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NATURALHY

"Preparing for the Hydrogen Economy by Using the Existing Natural Gas System as a Catalyst"
Project Contract No.: SES6/CT/2004/502661

NATURALHY is an Integrated Project funded by the European Commission's Sixth Framework Programme (2002-2006) for research, technological development and demonstration (RTD)

Work Package 5: End-Use Separation of Hydrogen

The transmission and distribution of hydrogen in natural gas networks provides a real opportunity for end users to obtain pure, or nearly pure, hydrogen for a variety of applications, thus helping to create "local hydrogen centres" and enabling the transition towards a hydrogen energy society. To achieve this, low cost and efficient means of separating hydrogen from the natural gas/hydrogen networks must be available. Providing options for hydrogen separation is an important aspect of NATURALHY.

Several partners within NATURALHY are engaged in developing advanced membranes capable of separating hydrogen from mixtures with natural gas. The objective is technically challenging, and because there will be a range of scales, the extraction of hydrogen can take place at different points in the network system over a range of supply pressures. The partners involved are the University of Warwick (UK), the Norwegian University of Science and Technology (NTNU) and CETH a French SME specialising in hydrogen technologies. The aim of the work is to provide the research data and know-how that will enable future manufacture of packaged units.

Several options are being addressed. The University of Warwick is preparing very thin palladium (Pd) alloy films (<8 microns) supported on porous substrates (Figure 1) while CETH is investigating the performance of proprietary Pd alloys supported on metallic substrates (Figure 2 - page 2). NTNU is developing alternative systems - carbon molecular sieve membranes derived from cellulosic materials doped with selected metals (Figure 3 - page 2).

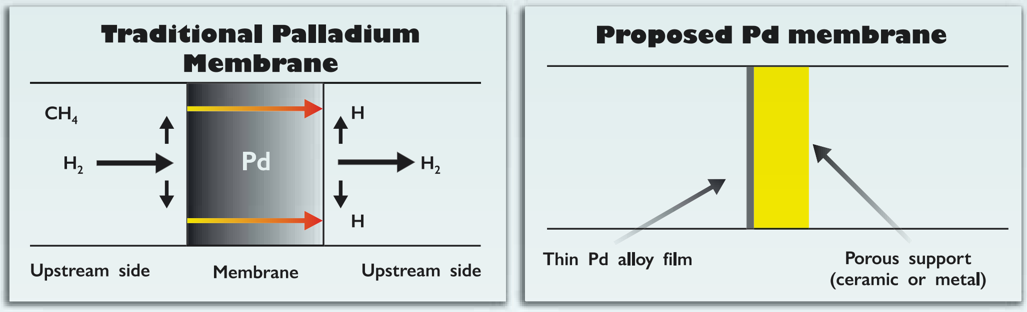

Figure 1: Schematic showing the approach to new Pd based membrane systems

There are alternatives to membranes for hydrogen separation. Pressure Swing Adsorption (PSA) is for example, widely used in the process and refinery industries, and these methods will be assessed and compared for the needs of NATURALHY. However, there are compelling reasons for developing efficient membranes, particularly cost and packaging advantages for smaller scale operations, and the ability to provide

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EDITORIAL

With this third Newsletter on the NATURALHY-project we would like to continue to inform you about our project, which investigates the potential of the existing natural gas system for the delivery of hydrogen. As a first logic step of the transition towards the hydrogen economy, this project focuses on the delivery of hydrogen/natural gas mixtures. The addition of hydrogen to natural gas affects the chemical and physical properties of the gas and will have an impact on the safety aspects related to the transmission, distribution and en use of the gas. In the main article of this issue we further focus on the research programme directed to the quantification of this impact. In the next newsletter we will pay attention to two other initiatives active in the transition field: the HYWAYS-project and the IAHE. If you have any questions or would like to discuss certain aspects of the NATURALHY-approach with us, than please react through our website **www.naturalhy.net.**

The project coordination team Onno Florisson, Friedrich Völlink and Gjalt Tiekstra

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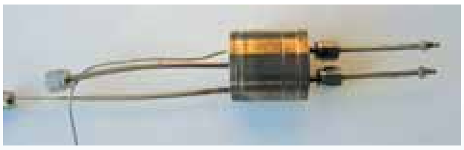

Figure 2: Pd membrane laboratory test module

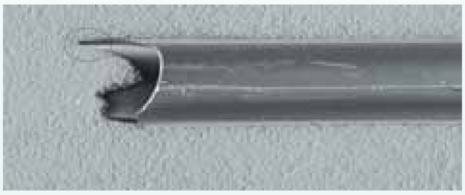

Figure 3: Hollow fibre carbon membrane

extremely high purity hydrogen if required. At the same time, the research programme is responsive to new developments in end-use applications, for example, the increasing capability of fuel cells to utilise a wider variety of feedstocks will influence the quality of the hydrogen purification required.

