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HYDROGEN DEBLENDING: FUTURE AND EMERGING TECHNOLOGY WATCH

(HYDROGEN DEBLENDING FEASIBILITY PHASE 2: FUTURE TECHNOLOGY WORKSTREAM)

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Hydrogen Deblending Future and Emerging Technology Watch

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1 INTRODUCTION

Hydrogen and hydrogen gas (H_2) are at the forefront of HM Government's strategy to achieve decarbonisation, explicitly highlighted in the 'British Energy Security Strategy' that builds upon 'The Ten Point Plan for a Green Industrial Revolution', the 'Net Zero Strategy' and the Energy Networks Association (ENA) hydrogen delivery plan.[1,2,3,4] In the latter instance, H_2 provides a low-carbon alternative energy gas to natural gas (NG) and the blending of H_2 into NG is a viable route for the transition into a decarbonised gas grid. Blending will introduce H_2 into the NG grid for storage and transportation, subsequently reducing the carbon dioxide (CO_2) emissions at the end point of use compared to an entirely NG stream.

However, upon the introduction of H_2, not all users will be able to immediately transition to a hydrogen enriched natural gas (H_2NG) network and incorporating H_2 into current NG infrastructure demands solutions to accommodate and support existing customers. Combustion control technologies currently installed could encounter issues accounting for the hydrogen fraction.[5] Other restrictions on H_2NG include compressed NG (CNG) filling stations which have a tolerance of 2% H_2 due to the specifications of vehicle tanks and the H_2 limit specifications for some gas turbines and engines.[6,7] To meet the requirements of these customers that cannot transition immediately to H_2NG it must be possible to separate the blended H_2 from the H_2NG stream to deliver suitable quality NG to the user. In addition, this separation of H_2 from the mixed gas stream will cater for pure H_2 end users.

Methods of H_2 separation or deblending would be required to deliver H_2-free NG or pure H_2 at multiple points in the network. The techniques required to separate H_2 at large scale have been investigated in previous reports, and these are noted in section 2.1.[8] In this report, the aim is to identify emerging technologies that have the potential to provide alternative systems to consider for future hydrogen separation at large scale. The existing hydrogen separation techniques proven on an industrial scale suffer from several shortcomings, most notably their large energy requirements, however energy efficiency data for novel technologies is not typically reported due to the focus on separation and permeability at research scale. For future work therefore, the technologies identified in this report demonstrating their energy efficiency and scalability to identify the most effective technologies would prove crucial for feasible H_2NG deblending.

2 SCOPE

This report provides a literature and technology review to identify future and emerging concepts that could disrupt the existing gas separation marketplace relevant to H_2 separation from NG. This includes but is not limited to:

- New, innovative, and potentially disruptive technology.
- New materials, designs and processes that may require scaling.
- Technology at laboratory or start-up scale.
- Technology that could be scaled up for gas transmission use.

2.1 PREVIOUS WORK

Previous research into H_2 separation from NG includes the European project HyGrid, which demonstrated direct separation from NG grids.[9] HyGrid combined membrane-based separation, electrochemical separation, and other technologies to achieve better value separation, and several of the published outcomes of this work are discussed in section 4.

This report is written in the understanding that previous work on relevant separation techniques for the National Grid identified several prevalent technologies for hydrogen deblending, including[8]:

- Pressure Swing Absorption (PSA)
- Polymeric Membranes
    - Polymeric hollow fibres
        - Polysulfone
        - Aromatic polyamides
        - Cellulose acetate
        - Polydimethylsiloxane (PDMS)
    - Non-polymeric materials
        - Molecular sieving carbon
        - Zeolites
        - Ceramics
- Palladium Membranes (have not been implemented in industrial applications)
    - Ceramics (tubular ceramic support, ceramic diffusion barrier layers combined with metal sinter support materials)
    - Preparation Techniques
        - Electroless plating (ELP)
        - Metal organic chemical vapor deposition (MOCVD)
        - Physical vapor deposition (PVD)
        - Plasma sputtering
        - Suspension plasma spraying (SPS)
- Cryogenic Separation
- Electrochemical Hydrogen Separation (EHS)
    - Proton Exchange Membranes (PEM)
        - Nafion™
        - Polybenzimidazole (PBI) using phosphoric acid

