Final Report Summary - HY2SEPS-2 (Hybrid Membrane - Pressure Swing Adsorption (PSA) Hydrogen Purification Systems)

Executive Summary:
The main goal of the Hy2Seps-2 project is the design and testing of hybrid separation schemes that combine Membrane and Pressure Swing Adsorption (PSA) technology for the purification of H2 from a reformate stream that also contains CO2, CO, CH4, and N2. The project focus is on small-scale PSA units, which operate at relatively low feed pressures and, as a result, there is less flexibility in operating modes in order to maintain high H2 purity without sacrificing recovery. Various possible configurations of the hybrid system have been evaluated depending on the material (H2 or CO2-selective membrane & adsorbent) properties, as well as on the operating conditions (membrane upstream or downstream the PSA unit).

The objectives of the project refer to: (i) optimization and scale-up of the carbon membrane synthesis
procedure, as well as testing under actual conditions, (iii) assessment of the benefits of using new or layered adsorbents on the PSA performance and generation of transport and adsorption data for the relevant materials, (iii) design, control and optimization of a hybrid membrane-PSA separation system and (iv) assembly and testing of a hybrid membrane – PSA separation system. The technical approach incorporates both materials development and process/system modelling.

The synthesis of carbon membranes includes the steps of deposition of a polymer layer and of thermal treatment at different temperatures. This cycle can be repeated for deposition of additional material and tuning of the separation performance. The permeation characteristics of the membranes have been evaluated in all stages of the evolution of the carbon layer starting from the initial polymer layer and through its curing and decomposition course as a function of thermal treatment at varying temperatures. Carbon membranes prepared on ceramic supports had poor H2/CO2 selectivity due to surface diffusion of CO2. Polymer membrane layers prior to pyrolysis showed moderate H2/CO2 selectivity of the order of 50 combined with a low hydrogen permeance. CO2-selective membranes were developed employing precursors based on ionic liquids mixed with suitable monomers, so that the final membrane is solid after curing. These membranes had a CO2/H2 selectivity up to 14 at low-to-moderate CO2 permeance. New membrane supports including nanostructured zirconia or alumina layers were developed in order to facilitate the synthesis of the aforementioned membranes.

New types of commercially available materials have been evaluated as adsorbents in the PSA process for improvement in performance under the specific operating conditions of small PSA units. The adsorption equilibrium of all relevant molecules contained in a reformate gas was measured and a new MOF material offering superior CO2 adsorption characteristics was identified. On the other hand, the performance of the new materials in adsorption of N2 was not better than the reference material. The selected adsorbent material has being evaluated in both fixed-bed operation and PSA process at lab-scale. A mathematical model, incorporating the equilibrium and kinetic data of the adsorbents, has been developed for the simulation of the dynamic behaviour of an adsorption column and of PSA processes. Due to the inferior characteristics of the selected material in adsorption of nitrogen, its performance in the PSA process is not better than current state-of-the-art adsorbents.

A dynamic mathematical model has been developed for the membrane and PSA modules as well as on the hybrid system. The model includes options both for steady state and dynamic simulation. In addition, the development of a gPROMS toolkit for optimisation of hybrid separation systems has been carried out. The process model was developed for the experimental PSA system for hydrogen purification built by HYGEAR and it also accommodates a hybrid membrane-PSA system based on a combination of the standalone experimental PSA system and an appropriate membrane.

A hybrid separation system consisting of a PSA and a membrane module capable of producing 1 Nm3/h of hydrogen has being assembled for carrying out pilot testing under actual conditions. A commercial membrane module incorporating a CO2-selective membrane was employed in the tests following reviewers’ recommendations, because a membrane module with target specifications was not obtained from project activities. The properties of the commercial module were far from optimal for the application, but, in any case, the obtained results showed that an increase in hydrogen yield at the same hydrogen purity is possible in the hybrid system compared to a standalone PSA unit. Technical and economic analysis showed that the specific hydrogen production costs for the hybrid enhanced hydrogen generation system are only 9% higher than for the state-of-the-art hydrogen generation system and there is ample room for improvement via development of membranes with better characteristics for the target application.
Project Context and Objectives:

Steam reforming of methane is currently the major route of hydrogen production. In a conventional methane steam reforming plant, methane reacts with steam resulting in a mixture of hydrogen, carbon monoxide, carbon dioxide, methane, nitrogen and water. A similar reformate product gas is also obtained from reforming of any kind of fossil or renewable hydrocarbon fuel. After water removal by condensation, hydrogen has to be separated from the remaining gases and purified. Pressure Swing Adsorption (PSA) is a process frequently used in hydrogen purification. Typical PSA units can produce 99.999+% H2. This, however, is linked to low hydrogen recoveries (70-75%), which have a negative effect on the cost of the produced hydrogen. Furthermore, one of the major greenhouse gases (CO2), is the dominant by-product of this process. Currently it is usually released in the atmosphere since the existing processes are not cost effectively designed for CO2 capture.

