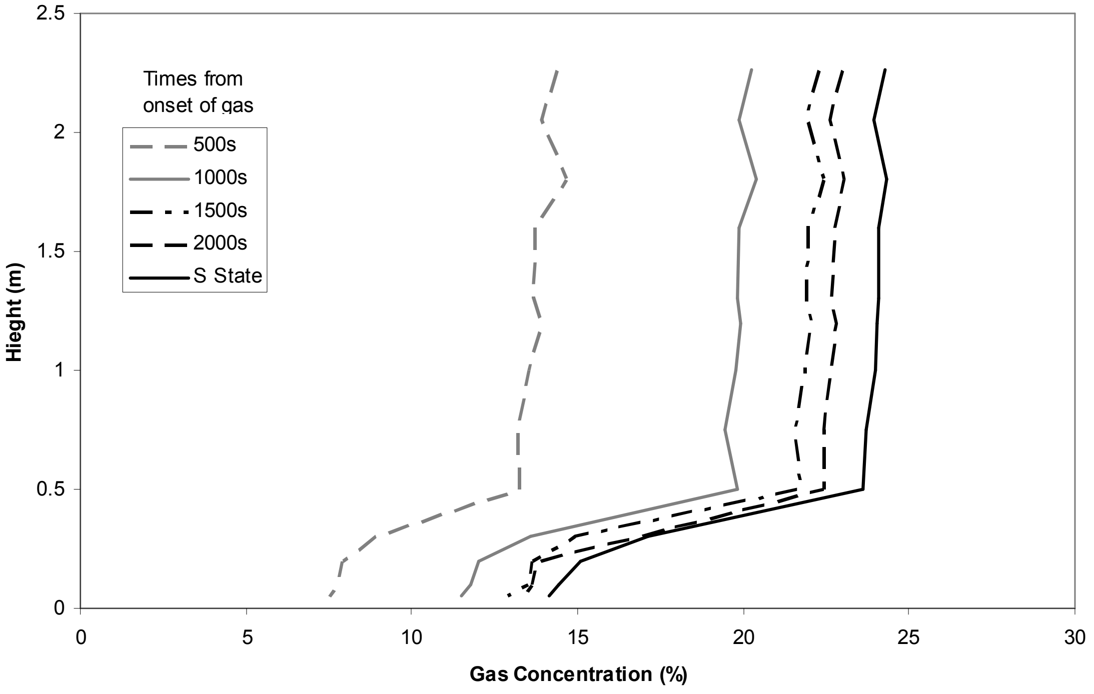

Figure 5. Gas Layer formation within the room during Test 8.

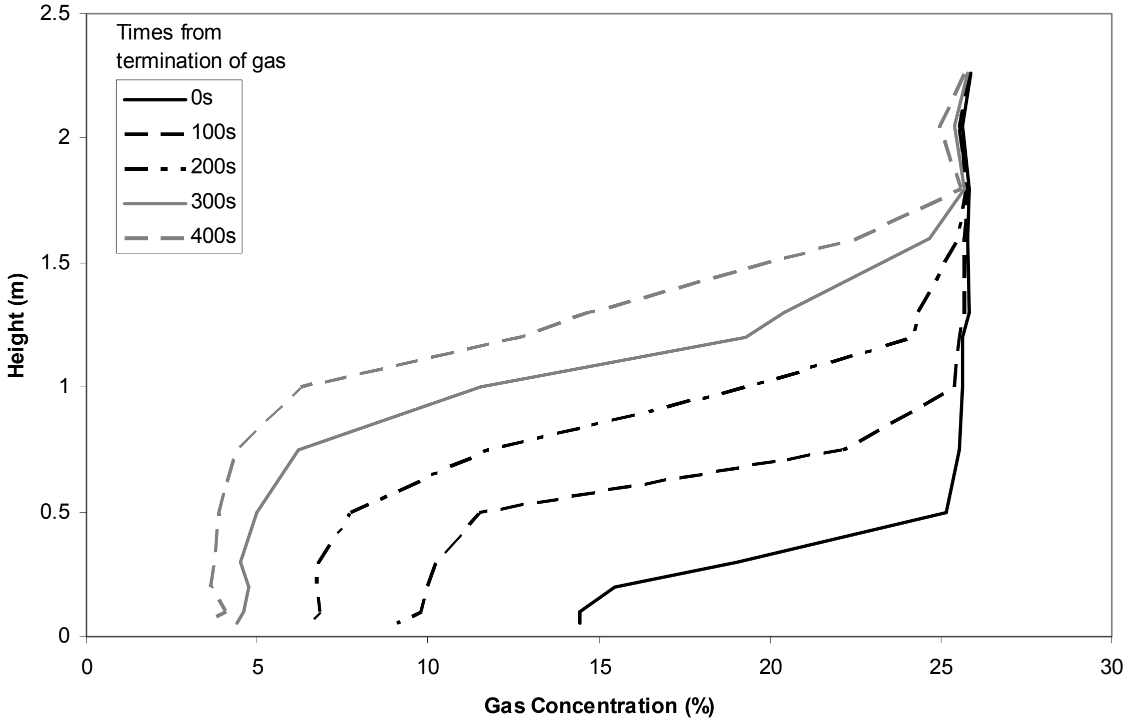

Figure 6. Gas layer dispersal during Test 8.

