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# Initial testing of an inside-out type palladium membrane reactor for recovery of hydrogen from hydrocarbons or water

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The ITER Tokamak Exhaust Processing (TEP) system relies on palladium membrane reactors (PMRs) for tritium recovery. The PMR consists of a palladium/silver membrane permeator filled with a catalyst, that can be used to recover hydrogen species (most importantly tritium) from methane and water impurities present in fusion reactor exhaust emissions. Two superimposed phenomena simultaneously occur inside the PMR: a chemical reaction onto the catalyst liberating hydrogen contained in molecules and permeation of this molecular hydrogen through the membrane. Applying a vacuum on the permeate side allows recovery of pure hydrogen from the molecules (including tritium). The inside-out configuration of the PMR improves vacuum conditions at the permeate side, thus enhancing decontamination factor and tritium recovery performances.

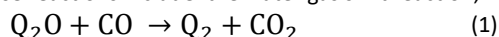
This paper presents the design, construction and initial commissioning of a newly erected test rig at UKAEA to perform experiments with protium on an inside-out PMR prototype in support of the ITER TEP. The efficiency of the PMR is assessed by both measuring flowrate through the permeate gas stream and analysing the composition of the retentate gas stream using gas chromatography. Permeation rate is assessed for protium for flowrates between 10 and 100 ml/min. The methane/water ratio, crucial for methane steam reforming tests, is assessed to optimise decontamination of hydrogen and minimise coking of the PMR. The hydrogen recovery fraction and decontamination factor are assessed for methane and water from flow rates of 10 to 60 ml/min.

**Keywords:** ITER, fuel cycle, fuel processing, palladium membrane reactor, PMR

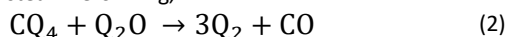
## 1 Introduction

A process to recover tritium from hydrocarbons, water, and other tritiated fusion exhaust is required for the sustainable fuelling of a fusion reactor. The ITER fuel cycle deals with, amongst other crucial functions, the exhaust gases through the Tokamak Exhaust Process (TEP) system [1]. A palladium membrane reactor (PMR) recovers tritium from fusion exhaust [2] and has been highlighted as a critical component of the ITER TEP system for dealing with air-like and water-like hydrogen processing [3]. Testing has been completed for outside-in type PMRs [4] [5] designed for high throughput-low hydrogen recovery, however little research has been conducted on inside-out type PMRs designed for low throughput-high hydrogen recovery. An outside in type PMR has a catalyst housed in a vessel, with permeation into an isolated palladium/silver tube; an inside-out type PMR has a catalyst housed in a palladium/silver (Pd/Ag) tube, with permeation into an isolated vessel.

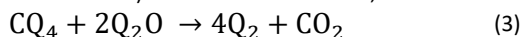
The PMR is a combined permeator and catalytic reactor used to promote reactions from hydrocarbon and water to molecular hydrogen. These reactions include: the water gas shift reaction,



And methane steam reforming,



These reactions occur simultaneously, complementing the process to form (where successful) the combined reaction,



Where Q represents the hydrogen isotopes Protium (H), Deuterium (D), and Tritium (T).

Constant removal of hydrogen through the Pd/Ag membrane overcomes equilibrium limitations and improves yield. Two product streams leave the PMR: a permeate stream consisting of ultrapure hydrogen; and a retentate stream consisting CO, CO<sub>2</sub>, unreacted feed gases, and any un-permeated hydrogen. This experiment is conducted cold (non-tritiated), using protium only.

## 2 Experimental Setup

### 2.1 PMR

The PMR, designed and supplied by GE Healthcare, featured a 152.4 mm ID by 755 mm stainless steel (316L) vacuum vessel (Figure 1, label 5) with a single outlet of 1" (2) through which a vacuum could be drawn. The Pd/Ag membrane (75%Pd/25%Ag) (6) has an OD of

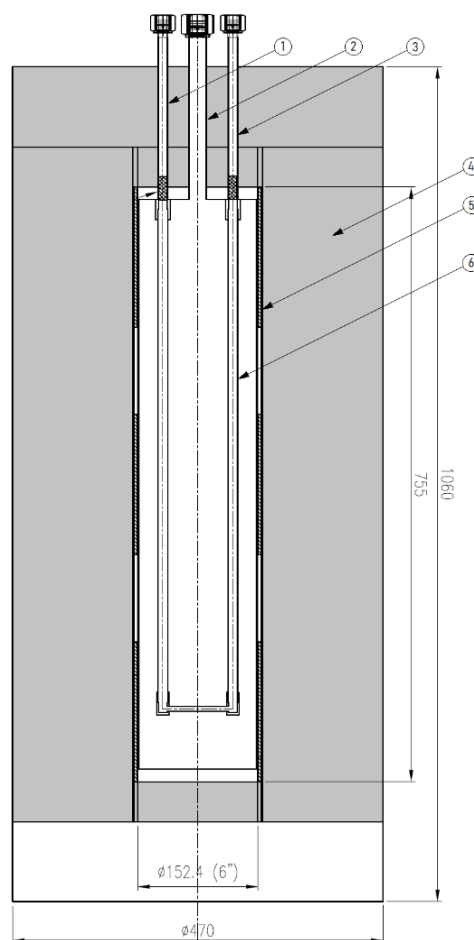


Figure 1: Palladium Membrane Reactor design.

