EXPERIMENTAL CHARACTERIZATION OF THE OPERATIONAL BEHAVIOR OF A CATALYTIC RECOMBINER FOR HYDROGEN MITIGATION

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ABSTRACT

One of the significant safety concerns in large-scale storage and transportation of liquefied (cryogenic) hydrogen (LH2) is the formation of flammable hydrogen/air mixtures after leakages during storage or transportation. Especially in maritime transportation hydrogen accumulations could occur within large and congested geometries. The installation of passive auto-catalytic recombiners (PARs) is a suitable mitigation measure for local areas where venting is insufficient or even impossible. Numerical models describing the operational behavior of PARs are required to allow for optimizing the location and assessing the efficiency of the mitigation measure. In the present study, the operational behavior of a PAR with a compact design has been experimentally investigated. In order to obtain data for model validation, an experimental program has been performed in the REKO-4 facility, a 5.5 m³ vessel. The test procedure includes two phases, steady-state and dynamic. The results provide insights into the hydrogen recombination rates and catalyst temperatures under different boundary conditions.

1.0 INTRODUCTION

The burning of fossil fuels is considered to be one of the main reasons for the increase in global temperatures. In our everyday lives relying on fossil fuels, greenhouse gases, such as carbon dioxide and methane, are released during both the extraction and use. Furthermore, countries are interested in diversifying their energy sources to limit the dependence on few or even single suppliers. One option that can enable both decarbonization and diversification of energy supply is utilizing renewable energy sources, such as solar and wind. However, renewable energy sources are fluctuating. In order to minimize disruptions to daily life there will be the need for storing excess energy as well as providing a fuel during energy production shortage.

In recent years, interest in the use of hydrogen both as an energy carrier and as a fuel has increased considerably. Hydrogen, when produced from electrolysis powered by renewable energy, is considered to be “green”. There are many storage and distribution options, specifically in the form of liquefied hydrogen (LH2). The increased density at cryogenic temperatures of 20 K and the high energy per unit mass compared to other common fuels makes LH2 favorable for transportation specifically in the maritime sector. As a popular example, Kawasaki Heavy Industries has built a LH2 carrier to demonstrate an intercontinental LH2 supply chain between Australia and Japan [1].

Both industrial engagement and public acceptance of LH2 heavily relies on the Regulations, Codes, and Standards (RCS) that will be required to implement safe technologies and procedures. Pre-normative research can support the drafting of appropriate rules by providing scientific knowledge on the phenomena and processes relevant to safety. One safety concern is the formation of an explosive hydrogen/air mixture as a result of an unintended leak. Now on the market, there are detectors to provide warnings of leaks to allow time for intervention, e.g. ventilation. In extreme situations, where there are no other means to vent a confined area in which a gaseous hydrogen leak is occurring, a mitigation strategy could use passive auto-catalytic recombiners (PARs).

The international STACY project (Towards Safe Storage and Transportation of Cryogenic Hydrogen) involving partners from France, Germany and Japan addresses some of the knowledge gaps related to the safety of LH2 [2]. One project activity aims to study the operational behavior of PARs under the low temperatures that would be expected in gas mixtures involving hydrogen from an LH2 leak as well as provide a numerical tool to assess the efficiency in accident scenarios.

2.0 PASSIVE AUTO-CATALYTIC RECOMBINERS

A PAR is considered to be a passive hydrogen mitigation device, as it does not need external energy in order to activate. It is self-starting and self-feeding and is used to mitigate the risk of hydrogen accumulation in unintended hydrogen release scenarios. The catalysts used are typically platinum or palladium which are already active at low temperatures [3]. Using these two precious metals as the heterogenous catalyst coating reduces the activation energy for the recombination reaction

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g) + 240\ \mathrm{kJ/mole} \tag{1}$$

that occurs exclusively on the catalyst surface according to the two-step mechanism called Langmuir-Hinshelwood [4]. PARs already implemented in nuclear power plants (NPPs) have been intensely studied and characterized [5].

