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Power-to-Gas full-scale demonstration of KHIMOD's innovative milli-structured Heat Exchanger Reactor technology at JUPITER 1000

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Abstract

JUPITER 1000 is one of the largest Power-to-Gas demonstration sites in the World [1]. The project, led by French gas grid operator GRTgaz and co-financed by the EU, the ADEME and the PACA region gathers 9 main industrial partners. The demonstration site, located at Fos-sur-Mer in the South of France, features two 500 kW electrolysers (one PEM, one alkaline), a carbon-capture unit from the chimney of a local steel manufacturer and a 25 Nm3/h methanation unit with injection of the produced synthetic methane into the local high-pressure natural gas transportation pipeline.

The fixed-bed methanation unit, designed and built by KHIMOD, features two Heat-Exchanger Reactor trains loaded with 2 different powder-based methanation catalysts. KHIMOD has successfully deployed its novel Heat Exchanger Reactor (HER) technology. These HERs are built using an innovative plate-based assembly process, using Hot Isostatic Pressing to produce steel monoblock HER cores. These cores are equipped with multiple millimetre-sized catalytic reaction beds with an intense network of cross-flow cooling channels. This reactor geometry allows to intensify the Sabatier reaction by efficiently using the full load of the catalyst employed with a very accurate control of the reaction temperature throughout the catalytic bed. KHIMOD's manufacturing process ensures reliable, easily operable and leak-tight HER, even at high pressures and high temperatures. This technology is particularly well-suited for kinetically-fast reactions operating at high pressures and temperatures where temperature control is of the utmost importance. This is the case of Power-to-X processes such as methanation, high pressure e-methanol synthesis, Fischer-Tropsch and Haber-Bosch notably.

KHIMOD with the help of CEA and GRTgaz has conducted several operating tests of its methanation unit at JUPITER 1000. It has been designed to be scalable to much larger industrial units without major scale-up development time. This paper will present the major results of these tests and draw a line of comparison with previous tests made on earlier methanation pilots operated by KHIMOD. The paper will then extrapolate on what can be technically expected for coming e-methane large-scale industrial plants, either coupled with biogenic or non-biogenic CO_2 or waste-fed pyrogasification plants. Finally, some conclusions will be presented concerning the overall technical production cost of the e-methane molecule and the main drivers affecting the bottom-line.

The JUPITER 1000 project

The JUPITER 1000 project [2] was launched in 2018 aiming to be one of the 1st industrial demonstrator of the Power-to-Gas concept [3]. Power-to-Gas involves using excess renewable electricity to produce a molecule, Synthetic Natural Gas (SNG) that can be stored in the pressure of the gas distribution network or in natural gas storage, such as salt caverns and used when needed. The Power-to-Gas concept allows very high energy storage capacities, in the GWh range, for day-to-day or seasonal storage. This long term renewable energy storage option allows to further decouple the intermittent production of renewable electricity from fluctuating demand and thus favours the penetration of renewables in the global energy mix.

Similarly, the methanation reaction deployed in the Power-to-Gas concept helps reduce CO_2 emissions of the industrial sector as one of the possible routes for the Carbon Capture & Utilization (CCU) scheme. The locally produced SNG marginally compensates some of natural gas consumption, thus reducing natural gas imports for gas importing countries.

The installation is based in Fos-sur-Mer, within the area of Marseille Grand Port Maritime (GPMM), in the South of France. Figure 1 shows an aerial view of the site.