PSA and Cryogenic Separation will not be discussed further in this report due to their established nature. The same is true of multiple polymeric, palladium and EHS membranes, however several of the technologies that have been identified in this review fall under those sub-categories previously reported. Thus, it is an aim in this review to highlight the new and novel aspects of these fields of research, especially where they are expected to show rapid growth or improve in applicability to separation of H_2 from NG. This review has searched a combination of papers, patents and companies as detailed in section 4 and in each case the technology in question was evaluated using the criteria outlined in the following section.

3 EVALUATION CRITERIA

The following criteria were considered during the review:

- Technology Readiness Level (TRL)
- Novelty
- Performance
- Material availability
- Sustainability
- Health and the environment
- Cost
- Durability
- Stability

A breakdown of the acceptance criteria applied to each, for inclusion within this review is provided in Table 1. Most of these criteria are self-explanatory and will be discussed for each technology in sections 4 and 5. Primary measurement of membrane performance are often permeability and selectivity, however these values were not comparable between membranes in the timescale of this report partly due to the variety of gases used for separation. In the case of stability, this specifies chemical stability and although this will vary with technology it is noted that the expectation is every technology will be subject to the same impurities present in the NG stream in-line with current regulations.[10] Minor components in NG may include CO_2, H_2S, water, C3+ hydrocarbons, inert gases and can impact the membrane performance in several ways; competing with H_2 permeation, blocking free volume, plasticising the membrane or poisoning the materials.

Table 1: Overview of acceptance criteria for parameters assessed

Parameter	Acceptance Criteria
Technology Readiness Level (TRL)	On the TRL scale of 1 to 9, where 1 and 9 represent 'basic principles observed' and 'actual system proven in operational environment' respectively, TRL of 4 or below will be in focus
Novelty	Quantity of research being carried out with this technology.
Performance	No fixed acceptance criteria, but included within review
Material availability	Materials are readily available
Sustainability	No fixed acceptance criteria, but included within review
Health & environment	Technology does not pose a significant risk to health or the environment
Cost	No fixed acceptance criteria, but included within review
Durability	No fixed acceptance criteria, but included within review
Stability	No fixed acceptance criteria, but included within review

4 TECHNOLOGY REVIEW

In the following section the technologies identified in recent literature were given a brief description and a discussion of the evaluation criteria outlined in the previous sections. Where possible, the technologies distinguished in this review have been categorised by a collective name and sub-categorised by the individual technology.

A total of 50 papers were reviewed covering a range of difference H_2 separation technologies.

The primary motivation for many of the papers was to generate pure H_2 from a gas stream or separate different gases. In general, those that did investigate separation from methane (CH_4) or H_2NG offered minimal information on the primary application of interest for this report, the content of H_2 remaining in the NG stream.

4.1 PALLADIUM-BASED MEMBRANES

Palladium (Pd) membranes have been covered in previous reporting due to their wide usage in gas separation research.[8] As an expensive and rare metal, Pd is not an ideal economic candidate for separation membranes however variants on Pd membranes offer cost savings while maintaining efficacy. Pd membranes are non-porous, dense membranes and rely on the dissociation of H_2 molecules into atomic hydrogen for transport through a solution-diffusion (Sol-D) mechanism.[11] In contrast, porous membranes rely on a mix of Knudsen diffusion, surface diffusion, capillary condensation and molecular sieving for molecular transport and are dependent on pore size.

4.1.1 Palladium Alloy Membranes

Pd has been combined with other metals including silver (Ag), copper (Cu) and gold (Au).[8,12,13,14] These Pd alloys have been previously noted as offering lower sensitivity to sulphur poisoning, lower phase-transition temperatures, high hydrogen permeabilities and lower costs to pure palladium and subsequently research into Pd alloy membranes may be of particular interest for emerging technologies.