Figure 1 shows a visual representation of the fundamentals of a PAR used in NPPs. Two areas that are of interests are the catalyst section and the chimney. In the catalyst section, the inlet gas mixture of hydrogen and air enters and reacts on the catalyst surface. Depending on the PAR manufacturer, the design of the catalyst as well as the spacing between catalyst elements will vary. The chimney, which is located directly above the catalyst section, helps to enhance the buoyancy-induced flow due to the temperature generated by the exothermic reaction on the catalyst.

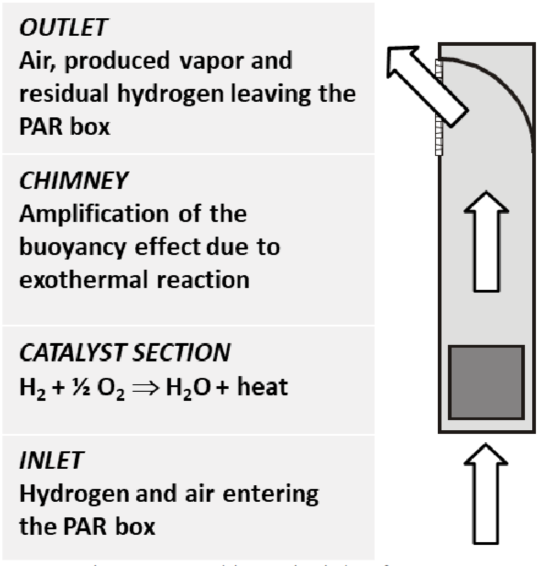

Figure 1. Visual representation of the fundamentals of a PAR [6].

Due to the increasing number of hydrogen applications in the context of the renewable energy transition, the transfer of hydrogen safety technologies from the nuclear field is increasingly considered. Especially in the maritime sector, PARs could become part of the hydrogen mitigation strategy, as was demonstrated by Kelm et al. [7]. In applications where there are size limitations, compact PAR designs could be suitable to mitigate risk from a hydrogen leak. New PAR designs have not yet been experimentally characterized under the boundary conditions that are present in LH2 release scenarios, which vary compared to NPP accidents.

The PARs investigated in the STACY project are different than those that are typically installed in NPPs. Figure 2 shows the Enersys-Hawker Hydrogen Eliminator that has been used for the experiments described within this paper. The compact design omits a chimney, which allows installation in restricted spaces. The PAR has a length of about 32 cm, a width of about 17 cm, and a height of about 8 cm. The gaps between the catalyst sheets promote a buoyancy-induced flow. The technical data sheet notes that the maximum concentration is 2 vol.% H2 for optimal recombination rate and the experimental program is designed not to surpass this limit.

Figure 2. The Enersys-Hawker Hydrogen Eliminator used in the test series.

The characterization of the PARs during basic operation is the first step towards studying the operational behavior under low temperatures and provide validation data for the numerical tool to be developed.

3.0 EXPERIMENTAL SETUP

The characterization of the PAR was performed by running an experimental program in the REKO-4 facility, located in the Hydrogen Laboratory on the campus of Forschungszentrum Jülich GmbH (see Fig. 3). The facility involves a 5.5 m³ steel pressure vessel with a design pressure of 25 bar. It has an internal diameter of about 1.4 m and an internal height of about 3.7 m. REKO-4 has 32 flanges which have been adapted over the years to allow for measurement to occur inside the vessel while also keeping it pressure tight. Injection of gases into the vessel takes place via mass flow controllers (MFCs). For the present tests, there are three MFCs for hydrogen, nitrogen, and air. Due to the dimensions of REKO-4, the characterization of the PAR can be obtained under natural convection. The experimental program described in this paper was performed under ambient conditions.

Inside the vessel, the PAR has been mounted with the help of carabiners on four chains anchored to the container ceiling, see Fig. 3 (right). In order to observe the PAR operation, six thermocouples and two hydrogen sensors have been placed around the recombiner (Fig. 4, left). The thermocouples are Ni-CrNi (type K) with 1 mm in diameter. The hydrogen sensors are XEN-3880 thermal conductivity sensors. Additional measurements are oxygen and humidity sensors near the top and bottom of the vessel. A well-mixed atmosphere during the experiments is achieved by a mixing fan. Temperature and hydrogen sensors close to the vessel ceiling serve to confirm well-mixed conditions.