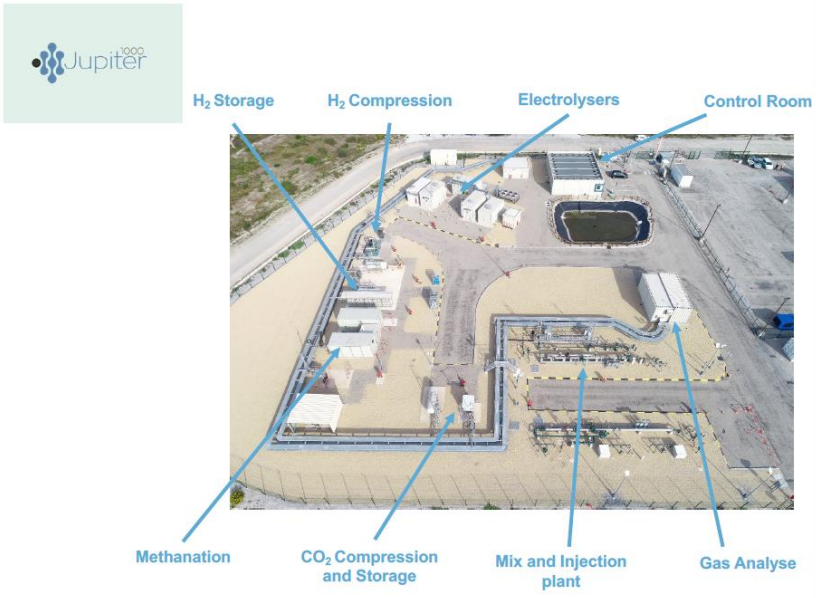

Figure 1: aerial view of JUPITER 100 site

Figure 2 shows an overall Block Flow schematic of the project. 1 MWe of renewable electricity from local photovoltaic and wind farms, operated by Compagnie Nationale du Rhône (CNR) is converted into 200 Nm3/h of green hydrogen using 2 different water electrolysis technologies: a 500 kWe alkaline stack and a 500 kWe Proton-Exchange Membrane (PEM) stack, both provided by McPhy Energy. The produced hydrogen can then either be directly injected into a local gas network pipeline with a limitation of 6% mol. Alternatively part of the hydrogen produced can be converted into 25 Nm3/h of SNG using CO_2 recovered from the local Ascometal steel factory, using a carbon capture process supplied by Leroux & Lotz. The produced SNG could then be mixed with fossil natural gas into the local gas network pipeline.

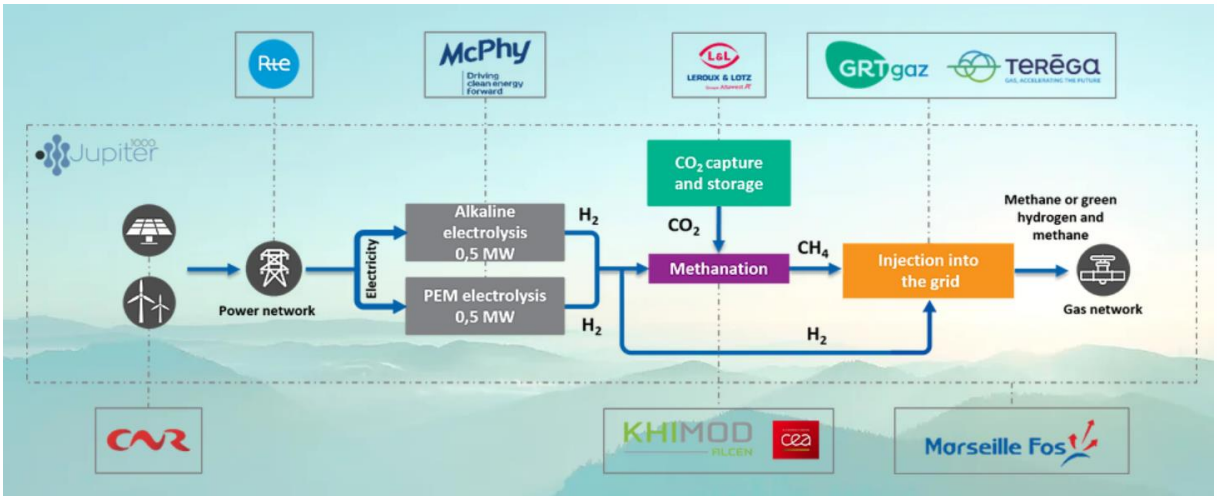

Figure 2: JUPITER 1000 overall Block Flow Schematic

The project is led by French gas network operator GRTgaz and involves 9 main industrial partners: GRTgaz, KHIMOD, CEA, CNR, Rte, McPhy, Leroux & Lotz, Terega, Marseille Fos and CMA-CGM. The Jupiter 1000 project is financed jointly by its partners, the European Union (ERDF), the French State (investments in the future, entrusted to the ADEME) and the Provence-Alpes-Côte d'Azur Region of France. The project is also approved by the Regulatory Commission of Energy (CRE) and the Capénergies competitive cluster.

KHIMOD is responsible for the design and manufacturing of the methanation unit with the assistance of the French Alternative Energies and Atomic Energy Commission (CEA). The first production of synthetic methane was achieved in 2022, followed by a series of performance tests. In this context, final performance tests were conducted on the methanation unit in the spring of 2024 and are the focus of this paper.

Methanation unit design

The methanation reaction discovered by French chemist Paul Sabatier and Jean-Baptiste Senderens in 1897 is a hydrogenation reaction of CO2 which produces SNG (CH4) and water with the reaction of Figure 3.

$$CO_2 + 4.H_2 \rightarrow CH_4 + 2.H_2O \quad \Delta H = -165\ kJ.mol^{-1}$$

Figure 3: Methanation reaction

It is a fast reaction with a high conversion ratio when catalysed by transition metals such as nickel, ruthenium or rhodium. The reaction is favoured by high pressures and is highly exothermic, with catalyst performance significantly affected by temperature. Therefore heat control of the catalytic bed is essential.

The methanation unit was designed for half of the hydrogen production capacity of Jupiter 1000: 500 kWe producing 100 Nm3/h of hydrogen. Using the theoretical H2:CO2 ratio of 4:1 from the chemical equation of Figure 3, this translates in 25 Nm3/h of associated maximum CO2 consumption and a maximum production capacity of 25 Nm3/h of SNG. This would represent 125 tpa if operated all year long. The unit has been designed to accommodate for a turndown ratio of 2.5, thus running from 40 to 100 Nm3/h of hydrogen.