The main goal of the project is the design and testing of hybrid separation schemes that combine membrane and Pressure Swing Adsorption (PSA) technology for the purification of H2 from a reformate stream that also contains CO2, CO, CH4, and N2. The general objectives comply with SP1-JTI-FCH.2010.2.3: “Development of gas purification technologies”, which is part of the application area SP1-JTI-FCH.2: “Hydrogen production & distribution”. A hybrid process should combine the very high throughput and purity of a PSA process with a membrane separation process which has lower operating costs. As a result a hybrid process is expected to increase the overall H2 recovery without sacrificing its purity. Furthermore, it provides the means for co-producing CO2 stream ready for capture and sequestration.

Based on this concept, the objectives of the project are:

- Optimization of carbon membrane synthesis procedure and production scale-up
- Detailed characterization & generation of transport & adsorption data for adsorbent and membrane materials
- Assessment of the benefits of using layered adsorbents on PSA performance
- Simultaneous design, control and optimization of a hybrid membrane-PSA separation system
- Evaluation of membrane material performance under real operating conditions
- Assembly and testing of a hybrid membrane – PSA separation system.

Large-scale PSA units have reached a mature stage allowing achievement of high H2 recoveries. This is primarily due to the high feed pressure (~30 atm or more) that enables the implementation of complex cycle patterns (i.e. Poly-Bed process, Lofin process, etc). For the same reason, it is also possible to design PSA processes for the co-production of CO2 and H2 (Gemini-9 process developed by Air Products). Current trends in large-scale PSA units are aiming at decreasing cycle times, which requires mechanical devices operating at rapid cycles, as well as adsorbents that are compatible with such cycles. These issues are also important for small-scale PSA units (<500 Nm3/h). Development of such units is extremely important for the implementation of the decentralized “hydrogen economy”. However, these units often have to operate at relatively low feed pressures (<10 atm), and as a result there is less flexibility in modifying the cycle steps and times in order to maintain high H2 purity without sacrificing recovery.

The commonly used PSA adsorbents are in the form of pellets. The perfect adsorbent must have high selectivity and adsorption capacity for CO2 as well as adequate adsorption/desorption kinetics at the operating conditions. In addition, it must exhibit high mechanical strength in order to withstand the repeated cyclic exposure to high pressures. The adsorbent material must be able to maintain its properties after extended periods of operation.
after several adsorption/desorption cycles. During the course of the previous HY2SEPS project the performance of three commercially available adsorbents based on carbon and zeolites was tested. The data indicated that in order to improve the performance of the PSA unit it is important to prepare adsorbent materials with improved adsorption capacity not only for CO2, but for N2 as well. A new adsorbent with enhanced selectivity towards carbon dioxide was prepared from commercial activated carbon extrudates by high temperature activation with carbon dioxide. Development of a new adsorbent with enhanced selectivity towards nitrogen involved ion exchange of a commercial 13X zeolite pellet with calcium, barium and lithium. Although adsorbents in the form of pellets might be appropriate for use in conventional PSA systems, they might not be suitable for use under rapid PSA cycles due to mass transfer limitations in the adsorption step, as well as due to issues related to heat transfer. Decreasing the size of adsorbents is not the solution, because in such a case the pressure drop along the bed might increase prohibitively. Moreover, issues related to bed fluidization might have to be addressed. These problems can be avoided by the use of structured adsorbents. Parameters like working capacity (moles of gas adsorbed/adsorbent unit mass), pressure drop characteristics, mass transfer characteristics and thermal management have to be optimized.

It is of interest to investigate the possibility of using structured adsorbents based on Metal-Organic-Frameworks (MOFs). MOFs are a relatively new class of crystalline porous materials with high diversity comprised of metal ions linked with multifunctional organic ligands. MOFs have the potential for making a significant impact in separation processes because they have large specific surface areas, large pore volumes, tunable pore sizes and functionality for specific applications. An extremely large number of MOF structures have been identified and reported in the literature. Preliminary studies have shown that the MOF Cu-BTC has four times higher working capacity for CO2 adsorption and lower heats of adsorption than zeolite 13X, while the effect of moisture on the stability and adsorptive properties of MOFs has to be clarified.