0.5", is inlet through (1) and outlet through (3), with a thickness of 0.345 mm. The inside of the Pd/Ag tube (6) was packed with catalyst (2% Pt on Alumina in 0.125" cylinder form). A total weight of 180.26 g of catalyst was added.

Three eltherm® ELK-MI/AY-T 14.5m heating elements provide

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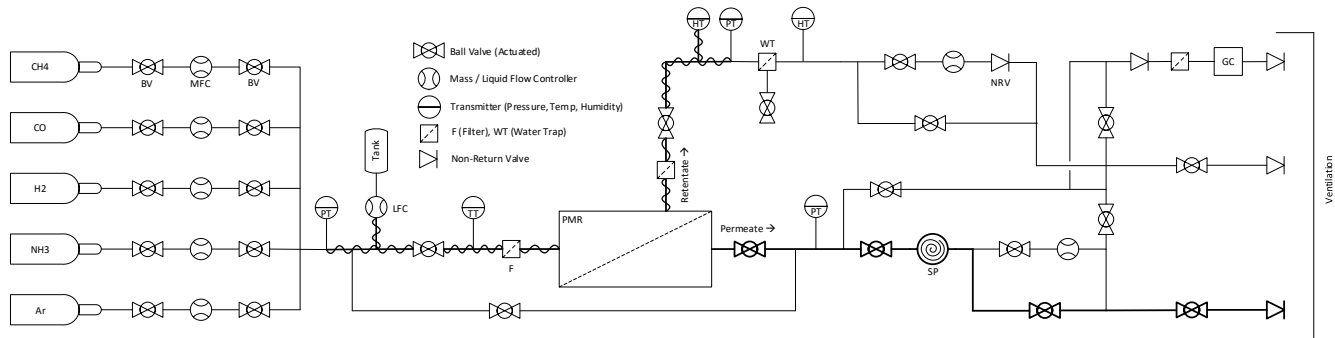


Figure 2: Simplified Process & Instrumentation Diagram (P&ID) of the PMR experimental setup.

2.28 kW heating each for a total maximum of 6.84 kW heating input. Six thermowells are spread across three heights, one set of three for measuring temperature, the other for overtemperature safety. To maintain the required process temperatures, the PMR is insulated with 150 mm of formed MICROTHERM® insulation resulting in a surface temperature below 40°C when the PMR vessel temperature is at its maximum (550°C).

## 2.2 Inlet System

Five high purity gas feeds supplied simulated fusion exhaust to the PMR system, individually controlled by Brooks GF040 mass flow controllers (MFCs) calibrated from 0 to 100 ml/min (converted from mass to volumetric flow rate equivalent at STP, applicable throughout), with stated  $\pm 1\%$  accuracy of the full scale. The gases included Methane (99.995%), Hydrogen (99.9995%), Carbon Monoxide (99.97%), 10% Ammonia in Argon (99.9995%), and Argon (99.9995%). Water was introduced in liquid form through a Bronkhorst L01V12 liquid mass flow controller and vaporised along 1.5m of heat traced  $\frac{1}{4}$ " stainless steel 316L tubing with the temperature stabilised between 100 and 120°C to ensure no liquid water was fed to the PMR, shown to the left of the PMR in Figure 2.  $\frac{1}{4}$ " stainless steel 316L tubing was utilised for the inlet system.

## 2.3 Retentate System

To ensure water was removed from the PMR, heat tracing extended from the retentate outlet of the PMR to a water trap, where it could be removed (if present) before potentially damaging the gas chromatograph (shown in the top right of Figure 2). Vaisala HMP7 humidity sensors are positioned before and after the water trap, first to indicate post-PMR water content (i.e. unreacted water) and second to ensure removal of water to levels that will not damage the gas chromatograph and not lead to build up of liquid water in pipes or the vacuum pump (when evacuating the system). A Brooks GF040 MFC was positioned on the retentate line to indicate retentate flow rate.  $\frac{1}{4}$ " stainless steel 316L tubing was utilised for the retentate system.

## 2.4 Permeate System

A vacuum was drawn on the permeate (shell) side of the PMR via an Edwards nXDS20i scroll pump, with 1" stainless steel 316L tubing to promote conductance. A turbo pump was considered, however due to the potentially high throughput of permeate gas, it was omitted. A Brooks GF040 MFC was positioned on the permeate line to indicate permeate flow rate. The permeate MFC showed a base flow rate prior to the introduction of system gases of  $0.563 \pm 0.047$  ml/min averaged over 30 minutes which was then deducted from the recorded permeate flow rate.