Table 2. Summary of gas layer formed at steady state.

Test	1	2	3	4	5	6	7	8
Gas composition	CH_4	50:50	CH_4	90:10	80:20	50:50	80:20	50:50
Release diameter (mm)	5	5	10	10	10	10	10	10
Calculated gas release rate (m^3 h^{-1})	4.21	5.68	20.6	21.6	22.8	27.4	23.1	27.3
Release height (m)	1.1	1.1	1.1	1.1	1.1	1.1	0.1	0.1
Height of interface (m)	1.4	1.4	1.2	1.2	1.2	1.3	0.3	0.2
Average gas concentration in layer at steady state (%v/v)	8.8	12.3	15.7	16.9	20.8	18.6	16.0	24.0
Wind speed at 10.75 m	4.5	2.5	1.9	6.5	9.2	1.3	4.4	5.4
Wind angle to inlet vent (0 degrees is normal to vent)	28	1	14	38	52	12	18	38

6.0 MATHEMATICAL MODEL OF GAS BUILD-UP

Due to the different wind conditions which prevailed over the test series and the different heights of the ventilation openings, it was not easy to compare directly the absolute concentration levels achieved during the tests. Such a comparison is best achieved with the use of a mathematical model.

Figure 7 shows, diagrammatically, the main elements of the model that has been developed. Gas was assumed to be released into the enclosure at a steady rate. The build-up of gas within the enclosure and the evolution of the upper buoyant layer was analyzed from onset of the release until steady state was achieved using a simple mathematical model.

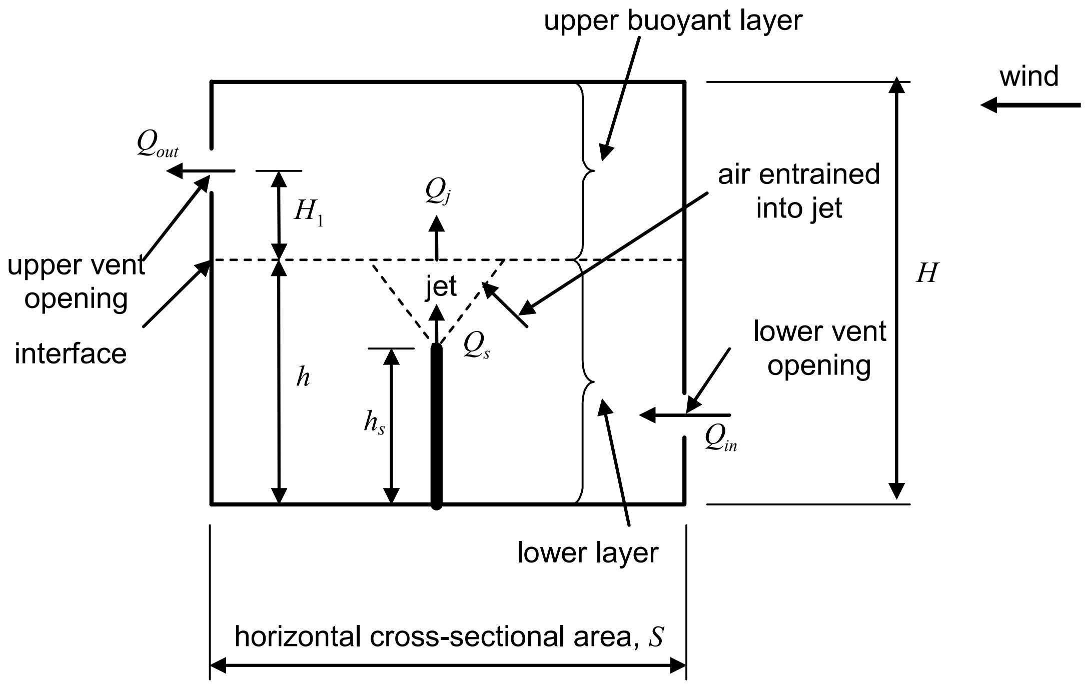

Figure 7. The main elements of the model

It was assumed that prior to the release of gas the enclosure was filled with air and that air flowed through the enclosure as a result of wind generated ventilation. Following commencement of the release of gas (lighter than air) a buoyant jet was formed into which air was entrained resulting in the formation of an upper buoyant layer of gas/air mixture and a lower layer of air. Within the upper layer the concentration of gas was assumed to be uniform. These assumptions are based on the observations made during the experiments. It was assumed that no mixing occurred across the interface separating the upper lower layers, and that the only transfer taking place was by means of the jet.