Membranes work essentially as a selective filter to increase the proportion of hydrogen in a gas stream. The filtering mechanism is based on molecular size (with or without the addition of surface or adsorption enhancement) to increase the concentration of hydrogen. Alternatively, the unique ability of palladium and its alloys to dissociate hydrogen reversibly and allow the interstitial diffusion of atomic hydrogen may be used to provide pure hydrogen.

Conventional palladium metal membranes have been tubular or in manifold sheet form but they are extremely expensive as the cost per unit flux of hydrogen is proportional to the metal thickness to the power of 2. The approach of NATURALHY is to achieve better performance at a lower cost by:

• Using very thin (<8 micron) Pd films supported on low cost substrates (for example porous ceramics); this reduces the metal loading, lessens the diffusion path thereby speeding up hydrogen diffusion, and lowers operating temperature to below 400°C.

• Alloying palladium with silver or copper to improve mechanical stability, hydrogen flux rate and resistance to poisoning from sulphur in the odorant and other trace components of natural gas.

• Using carbon- based polymer membranes and mixed phase membranes which have the advantage of operation at relatively low temperatures typically around 100°C. In addition, they are based on inexpensive materials and can be manufactured into packaged systems by inexpensive polymer processing technologies.

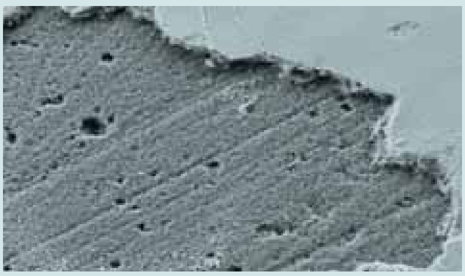

Figure 4: Electron micrograph showing commercial ceramic support with defects and the effect of applying more uniform porous ceramic layer

Figure 5: Pd thin film membrane supported on tubular ceramic substrate

To achieve our research objectives, we are conducting basic research into materials formulation and characterisation, particularly the preparation of thin films and control of porosity and surface structures. The progress made so far is encouraging.

Initial preparations of thin Pd membranes supported on ceramic supports show promising hydrogen flux and selectivity but, indicate that the texture and pore structure of the support material are critical to obtaining pin-hole free membranes. Most porous ceramic supports have defects in the form of large pores (>10micron diameter). These pores may not be covered by thin palladium films, and hence remain as pin holes in the membrane, greatly reducing separation factor. In addition they may act as stress points in thicker films. Techniques have been developed to apply a coating of alumina that covers these defects, leaving a much more homogeneous surface for subsequent coating of Pd films. Figure 4 is an electron micrograph showing a typical defect in an alumina support, and how the applied washcoat provides a smoother surface for obtaining a more coherent membrane (Figure 5).

For carbon membranes, improving hydrogen selectivity requires close control of the pyrolysing procedures used in manufacture from the polymeric precursor film. Similarly, for mixed phase membranes, achieving an understanding of the fundamental processes controlling selective diffusion and pore tailoring by design requires basic research in addition to the more empirical approach.

For packaged Pd alloy systems (Figure 6) the operational envelope of fabricated systems is being defined and work continues to determine how the systems could contribute to end use applications within the scope of potential future NATURALHY scenarios.

The End-Use Work Package is also focussed on examining the impact of hydrogen addition to natural gas on domestic and industrial appliances. This work involves

• Gathering all available data on combustion properties and effects on appliances of different hydrogen/natural gas mixtures. This activity is led by Gasunie, the Netherlands.

• Carrying out field test on typical domestic boilers under real conditions. This programme is being carried out by DGC (Danish Gas) and by Naturgas Midt-Nord.

These aspects of End-Use will be covered in a future article. ❖

Ashok Bhattacharya and Costa Komodromos
WPTG/University of Warwick
WP Leader

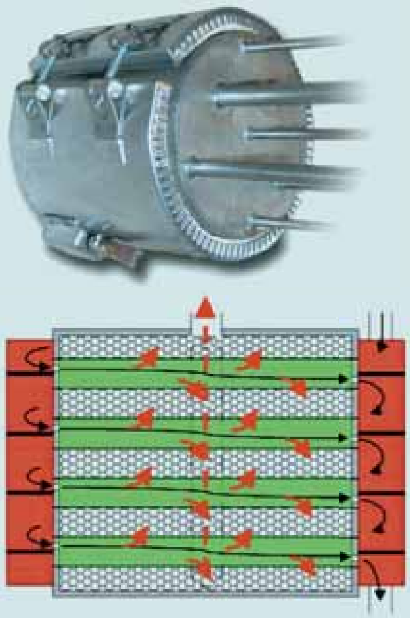

Figure 6: Packaged separator module integrating the membranes & heating system, and showing the internal flow pattern

Burning Velocity Measurements of Mixtures of Hydrogen & Methane

The Safety Work Package (Work Package 2) of the NATURALHY Project is designed to identify and quantify the consequences and level of risk resulting from accidental releases of natural gas-hydrogen mixtures during the transmission, storage, distribution and delivery of such mixtures by means of existing natural gas infrastructures. The potential safety issues are overwhelmingly ones of leakage, ignition and combustion. The need to undertake this work stems from the fact that hydrogen is far more reactive than methane, the main constituent of natural gas, and its addition to natural gas is therefore likely to increase some hazards through increased flame temperatures and burning velocities.