## 2.5 Gas Analysis

Analysis of the retentate gas is the highest accuracy measurement of PMR efficacy available on this experiment (detection limits below 0.05% stream composition for Agilent 490 Micro GC, available for multiple gas species in a single sample, while mass flow controllers typically do not differentiate gas species and (for Brooks GC040) have a stated standard deviation of 0.2%). High levels of carbon dioxide indicate successful conversion of methane and water through the water gas shift reaction and methane steam

reforming. Presence of carbon monoxide indicates a partial reaction, potentially due to high flow rate, or due to lower temperatures promoting the water gas shift but not methane steam reforming. Presence of hydrogen indicates failure to permeate, either due to high flow rate or coking of the membrane (but not the catalyst). Presence of methane indicates reaction failure, or potentially membrane coking leading to re-combination carbon and hydrogen after the initial molecular decomposition. As the gas chromatograph does not detect (and is damaged by) water, methane presence also infers water in the retentate stream; any methane should react with water, therefore its presence implies water also did not react.

Although isolated from each other during normal operation, the permeate and retentate streams could be routed to an Agilent 490 Micro Gas Chromatograph (GC) for gas analysis. The entire retentate flow stream was routed through the GC filter/bypass which allowed the GC to sample a highly representative retentate stream at regular intervals. An adjustable non-return valve was set to approximately 1.25 bar(a) and placed after the GC to regulate the retentate and inlet pressure to process relevant levels and maintain a constant and repeatable pressure for the GC. The GC's baseline pressure was set to 200 kPa and the carrier gas utilised was Argon (N5.5) to better identify hydrogen.

The GC was fitted with two columns: a Molsieve 5A column designed to separate and detect hydrogen, carbon monoxide, methane; and a PoraPlot U column designed to separate and detect hydro- and halocarbons, and carbon dioxide. For ammonia detection, one column can be replaced with a CP-Volamine column used for separating amines. Calibration of the GC was conducted using Agilent Universal Calibration Gas (5184-351) as well as interval concentrations of pure gases (Hydrogen, Methane, and Carbon Monoxide).

# 3 Methods

## 3.1 Pd/Ag Membrane preparation

As received, the membrane may not be permeable to hydrogen even at elevated temperatures. Activation and conditioning of the membrane are steps to achieve optimal performance of the PMR unit [6] [5]. Conditioning of the membrane is achieved in two steps: 1) activation of the membrane using air; and 2) conditioning of the membrane using hydrogen. Previous studies have shown that exposure to air (50% air / 50% argon in one study [4] and 10% air mixture in another [5]) increases permeation rate. Further, it both reduces the probability of a decrease in permeation over time and the rate of decrease. Hydrogen conditioning also aids permeation during non-hydrogen feed experiments [6] [4].

## 3.2 Permeation of the membrane

Quantification of the ability for hydrogen to permeate the Pd/Ag membrane is shown by feeding pure hydrogen to the PMR and measuring the permeate flow rate. The permeation coefficient, the measure of membrane permeability, is calculated using the following equation [6]:

$$P(H_2) = \Pi \cdot \frac{A}{t} \cdot (p_f^{0.5} - p_p^{0.5}) \quad (4)$$

Table 1: Permeation coefficient variables.

	Variable	Value	Unit
$P(H_2)$	Permeation flow rate ( $H_2$ )	measured	$\text{mol}\cdot\text{s}^{-1}$
$A$	Permeation surface area	0.0602	$\text{m}^2$
$t$	Membrane thickness	0.000345	$\text{m}$
$p_f$	Pressure ( $H_2$ feed)	measured	$\text{Pa}$
$p_p$	Pressure ( $H_2$ permeate)	measured	$\text{Pa}$
$\Pi$	Permeability	calculated	$\text{mol}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-0.5}$

The theoretical permeability has been calculated for  $H_2$  as  $\Pi_T = 3.85E-8 \exp(-5730/RT)$ , where  $R$  is the gas constant ( $8.31 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $T$  is the measured temperature of the reactor (K).

Permeation measurement was conducted by evacuating the system to a pressure less than  $5E-2$  mbar(a) with the PMR temperature stabilised at  $400^\circ\text{C}$ . Hydrogen was introduced through the hydrogen inlet MFC between 4.5 and 92 ml/min, where it permeated the palladium membrane tube and was exhausted from the system. Permeation measurement was conducted pre- and post-activation of the Pd/Ag membrane.

### 3.3 Activation of the membrane

The system was evacuated to a pressure less than  $5E-2$  mbar(a) through to the Argon inlet MFC and the temperature of the PMR stabilised at  $400^\circ\text{C}$ . Air was introduced through the Argon inlet MFC until the pressure in the Pd/Ag tube reached approximately 100 mbar(a), whereupon the air inlet was stopped and the pressure held for 30 minutes. The system was evacuated of gas afterwards.

### 3.4 Conditioning of the membrane

The system was evacuated to a pressure less than  $5E-2$  mbar(a) through to the Hydrogen inlet MFC and the temperature of the PMR stabilised at  $410^\circ\text{C}$ . Hydrogen was introduced through the hydrogen inlet MFC until the pressure in the Pd/Ag tube reached approximately 100 mbar(a), whereupon the hydrogen inlet was stopped and the pressure held for 45 minutes. The system was evacuated of gas afterwards.