It was assumed that the wind driven ventilation flow entering the enclosure through the lower vent (and hence entering the lower layer) was augmented by buoyancy generated ventilation flow. It was also assumed that gas/air mixture at the concentration prevailing in the upper layer flowed out of the enclosure through the upper vent.

The objective of the analysis was to determine both the variation in the volume of the upper layer, V_1 (m^3), (i.e. the change in position of the interface, h (m)), and the build-up of gas in the upper layer, c (%), during the transient part of the release and also their steady state values.

Firstly, it was necessary to consider the evolution of the volume of the upper layer. Following Kaye and Hunt [1] the rate of change of the volume of the upper layer can be expressed as:

$$\frac{dV_1}{dt} = Q_j - Q_{out} = Q_j - (Q_{in} + Q_s) \tag{2}$$

Q_j – flow rate of gas/air mixture in the jet at the point of entry to the upper layer, m^3 s^{-1}; Q_{out} – flow rate of gas/air mixture leaving the enclosure, m^3 s^{-1}; Q_{in} – flow rate of air entering the enclosure, m^3 s^{-1}; Q_s – flow rate of gas entering the enclosure, m^3 s^{-1}; t – time, s.

Secondly, it was necessary to consider the build-up of gas in the upper layer. The rate of change of volume of gas in the upper layer can be expressed as:

$$\frac{d(V_1 c)}{dt} = V_1 \frac{dc}{dt} + c\frac{dV_1}{dt} = Q_s - c(Q_{in} + Q_s) \qquad (3)$$

Substituting for $\frac{dV_1}{dt}$ from equation (2), gives:

$$V_1 \frac{dc}{dt} + c\big(Q_j - (Q_{in} + Q_s)\big) = Q_s - c(Q_{in} + Q_s)$$

Therefore the rate of change of the concentration is given by:

$$V_1 \frac{dc}{dt} = Q_s - cQ_j \qquad (4)$$

To solve the pair of equations (2) and (4) numerically, it was necessary to establish relationships for the volume flow rate of ventilation air into the enclosure through the lower vent, Q_{in}, and the volume flow rate of gas/air mixture from the jet into the upper layer, Q_j.

To determine Q_{in}, the approach described in Warren and Webb (1980) [2] was followed in which:

$$Q_{in} = \sqrt{Q_B^2 + Q_W^2} \qquad (5)$$

Q_B - ventilation flow generated by buoyancy in the absence of wind, $m^3\ s^{-1}$; Q_W - ventilation flow generated by the wind in the absence of buoyancy, $m^3 s^{-1}$.

Considering the effective height of the upper buoyant layer as the vertical distance from the interface to the centre of the upper vent, H_1, (m) then the ventilation flow generated by buoyancy can be expressed as:

$$Q_B = \frac{C_d A_v}{\sqrt{2}} \sqrt{2g' H_1} \qquad (6)$$

C_d – coefficient of discharge of the vent (A value of $C_d = 0.8$ was used.) ; A_v – area of vent opening, m^2; g' - reduced gravity, $m\ s^{-2}$.

Where $g' = \left(\frac{\rho_{air} - \rho_1}{\rho_{air}}\right) g$

g – acceleration due to gravity, $m\ s^{-2}$; ρ_{air} – density of air, $kg\ m^{-3}$; ρ_1 – density of gas/air mixture in the upper layer, $kg\ m^{-3}$.

The ventilation flow generated by the wind can be expressed as:

$$Q_W = \frac{C_d A_v}{\sqrt{2}} U_W \qquad (7)$$

U_W – component of the wind velocity normal to the ventilation opening, $m\ s^{-1}$.

To determine Q_j, the model for a buoyant jet of Lane-Serff et al (1993) [3] was adopted. The two main assumptions of this approach are the Boussinesq approximation (discussed in detail by Turner

(1973) [4]) and relating entrainment into the jet as proportional to the local mean jet velocity. The constant of proportionality is called the entrainment constant, α.

An entrainment constant was first used explicitly by Morton, Taylor and Turner (1956) [5]. Numerous experimental studies have provided values of the entrainment constant such as Rouse, Yih and Humphreys (1952) [6], Chen and Rodi (1980) [7]. A value of $\alpha = 0.05$ taken from Rodi (1982) [8] was used in this analysis.

Following Lane-Serff et al (1993) [3], Conservation equations for mass, momentum and buoyancy were written as:

$$\frac{d\left(U_j R^2\right)}{dZ} = 2R\alpha U_j \tag{8a}$$

$$\frac{d\left(U_j{}^2 R^2\right)}{dZ} = g'(\lambda R)^2 \tag{8b}$$

$$\frac{d\left(g' U_j R^2\right)}{dZ} = 0 \tag{8c}$$

U_j – local mean jet velocity, m s^{-1}; R – local jet radius, m; Z – height above the source of the gas, m; λ – ratio of the transverse length scales of density and velocity. (Following Lane-Serff et al (1993) [3], a value of λ of 1.1 was adopted.)