In the course of the previous HY2SEPS project the performance of FAU and DDR zeolite type membranes was tested. Members of the consortium prepared the FAU membranes, while the DDR membranes were acquired from NGK (Japan). Both membranes were CO2 selective. The FAU membrane performance depends on the presence of humidity, while its synthesis scale-up on long tubes was faced with difficulties. The performance of DDR membranes was not affected by the presence of humidity, but such membranes could not be delivered for building a pilot plant membrane unit. On the other hand, carbon membranes on ceramic tubular supports can be prepared by pyrolysing polymer coated tubes. The permeance and ideal selectivity of these membranes depend on the number of coatings and the pyrolysis temperature. Carbon membranes can act as molecular sieving or selective surface flow materials depending on the mechanism for the gas component separation. In carbon molecular sieve membranes, the pore size distribution and the adsorption capacity, which control the selectivity of gas separation, can be tailored during fabrication by controlling parameters such as the pyrolysis temperature, time, and flow rate of the sweep gas present during pyrolysis.

A hybrid PSA-membrane separation process can be envisaged in several different possible configurations depending on the membrane properties, as well as on the operating conditions.

Configuration #1: Treatment of the feed stream with a H2 selective membrane. In this configuration, the membrane module produces a low-pressure, H2-rich permeate and a CO2, CH4, CO-rich retentate stream at membrane feed pressure. Depending on its composition, the former can be fed to the PSA either
at an intermediate step of a cycle (i.e. purge) or at the adsorption step after recompression. The retentate stream can be used either as fuel, or as captured CO2. Additional capital and operating costs are needed for compressor units.

Configuration #2: Treatment of the feed stream with a CO2 selective membrane. In this configuration the membrane module produces a high-pressure, H2-rich retentate and a CO2, CH4, CO-rich permeate. The retentate can be fed to the PSA unit without the need for additional compression. The permeate can be used either as a fuel or if its composition is within specifications it can be compressed and used as captured CO2. This configuration has the advantage that there is no need for recompressing the retentate in order to feed it to the PSA process.

Configurations #3 & #4: Treatment of the off-gas stream with a H2 or CO2 selective membrane. In this configuration the PSA off-gas is compressed and mixed with the high pressure fraction of the depressurization gas. This configuration minimizes the compression needs before the membrane feed. The H2-rich stream of the membrane module (the retentate for the CO2 selective or permeate for the H2 selective) has to be recompressed and recycled to the PSA feed. These configurations are rather complex and their optimal operation requires the design and possibly control modifications of the PSA unit.

A hybrid unit shows improved performance for the separation of CO2/N2 and CO2/CH4 compared to standalone membrane or PSA units. For a successful implementation of the hybrid process it is necessary to develop cost-competitive membrane materials with appropriate properties for hydrogen-carbon dioxide separation at a scale that can treat the flow rates of the PSA feed or effluent streams.

Project Results:
The technical approach incorporates both materials development and process/system modeling. In terms of material development, the main project activity refers to optimization of procedures for synthesis of carbon membranes on ceramic tubular supports tuned to being either H2 or CO2-selective. The adopted protocols should be easily transferable to scaled-up production. An additional activity refers to the assessment of alternative, newly developed adsorbents for the PSA unit. At the same time, the study of membranes and adsorbents generates transport & adsorption data, which have been used in the course of the project. Mathematical models have been employed in the conceptual design and optimization of a membrane – PSA hybrid system with goal to maximize H2 recovery without sacrificing purity. Dynamic optimization of the overall system has been carried out for selected flowsheet configurations. Design and control issues are considered simultaneously. In the last stage, construction and testing of a membrane-PSA hybrid system at the scale of 1 Nm3 H2 h-1 has been done.
Activities have been organized into four work packages according to the approach presented above. The main S & T results in each work package are described in the following.
Work Package 2 – Carbon membrane material and module design

The purpose of WP 2 is to optimize the carbon membrane synthesis procedure in order to improve permeation flux without sacrificing selectivity and ensure long-term stable performance. The adopted procedure should be applied to multi-channel tubular supports in order to increase the membrane area per support volume. Another objective is to scale-up the carbon membrane synthesis to tubes up to 1 m long from the 0.07 m long laboratory prototypes. The final objective is to design, optimize, and assemble a pilot-scale module. Other activities include the optimization of the design and fabrication of the hybrid systems.
carbon membrane module. Since activities on carbon membrane synthesis did not lead to materials satisfying the application requirements, additional work focused on the study of the performance of resin membranes (before pyrolysis to carbon), as well as of membranes prepared from combination of resins with ionic liquids. This was done according to reviewers’ suggestion based on the mid-term review outcome.

FORTH, in collaboration with CTI, carried out the activities referring to synthesis and testing of carbon membranes on ceramic tubular supports. The focus was on the identification of the simplest procedure possible, since a lengthy, multi-step protocol will render the process unattractive in terms of production cost. The supports had a pore size in the selective layer ranging from 0.8 μm to 15 kD. The membrane synthesis was based on dip-coating of the supports into a furaldehyde-furfuryl alcohol precursor solution followed by curing and pyrolysis in the temperature range of 500-900°C. Several experimental parameters were varied, including the composition of the precursor solution, the presence of solvent, the number of coating cycles and the pyrolysis temperature.