### 3.5 Hydrogen Recovery Fraction and Decontamination Factor

The hydrogen recovery fraction (HRF), a measure of the relative total of hydrogen recovered from the feed, can be calculated using two different methods. Firstly, based on feed and retentate measurements:

$$HRF = 100 \left( 1 - \frac{F_{ret}(x_{H_2} + 2x_{CH_4} + x_{H_2O})}{F_{H_2O}} \right) \quad (5)$$

And secondly by using feed and permeate measurements:

$$HRF = 100 \left( 1 - \frac{F_{H_2O} + F_{perm}}{F_{H_2O}} \right) \quad (6)$$

The accuracy of the GC far surpasses that of the permeate MFC, therefore Equation (5) was used to determine the hydrogen recovery fraction throughout this experiment. As water is removed before entering the GC due to damage possibilities, the retentate flow rate of water,  $F_{ret}(x_{H_2O})$ , was calculated from the presence of methane.

The decontamination factor is a ratio of the total hydrogen in the feed against the total hydrogen in the retentate. It is calculated for Methane Steam Reforming using Equation (7) [4].

$$DF = \frac{2F_{CH_4} + F_{H_2O}}{F_{ret}(x_{H_2} + 2x_{CH_4} + x_{H_2O})} \quad (7)$$

### 3.6 Carrier gas effects

To aid in the speed of the experiment, a carrier gas can be used to increase the flow rate of the experimental gases. The effect of the carrier gas is assessed by varying the flowrate of the carrier gas without altering the experimental gas volume. Whilst in steady state methane operation (shown in Section 3.7) the carrier gas feed flow rate is altered. With a methane feed of 10.563 ml/min and steam at 19.437 ml/min (0.937 g/h), the argon inlet flow rate is varied.

### 3.7 Methane Operation

Firstly, the system is initialised into a state ready for the

introduction of gas. It is evacuated to a pressure less than  $5E-2$  mbar(a) and the temperature of the PMR raised, at a rate of  $5^\circ\text{C}$  per minute to protect against thermally induced mechanical stresses, to between  $450$  and  $550^\circ\text{C}$ . Below this temperature, methane steam reforming may not occur, and above this temperature, there is a risk of melting or damaging the Pd/Ag tube. The temperature of the PMR inlet and outlet heat tracing is raised to between  $100$  and  $120^\circ\text{C}$  to ensure no liquid water was fed to the PMR, which can cause corrosion or damage via a pressure increase onset by rapid water vaporisation.

The system control software is initiated, logging pressures, temperatures, valve positions, actual MFC & LFC flow rates, pump demand, and humidity at one second intervals. The retentate and permeate streams are isolated, with the retentate stream routed through the GC and then exhausted, and the permeate stream routed (after the permeate MFC) straight to the exhaust ventilation. Argon (N5.5) is introduced at 100 ml/min. Once the system equilibrates, the GC can be initiated, with samples taken in 4-minute intervals (to balance residence time for identification of carbon dioxide). Water is then introduced up to 2 g/h (41.481 ml/min using 18 g/mol conversion). Introducing water first reduces the chances of coking caused by methane. Shortly after water introduction and stabilisation (between 10 and 30 seconds), methane is introduced at a ratio of 1:1.84 methane to water. Although the range of ratios is considered broad (good results obtained in previous study consider 1.75-1.84 [5]), 1:1.84 balances the risk of coking with a lower ratio to detrimental hydrogen recovery fractions with a higher ratio. The pure Argon feed is reduced to complement the methane/water mix, balancing for a total flow rate of 100 ml/min. Methane/water experiments are run as follows:

Table 2: Methane/water experimental schedule.

CH <sub>4</sub> ml/min	H <sub>2</sub> O ml/min	Total ml/min	Argon ml/min	Total ml/min
3.521	6.479	10	90	100
7.042	12.958	20	80	100
10.563	19.437	30	70	100
14.085	25.915	40	60	100
21.127	38.873	60	40	100

Temperature is varied at  $450$ ,  $500$ , and  $550^\circ\text{C}$ . The length of an experimental run is a minimum of 2 hours, with consideration given to extending this whether equilibrium is attained. Selected runs are tested for an extended period of between 10 and 12 hours.

## 4 Results and Discussion

Characterisation and testing of the experimental setup and process strategy included assessing the membrane permeation efficiency and quantifying the effects of carrier gas ratios, before performing initial experimental runs both at standard length (approximately 2 hours, or more than seven times process gas replacement) and extended length (more than 10 hours).

### 4.1 Permeation of the membrane

Characterisation of the Pd/Ag membrane permeation rate is presented in Figure 4.