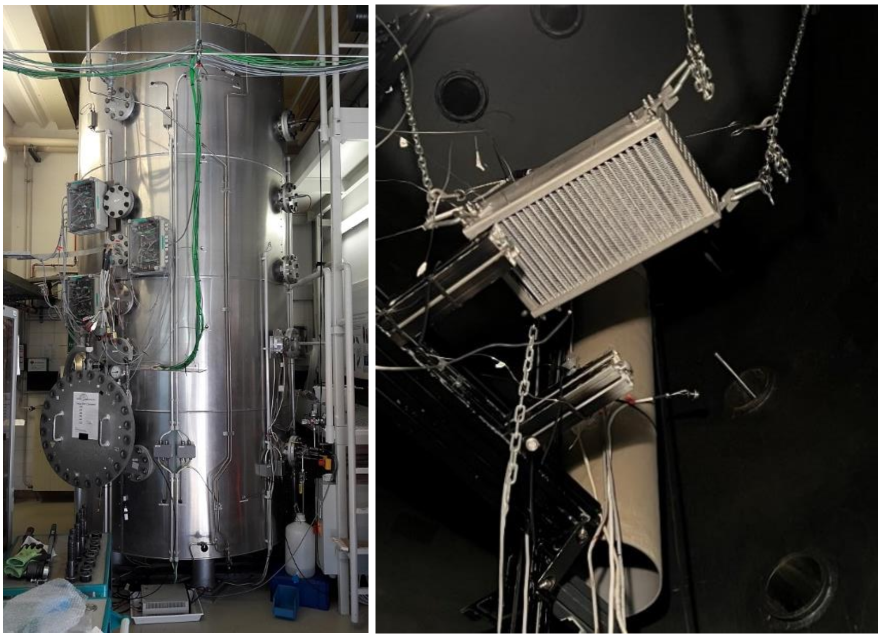

Figure 3. REKO-4 facility (left), PAR installation next to the mixing fan (right).

Figure 4 (right) shows the placement of four thermocouples that measure the catalyst temperature. They are located inside two catalysts in top and bottom position, respectively.

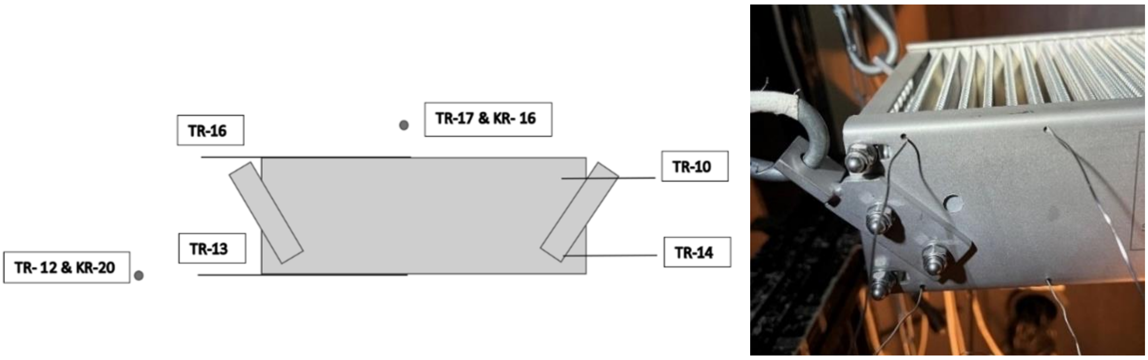

Figure 4. Sensors locations at the PAR (left), PAR with thermocouple instrumentation (right).

Figure 4 (left) shows a sketch of the location of thermocouples (TR) and hydrogen sensors (KR) around the PAR. The inlet gas temperature measurement occurs with the thermocouple TR-12. The hydrogen sensor in the same position (KR-20) measures the inlet hydrogen concentration of the PAR. Both sensors are located to the side of the PAR as to not be influenced by heat radiation from the catalyst. There are four thermocouples that measure the catalyst temperature: TR-10, TR-14, TR-13, and TR-16. The thermocouples TR-10 and TR-14 are located at the top and bottom of the last most catalyst sheet within the PAR respectively (see also Fig. 4, right). The thermocouples TR-16 and TR-13 are located at the top and bottom of an inner catalyst sheet, respectively. TR-17 and KR-16 are the thermocouple and hydrogen sensor located at the outlet of the PAR.