Pd-Ag membranes offer high H_2 selectivity and purity, but are subject to H_2 embrittlement and sulphur contamination.[12] Previous reporting has noted the research into thin Pd membranes supported on ceramic substrates and the potential fabrication issues.[8] Nordio *et al.* tested a range of Pd-Ag configurations; ceramic supported thin and normal Pd-Ag membranes (c-tPd and cPd), ceramic supported double-skin Pd-Ag membranes (c-PdDS) and metallic supported Pd-Ag membranes (m-Pd) and found reduced energy consumption with single c-tPd membrane modules but improved purity with two membrane modules in a low-pressure grid. m-Pd configurations further improved purity but increased energy consumption. This research also considered the implications of two membrane modules in series and the removal of humidity before separation and then reinjecting into NG, but not the removal of sulphur compounds before separation and then reinjecting into NG. Pd-Ag membranes have been tested for the separation of H_2 from NG at approximately 15% concentration with no significant effect from the NG components on the membrane.[13]

Pd-Cu membranes demonstrate lower costs and a degree of resistance to surface poisoning when compared to other Pd-based membranes.[14] Nayebossadri *et al.* have investigated additional alloying of Pd-Cu with transitional metals, highlighting small percentage additions of Zirconium (Zr) in Pd-Cu-Zr membranes exhibiting improved chemical stability and hydrogen permeation. Pd-Cu membranes have been tested at H_2 concentrations in NG of approximately 25% and showed almost full recovery of performance after the experiment.[13]

Pd-based membranes have been combined with other methods of separation to generate a higher purity final H_2 stream.[12] Existing Pd-based membranes are in use for H_2 production and carbon capture, utilisation and storage (CCUS) at TRLs as high as 5-6, however the purity requirements for production and CCUS differ significantly to that of gas network and the use of novel Pd-based membranes for H_2 separation from NG remains at low scales.[15,16,17] Nordio *et al.* have estimated a cost of between 3.56 and 9.80 €/kg_{H2} for various combinations of Pd-alloy membranes and additional purifying steps compared to estimates that the average at-the-pump price of onsite renewable hydrogen in Europe was 11 €/kg_{H2} in 2020.[12,18]

4.1.1.1 Platinum Membranes

Platinum (Pt) based membranes have been included in this report as a subset of Pd membranes and much like Pd membranes they have high hydrogen selectivity while remaining very sensitive to surface contamination and relatively expensive.[11] However, Pt is currently less than half the price of Pd and this may lead to preferential usage of Pt over Pd for some applications in the future[19] Despite this, in the timeline of this report significantly less research into relevant Pt based membranes was identified compared to Pd membranes, and often the primary focus of Pt based membrane research was into Pd membranes. Pd, Pt and other rare metals also play a role in Proton Exchange Membranes (PEMs) as electrocatalysts.[11,20]

4.2 POLYMER MEMBRANES

For H_2 separation, typically glass-like polymers with H_2 selectivity are used for membranes with predominant H_2 permeability.[21] Conventionally this has involved dense polymeric membranes including cellulose acetate and polysulfone membranes. For polymer membrane performance there is a limitation in the balance between permeability and selectivity known as Robeson's upper bound, however the value of this for H_2 permeability and H_2 /CH_4 selectivity will increase as advances in polymer membranes are made.[10] Such advancements include polymers of intrinsic microporosity (PIMs), thermally rearranged (TR) polymer membranes and mixed matrix membranes (MMMs).

Microporous organic polymers (MOPs) and organic molecular sieve membranes (OMSMs), defined as membranes composed of organic constituents with rigid micropores include PIMs, TRs, and Covalent organic frameworks (COFs), but also hydrogen organic frameworks

(HOFs), porous aromatic frameworks (PAFs), and porous organic cages (POCs) amongst others.[22,23] PIMs, TRs and COFs and briefly discussed due to their use in MMMs with inorganic counterparts.