An essential first step in assessing combustion hazards is the determination of the relevant parameters of natural gas-hydrogen mixtures pertinent to turbulent premixed combustion to enable the use of mathematical techniques for predicting the consequences of explosions, and subsequently in the design of mitigating measures. This part of the project, being performed as Task 1 of Work Package 2, therefore involves measurement of the turbulent burning velocity of natural gas and natural gas-hydrogen mixtures with air using a unique fan-stirred "explosion bomb" which is being used to provide a fundamental understanding of the combustion of such mixtures.

The explosion bomb, pictured in Figure 1, is housed within the School of Mechanical Engineering at the University of Leeds, with the current project being a collaboration between academic staff of that School and the School of Process, Environmental and Materials Engineering. The bomb allows both laminar and highly turbulent flames to be studied up to the point of extinction (due to turbulence extinguishing the combustion process) with a full range of advanced laser diagnostic techniques. Ignition of flammable mixture within the bomb is at its centre, giving rise to a single flame kernel, with the flame propagating in either a laminar mixture, or a turbulent mixture with a predetermined level of turbulence generated by four fans within the bomb; examples of turbulent flame propagation are shown in Figure 2.

The aim of this experimental work is to generate a new and comprehensive data base on the burning velocity of hydrogen-methane mixtures. Work is being undertaken at atmospheric pressure, and with various initial temperatures, and using both laminar mixtures and fluctuating turbulence velocities that range from low to very high levels (with root mean square, rms, fluctuating velocities varying from 0.5 to 10 m s^{-1}). Mixtures with air of pure methane, 10%H_2-90%CH_4, 20%H_2-80%CH_4 and 50%H_2-50%CH_4 are being considered, with equivalence ratios ranging from 0.5 (fuel-lean) to 1.7 (fuel-rich). To date, the majority of this data has been gathered, although a significant amount of data analysis remains to be performed.

The ability of comprehensive chemical kinetic models to predict the laminar burning velocity of these mixtures is also being investigated. So far, two schemes have been evaluated against the experimental laminar burning velocity data produced, with one of them showing excellent agreement with observations. These schemes have also been used to establish that the addition of hydrogen to methane affects changes in laminar burning velocity that are far greater than those observed between the different compositions of natural gas used across EU member states, with the addition of 10% hydrogen increasing the burning velocity by twice the amount of variability observed between the minimum and maximum burning velocity natural gases currently in use.

Some preliminary results of this work are shown in Figure 3. The figure shows the burning velocity of pure methane (in black) and 50%H_2-50%CH_4 mixture (in red) against the equivalence ratio, ϕ, at two levels of turbulence within the bomb – for rms turbulent fluctuating velocities (u') of 2 and 6 m s^{-1}. These data clearly show the influence of hydrogen addition to methane in increasing turbulent burning velocities across all stochiometries, as well as the significant influence that increasing turbulence levels has.

Once all the data have been analysed, it will be presented in a compact ▸▸ PAGE 4

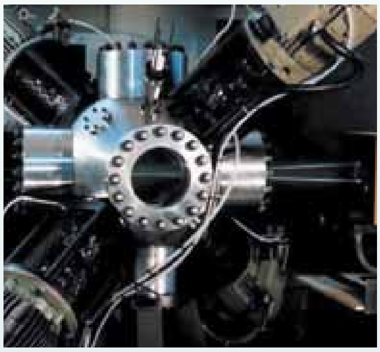

Figure 1: The explosion bomb being used for burning velocity measurements, with the four fans used to generate turbulence within the central spherical vessel seen around its periphery.