Equations (8a) to (8c) were non-dimensionalised and transformed as described by Lane-Serff et al (1993) [3] and integrated at each time step during the solution of equations (2) and (4) to determine the mean jet velocity, U_j, and the jet radius, R, at the height at which the jet entered the upper buoyant layer. This enabled the flow rate of gas/air mixture into the upper layer, Q_j, to be calculated.

7.0 RESULTS FROM THE MODEL

Figure 8 shows a comparison of the model predictions with experimental measurements of the build-up of gas within the upper layer of the enclosure during Tests 6 and 8.

The predicted steady state level of the interface between the upper and lower layers was 1.33 m and 0.22 m for Tests 6 and 8, respectively. These values compare with experimental measurements of 1.3 m and 0.2 m, for Tests 6 and 8, respectively.

Figure 9 shows the steady state concentration predicted by the model compared with the steady state concentration measured during all the experiments.

Figure 10 shows the effect of varying the percentage of hydrogen in the released methane/hydrogen mixture on the gas accumulation in the upper layer in the enclosure and on the height of the interface between the upper and lower layers predicted by the model.

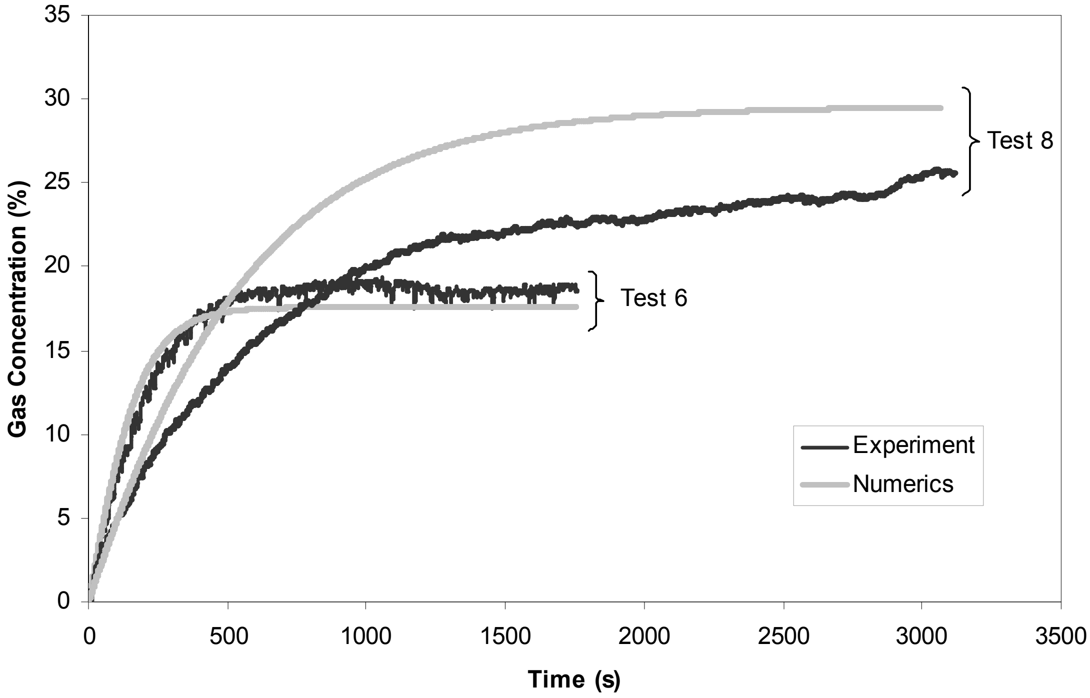

Figure 8. Gas concentration with time, Tests 6 and 8.