4.2.1 Polymers of intrinsic microporosity

PIMs were first reported in 2004 by Budd *et al.* as PIM-1 with a rigid polymer chain structure that forms micropore networks and PIMs have since been shown to exhibit good gas permeability and selectivity.[24] As a glassy polymer PIMs vary in permeability and selectivity as they age, and significant research has focused on optimising this aspect. PIMs have been incorporated into MMMs for gas separation to provide a better balance of permeability and selectivity in age.[24,25] Variations on PIM-1 have shown a comparable stability, only degrading at high temperatures.[24] As with many glassy polymers, PIMs tend to offer a lower cost membrane solution due to the reduced surface area requirements from their high permeability, however limited cost estimations have been made on production and without comparable metrics to Pd based membranes.[25,26]

4.2.2 Thermally rearranged polymers

TR polymers are a subset of microporous polymers that exhibit notable gas permeability due to their rigid polymer structure formed during post-fabrication thermal treatments.[27] Optimising TR polymers for gas separation has included incorporating fluorinated monomers and combining 2D materials with TR polymers in MMMs.[27,28] Functionalised TR polymers offer improved performances based on selectivity and permeability in a variety of gases and lower material costs over homopolymers, and show comparable temperature stability to PIMs.[27]

4.2.3 Covalent Organic Frameworks

COFs are porous structures similar to metal organic frameworks (MOFs), however consisting of covalent organic linkages, exhibiting larger pores and a lamellar superstructure due to the weak interactions between layers.[29] The durability of COFs appears somewhat restricted by the loose stacking structures, but COFs have been implemented for H_2 storage. COFs have been optimised with conflicting pores and on ceramic supports to increase stability and enhance selectivity for H_2 in CH_4.

4.2.4 Polybenzimidazole membranes

Polybenzimidazole (PBI) membranes were previously reported for their use in hydrogen separation, notably doped by phosphoric acid (PA).[8,30]

Organic polymer membranes benefit from practical and economic manufacturing methods but suffer from poorly constrained selectivity and permeability.[31] Inorganic membranes benefit from their stability and controllable selectivity and permeability.[11] Combining these benefits with the low manufacturing costs of organic polymer membranes are MMMs made of composite materials with continuous polymeric matrices imbedded with inorganic particles.

PBI membranes incorporated with Pd nanoparticles have been tested to capitalise on the benefits of both materials, and the mixed-matrix membrane showed a marked improvement compared to solely PBI membranes. [31]

4.2.5 Nafion™

Nafion™ membranes were briefly mentioned in previous reporting but cover a range of membrane compositions, mainly perfluorinated sulfonic acid (PFSA).[8,20] Nafion™ membranes are designed to work as cation exchange membranes (CEMs), analogous to PEMs and will completely retain common non-polar gases with no permeation or differentiation.[32] Nafion™ membranes provide separation of hydrogen and oxygen over a broad range of pressure and temperature during water electrolysis and claim high durability and stability, however have been reported showing performance degradation.[33,34] Nafion™ membranes have been used in conjunction with a range of catalysts; variations of Pt, ruthenium (Ru), Pd, iridium (Ir), nickel (Ni) and cobalt (Co).[11] In the field of fuel cells Nafion™ membranes have been combined into MMMs with other polymer and two-dimensional (2D) membrane materials, and in one case polyacrylate carboxyl microspheres (PCMs) to improve proton conductivity.[35,36] Existing Nafion™ membranes, for example Nafion™ 117 is sold at $2600 per square metre from third party suppliers.[37]

4.2.6 UniSieve

UniSieve develop separation membranes for multiple applications, using a combination of molecular sieve and polymeric membranes.[38] Limited publicly available information was identified for UniSieve, however it has been included in this report due to the patent filed by the company for the processing of polyolefins noting the embedding of MOFs into polymeric membranes.[39]