It was found that carbon membranes offering good H2/CH4 and H2/N2 selectivity are possible combined though with low H2/CO2 selectivity. In many cases, produced membranes were actually slightly CO2 selective, which indicates the presence of surface diffusion during permeation of CO2. This translates to a H2/CO2 separation factor during testing of H2/CO2 mixtures, which is lower than the ratio of ideal selectivity. The onset of selectivity requires also a large number of coating/pyrolysis cycles. This means that the preparation of the final carbon membrane is time-consuming with a high production cost.

Because of the aforementioned findings, it was decided to examine the permeation characteristics of the membrane layer prior to pyrolysis and, more specifically, during the curing treatment up to the onset of resin decomposition at temperatures around 300-400°C. It was found that the composition of the precursor solution (furfuryl alcohol/furaldehyde molar ratio) is decisive for the initially impermeable character of the deposited layer. Generally, furfuryl alcohol-furaldehyde mixtures of any composition turn to gel in the presence of acid catalyst, but the time to gelation is a strong function of the composition. Decomposition of the polymer layer starts at around 200°C and the rate of decomposition gets maximized at ~350°C, at which temperature the membrane layer transforms into one presenting Knudsen diffusion characteristics combined in many cases with surface diffusion of CO2 as well as high permeance, albeit smaller than the one of the blank tubular support. This behavior has been observed invariably in a multitude of different tubes. It is understandable that successive coatings will lead to gradual decrease of the pore size and the onset of selectivity due to the function of the microporous carbon layer. Generally, resin membranes are hydrogen selective up to a temperature of around 300°C, i.e. before appreciable decomposition of the resin layer takes place. The highest H2/CO2 selectivity was 65 and there are some examples offering H2/CO2 selectivity in the range 20-50 combined with a H2 permeance below 10-9 mol m-2 s-1 Pa-1. The highest H2/CH4 selectivity, on the other hand, was 125. There are some membranes offering H2/CH4 selectivity in the range 20-120 and there are two examples of membranes combining H2/CH4 selectivity higher than 30 and hydrogen permeance approaching values of the order of 10-8 mol m-2 s-1 Pa-1. Based on these results, it can be concluded that no resin membrane offers selective behavior combined with permeance high enough to be considered attractive for scale-up and pilot testing.

The best membranes were those prepared from solutions rich in furfuryl alcohol. At the same time, the observed separation behavior is on par with the one obtained for a carbon membrane prepared after 14 coating/pyrolysis cycles.

Since resin membranes did not provide the required performance, additional testing was carried out with membranes prepared from combination of furfuryl alcohol-furaldehyde solutions with ionic liquids. The
addition of ionic liquid renders the membranes CO2-selective. The highest CO2/H2 selectivity was ~14 at a CO2 permeance of ~10-9 mol m-2 s-1 Pa-1 and was observed in the case of humidified feeds. The highest CO2 permeance is ~10-8 mol m-2 s-1 Pa-1, but in this case the observed selectivities are lower. The typical CO2/CH4 selectivity values are around 20 and values up to 37 were measured. Although the selectivity of these membranes can be considered adequate, their permeance is quite low for a practical application.

Additional studies were carried out for synthesis of membranes from gluconate salts of sodium and calcium. Gluconate salts decompose with foaming creating carbonaceous sheet structures and it was thought that this could provide selective membranes. Decomposition of sodium gluconate membranes starts at 180-200°C and is almost completed at 400-500°C. There is no major improvement in selectivity during the transition from a gluconate salt layer to a carbon layer. It was found that in the presence of moisture the permeance decreases considerably, presumably due to capillary condensation of water and pore plugging.

Since the membrane development activities did not lead to successful candidates for scale-up and taking into account the limited time frame of the project, a commercial CO2-selective polymeric membrane was selected for application in the pilot unit at HyGear (PermSelect silicone membrane produced by MedArray) according to reviewers’s suggestion following the mid-term project review. This membrane was measured in the form of a small lab-scale module and was found to have a CO2 permeance of 2x10-8 mol m-2 s-1 Pa-1 combined with the following selectivities: CO2/H2 = 5, CO2/CH4 = 3.4 CO2/N2 = 11.6. In comparison, the ionic liquid membrane developed in the project has one order of magnitude lower permeance but a higher CO2/H2 selectivity by 2-3 times.

New ceramic supports incorporating a nanofiltration layer of γ-alumina or zirconia were developed during the project in order to provide a less defective substrate for deposition of the final membrane. It was confirmed that these new types of supports are better suited for development of the final membrane for separation of the reformate gas mixture. Preparation of the zirconia NF tubes was rendered possible by a specific zirconia sol which remains stable for a longer time period. Membrane modules for membrane tubes of a length of 40 cm have been constructed. The design can be adapted for longer tubes, since the module is built of two sections connected to each other through flange connections.