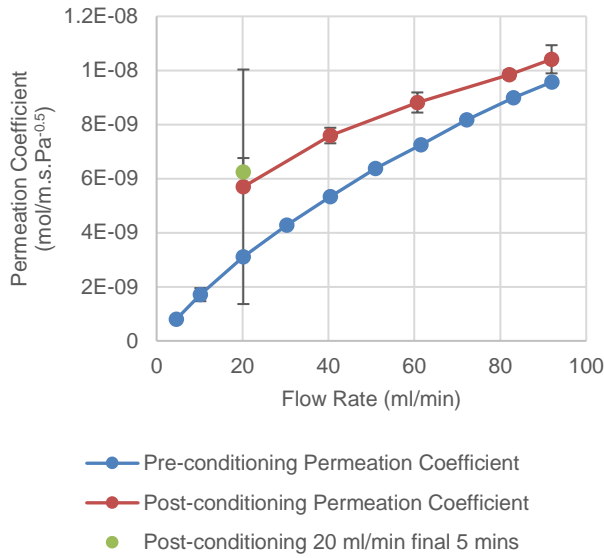


Figure 3: Permeation coefficient against hydrogen inlet flow rate pre- and post-conditioning of the PMR.

The large error for the post-conditioning 20 ml/min data point comes from the increase in measured permeate pressure as the system was initially filled with hydrogen. The data point was represented a second time for the final 5 minutes of the 20 ml/min experiment, marked as the green data point, which provided a much-reduced standard deviation.

#### 4.2 Initial tests

##### 4.2.1 Argon carrier gas effects

The effect Argon carrier gas has on the permeation of hydrogen is characterised.

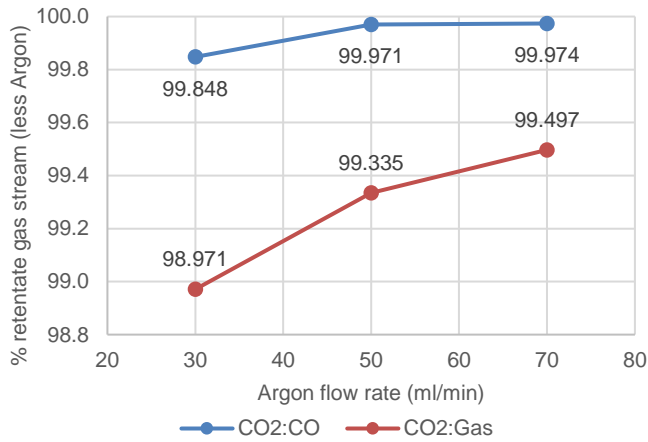


Figure 4: GC data showing percentage of CO<sub>2</sub> in the retentate gas stream (less argon (i.e. removing argon from the account)) as a ratio of CO and for all gases, for varying Argon carrier gas flow rates.

Data is averaged over an hour's operation from when steady state is achieved. Standard deviation varied from  $\pm 0.344$  % for 70 ml/min Argon feed to  $\pm 1.883$  % for 30 ml/min argon feed. Methane and water inlet flow rates were kept constant and measured at  $10.549 \pm 0.0096$  ml/min and  $19.023 \pm 0.0340$  ml/min respectively for the duration of the argon carrier gas effects experiment, sustaining a CH<sub>4</sub>:H<sub>2</sub>O ratio slightly below desired at  $1.803 \pm 0.0036$ . The temperature was maintained at  $520 \pm 3.3$  °C. Inlet and retentate pressure dropped as the argon inlet flow rate was reduced while the permeate pressure remained constant.

The higher fraction of "other gases" shown in Figure 4 for lower argon flow rates represents a disproportional increase in CH<sub>4</sub> and CO, although H<sub>2</sub> remained the dominant gas after CO<sub>2</sub> for all experiments. This potentially indicates coking of the membrane – both from the increased presence of methane and of hydrogen, or the increased hydrogen could be due to the reduced inlet pressure

(Table 4), resulting in a smaller differential pressure across the membrane. It should also be noted that the carrier gas flow rate was lowered over the experiment (meaning the 70 ml/min argon flow was the first permeation experiment conducted, and 30 ml/min argon flow the last); it may be that the reduction in hydrogen recovery was due to a small, cumulative coking effect. The experiment will be reconducted in a different order to explore this possibility.

The CO<sub>2</sub>:Gas ratio (the ratio of CO<sub>2</sub> to all other retentate gases) relates closely to the hydrogen recovery fraction. With the variability of the decontamination factor, this is harder to track:

Table 3: Variability in CO<sub>2</sub>:Gas ratio, hydrogen recovery fraction, and decontamination factor for varying Argon carrier gas flow rates.

Argon inlet (ml/min)	CO <sub>2</sub> :Gas Ratio	Hydrogen Recovery Fraction	Decontamination Factor
30	98.971 $\pm$ 1.883	98.940 $\pm$ 0.479	140.9 $\pm$ 89.4
50	99.335 $\pm$ 1.054	99.308 $\pm$ 0.550	206.6 $\pm$ 76.3
70	99.497 $\pm$ 0.343	99.454 $\pm$ 0.107	209.8 $\pm$ 42.9

When hydrogen removal rises above 98% (equating to a decontamination factor of roughly 50), small experimental errors can lead to significant changes in decontamination factor [4].