4.2.7 H24US

H24US claim a "disruptive membrane technology" for H_2 separation applied in the form of Deblending Units (DBU).[40] The type of membrane technology currently used by H24US is not given on their website, however they make it clear it does not involve "precious metals or other expensive materials" and uses low differential pressures to separate H_2 suggesting it is an MMM. Additionally, H24US filed a patent in 2021 for a multi-layer membrane for H_2 purification from multi-component gases including CH_4 and CO_2, and it is described as using "a molecular pre-treatment, a transition metal, fluorine containing polymer, carbon fibers and carbon matrix sintered on a supportive screen."[41] H24US explicitly list natural gas pipelines as an application for their DBU technology along with the potential for practical H_2 storage using existing a solid metal hydride solution called Hydrostik Pro.[40,42]

4.3 INORGANIC AND 2D MATERIALS

Multiple inorganic 2D materials have been researched for potential application to H_2 separation.

4.3.1 Carbon Molecular Sieve Membranes

Carbon molecular sieve membranes (CMSMs) are a low cost alternative membrane with low temperature stability.[12] CMSM are an example of porous membranes and are formed of amorphous high-carbon materials with notable thermal resistance, chemical stability, and pressure stability, while a combination of adsorption and molecular sieving lead to high selectivity for H_2/CH_4.[11,12,43]

Composite alumina carbon molecular sieves membranes (Al-CMSM) have been successfully tested by Llosa Tanco *et al.* to separate up to 20% H_2 from CH_4.[44] The motivation for this research came from the requirement for H_2 to be separated at high purities and subsequently has limited details on the hydrogen remaining in the CH_4.

Al-CMSM have also been used in combination with Pd membranes to improve the H_2 purity with reduced operating temperatures.[12]

4.3.2 Graphene and Graphene Oxides

Graphene-based membranes are one of several 2D materials that are the focus of research into 2D H_2 separation membranes.[45] These membranes can be categorised into single-layer graphene, multi-layer graphene laminates and graphene-based composite membranes or MMMs. It is not possible for gas molecules to permeate a defect-free single-layer graphene, instead the nanopores serve as gas transport channels and single-layer graphene does not offer practical applications due to its scalability. Alternatively, multi-layer graphene offers a robust development opportunity for membrane materials such as nano-porous graphene (NPG) or the synthesis of graphene oxides (GO).[45,46]

GO are a noteworthy candidate for H_2 separation from graphene-based membranes, as they exhibit the high H_2 permeability and selectivity required of separation membranes, notably due mechanisms of interlayer pathways.[29] GO shares the monatomic thickness of graphene nanosheets, however also contains epoxy, hydroxyl, carboxyl and other O_2 containing functional groups that form the interlayer pathways. The poor mechanical strength of ultrathin GO membranes incites the use of ceramic supports as with other membranes discussed, however the interlayer pathways remain functional. Selectivity for H_2 in CH_4 has been investigated using crosslinked GO membranes with adjusted interlayer spacing. Further research into generating porosity into GO membranes offers additional gas transport mechanisms and increased H_2 permeability.

Graphene may also act as a filler in composite membranes.[45] MMMs make use of the graphene and GO interlayer pathways for selectivity and their mechanical properties to improve upon single component membranes. Graphene-based MMMs have led to the development of 3D structures with varying porosities, made in combination with other membrane and 2D materials. This includes GO MMMs made with PIMs to offer improved membrane lifespans and with CMSMs to improve CO_2 and N_2 separation.[47,48]

4.3.3 Metal carbides, nitrides and carbonitrides.

Transition metal carbides, nitrides and carbonitrides (MXene) are 2D materials that can be incorporated into metal and ceramic matrices to offer favourable properties.[49] MXene membranes have very similar structure to GO membranes, with hydroxyl, fluoro, and oxide groups creating interlayer pathways resulting in the high H_2 permeability and selectivity.[29] The use of high toxicity hydrogen fluoride (HF) in MXenes manufacture and their susceptibility to oxidation appear to be just two of numerous issues that must be overcome to implement them effectively.[50]