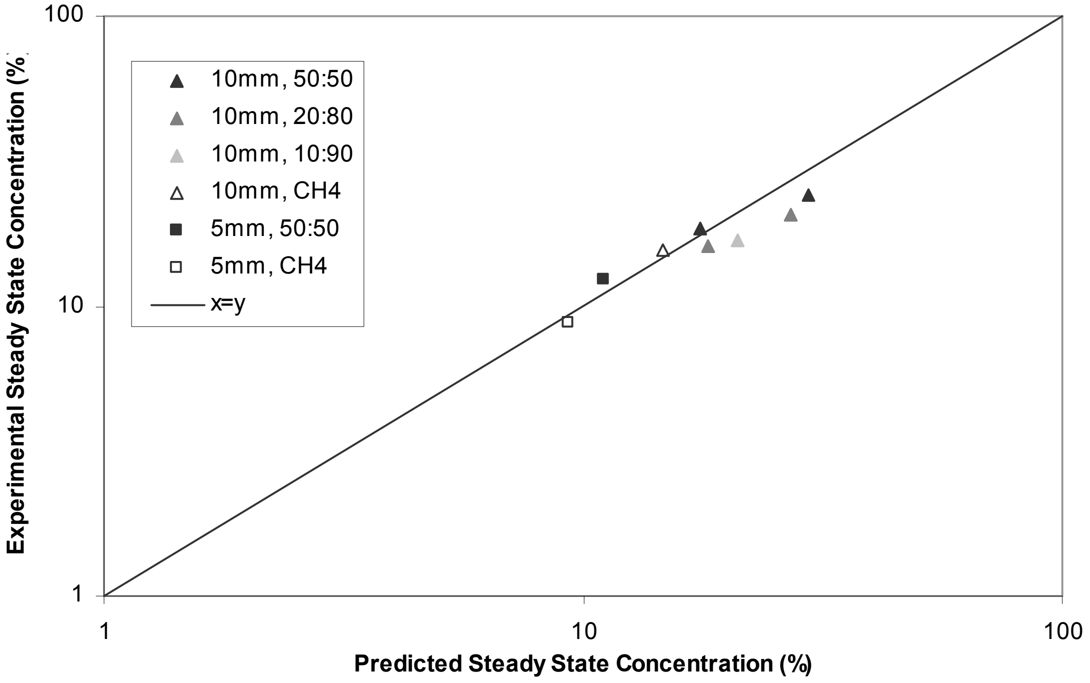

Figure 9. Steady state gas concentrations for all tests.

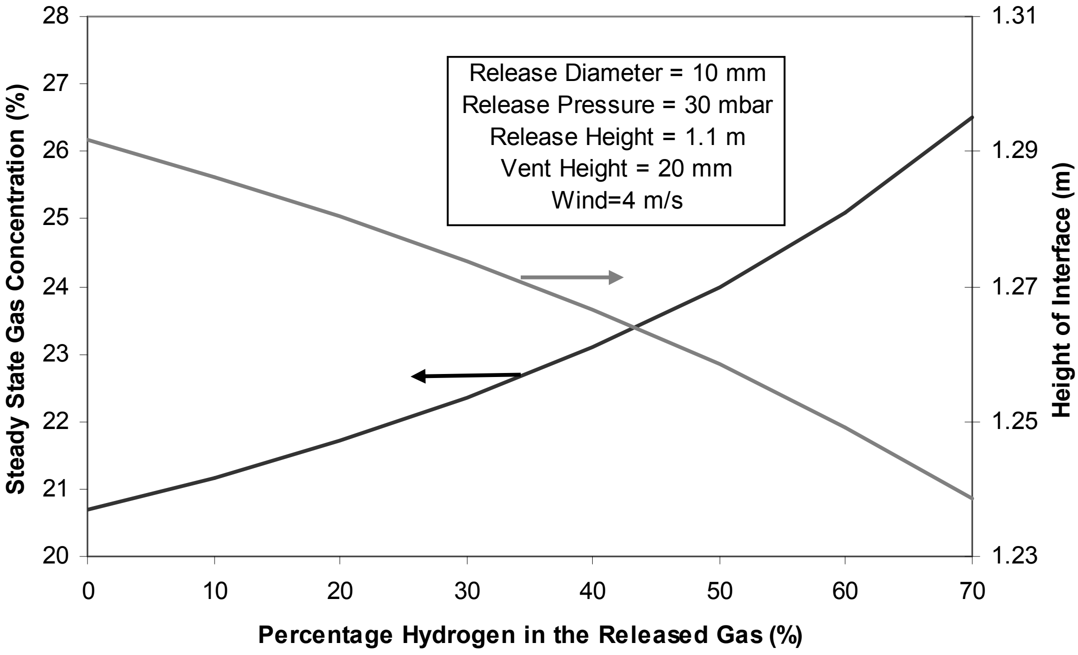

Figure 10 Steady state gas concentration and height of interface with amount of hydrogen in the released gas

8.0 DISCUSSION

The predictions of the model showed good agreement with the experimental data and demonstrate that the model performs well for the upward directed relatively low momentum releases of buoyant gas into the ventilated enclosure under consideration. Consequently, the model was used to investigate the influence on the gas accumulation of changes in different parameters. The Naturalhy project is concerned with the introduction of hydrogen into existing natural gas infrastructures. Therefore, it is of interest to understand the difference in behaviour of releases of different composition under identical release conditions.

The predictions presented in Figure 10 shows the effect of varying the percentage of hydrogen in the released methane/hydrogen mixture on the gas accumulation in the upper layer in the enclosure and on the height of the interface between the upper and lower layers. As a consequence of raising the percentage of hydrogen, the volume flow rate of the gas released into the enclosure increased. This results in a rise in the gas concentration and an increase in the volume of the region in which the gas accumulates. However, the rise in hydrogen content of the released gas also leads to enhancing the buoyancy which in turn leads to an increase in the ventilation air flow. Consequently, the rise in concentration is not as great as might otherwise have been expected. Nevertheless, the concentrations are higher and, due to the wider flammable limits, the duration over which a flammable inventory is present will also be increased. Both these factors will need to be considered when assessing the change in risk presented to the domestic customer as a result of introducing hydrogen into the supplied gas. The experimental data and the mathematical model described herein will facilitate quantification of this change in risk.