Table 4: Change in average pressure with change in argon inlet flow rates.

Argon inlet (ml/min)	Inlet pressure (bar(a))	Retentate pressure (bar(a))	Permeate pressure (mbar(a))
30	1.211 $\pm$ 0.0115	1.203 $\pm$ 0.0113	0.671 $\pm$ 0.0552
50	1.295 $\pm$ 0.0140	1.286 $\pm$ 0.0138	0.628 $\pm$ 0.0198
70	1.387 $\pm$ 0.0076	1.378 $\pm$ 0.0076	0.625 $\pm$ 0.0148

The contribution of retentate pressure must be further assessed, however the use of argon carrier gas to increase flow rate and system response time does not significantly affect the experiment, with the hydrogen recovery fraction *increasing* with higher argon carrier gas flow rates (though the cause of this needs exploring).

##### 4.2.2 PMR sensitivity

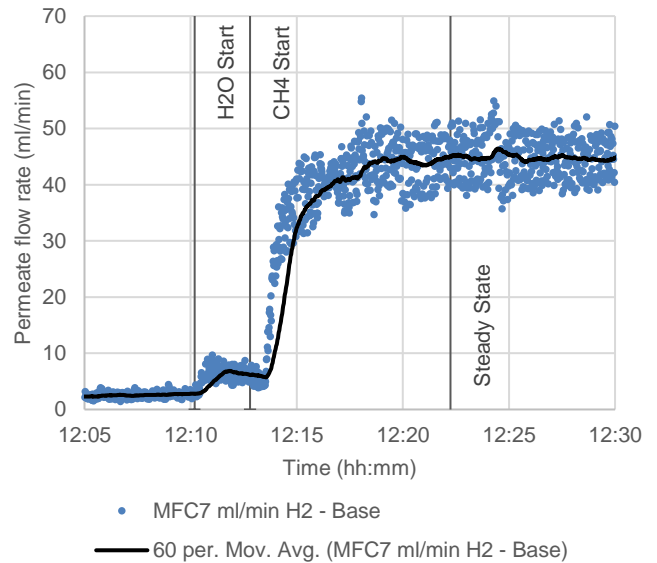


Figure 5: PMR system response time upon inlet of water and methane during the first Argon carrier gas experiment, setup as described in Section 4.2.1 (70 ml/min Argon flow rate).

For the argon carrier gas experiments (starting with 70 ml/min Argon) the response time is shown in Figure 5. Water was introduced at 12:10:11 (T = 00:00:00), at T + 00:00:18, a small rise in permeate flow rate was observed possibly due to reaction with residual coking



of the membrane and catalyst. Methane was introduced at T + 00:02:37 with reaction and permeation less than thirty seconds later, at T + 00:02:54. Steady state was reached less than ten minutes after methane introduction, at T + 00:12:04. Steady state was corroborated by steady state temperature, pressure, and humidity.

#### 4.2.3 Methane runs

Initial standard experimental runs were conducted for varying flow rates of methane and water to assess the efficacy of the experimental setup.

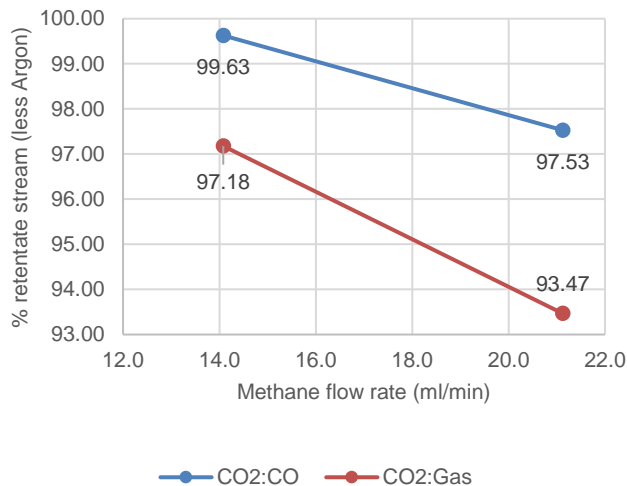


Figure 6: GC data showing percentage of CO<sub>2</sub> in the retentate gas stream (less Argon) as a ratio of CO and for all gases, for varying methane inlet flow rates.

Data is averaged, once steady state is achieved, over 2-3 hours continuous operation. Standard deviation varied from  $\pm 1.25$  % for 14.085 ml/min CH<sub>4</sub> feed to  $\pm 1.30$  % for 21.127 ml/min CH<sub>4</sub> feed. Inlet parameters were as per Table 5 (shown as returned values).

Table 5: Feed parameters for initial CH<sub>4</sub>/H<sub>2</sub>O experiments.