Work Package 3 – New (structured and/or MOF) adsorbents
The purpose of WP 3 is to characterize new adsorbent properties, identify the optimum geometric characteristics of an adsorbent PSA bed with the new adsorbents and finally to evaluate the improvements of H2 purification in PSA units using these new materials.

Task 3.1 refers to characterization & testing of new (structured and/or Metal-Organic-Framework) adsorbents. In order to achieve the goals of this task, three different MOFs (CuBTC, FeBTC and Mil-53(Al)) and an activated carbon monolith were selected for study. These materials were screened based on the adsorption equilibrium of CO2, CO, CH4, N2 and H2 at 303 K. It was found that the best material for CO2 adsorption was shaped CuBTC from KRICT (S. Korea). Regarding the adsorption of N2, the limiting contaminant in H2 product, none of the materials presented a higher adsorption capacity than the zeolite 13X studied in Hy2Seps project. Adsorption equilibrium isotherms of CO2, CO, CH4, N2 and H2 were determined up to a pressure of 7 bar at three different temperatures. The following order of adsorption selectivity was established according to the adsorption selectivity in CO2/CO
adsorption (from the most to the least adsorbed compound) was observed in this sample: CO2 > CO > CH4 > N2 > H2. The equilibrium data were fitted with the Langmuir isotherm. The Zero Length Column (ZLC) technique was used to evaluate the transport kinetics of pure gases on CuBTC (KRICT). It was found that diffusivity was too fast and that the transport parameters could not be determined by ZLC.

The purpose of Task 3.2 was to develop a complete mathematical model for the simulation of the dynamic behavior of an adsorption column and of PSA processes. The mathematical model, that incorporates both the equilibrium and kinetic data, was developed and implemented in gPROMS (PSE Enterprise, UK). The validation of the model was done, at a first stage, against experimental binary and ternary breakthrough curves (obtained in Task 3.3).

The objective of Task 3.3 was to evaluate the performance of the selected adsorbent material in both fixed-bed operation and PSA process at lab-scale. This task started with the measurement of breakthrough curves using CuBTC (KRICT). Tests at 303 K and a pressure of 2 bar for CO2-He, CO2-H2, CO2-H2-CH4, CO2-H2-N2, CO2-H2-CO mixtures were performed. At the beginning of each experiment, the column, initially saturated with He or H2, started to be fed with the feed mixture. After saturation of the column with each feed stream, the inlet stream was changed at starting time of desorption either to helium or hydrogen at the same total flow rate, starting a desorption step. During the adsorption and desorption steps, the temperature histories and the molar flow rate were registered. Additionally, samples were collected for subsequent determination of the molar composition of the exit gas in the gas chromatograph. PSA tests were performed using a four steps cycle: cocurrent pressurization with feed; feed; countercurrent blowdown and countercurrent purge with hydrogen. A temperature of 303 K, a high pressure of 3.5 bar and a low pressure of 1 bar were employed. Different feed mixtures were used. At the beginning of each PSA experiment the column was filled with hydrogen.

A complete mathematical model that describes the dynamic behavior of multicomponent adsorption in a fixed bed, composed of material, momentum and energy balances, was developed. The model consists of a set of non-linear partial differential equations in time and space. Appropriate boundary and initial conditions were defined in order to simulate both fixed-bed and PSA operations. The model was implemented in gProms and solved using orthogonal collocation in finite elements as the numerical method. All the experimental tests performed (breakthrough and PSA) were simulated using this model. A good prediction is obtained from the model, which is therefore validated.

PSE used the mathematical model described above to validate the model implemented in a complex simulation program that represents the flow sheet of the HyGear set-up. UPORTO reviewed the flow sheet program and transferred to PSE necessary input data for the simulation of the HyGear tests, namely adsorption equilibrium and transport parameters values. Furthermore, the mathematical model developed in WP3 was used to simulate more complex PSA cycles not feasible in the lab-scale unit. These simulations were performed using the data for the CuBTC spheres from KRICT.