4.3.4 Metal organic frameworks

MOFs are crystalline compounds formed by coordinating metal ions with organic bridging ligands that can form nanosheets with a porous structure capable of molecular sieving.[29] Zinc (Zn) MOFs have been prepared on ceramic tubular supports and in combination with GO. The instability of MOFs to water poses a particular challenge for H_2 separation. Similarly, to Graphene-based membranes, MOFs have been combined with PIMs in MMMs.[51] A noteworthy subclass of MOFs are zeolitic imidazolate frameworks (ZIFs), that often exhibit superior stabilities due to the imidazolate links and they have been demonstrated as candidates for H_2 permeability.[52] MOFs predominantly remain at low TRL and laboratory scale work has been critically assessed.[53] MOFs may successfully move to larger scales through individual companies.

4.3.4.1 Immaterial

Immaterial are a Cambridge based company that develop porous materials, notably MOFs through high throughput computational design and manufacture.[54] Immaterial's unique monolithic MOFs claim to provide more practical manufacture and application opportunities, with access to the University of Cambridge database of 100,000 known MOF structures, maintained by the Cambridge Crystallographic Data Centre. Immaterial perform Grand Canonical Monte Carlo (or GCMC) simulations to identify structures with the greatest selectivity due to unbounded variations in functional sites and porosity. Immaterial's MOFs may provide 'drop-in' replacements, or the use of computational fluid dynamics (CFD) and a recently developed pilot facility to explore protypes with the aim of achieving a first commercial facility in 2024.

4.3.5 Zeolite Nanosheets

2D zeolite nanosheets exhibit the same large porous structure of COFs and have been investigated for H_2 separation from other gases.[29] Constructing high performing zeolite nanosheets pose a larger challenge then MOFs and COFs and have subsequently been incorporated into polymers.

4.3.6 Further materials

Several membrane materials were identified in this report but not in detail. This includes 2D transitional metal dichalcogenides (TMD) and 2D layered double hydroxides (LDH).[45,45]

4.4 ELECTROCHEMICAL HYDROGEN SEPARATION

Electrochemical H_2 separation (EHS) aims to overcome some of the issues raised by membrane technologies, including their dependence on pressure and subject to H_2 embrittlement.[11] A significant number of the membrane technologies detailed have been implemented in EHS systems, typically as CEMs/PEMs.

4.4.1 Proton exchange membranes

PEMs are used in EHS to allow the permeation of protons between the cathodic and anodic sides of electrochemical cells.[11] The role of the anode and cathode is to oxidise H_2 into protons and electrons and then reduce them back into H_2 respectively. Due to the requirements of a PEM to exhibit the desired permeability, selectivity, and integrity there is a distinct overlap in the potential application of the membranes previously discussed, however commonly Nafion™ and PBI-based PEMs have been used in the presence of Pt-based catalysts to carry out EHS.[11,30] Inorganic membranes are starting to be tested for EHS but these are at the early stages of development.[55] Evidence is lacking into the durability and stability of PEMs used in EHS, however the applications of these membrane types in research into fuel cells and electrolysers may help provide the missing evidence for these technologies.

4.4.2 Electrochemical Hydrogen Pumping

Electrochemical H_2 pumping (EHP) or concentrators were developed in tandem with initial PEM technologies, and typically used previously discussed Nafion™ membranes.[56] High-temperature EHP has been investigated for H_2 separation using PBI-based membranes, and this has included composite membranes previously discussed.[11,56] EHP can simultaneously separate and compress H_2, and has been demonstrated to produce 99.3% purity H_2 from syngas.[57]

4.4.3 Electrochemical Hydrogen Compression

An electrochemical hydrogen compressor (EHC) has been used in combination with other separation methods to deliver a purer final H_2 stream.[12] EHC is a primary focus of the HyET group of companies that enable the development and scaling of technologies.[58]