CH <sub>4</sub> ml/min	H <sub>2</sub> O ml/min	Argon ml/min	Inlet Pressure bar(a)	PMR temp (av.) °C
14.079	25.913	59.865	1.354	549
$\pm 0.0094$	$\pm 0.0546$	$\pm 0.7412$	$\pm 0.0215$	$\pm 8.6$
21.121	38.874	39.913	1.277	557
$\pm 0.0095$	$\pm 0.0585$	$\pm 0.0060$	$\pm 0.0192$	$\pm 10.1$

The CH<sub>4</sub>:H<sub>2</sub>O ratio was maintained at  $1.841 \pm 0.0050$ . Permeate pressure rose quickly above the maximum range of the high accuracy permeate pressure sensor (max. range 1.333 mbar(a)). The permeate pressure on the low accuracy-wide range pressure sensor averaged  $5.15 \pm 1.47$  mbar(a) and  $7.79 \pm 0.91$ , however with the proximity to the bottom of the sensor range these often show higher (3 to 4 mbar) than dedicated low pressure (less than 2 mbar(a) full range) sensors. The decontamination factor spiked early in the 14 ml/min CH<sub>4</sub> experiment, rising above 2000 for a short time before settling at  $22.1 \pm 8.1$  at T + 01:01:59, comparable with the second experiment, 21 ml/min CH<sub>4</sub>, with a decontamination factor of  $19.3 \pm 11.2$ . The hydrogen recovery fraction was  $94.61 \pm 2.11$  % and  $92.26 \pm 5.08$  % in the 14 and 21 ml/min CH<sub>4</sub> experiments respectively, equalling a 3.7% reduction in efficiency between these CH<sub>4</sub> flow rates.

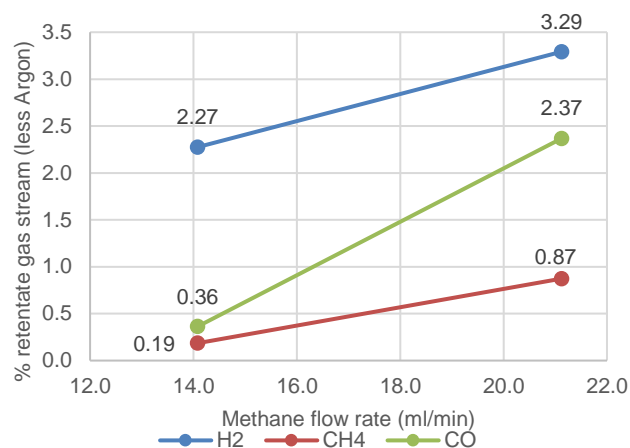


Figure 7: GC data showing percentage of gases other than CO<sub>2</sub> in the retentate gas stream (less Argon) for varying methane inlet flow rates.

The relatively large increase in CO compared to H<sub>2</sub> and CH<sub>4</sub> indicates partial completion of the reaction. Increase in membrane saturation may cause H<sub>2</sub> to remain present for longer and recombine with O<sub>2</sub>.

#### 4.2.4 Extended Methane run

The extended experiments test the PMR system over a longer period, aiming to gauge whether any issues arise – such as coking – when the membrane is continually used, and whether permeation remains efficient in extended use.

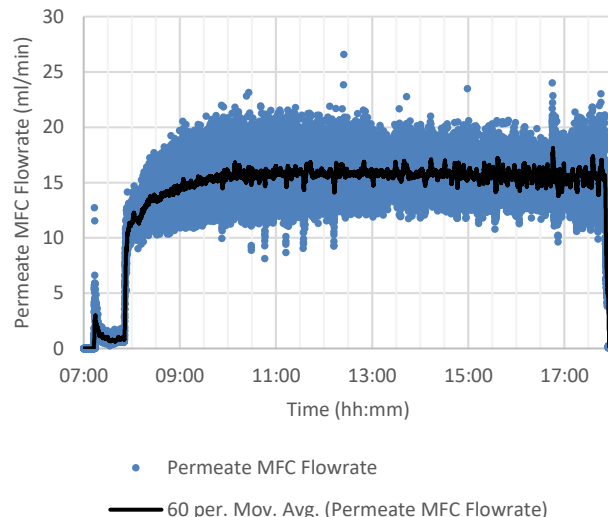


Figure 8: Permeate MFC flowrate during extended methane experiment.

Methane, water, and argon inlet flow rates were kept constant and measured at  $3.514 \pm 0.0112$  ml/min,  $6.484 \pm 0.0920$  ml/min, and  $89.889 \pm 0.0151$  ml/min respectively. The inlet pressure remained steady at  $1.396 \pm 0.0037$  bar(a), however the temperature fluctuated, averaging  $542 \pm 6.4$  °C. Figure 8 shows that once steady was achieved, the flowrate as measured through the permeate MFC stayed constant at  $15.761 \pm 1.817$  ml/min (corrected for baseline throughput). System steady state was achieved much more slowly than during subsequent experiments, at T + 05:12:43 (where T is methane inlet at 07:48:35 with steady state at 13:01:18) potentially due to the low flow rate of reactant gases compared to Argon. Water inlet was initiated earlier, as well, at T - 00:09:29; this experiment was conducted early in the experimental campaign when the operation of the liquid flow controller feeding H<sub>2</sub>O to the experiment was not fully optimised. Subsequent experiments used a reduced time between H<sub>2</sub>O and CH<sub>4</sub> feed, with an optimised liquid flow controller operating procedure that drastically reduced time to steady state input. This will be explored further.