The simulation of a 6 step four-column PSA process was carried out. The column dimensions considered were 44.5 cm in length and 7.2 cm in diameter which correspond to the dimensions of the columns in HyGear’s set-up. The feed composition was also taken from data provided by HyGear corresponding to reformate gas from a methane steam reformer. The operating parameters, namely flow rates and steps duration, were optimized in order to obtain a H2 product with purity above 99.99+%, maximizing the hydrogen recovery. The best result was obtained for a feed flow rate of 12.3 SLPM, a purge flow rate of 1.68 SLPM, a feed and purge duration of 110 s, a pressurization and blowdown duration of 60 s and a pressure equalization duration of 50 s. A hydrogen purity and recovery of 99.995% and 32.2%, respectively, were obtained with an adsorbent productivity of 2.17 molH2/kg/h. It was found that nitrogen
is the limiting contaminant; it reaches the end of the bed while the other impurities are still well within the bed. The results showed that the recovery of the PSA process using CuBTC as adsorbent was very low. This is due to the very low adsorption capacity of CuBTC for N2. Although this material has adsorption capacity for CO2 approximately double that of the currently used activated carbons, it has a lower capacity for N2 which turned out to be very unfavourable for the hydrogen purification process under consideration. Since the use of a single adsorbent bed with CuBTC resulted in very low process recoveries, the use of CuBTC was further investigated by simulations of layered bed processes. Beds with an initial layer of CuBTC and a second layer of zeolite were considered. The data of the zeolite material studied in project Hy2Seps were used. A second layer of zeolite is used because this adsorbent has enhanced capacity for N2. A mathematical model that represents the layered bed was implemented in gPROMS. Simulations with the same 6-step cycle as described above were performed. Once again, the operating parameters, namely flow rates and steps durations, were optimized in order to obtain a H2 product with purity above 99.99+%, maximizing the hydrogen recovery. The best result was obtained for a feed flow rate of 11.8 SLPM, a purge flow rate of 1.60 SLPM, a length of CuBTC of 20 cm, a feed and purge duration of 210 s, a pressurization and blowdown duration of 115 s and a pressure equalization duration of 95 s. A hydrogen purity and recovery of 99.992% and 65.3% respectively were obtained with an adsorbent productivity of 4.22 molH2/kg/h. This result shows that the process recovery doubles when compared to the results obtained with the single CuBTC bed.

The final assessment of the selected adsorbent material has to take into account its production cost, which appears to be rather high compared to existing adsorbents.

Work Package 4 – Model-based design of hybrid membrane separation system

The objectives of Work Package 4 refer to the conceptual design and optimization of a membrane-PSA hybrid system for maximization of H2 recovery, the design of state-of-the-art controller for the optimal hybrid separation system and the evaluation of the possibility of H2 and CO2 co-production using hybrid membrane-PSA systems. The designed mathematical model of the membrane consists of three different subsystems i) the tube side, ii) the shell side and iii) the membrane and includes mass, energy and momentum balances as well as, dynamic representation of the thermo-physical properties of the system. In the developed model, optimization and simulation studies were performed to identify the optimal design of the membrane module (number of tubes, pressure drop, membrane length and diameter).

PSE developed a dynamic mathematical model for the membrane module based on the design provided by CTI. The developed model was based on mass, energy and momentum balances as well as, dynamic representation of the thermo-physical properties of the system. Moreover, the model includes the option for steady state simulation, which is ideal for optimization studies, and dynamic simulation which has been used for experimental validation of the model. Moreover, the limitation of the process was included for the maximum pressure drop difference between the tube and shell side for the unit located at Hygear.

Simulation and optimization studies were performed to investigate the optimal configuration of the membrane in order to achieve the desired hydrogen production (1Nm3/h). The results showed that a feasible configuration of the system, with low pressure difference, can be achieved only for the case of multichannel tubular supports (7 channels) and with maximum length of the tubes (1178 mm). For the case of a single-channel tube, a compressor should be considered in the inlet or outlet stream of the membrane in order to achieve high levels of hydrogen recovery.

Subsequent activities in WP 4 focused on the design and control strategy of hybrid membrane-PSA systems given the developments for gPROMS in the field of hybrid membrane. The overall objective is to design and develop a control system for the hybrid membrane-PSA system that maximizes the performance and efficiency of the system while ensuring safety and reliability. The control system should be able to adapt to different operating conditions and optimize the performance of the system in real-time.

The control system should integrate various sensors and actuators to monitor and control the process parameters, such as pressure, flow rate, temperature, and composition, to ensure optimal operation. The control system should be able to detect and respond to deviations from the desired operating conditions, and adjust the process parameters accordingly. The control strategy should be designed to minimize energy consumption and maximize process efficiency.

The control system should be capable of adapting to changes in the feed composition, throughput, and other operating conditions. The control parameters should be optimized based on the real-time data collected from the sensors. The control system should be able to handle disturbances and provide robust and reliable control of the process.

In addition, the control system should be designed to ensure safety and reliability of the system. The control system should be able to detect and respond to potential safety hazards, such as excessive pressure or temperature, and initiate appropriate actions to prevent accidents. The control system should also be able to handle failures and degraded components, and provide uninterrupted operation of the system.