4.4.4 Temperature swing adsorption

Temperature swing adsorption (TSA) has been used in combination with EHS and other separation methods to deliver a purer final H_2 stream, particularly to remove water.[12] Compared to PSA, TSA can avoid the need to pressurise both H_2 and NG streams and the temperature driven technique presents a dramatically reduced number of cycles and lower energy costs from heat sources. Combinations of PSA and TSA are also possible.[59] TSA has achieved high TRLs for CCUS applications including large pilot tests for commercial plants but will fall to lower TRL for H_2 separation from NG.[60]

4.4.4.1 Svante

Svante offers an advanced TSA for application to CCUS called intensified rapid cycle TSA, that operates magnitudes quicker than conventional TSA.[61] The applicability of this to H_2 separation from NG is not evident.

4.5 FURTHER COMPANIES

There were several companies identified in this review that did not have publicly available information to identify the class of technology, respond to information requests or show a direct applicability to H_2 separation. Two of these have not been included in the previous sub-categories but merit note due to their potential in this area in the future.

4.5.1 FORBLUE™

AGC's FORBLUE membranes cover a range of applications from humidification to CEM and are already used for electrolytic manufacturing of H_2.[62]

4.5.2 ZIRFON

AGFA's ZIRFON membranes were developed for alkaline electrolysis and claim high durability and condition flexibility but are currently not applicable as gas separation membranes.[63]

5 SUMMARY

The information gathered in the previous section regarding the various technologies under development for H_2 separation has been summarised in Table 2 in line with the evaluation criteria defined in section 3. In section 4, at least 28 distinct technologies were identified including 7 existing companies. Excluding the companies, 14 of these are summarised in Table 2 due to the sufficient resources available, and of the remaining technologies several were not discussed in detail including HOFs, PAFs and POCs, and TMD and LDH. These were mentioned in two references respectively and have not been included in the summary due to the limited information obtained. Where a particular criterion poses a notable hinderance to development these have been highlighted in red. For a significant number of technologies and evaluation criteria, limited or no references were identified to summarise the technology. This indicates a requirement for further research and comparable measurands, particularly to cover material availability, sustainability, health, and environmental criteria. In these cases where no quantitative or qualitative information was identified for a particular parameter this criterion was not commented on.

Table 2: Summary of technologies through evaluation criteria.

Technology	Acceptance Criteria								
	TRL*	Novelty**	Performance ***	Material availability	Sustainability	Health & environment	Cost	Durability	Stability
Palladium-based membranes									
Palladium alloy membranes	1-5	104 results	99.92-99.99% H_2 purity	Rare Metals	Rare Metals	-	High cost of Pd, but low process cost possible (3.56-9.80 €/kg_{H2})	Subject to H_2 embrittlement	Surface poisoning but full recovery shown with NG
Polymer membranes									
PIMs	1-3	31 results	-	-	-	-	Benefits from low-cost polymer components. Estimated at $45 per m^2	Thermal decomposition occurs at high temperature	Plasticisation effects require further evaluation
TR polymers	1-3	30 results	-	-	-	-	Benefits from low-cost polymer components	Thermal decomposition occurs at high temperature	Limited evidence identified
COFs	1-3	54 results	-	-	-	-	-	Basic lamellar structure subject to exfoliation	Long-term stability achieved by staggered stacking
PBI membranes	1-5	49 results	-	-	-	Not harmful, but not biodegradable	Benefits from low-cost polymer components	Thermal decomposition occurs at high temperature	Unstable at mid-temperatures and high flow rates with specific functionality
Nafion™	1-5	62 results	>99.9% H_2 purity	-	-	Not harmful, but not biodegradable	$2600 per m^2	High mechanical integrity	High chemical stability
Inorganic and 2D materials									
Graphene and GOs	1-3	145 results	-	Inexpensive graphite raw material	-	Long-term stability requires improvement	Production at scale not realised	Requires further development	Long-term stability requires improvement
MXenes	1-3	64 results	-	-	-	Use of high toxicity HF in manufacture.	-	-	Susceptible to oxidation
MOFs	1-5	308 results	-	-	-	-	Higher cost than other 2D materials	-	-
Zeolite Nanosheets	1-4	292 results	-	-	-	-	Lower cost than other 2D materials	-	-
Electrochemical hydrogen separation									
PEMs	1-5	70 results	-	-	-	-	-	-	Catalyst poisoning. Dependent on membranes
EHP	1-5	5 results	99.3% H_2 purity	-	-	-	-	-	Dependent on membranes
EHC	1-5	4 results	10 kg/day	-	-	-	-	-	-
TSA	1-5	4 results	-	-	-	-	Process equipment is significant proportion of costs	Effect of temperature should be considered	-