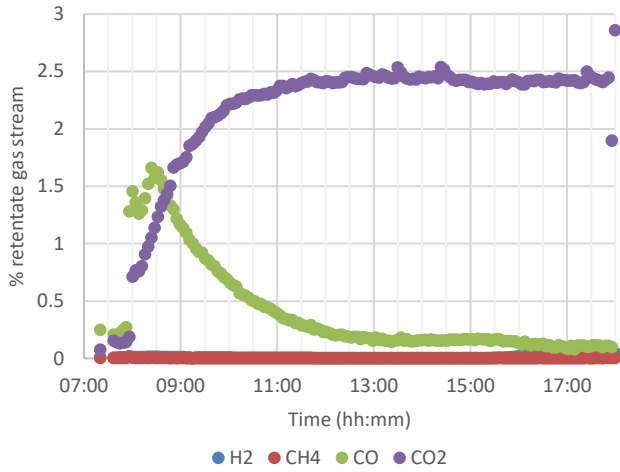


Figure 9: GC data showing percentage of retentate gases in the extended methane run experiment.

Figure 9 shows an initial surge in CO production without further reaction to CO<sub>2</sub>, however the water gas shift reaction took hold and peaked CO<sub>2</sub> production at the steady state milestone (T + 05:12:43). The speed of this compared to the subsequent argon carrier gas effects experiments could have been due to the low ratio of reactant gases to argon carrier gas, considering relatively little change in other parameters (pressure, humidity, temperature) for the duration of the experiment. During steady state, the ratio of CO<sub>2</sub> to CO reached  $94.282 \pm 0.601$  % (CO<sub>2</sub>) with the hydrogen recovery fraction averaging  $94.192 \pm 0.350$  % and the decontamination factor averaging  $17.650 \pm 1.162$ .

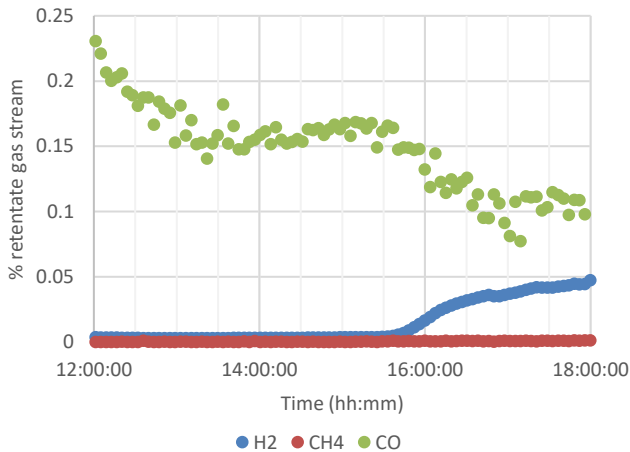


Figure 10: GC data highlighting change in hydrogen and carbon monoxide presence towards the end of the extended methane run experiment.

Towards the end of the experiment, starting at approximately T + 07:48:15 and continuing through to the end of the experiment at T + 10:01:31, CO dropped from its steady state  $0.203 \pm 0.065$  % towards 0.1%, with the hydrogen fraction eventually increasing. The hydrogen fraction increase indicates potential coking of the membrane, reducing the ability for hydrogen to permeate.

## 5 Conclusions

Results achieved were comparable with previous experiments [4] [5] and corroborated internally with secondary instrumentation (i.e. GC results matched permeate MFC flow rates). System data-capture facilitates in-depth analysis of relevant hydrogen recovery information, including pressure, temperature, humidity, and flow rate at a minimum capture rate of one datapoint per instrument per second. The gas chromatograph adequately analyses retentate gas composition.

Carrier gas to process gas ratio affects hydrogen recovery

fraction; increasing carrier gas flowrate improves recovery (98.9 % HRF at 30 ml/min Ar feed to 99.5 % HRF at 70 ml/min Ar feed). Further analysis is required to isolate influence of inlet and retentate pressure (0.17 bar increase in pressure between 30 and 70 ml/min Ar feed during experiments, Table 5). Initial methane run results indicate a reduction in permeation efficiency with increased feed flow rate, equalling a 3.7% reduction between 14.1 and 22.1 ml/min CH<sub>4</sub> feed flow rate. This equates to a 0.46% drop in efficiency per ml/min CH<sub>4</sub> feed flow. The extended experiment, totalling 10 hours of continuous operation, experienced an uncharacteristic slow steady state achievement time of more than 5 hours, with a minor drop in permeation ability after approximately 8 hours of operation.

Further data capture during the full experimental campaign will highlight hydrogen recovery and decontamination changes of hydrocarbons, water, and ammonia with respect to temperature, carrier gas flow rate, and process gas feed flow rate.

## 6 Data Availability

Datasets related to this article are available upon request.

## 7 Declaration of Interests

None declared.

## 8 Acknowledgements

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