9.0 ACKNOWLEDGEMENTS

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Predictions of the consequences of natural gas-hydrogen explosions using a novel CFD approach

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Abstract

There is increasing interest in the use of hydrogen as an energy carrier. A hydrogen delivery system is required, and one solution is its addition to existing natural gas pipeline networks. A major concern is the explosion hazard may be increased should an accidental release occur, and this paper presents results from the mathematical modelling of confined, vented explosions of mixtures of methane with 0%, 20% and 50% hydrogen dilution by volume. The flow field in an explosion was predicted through solution of the averaged forms of the Navier-Stokes equations, with these equations closed using both k-ε and second-moment turbulence models. Accurate representation of the turbulent burning velocity of the various mixtures was necessary, and this was achieved using correlations obtained from the analysis of extensive experimental data sets on H_2-CH_4 mixtures. Results, derived for explosions in a $70m^3$ confined vessel with and without pipe congestion, demonstrate that hydrogen addition can have a significant effect on overpressure generation, particularly if turbulence generating obstacles are present.

Keywords: CFD, deflagration, safety, hydrogen

1. Introduction

There is presently an increasing interest in the use of hydrogen as an energy carrier as an essential part of achieving a sustainable economic development. The work described was carried out as part of the NATURALHY project (see http://www.naturalhy.net), the main objective of which is to considering the potential for using the existing natural gas system as a means of transporting the hydrogen from a site of production to a point of use. Hydrogen would be transported in the gas network as a mixture and some hydrogen extracted for hydrogen powered applications. However, some hydrogen would remain mixed with natural gas and be delivered to existing gas customers where it would be burned as a mixture.

One major concern in this work is that the explosion hazard may be increased, as in contrast to natural gas, hydrogen has a relatively high burning velocity, and can easily make the transition from deflagration to detonation. It is therefore essential to investigate the possible behaviour of such gaseous mixture releases in both confined and unconfined areas of industrial relevance. Subsequently, the information obtained can be used in the design of equipment and plant, and to improve safety and reduce the risk of both deflagrations, and deflagration to detonation transitions.

This paper presents results from the mathematical modelling of confined, vented explosions with and without internal pipe-work congestion. The mixtures investigated comprised methane, used to represent natural gas, with 0%, 20% and 50% hydrogen dilution by volume. One objective of this study was the comparison of turbulence model performance, and the turbulent flow field was resolved by the application of both a two-equation and a second-moment turbulence closure, supplemented with transport equations for the reaction progress variable and the total energy. Accurate representation of the turbulent burning velocity of the various mixtures is necessary, and this was introduced into the calculation via the diffusion coefficient and the source term of the reaction progress variable. The burning velocity was represented by correlations obtained from the analysis of recent experimental data gathered at the University of Leeds, and a simple eddy break-up reaction model using a one-step irreversible reaction was applied in the prescription of the turbulent combustion model.

The calculations presented are representative of confined, vented explosion experiments undertaken by Loughborough University in a 70m^3 confined vessel with and without internal pipe-work congestion. The results are conforming to experimental observation (Hankinson and Lowesmith, 2007), however a full experimental dataset remains in preparation and as such, is not reported in the present work. Future publication will provide full comparisons.

2. Experimental Arrangement

The predictions presented in this paper are a selection taken from a number of simulations of large-scale experiments undertaken by Loughborough University (Hankinson and Lowesmith, 2007). A full account of the experiments performed and the results obtained will be presented elsewhere, hence only a brief overview is given here.

The experimental rig was of steel construction, and measured 8.25m in length, 3.0m in width, and 2.8m in height. One 3.0 × 2.8m end was effectively open to the atmosphere for the purpose of the tests, being covered with a polythene sheet to retain the gas-air mixture prior to ignition. Figure 1 depicts the rig, and indicates the configuration of pipe-work congestion and the spark ignition points, although not to scale.

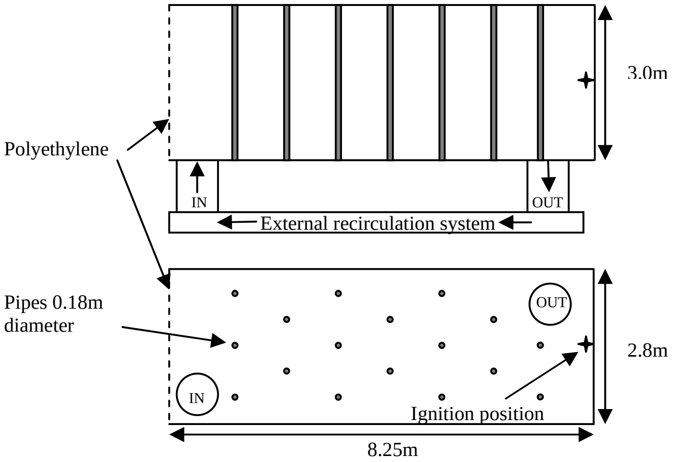


Figure 1. Schematic diagram of the experimental rig.

The gases investigated were mixtures of methane, hydrogen and air, with the methane-to-hydrogen ratio by volume being 100:0, 80:20 and 50:50. Five tests for computational investigation were chosen as a representative sample of the total number of experiments performed, and these configurations are reported in Table 1.