*Estimated range based on the current levels of development for example laboratory research or pilot scale.
**Novelty has been taken from available publications when the combination of key words of each technology (for example 'PIM') and 'hydrogen separation' are included in a search of abstracts on the Web of Science™ data base.[64]
*** Several parameters including permeability, selectivity and kinetic diameter are more appropriate measures of efficiency at laboratory scale but remain beyond the scope of this report.
- No conclusive evidence identified.

6 CONCLUSION

This report has provided a literature and technology review of novel and emerging techniques for gas separation, with particular attention to technologies that could disrupt the existing gas separation marketplace relevant to H_2 separation from NG. In the summary shown in section 5, 14 distinct technologies were highlighted, and a further 14 were identified in section 4 including 7 from existing companies. The review of new, innovative, or potentially disruptive technology demonstrates a wide field of research into gas separation, and specifically H_2. Most technologies identified were applied to the broader application of separating different gas pairs for example H_2/CO_2, but several did investigate H_2 separation from CH_4 or NG. As each technology is developed further it is probable that their degree of applicability to separation of H_2 from NG will be established.

Gas separation research is profuse with membrane-based technologies, typically new materials, designs and processes that require scaling. Predominantly these are under development at laboratory, start-up, or small business scale. For each technology the evaluation criteria outlined in section 3 was considered. No single, standout technology with a high propensity for rapid growth or scaling for transmission use has been identified based on the applied criteria.

Overall, there was a limited amount of information apparent to satisfy the criteria and in several cases no evidence was identified. The most promising opportunities identified in this review were either technologies at a very early stage of development offering the broadest potential applications or more mature technologies under-development at private companies. It is evident that more experimental data is required to be gathered on each type of technology before the application to H_2 separation from NG can be fully assessed, and this reflects that the topic of gas separation, especially H_2 from NG is a key target for many companies and it is expected that there will be new developments hereafter.

7 FUTURE WORK

As a follow on from this project, a proposal is being drafted for National Grid to identify suitable technologies for development from TRL 1 to 4 and fund this development.

7.1 TECHNOLOGY DEVELOPMENT AND VALIDATION

The further development of certain technologies would provide the potential for scale up, for example:

- H24US have limited publicly available information, however if the DBU technology are truly at a commercial stage they would be a prime candidate for a scale validation.[40,41]
- Although Immaterial are not directly targeting H_2 separation at this stage, they have reached the scale up stage for their monolithic MOFs so could be able to deliver a testable technology.[54]

A traceable validation of technologies would be required to demonstrate their effectiveness for the proposed application. This would be achieved via a study to look at the following.

- An **efficiency** study would involve using synthetic H_2NG to feed the separation technology at various compositions and pressures and measure the output compositions and impurity content to ensure end user requirements can be met.
- A **durability** study would involve testing the technology over the full range of expected environmental and gas feed conditions (e.g., temperature, pressure, humidity, feed gas impurities).
- A **stability** study would involve testing of the technology over a defined period under expected operating conditions to assess its long-term performance.
- In addition to these studies, a better understanding of **cost**, cost drivers and cost reduction would be significant in determining the feasibility of each technology.

8 REFERENCES

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