The water vapor produced from the catalytic reaction (see eq. 1) influences the hydrogen sensor measurements due to the change of thermal conductivity. During the post-processing, the data has been corrected. For this purpose, the average of the humidity measurements is used to derive a correction factor.

4.0 TEST PROCEDURE

The same PAR has been used for all tests. After the PAR and sensors are in place, the REKO-4 vessel is sealed. A fan is started to ensure well-mixed conditions inside the vessel throughout the entire test sequence. Figure 5 shows an example of the test procedure where relevant points are highlighted by the black dashed lines labeled A-F.

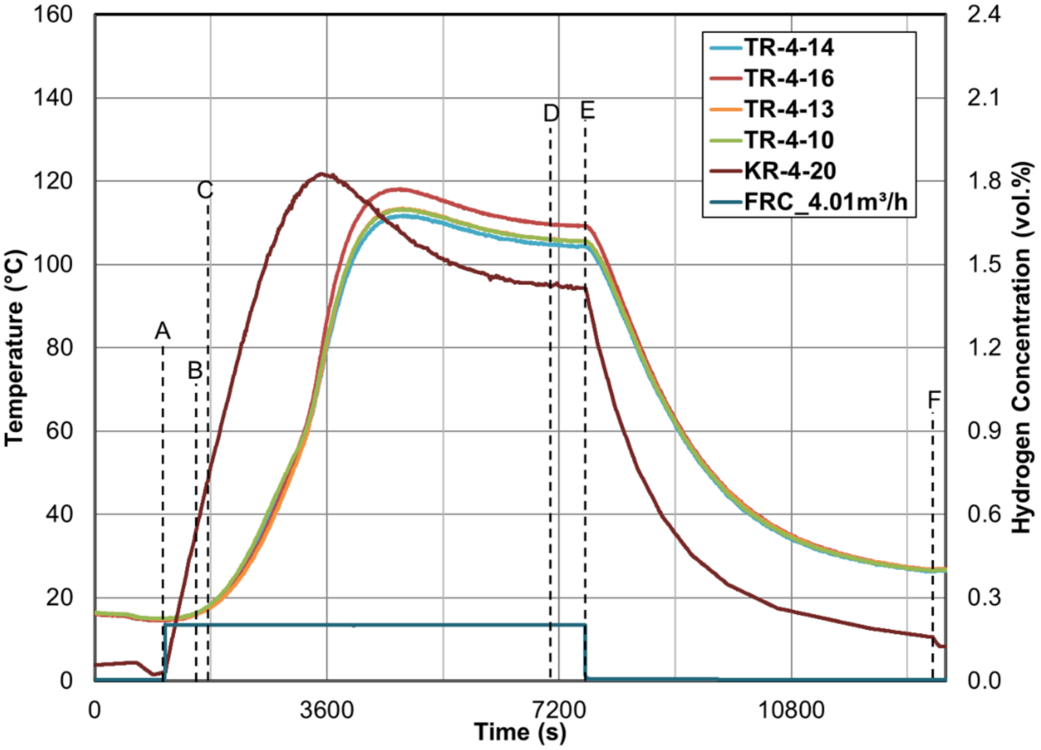

Figure 5. Example of the test procedure (steady state and dynamic phase)

Line A marks the start of the injection of hydrogen. The MFC continuously injects hydrogen at a constant rate until a quasi-steady state is reached. In this example, the hydrogen injection rate is 0.2 n-m³/h (blue line labeled FRC_4.01). Line B marks the time where the catalyst temperature has increased by 1 K, indicating that the reaction is occurring. For this example, it takes approximately 8 minutes after start of the injection for the catalyst temperature to increase, with a corresponding hydrogen concentration of 0.5 vol.%. Line C marks the light off of the catalyst. The catalyst light off time and temperature are registered when the recombination reaches 50% of the maximum recombination rate. For this example, the light off temperature is 17 °C and the hydrogen concentration is 0.7 vol.%.