Table 1. Experimental conditions.

Experiment number	Fuel / CH_4:H_2	Congestion / pipes	Ignition location
7	80:20	None	Rear
8	50:50	None	Rear
9	80:20	17	Rear
10	50:50	17	Rear
13	100:0	None	Rear

3. Mathematical Modelling

3.1. Turbulent Flow Field

The flow fields within the experimental rig were resolved by solution of the two- and three-dimensional forms of the density-weighted, partial differential equations describing the conservation of mass, momentum, and total energy. Time-dependent, and written in their high Reynolds number forms, the averaged equation set was closed in the first instance by the standard k-ε turbulence model of Jones and Launder (1972). Modelling constants used were the widely accepted standard values, as reported in Jones and Whitelaw (1982). For comparison, a second-moment method of turbulence closure was investigated, being that described by Jones and Musonge (1988). In this original aspect to the modelling approach, the shear and normal stress terms are closed by the solution of their individual transport equations, the modelling constants employed being a modified set, as described in Jones (1994).

The geometry was modelled using three approaches. In the first instance, a central section of that shown in Fig. 1, assuming symmetry properties of two of the computational boundaries, was used. Fig. 2 depicts this geometry, where the left boundary represents a solid wall, and the right an outflow. Initially, a small area of burned gas, represented by a region where the progress variable, *c*, equals 1.0, is located adjacent to the former boundary, which is used to instigate the numerical reaction. Secondly, a two-dimensional slice of the geometry was modelled using three solid wall boundaries, and containing a representation of all the specified obstacles. Thirdly, a full three-dimensional version of the confined region was modelled.

3.2. Combustion Model

In addition to that for total energy, *E*, the premixed combustion model implemented requires the solution of a conservation equation describing the reaction progress variable. The source term of this equation is represented by a modified form of the eddy break-up reaction rate expression as:

$$\overline{\rho S_c} = \bar{\rho} R \tilde{c}^4 (1-\tilde{c}) \left({\rho_b}/{\rho_u} \right) \tag{1}$$

where reactants are assumed to go to products in a single-step irreversible reaction, and a superscript bar and tilde represent, respectively, Reynolds and density-weighted averaged mean values. Also, R represents the reaction rate established in line with discussion in Catlin et al. (1995), and ρ the densities of the burned and unburned gases indicated by the subscripts. This form of the reaction rate expression eliminates the cold-front quenching problem by prescribing variation of the reaction rate through the flame using a power law expression (Catlin et al., 1995). Equation (1) can be subsequently used in the closure of the source term for total internal energy by convolution with a representation of the specific heat release.

The two components of this model are to firstly provide solutions which give rise to a flame which accurately reproduces specified burning velocities, and secondly provide a representative prescription of these velocities given known mixture and flow field parameters. Following Catlin et al. (1995), the source terms and diffusion coefficients in the equations for E and c can be defined as functions of the turbulent burning velocity, and here, correlations derived from the most recent experimental evidence (see, for example, Burluka et al., 2007) have been implemented.

3.3. Method of Solution

Integration of the equations employed a second-order accurate finite-volume scheme in which the transport equations were discretised following a conservative control-volume approach, with values of the dependent variables being stored at the computational cell centres. Approximation of the diffusion and source terms was undertaken using central differencing, and a second-order accurate variant of Godunov's method applied with respect to the convective and pressure fluxes. The fully-explicit time-accurate method was a predictor-corrector procedure, where the predictor stage is spatially first-order, and used to provide an intermediate solution at the half-time between time-steps. This is then subsequently used at the corrector stage for the calculation of the second-order fluxes. A further explanation of this algorithm can be found elsewhere (Falle, 1991). An adaptive-grid method was employed to allow the generation of fine grids in regions of steep spatial and temporal variation, and the implementation of coarser grids in smooth regions of the flow. Adaption of the rectangular mesh was employed by the overlaying of successively refined layers of grids, with each layer generated from its predecessor by the doubling of the computational cell number in each spatial dimension. Again, further details regarding the algorithm can be found in Falle and Giddings (1993).

4. Results and Discussion

Figure 2 provides an example of a sample stage of solution during the calculation of experiment number 10, using the Reynolds-stress approach to the turbulence closure. From an assembly of a time-lapse sequence of the reaction progress variable such as this, the behaviour of the flame front can be seen to be in-line with expectation. Initially progressing at a relatively slow rate, the reaction zone subsequently accelerates through the unreacted fluid upon each obstacle interaction, returning to a constant velocity in between these areas of turbulence generation.