The CO2 feed is provided by a carbon capture unit capturing CO2 from the flue gas of the furnace of the Ascometal steel factory located nearby. This process provided by Lerox & Lotz features a condenser, a membrane MonoEthanolAmine (MEA) contactor and a stripping column. The CO2 is then dried prior to being compressed and injected in a pipeline towards the Jupiter 1000 site where it is stored in a buffer feed tank.

The H2 feed is provided by either of the 2 electrolysis units present on site, through an intermediate storage tank.

A nitrogen supply by gas cylinders is used during start up and for inerting the installation in case of shutdowns.

Figure 4 shows a simplified Process Flow Diagram of the methanation unit process.

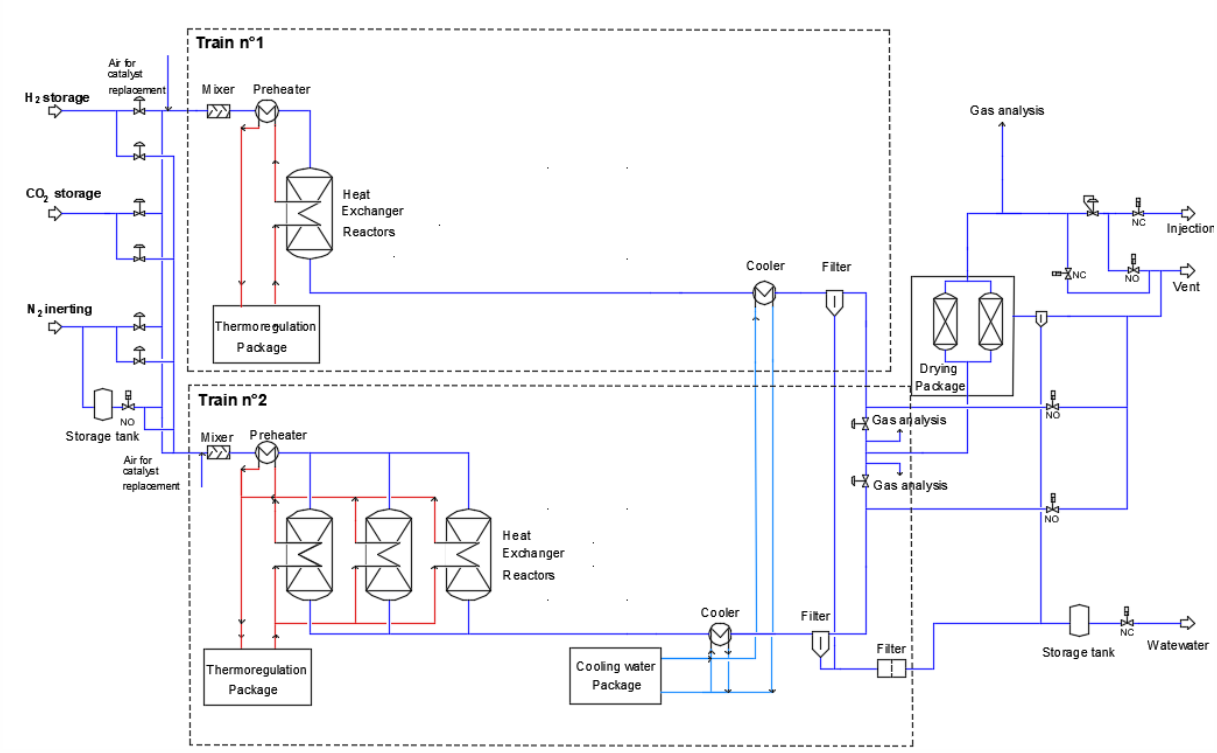

Figure 4: simplified PFD of the methanation process

The process has 2 independent trains, each equipped with 3 methanation reactors. In each train, the flow-controlled H2 and CO2 feeds are mixed together in an in-line static mixer. The H2:CO2 ratio is controlled by an infrared CO2 analyser. The feed gas is then preheated in a shell and tube heat exchanger, using hot mineral oil, at a temperature close to the methanation reaction temperature of 300°C. The 3 parallel methanation reactors per train are KHIMOD's milli-structured Heat Exchanger Reactors (HER) which will be detailed in the next section. The methanation reactors are cooled by mineral oil to maintain an almost isothermal behaviour. The produced SNG + produced water and non-converted CO2+H2 are then cooled in a shell and tube condenser using refrigerated water and glycol. Water is then separated in a vertical gas-liquid separator.

The gas coming out of the gas-liquid separators is then sent to a Temperature Swing Absorption (TSA) unit to bring the water content of the produced gas to the export specification before being compressed at a pressure. After the gas is analysed using an in-line FTIR analyser, it is directly injected in a GRTgaz natural gas pipeline delivering gas to nearby industrial use. In this application there is no need to add a membrane separation unit to increase the CH_4 content as the dilution ratio of the injected SNG volumes in the flow of

fossil natural gas guarantees that the mixture is suitable for type H reinjection specifications listed in table 1.