The time between lines C and D allows for the PAR operation to reach a quasi-steady state. Line D marks the beginning of the quasi-steady state. It was determined from an initial test that two hours was a sufficient amount of time to allow for an equilibrium to be reached. When the hydrogen injection is stopped (E), the steady state phase of the test ends and the dynamic phase of the test begins. In the dynamic phase, the PAR continuously removes hydrogen from the atmosphere. Line F marks the end of the dynamic phase of the test when purging of the vessel begins. At this time, it can be concluded that the catalyst of the PAR has stopped reacting, which is confirmed by the stability of the temperature sensors, signifying the end of the dynamic phase of the experiment.

Depending on the experiment, several hydrogen injection rates were performed in succession in order to obtain multiple quasi-steady states before the dynamic phase was initiated. The following four hydrogen injection rates were applied: 0.25 n-m³/h, 0.20 n-m³/h, 0.15 n-m³/h, and 0.10 n-m³/h.

The first step in the post processing is to correct the hydrogen sensor measurements. Since the hydrogen sensors are thermal conductivity sensors and calibrated in dry gas, the thermal conductivity of the mixture is recalculated to account for the humid air. The second step is the determination of the reaction rate. A molar balance of hydrogen inside the vessel

$$\frac{dn}{dt} = \dot{n}_{in} - \dot{r}, \tag{2}$$

where $\frac{dn}{dt}$ – change of the hydrogen inventory inside the vessel, mole/s; $\dot{n}_{in}$ – molar flow rate injected by the MFC, mole/s; $\dot{r}$ – recombination rate of the PAR, mole/s, is used to obtain the recombination rates. The injected molar flow is determined from the MFC signal. In case of a well-mixed ideal steady state, the recombination rate would equal the injection rate. For the present tests, the change of the molar hydrogen inventory is calculated as an average value between points D and E (Fig 5). Thus, the difference between the molar flow rate and the change in the moles over time determines the reaction rate of the PAR.

5.0 RESULTS

Table 1 shows the test number with the associated injection rate. The maximum number of quasi steady states performed in one test was four. The fastest injection rate was 0.25 n-m³/h and the slowest was 0.10 n-m³/h of hydrogen. Gray cells mark test sequences from the first two tests where the executed time was not sufficient to obtain a proper steady state. After tests 1 and 2, it was determined to start with the highest injection rate so the temperature and hydrogen concentrations stabilized within the two hour period as described in the test procedure.

Table 1. The injection rates for each test preformed.

Test #	Injection Rate 1 (n-m³/h)	Injection Rate 2 (n-m³/h)	Injection Rate 3 (n-m³/h)	Injection Rate 4 (n-m³/h)
1	0.10	0.15	0.20	0.25
2	0.10	0.15	-	-
3	0.25	0.20	0.15	0.10
4	0.20	-	-	-
5	0.25	0.20	0.15	0.10
6	0.15	-	-	-

The time for the catalyst to reach 1 K above the starting temperature due to the exothermic reaction is show in Tab. 2. The differences between the starting times for each tests can be attributed to the initial conditions (temperature, humidity) as well as the rate of the hydrogen injection.

Table 2. Hydrogen concentration and average catalyst temperature at the initial reaction start.

Test #	Hydrogen Concentration (vol.%)	Average Catalyst Temperature (°C)	Time (min)
1	0.25	19.0	8.1
2	0.16	20.7	5.6
3	0.23	21.3	3.1
4	0.54	16.2	8.1
5	0.51	18.1	6
6	0.42	20.1	7.8

The average catalyst temperature and hydrogen concentration at the light off point is shown in Tab. 3 for each of the tests. The resulting values are influenced by the hydrogen injection.

Table 3. Average catalyst light off temperature and hydrogen concentration

Test #	Average Catalyst Temperature (°C)	Hydrogen Concentration (vol.%)	Time (min)
1	22.7	0.53	17.4
2	33.6	0.45	22.7
3	34.5	0.81	11.2
4	17.4	0.71	10.8
5	20.9	0.82	10.1
6	21.4	0.59	11.4

Figure 7 shows the temperature and hydrogen concentration measurements over the 8 hours of test 3. During test 3, four quasi-steady states were reached for four different injection rates.