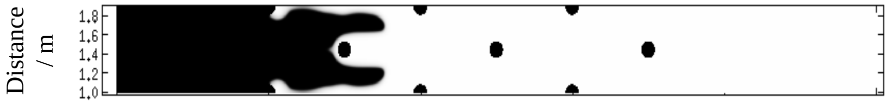
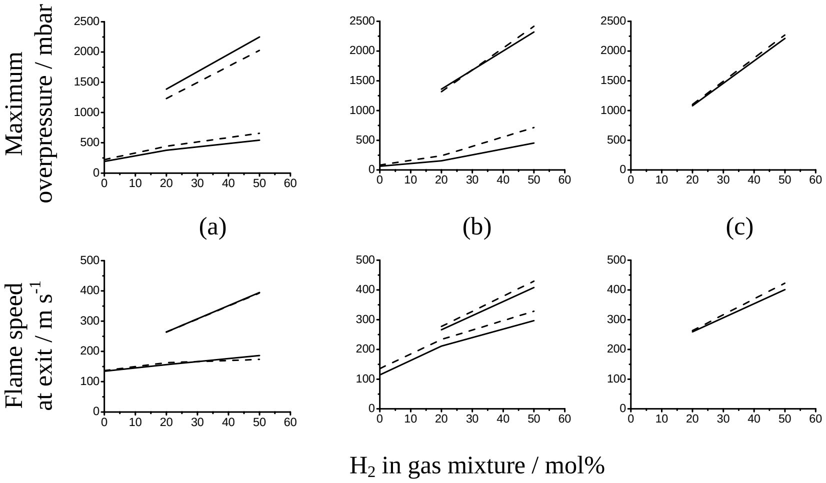


Figure 2. Sample two-dimensional symmetry progress variable predictions of experiment 10.

Analysis of the results provides the maximum overpressures achieved and the flame-front vessel-exit velocities predicted by the models, which are presented in Fig. 3. It is evident from these results that, in general, the magnitude of the predictions, and hence ultimately their conformity with experiment, depends upon the turbulence model, which in turn has a performance dependency upon the domain geometry and the fuel investigated. This is less evident for the three-dimensional approach, although results based on the Re-stress model are generally more in line with available data.

For the two-dimensional symmetry simulations run involving internal pipe-work, the more reliable Reynolds-stress model is seen to be at variance with its two-equation counterpart with respect to recorded maximum overpressures. Predicted exit flame-speeds do, however, show little difference in the performance of the two turbulence models. At the higher turbulence levels associated with the congested cases, the flow becomes increasingly less isotropic and it appears a notable component of the turbulence stress-tensor is not being represented in the k-ε case. Scrutiny of the calculated results also reveals a relative deterioration of the k-ε model's predictive ability in the cases of higher hydrogen content, this being due in part to the introduction of hydrogen effecting an increase in both the laminar and turbulent burning velocity, and hence an increase in the turbulence generated. The varied performance of the models is further highlighted when the results obtained from the calculations of the empty rig are considered. Here, conversely to that seen in the relatively high turbulence case, the Reynolds-stress model is seen to predict lower maximum overpressures than its k-ε counterpart, over the three fuels considered. Again, predictions of exit flame-speed velocity are similar for the three cases investigated, with little difference observed between the two turbulence model predictions.



(a) (b) (c)

Figure 3. Maximum overpressures and exit flame-speeds obtained using the k- ε (dashed line) and Reynolds-stress (solid line) models for the 17-pipe (upper) and 0-pipe (lower) configurations using the (a) symmetry, (b) two-dimensional and (c) three-dimensional approaches.

With reference to the two-dimensional calculations (Fig. 3b), the increase in geometry complexity is seen to bring predicted overpressures more in line in the congested cases, although a less conforming result is seen for the empty vessel. Also, predicted exit flame speeds comply with this observation, which raises questions regarding the validity of the model in such low turbulence regimes. Based on these observations, and the long computational time of approximately 80 hours using a 3 GHz processor, three-dimensional calculations were undertaken of the high-turbulence cases only, and results are depicted in Fig. 3(c). Both predicted overpressure and flame speed are noted to be of lower magnitude than the previous approaches, with the k-ε model typically over predicting Re-stress results in the cases with the higher hydrogen concentration and hence the higher level of turbulence.

One further consideration is the accuracy to which either of these turbulence models can be expected to predict a flow that is substantially laminar, as in the case of explosions within vessels without internal obstacles. Further work has therefore focussed on those experimental tests performed using internal, turbulence generating pipes. Additional investigations are also being undertaken to assess the model's performance in the modelling of similar, but unconfined cases.

5. Conclusions

For the first time, a Reynolds-stress turbulence model has been applied to the prediction of large-scale vented explosions, coupled to a turbulent premixed combustion model. Maximum predicted overpressures and flame-front velocities for five test cases are presented, and comparisons made to calculations based on the k-ε model. The Reynolds-stress model is seen to generally be at variance with the isotropic approach, although in terms of predicted overpressures and flame-front velocities these differences are often small. However, the increase in turbulence anisotropy caused by internal pipe work within a vessel necessitates the use of a Reynolds-stress model on physical grounds alone. These observations are valid for the three approaches used to represent the geometry considered, with the level of conformity observed in the two-dimensional cases making them viable for use in future studies.

6. Acknowledgements

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