Higher Heating Value (HHV) at 25°C	10.67 – 12.77 kWh/Nm^3
Wobbe Index	13.6 – 15.66 kWh/Nm^3
Specific Gravity at 25°C	0.555 – 0.7
CO_2 content	Max. 2.5 % mol.
CO content	Max. 2% mol.
H_2 content	Max. 6% mol.

Table 1: Type H main gas specifications

Each train is equipped with mineral oil thermal regulation package for both heating and cooling mineral oil. This thermal oil regulation package capacity is about 10 times what is required for normal operations. This overcapacity is determined by Power-to-Gas concept which necessitates the ability to perform a cold start in about 30 minutes. The cooling water-glycol mixture feeding the condenser is supplied by a water cooling package.

Figure 5 provides a simplified 3D model of the process equipment. All process equipment fit into a 20 ft container and main utilities (oil thermal regulation packages, water cooling package, compressed air system, nitrogen blanketing system ...) fit in another 20 ft container. A 3rd 10 ft container encloses all electric, safety and process control cabinets, and is used as a mini local control room. The unit has no gas emissions except for normal and emergency shutdowns, when the gas content is flushed with nitrogen and routed to the vent.

Figure 5: Simplified 3D model of the process equipment

Figure 6 shows an overall view of the process container.

Figure 6: view of the process container (before thermal insulation was installed)

Methanation Reactors

The methanation reactors are using KHIMOD's Heat-Exchanger Reactor (HER) technology [4]. The core of the reactor features millimetre-size catalytic reactive channels that can be seen on side A of Figure 7. These tubular channels have an internal diameter ranging typically from 2 to 12 mm. Perpendicular to the catalytic channels, millimetre size heat-transfer channels, shown on side B, cool down the catalytic bed in a cross-flow heat exchanger pattern, to achieve a thermal profile as isothermal as possible.

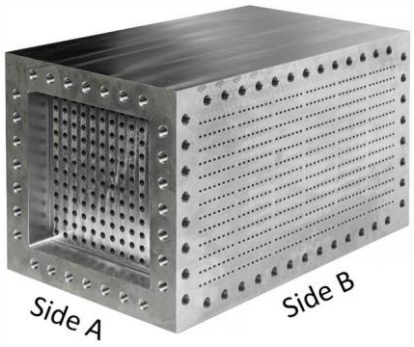

Figure 7: Typical view of a K3-size HER core module (Side A: reactive channels; Side B: heat transfer channels)

The reactor core is produced through a plate-based manufacturing process where plates containing reactive and heat transfer channels are assembled using a complex series of Hot Isostatic Press (HIP)

operations to create a metallic monoblock. This metallic monoblock is then machined to provide an HER core onto which gasketed flange connections can be attached. For methanation, AISI 316 L grade is used, although other metals can be used for more severe applications.

Compared to other catalytic rector technologies, KHIMOD's HER offer unique features that are highly beneficial for the methanation reaction:

- The reactive channel diameter is one order of magnitude less than traditional tubular water-cooled fixed bed reactors, leading to a much higher surface-to-volume ratio and allowing to extract the heat generated by the reaction much more efficiently. This guarantees a thermal profile closer to the isothermal ideal conditions which favours better overall catalyst performance and lifetime.
- The reactive channels are very short in length, typically in the range of several hundreds of millimetres. This is an order of magnitude shorter than common tubular reactor, resulting in a low pressure drop, typically less than 0.1 bar.
- The reactive channels can withstand very high pressures, up to hundreds of bars. Although this is not necessary for the current application, the possibility to operate at higher pressure can enhance the CO_2 conversion at a given space velocity for reactions that are thermodynamically favoured by increased pressure, such as the methanation reaction.
- The HERs are relatively compact with a low lateral distribution in the typical range of several tens of millimetres. This results in a high Peclet number with a subsequent narrow Residence Time Distribution (RTD) allowing better control of the reaction.
- A Khimod HER can be regarded as an array of individual tubular reactors, each with a catalyst volume close to 10 mL. This volume is comparable to that of continuous flow catalyst test benches typically employed in research institutions. Consequently, the scale-up from new laboratory-scale catalyst development to Khimod HER technology is simpler. This generally occurs in two stages: first, from laboratory-scale to the K1-size (12 reactive channels HER) and subsequently from the K1-size to the commercial HER size, such as the new K5, equipped with 784 reactive channels. The K5-size HER reactor core is shown in Figure 8.