On the primary y-axis the temperature is plotted over time. Both the PAR inlet and outlet temperature (TR-4-12 and TR-4-17) show the starting temperature of the atmosphere of approx. 16 °C. The atmosphere temperature increases over the course of the test and the final temperature is around 24 °C. The four thermocouples located on the catalyst of the PAR are consistently close together throughout the duration of the test. The catalyst temperatures are decreasing with decreasing injection rate, as a result of less reaction occurring on the catalyst surface.

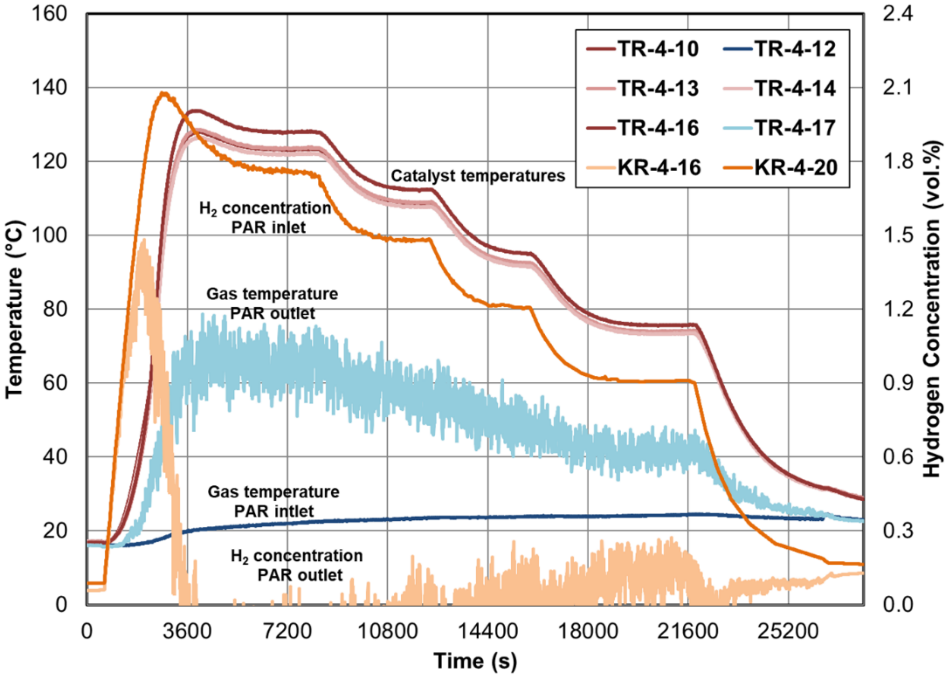

Figure 6. The PAR temperature and hydrogen concentration over course of test 5

On the secondary axis, the hydrogen concentration in vol.% is plotted with respect to time. Sensor KR-4-20 shows decreasing hydrogen concentration at the PAR inlet for decreasing injection rates with a stable reading due to its location next to the PAR inlet. In contrast, sensor KR-4-16 shows strong fluctuations due to the location above the PAR. Here, the combined effects of fluctuating flow patterns, high temperature and high humidity, which can also be observed in the gas temperature measurement above the PAR (TR-17).

Figure 7 shows a representative zoom on the end of the dynamic phase in test 5. When both PAR inlet and outlet concentration meet, the catalytic reaction has come to an end. The data shows that the PAR operates until approximately 0.2 vol.%. It should be noted that this value is significantly below the light off concentration (see Tab. 3).