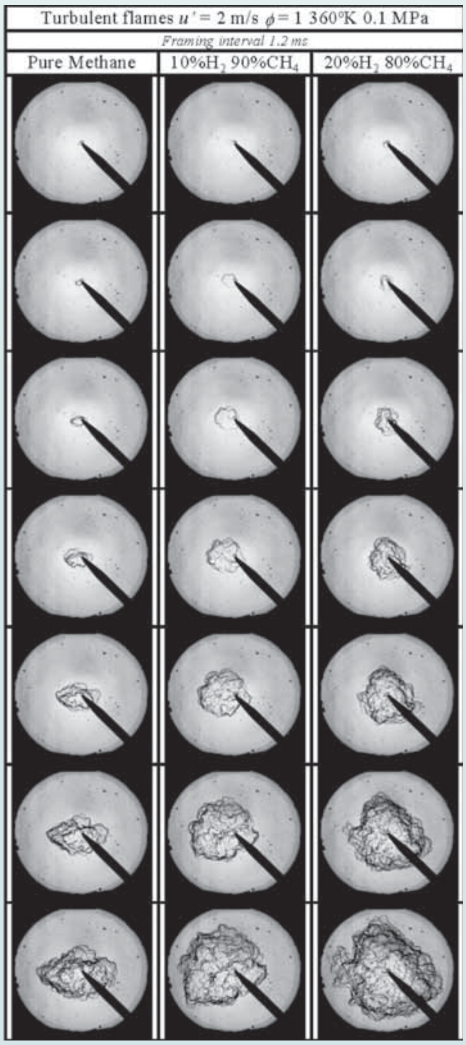

Figure 2: Flame development with time for turbulent mixtures of pure methane, 10%H_2-90%CH_4 & 20%H_2-80%CH_4. The individual frames correspond to the same times, and clearly illustrate the influence of hydrogen addition in increasing flame speeds.

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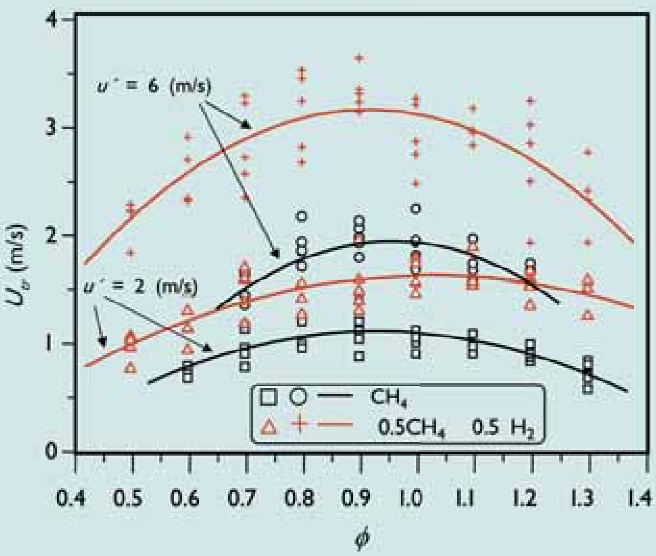

Figure 3: Turbulent burning velocity variation with equivalence ratio for a mixture of 50%H_2-50%CH_4 at two levels of turbulence intensity.

form for subsequent use in explosion models. Attempts will therefore be made to collapse all the data in to generalised correlations using non-dimensional groups based on the laminar and turbulent burning velocities, and parameters such as the rms turbulent velocity, Karlovitz stretch factor and turbulent Reynolds number. These correlations will then be used within computational fluid dynamic and phenomenological models of explosions, within other parts of the Safety Work Package, to permit assessments of the influence of hydrogen addition to natural gas on the overpressures generated in explosions. The data base of burning velocity information to be generated will also be of interest to those working on gas utilisation issues, and in particular to the use of hydrogen-natural gas mixtures in domestic, commercial and industrial equipment based on premixed combustion processes, as well as to those involved in the supply of such mixtures for use in internal combustion engines. ❖

M. Fairweather, M.P. Ormsby, C.G.W. Sheppard and R. Woolley, University of Leeds

NEWS

The first NATURALHY project workshop was held on November 22, 2005 during the 2nd European Hydrogen Energy Conference EHEC 2005 (Zaragoza - November, 22nd -25th, 2005). EHEC is a forum for all latest developments and advances in the field of Hydrogen and is devoted to the exchange of scientific and technical information. **http://ehec.info**

The workshop provided the opportunity to make brief overview of the project objectives and results and brought together more than 50 industry experts to discuss and explore various topics related to the project work packages on Life-Cycle Analysis, Safety, Durability, Integrity, End-Use and the Decision Support Tool.

All workshop presentations are available from the project website:
http://www.naturalhy.net/ehec2005.htm

UPCOMING EVENTS

NATURALHY will participate in the following events:

5-9 June 2006

23rd World Gas Conference (WGC)
Amsterdam, the Netherlands
www.wgc2006.nl

13-16 June 2006

16th World Hydrogen Energy Conference (WHEC) Lyon, France
www.whec2006.com

1-5 June 2008

17th World Hydrogen Energy Conference (WHEC) Brisbane, Australia

16-21 May 2010

18th World Hydrogen Energy Conference (WHEC 18) Essen, Germany
www.18whec2010.de

CONTACT US

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