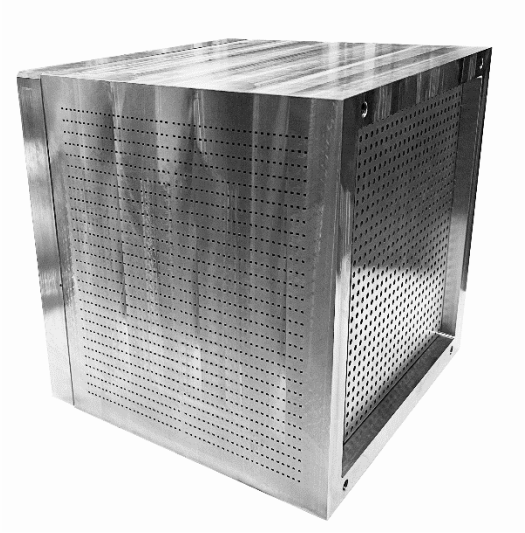

Figure 8: Typical view of a K5-size HER core module

The HERs used in Jupiter 1000 were developed in the years 2017-2018 in partnership with the CEA. The initial unit design featured 2 trains of 5 HERs, based on the optimal operating conditions for methanation catalysts known at the time. Advances in the field have since enabled a reduction in the number of HERs per train to 3, as illustrated in Figure 9.

Figure 9: installed 3 parallel HERs train bundle

Methanation Catalyst

Khimod HER use powder-based catalyst with a particle size below 500 µm suitable for the reactive channel diameter.

Different catalysts have been used in train number 1 and train number 2.

Train number 1 has been loaded with a specially developed powder-based nickel on alumina catalyst. The catalyst is reduced on site before being put on stream. Progress in the knowledge of this catalyst allowed to decrease the number of reactors from 3 to 1 for the same 50 Nm3/h H2 feed. Operational results from screening and tests has shown that the performance of this charged catalyst is able to process higher values of inlet flow, for instance 1 K3-size reactor can proceed the 50 Nm3/h which was initially designed for the whole train of 3 K3 reactor size (c.f. Figure 7).

Train number 2 has been loaded with another commercial pellet-type catalyst crushed and sieved to meet the particle size requirement. This catalyst is also a nickel on alumina catalyst. The catalyst is pre-reduced, followed by a partial re-oxidation. It is then further reduced on site before being put on stream.

Performance test program

The performance tests conducted in the spring of 2024 aimed to evaluate the catalytic reactor performance of each reactor train. The assessment focused on several key parameters: CO_2 conversion rate, CH_4 content in the produced SNG, pressure drop across the reactor, power requirement and energetic yield of the methanation unit. Additionally, the tests measured the transient time required to achieve steady production from both hot and cold stand-by mode, as well as the associated power consumption.

The operating window has been as wide as possible, taking into consideration the unit design and actual performance limitations of the unit in its overall environment at Jupiter 1000 site:

- H_2 flowrate : 20 – 45 Nm3/h
- H_2:CO_2 ratio : 3.8 – 4.4
- Reaction temperature : 270 – 310 °C
- Reactive pressure : 3 – 7 bar g

Due to operational constraints, parametric study was only possible for train number 1, while only the full load test could be achieved on train number 2. However, as discussed in the next section, the results from

train number 1 proved to be particularly valuable, as its catalyst exhibits significantly better performance compared to that of the train number 2.

Performance tests results

Data validation

Production data was acquired from the unit SCADA at a rate of 1 operating point every 10 seconds. To ensure reliable results, parametric test conditions were maintained to achieve at least 15 minutes of steady operation per operating point. Data was then filtered and cross-checked using a mass balance closing procedure. Finally, the data were filtered using a Savitzky-Golay filter [5].

CO2 conversion rate

The CO2 conversion rate is expressed as:

$$CO_2 Conversion = \frac{Q_{mol}(CO_2, in) - Q_{mol}(CO_2, out)}{Q_{mol}(CO_2, in)}$$

All inlet flowrates have been normalised using Gas Hourly Space Velocities in h-1 expressed as:

$$GHSV = \frac{Q_{vol}(CO_2 + H_2, Normal\ Conditions, in)}{Volume_{Catalyst}}$$

Figure 10 shows the CO2 conversion as a function of GHSV and H2:CO2 ratio. The CO2 conversion is very high, above 92%mol in all cases. The conversion is hardly affected by the increase in GHSV up to a very high GHSV value of 25 000 h-1 indicating that the GHSV could be increased even further. The conversion is affected by an increase of the H2:CO2 ratio. A 10% overflow of H2 compared to the stoichiometric ratio of 4.0 shown in the equation of the reaction in figure 3, sets the CO2 conversion close to 99%vol. which is very close to the thermodynamic optimum at these (pressure, temperature) conditions. However this over-stoichiometry induces increased amounts of non-converted H2 in the SNG. H2 is by far the governing factor in SNG economics so in units which do not recycle the non-converted H2 such as Jupiter 1000, we should stick to the stoichiometric H2:CO2 ratio of 4.0. However for units equipped with a downstream membrane separation unit and a recycle compressor, we should increase the H2:CO2 ratio to 4.4 in order to bring the CO2 conversion to the optimum.