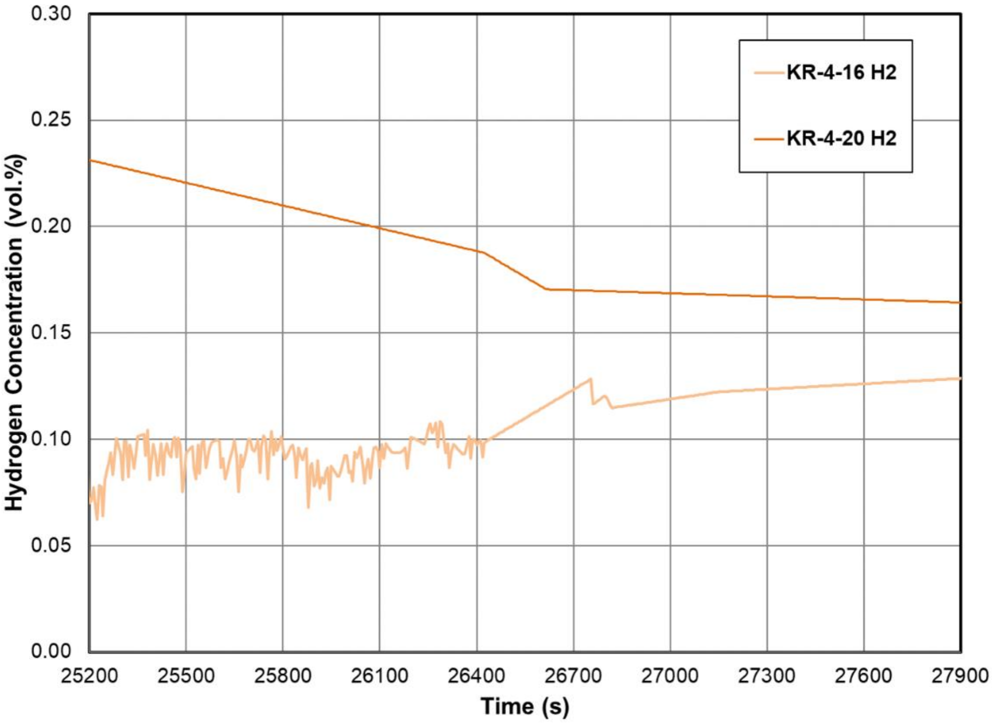

Figure 7. Hydrogen concentration at the end of the dynamic test 5.

The average catalyst temperatures during the quasi-steady states are presented in Fig. 8. TR-16 measures a significantly higher temperature than TR-13 for all four injection rates. Similarly, TR-10 measures a slightly higher temperature than TR-14 for all four injection rates. TR-16 has an increased temperature due to the heat generated and subsequently transferred from the adjacent sheets. A result of the lack of adjacent catalyst sheets on either side, TR-10 has a lower temperature in comparison to TR-16. The difference between the temperatures of an inner catalyst sheet and an outer sheet is a similar result as previously studied PARs. However, opposite than previously studied PARs the top edge of the catalyst sheets has a higher temperature then the bottom edge of the catalyst sheets. In previously studied PARs the bottom edge, which the inlet gas comes into contact with first is significantly hotter than the top edge, as there is more of a reaction occurring at the bottom edge than the top due to a boundary layer formed over the sheets.

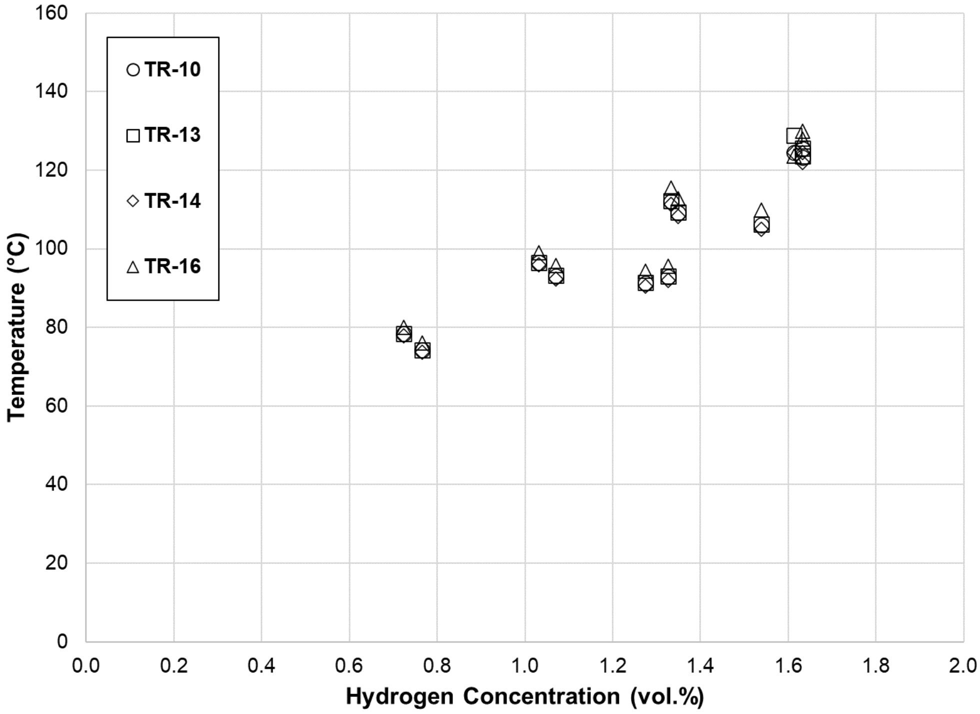

Figure 8. Catalyst temperature vs hydrogen concentration at the respective steady state tests.