The development of the control system requires a multidisciplinary approach involving expertise in process control, systems engineering, and membrane technology. The control system should be designed to ensure the safe and efficient operation of the hybrid membrane-PSA system, while maximizing the performance and minimizing the energy consumption.
separation systems and on the development of a gPROMS toolkit for optimisation of hybrid separation systems. The process model was developed for the experimental PSA system for hydrogen purification built by HYGEAR and it also accommodates a hybrid membrane-PSA system based on a combination of the standalone experimental PSA system built by HYGEAR and an appropriate membrane. The models are developed in PSE’s gPROMS ModelBuilder and are based on the hybrid separation system toolkit. This makes them easily reconfigurable: simulations which consider modifications of the system flowsheet, the use of different adsorbents and membrane and changes in the operating schedule can be done with limited effort. The model includes all of these design parameters in its description of the process. The approach followed was first to develop a standalone PSA-system model that matches the HYGEAR PSA system. Subsequently, a membrane model was coupled to this PSA system, a control system was designed and the resulting hybrid configuration was simulated. At that stage, some further clarifications were obtained from HYGEAR regarding the details of the experimental setup, following which the standalone PSA-system model was modified accordingly.

The 4-bed PSA process of HYGEAR has been modelled in gPROMS using the toolkit developed during the project. The mass flow controllers (MCV) supplying each pure component to the mixer have been modelled as a single process material source for the mixed feed (hydrogen, methane, CO, CO2, N2). To achieve the specified volumetric flowrate in the model, a valve with a control system has been modelled. The mixed feed is supplied to a buffer which represents the holdups in the piping system. From the buffer, the feed can flow to each of the beds. This flow is controlled by a single valve for each bed, for which the “Valve” model from the toolkit is used. The purge of the bed is done through a purge valve, and the purge streams from all the beds are merged into a common holdup. On the product side, each bed produces through a product valve which is modelled as a controlled proportional valve. The product flow from each bed is merged into a product storage vessel which is controlled at 7.5 bara. From this product vessel, the product can flow to a large storage tank which is maintained at 1 bara.

The operation of the PSA process was simulated over 158 cycles of total duration of 3h 52 minutes, in order to arrive close to a cyclic-steady state. The cycle time parameter, T_CYCLE, was set at 22 s. The final hydrogen purity achieved was 99.82 mol%, which corresponds to a value of 2.74 on the purity log scale (-log10(1 - mol% H2/100)). Comparing the experimental result at an adsorption time of 22s, a log transformed purity of around 6.15 with the simulation result, a log transformed purity of 2.74 there is a gap between the purity achieved in the experiments and that predicted by the model. Possible reasons for this could be the measurement errors associated with flowrates supplied to the PSA beds in the experiments. The HYGEAR experiments did not measure the composition of the purge gas, and therefore the mass balance for the experiments could not be closed. Another possibility is the numerical dispersion, since the beds were run using an orthogonal collocation-based discretisation of the spatial variations with 20 collocation points. This might have been inadequate for the purity achieved.

Modelling and simulation of the hybrid system was also performed. The hybrid separation flowsheet consists of a membrane followed by the PSA system. The membrane is hydrogen selective; consequently, the permeate of the membrane flows to a buffer and then is compressed to the desired PSA system operating pressure.

To facilitate studies involving different configurations and different materials/adsorbents, a modelling toolkit is required that allows rapid design, configuration and optimisation of hybrid separation systems. The
hybrid separation toolkit contains the component models used to construct the flowsheets together with a number of models that have been added or improved upon to enhance usability and to fulfil functional specifications. The toolkit is implemented in gPROMS ModelBuilder 4.0.0 in a manner which allows its interfacing to other general process equipment models included with gPROMS ModelBuilder 4.0.0. The toolkit meets the functional requirements and allows the construction of flowsheets for hybrid separation systems in just a few hours purely by using drag-and-drop flowsheet and dialog configuration. This toolkit has been used in the context of the project. The main limitations of the current toolkit are in two areas. The first is related to the modelling assumptions used in developing the main component models:

- no radial flow distribution taken into account in the adsorption bed
- intra-pore mass transfer and boundary layer-mass transfer modelled using a single mass transfer coefficient
- a simplified permeability relation in the membrane,
- no detailed modelling of the geometry of certain types of membranes.

Future developments may relax or altogether remove some of these assumptions.

Secondly, there are limitations with respect to the optimisation strategies that can be applied to the process. The gPROMS built-in optimisation functionality permits gradient-based optimisation of a user-defined optimisation criterion for general dynamic simulations. However, there are currently no purpose-built optimisation algorithms for processes, such as PSA, operating at cyclic steady states.

Work Package 5 – Construction & testing of prototype hybrid separation system

The objectives of Work Package 5 refer to the construction of the membrane module as well as the construction and operation of the membrane – PSA hybrid system. Additionally, the hybrid separation system has been evaluated from an industrial point of view.