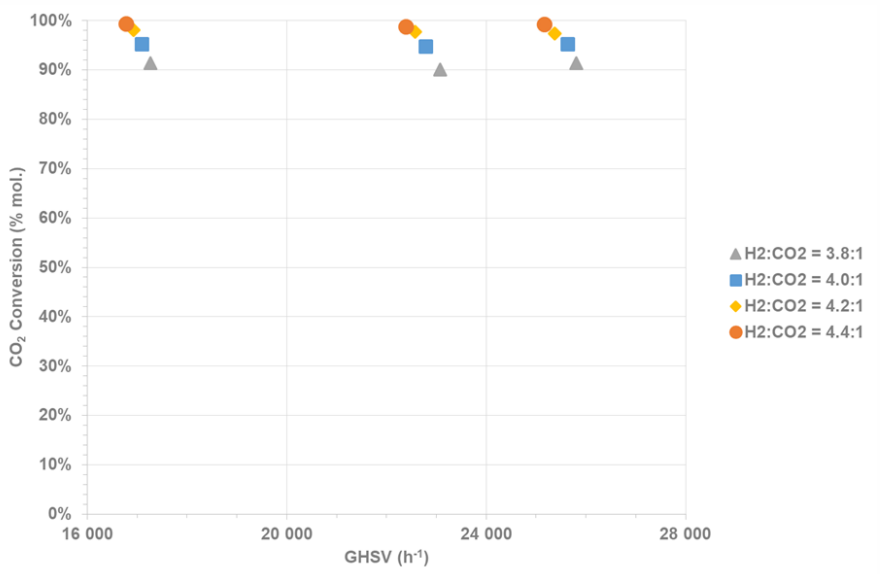

Figure 10: CO2 conversion as a function of GHSV for various H2:CO2 ratios, for Operating Pressure = 5 bar g and Operating Temperature = 300°C

Figure 11 shows that the CO2 conversion increases as the operating temperature is increased. An asymptotic behaviour seem to be reached at temperatures above 310°C. However thermal degradation of the catalyst might become an issue at temperatures above 310°C. Therefore the operating temperature should be kept at 300°C.

Figure 11 shows a comparison of the performance of the catalyst of train n°1 and train n°2 in terms of CO2 conversion. The performance of the catalyst of train n°2 is very close to the one of train n°1. However train n°2 has 3 reactors whereas train n°1 has only 1. Therefore the GHSV of train n°2 is only 8 500 h-1 versus the conversion of train n°1 which is 25 000 h-1 for the same H2 intake of 45 Nm3/h. A higher GHSV means a higher SNG yield per catalyst volume and therefore per HER, explaining why the catalyst of train n°1 is favoured for commercial applications.

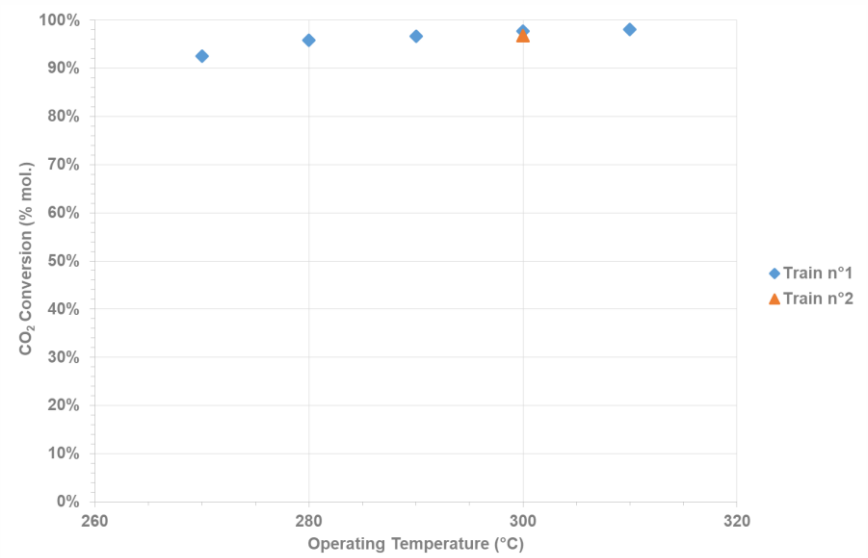

Figure 11: CO2 conversion as a function of Operating Temperature, H2 Inlet Flowrate of 45 Nm3/h, Operating Pressure = 5 bar g and H2:CO2 Ratio = 4.2:1

CH_4 content

Figure 12 shows that the methane content in the SNG slightly drops as a function of GHSV. The methane content does not exceed 79% vol. as the over-stoichiometry involves that a significant proportion of H2 is present in the reactor outlet. Therefore, the produced SNG does not comply as such with type H gas specifications of table 1. It does so however as the produced SNG is diluted in a large quantity of natural gas in the export pipeline. For larger units however, a membrane separation unit + recycle compressor would entrust to meet the export specification directly out of the methanation plant.