Figure 9, shows the steady state recombination rates calculated using equation (2). The injection of hydrogen using the MFC has an absolute error of +/- 0.02. For the hydrogen sensors, an absolute error of +/- 0.1 vol.% has been considered.

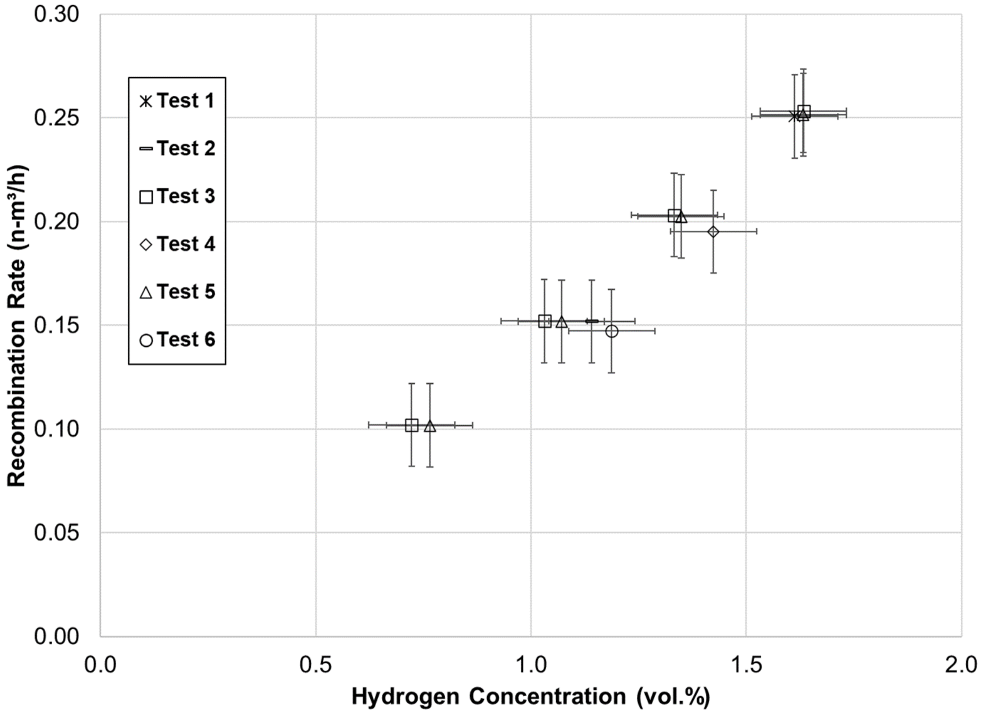

Figure 9. Recombination rates for the PAR at different hydrogen concentrations.

6.0 CONCLUSION

The STACY project aims to assess the efficiency of PARs for hydrogen mitigation in maritime LH2 transportation. For this purpose, a numerical tool to simulate PAR operation is being developed. The present paper presents the first experimental results obtained to characterize the operational behavior of a PAR with a compact design.

The characterization of PAR operation was achieved by determining the reaction rate at different hydrogen concentrations. The data collected showed some interesting operation characteristics, from fast start-up at low concentrations to prolonged usage. One of the most interesting point was the higher temperature at the top edge of the catalyst sheet instead of the bottom edge. This could be due to the fact that there is no chimney creating high flow velocities and a well-developed boundary layer.

Further experiments will be carried out at a higher injection rates and different atmospheric conditions. In particular, the expansion of the temperature range in the direction of cryogenic temperatures will be advanced during the project. All the data collected from the experiments will be used for numerical model development and validation.

7.0 ACKNOWLEDGEMENTS

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