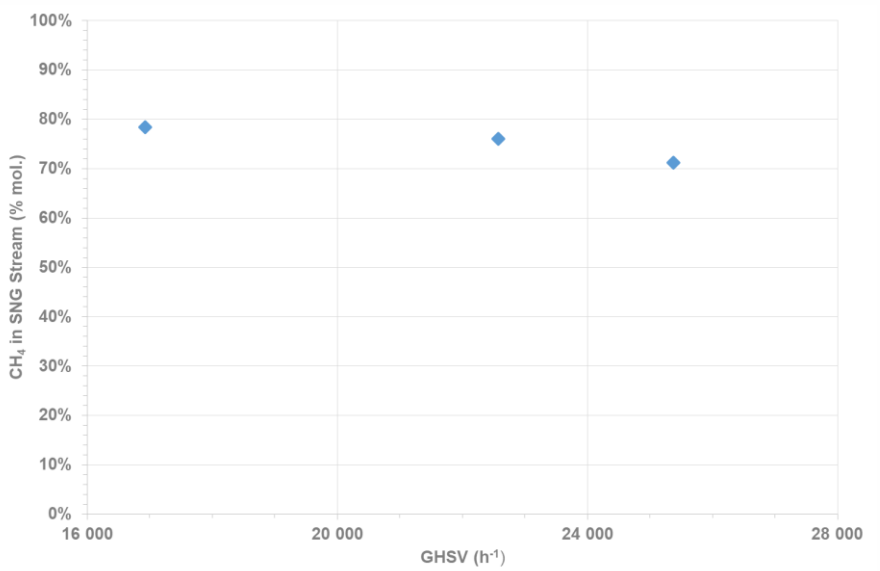

Figure 12: CH_4 content in the SNG Stream as a function of GHSV, for Operating Temperature = 300°C, Operating Pressure = 5 bar g and H_2:CO_2 ratio = 4.2:1

Power consumption

The overall power consumption of the unit per unit volume of produced SNG is decreasing as a function of GHSV as can be seen in Figure 13. Indeed a large proportion of the energy is needed to keep the unit running independently of the gas produced. As the amount of gas produced increases, the power consumption per unit of gas produced decreases. However, the amount of power consumption is below of 1 kWh/Nm3 of CH4 produced, which is relatively small. Nevertheless, the high GHSV value of 25 000 h-1 only corresponds to 45 Nm3/h of H2 intake which corresponds to a small pilot unit size.

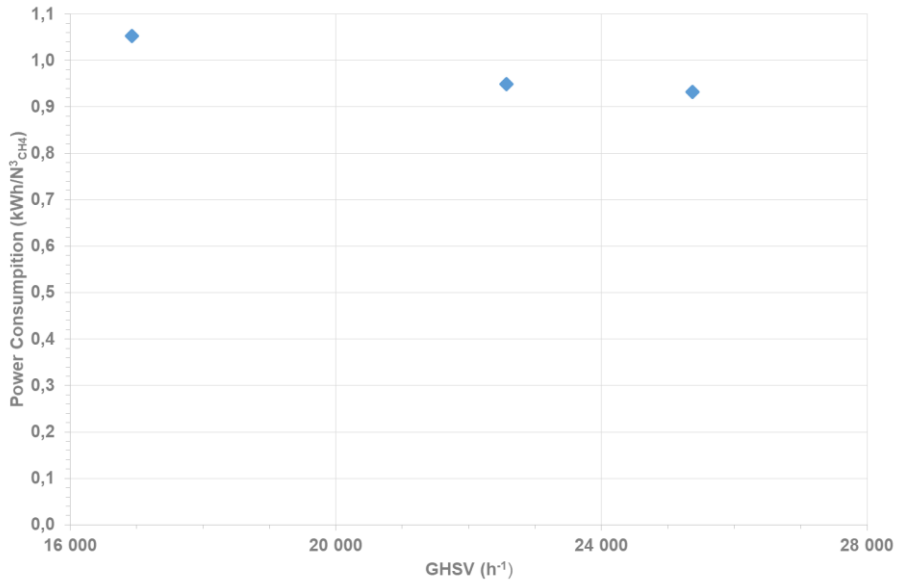

Figure 13: Power consumption as a function of GHSV, for Operating Temperature = 300°C, Operating Pressure = 5 bar g and H_2:CO_2 ratio = 4.2:1

Energy yield

The energy yield is defined as:

$$Energy\ Yield = \frac{HHV_{SNG\ produced}}{HHV_{H2\ feed} + Power\ Consumption}$$

The energy yield increases as the GHSV increases. This is due to the decrease of the overall power consumption of the unit as the GHSV increases that was discussed above. The energy yield curve is however relatively flat ranging from 74% to 75%. It is a relatively high value considering that around 20% of HHV of hydrogen is lost naturally during the methanation reaction in the form of heat. This heat is then dissipated by the air coolers of the mineral oil thermal regulation package, while it could instead be valorised at 250°C as heat for local heat demand of converted back into electricity using an Organic Rankine Cycle. Alternatively, it could be used in the CO2 capture by amines as the process requires temperatures of around 150°C, thus reducing the energy consumption of this unit. Thermal optimisation is of paramount importance for Life Cycle Assessment of the overall process and is a key focus in a commercial application. However, the size of this demonstrator did not allow to address the thermal optimisation issue at this stage.

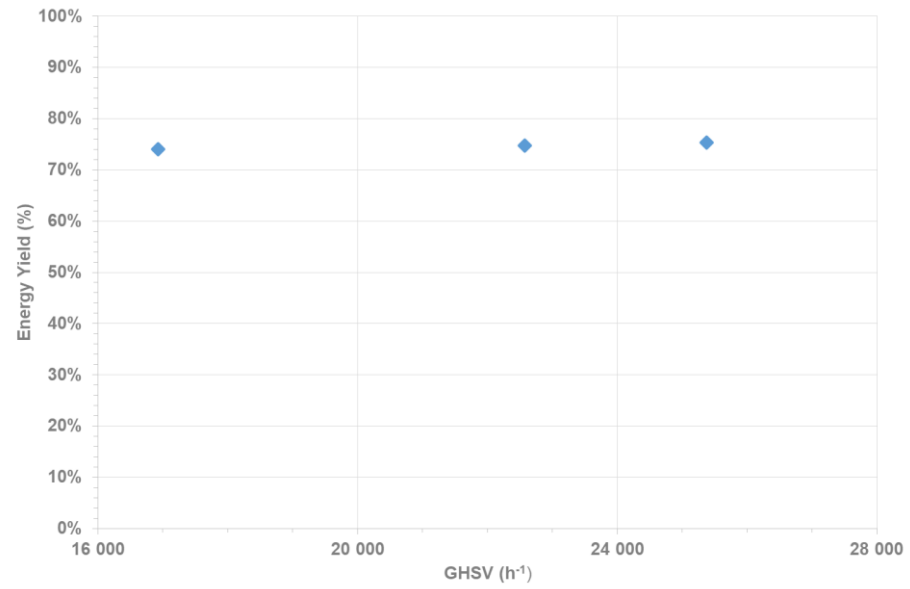

Figure 14: Energy yield as a function of GHSV, for Operating Temperature = 300°C, Operating Pressure = 5 bar g and H_2:CO_2 ratio = 4.2:1

Start-up times

One of the goals of Power-to-Gas is to be able to be responsive to the supply-demand equilibrium of the power grid and to be able to start fast to store temporary excess supply of intermittent renewable power.

Figure 15 shows the evolution of the main operating parameters after a cold start. The heat regulation package of train n°1 takes around 50 minutes to bring the oil circulation to the 300°C operating temperature setpoint, and then 28 additional minutes to reach steady operating conditions at maximum throughput. However changes in operating conditions while the unit is maintained hot during a hot start, take a few minutes to reach steady operating conditions. Thus the methanation unit complies with the Power-to-Gas requirements. However when a fast cold start is not required, this would translate into a smaller heat regulation package sizing.

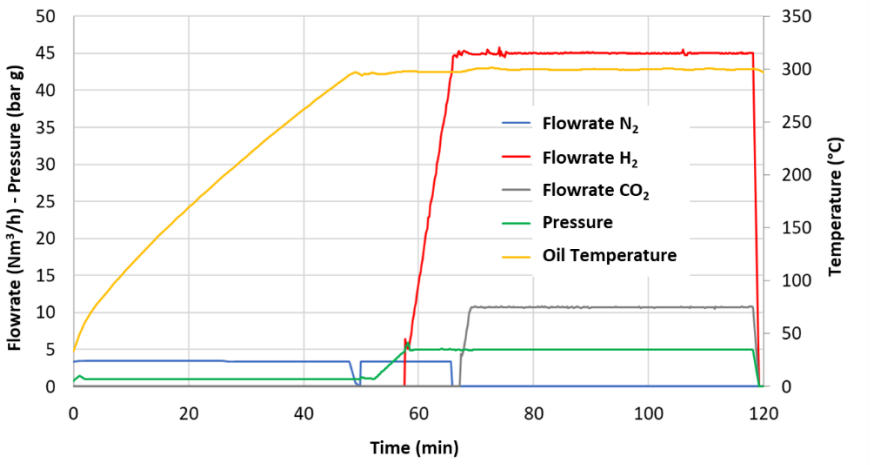

Figure 15: evolution of the main operating parameters after a cold start (train n°1)

Conclusion

The methanation unit of Jupiter 1000 demonstrates that methanation using heat exchanger reactors is a mature technology, flexible and operational with a high level of performance. High conversion rates have been demonstrated at high GHSV, allowing a very compact design for the methanation Heat Exchanger Reactors. Further improvements can however be made to increase the energy efficiency of the reaction for larger scale industrial units.

Acknowledgments

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