The construction of the PSA part of the hybrid separation system used as a basis the PSA system from the preceding project Hy2Sebs, which was revamped to meet current requirements. New valves were mounted into the PSA to provide the suitable flows for the production of 1 Nm3/h of hydrogen. The control of the PSA unit was revised based on results from Task 4.4 of WP 4 (Design the control of the hybrid separation system).

Since a membrane with the target specifications could not be developed during the project, the project reviewers (mid-term review meeting) advised the project consortium to test a commercially available membrane module to approve the viability of a hybrid separation system. Thus, HyGear did a search on potential suppliers of membrane modules that can be used for the hybrid membrane-PSA separation process. Three potential suppliers were identified, among which only the PermSelect membrane module from MedArray could be procured, since modules from other suppliers were too large for the purpose of the project (capacity of 40 Nm3/h compared to desired capacity of 1 Nm3/h of hydrogen). With respect to the short project duration, the MedArray system was chosen to be the one tested at HyGear’s facilities in Arnhem.

The membrane module was tested in first instance as separate unit before connecting it to the pressure swing adsorption system. The tests on the membrane module were carried out applying different transmembrane pressures (TMP). The highest TMP resulted in the highest hydrogen yield (97%). Since the maximum allowable pressures of the membrane module were too low (and there was no suitable compressor available), it was impossible to connect the membrane to the PSA and thus to setup the hybrid separation system. The construction and testing of the PSA with the membrane module failed.
hybrid separation system. Therefore, it was decided to feed the PSA with simulated gas, corresponding to the flow and composition of the permeate of the membrane experiments. This should have no influence on the performance of the hybrid system, since the operation of the PSA does not affect the operation of the membrane. The composition of the synthetic feed gas was: 75.2% H2, 3.3% N2, 3.3% CH4, 2.6% CO and 15.6% CO2.

For the comparison of performance, test results on the standalone PSA as well as on simulated hybrid test were taken. Comparison of the yield vs. purity curves for the standalone PSA and Hybrid tests showed that the hybrid system has a better performance than the standalone PSA and an increase of up to 4% in H2 yield can be achieved at a hydrogen purity of 5.0. The results also indicate that combining a membrane separation module with a PSA unit will lead to an increased adsorption time of the PSA of 8%. This is important for the PSA operation itself. An increased adsorption time means an extended lifetime for the employed valves, that have to switch between the different adsorption steps and thus connecting different adsorbers to each other, due to the decreased time to switch. However, predicting the lifetime of the valves is not possible as the lifetime of the valves depends also on other variables, e.g. dust-free gas or reliable solenoids to operate the valves. The most important result is that the hydrogen yield of the overall system can be increased by 4%.

It can be concluded that although the employed membrane was far from optimal, the hybrid system was found capable of increasing the overall H2 yield and adsorption time, without sacrificing the purity. The question is, however, whether these cost reductions outweigh the additional costs of the membrane and compressor.

The evaluation from an industrial point of view was performed on the basis of an existing hydrogen generation system (HGS) of HyGear. The assessment was done identifying the capital expenditure costs (CAPEX) of the HGS and the resulting operation and maintenance expenditures (OPEX). The economic evaluation also considered the auxiliary costs that occur during the operation of such unit. Finally, the hydrogen production costs per kilogram were considered.

The capital or investment cost of the hydrogen generation system is comprised of the hydrogen generation system itself, the hydrogen booster (compressor) to fill the hydrogen storage, the hydrogen storage unit, the piping and controls for the installation and operation at the customer site and the hourly operator costs. It was assumed that the machine is operated for ten years, the interest on the investment is 6% and the operation and maintenance cost will account for 5% of the CAPEX.

The CAPEX and OPEX costs for the hybrid enhanced hydrogen generation system are different. The reason for this is that a membrane separation module is applied to the system. As the membrane separation module delivers the permeate gas at lower pressures than demanded for the PSA inlet, an additional compressor is required. The compressor will be at the same cost level than the compressor for filling the hydrogen storage. Compressors that have to compress gas mixtures are in general more expensive than pure gas compressors. Mainly the sealing of these types of compressors/boosters increase the price, especially if ATEX standards are applied (the case in the present assessment). This added to the lower prices of gas boosters compared to compressors results in same cost levels. One uncertainty in the calculations for the hybrid hydrogen generation system is related to the cost of the membrane separation module for the production of 50 Nm3/h of hydrogen. Assuming a membrane cost of € 50.000 for a capacity of 50 Nm3/h of hydrogen, it turns out that due to the higher CAPEX and cost of the hybrid system the annual OPEX cost and thus the OPEX costs per kg of produced hydrogen are 13% higher than for the state-of-the-art HGS.

The calculation of the costs per kg of hydrogen of both examined systems takes into account the fuel costs and the costs for the CAPEX and OPEX as well as the operation and maintenance costs. The calculation shows that the hybrid system has a better performance than the standalone PSA and can achieve an increase of up to 4% in H2 yield at a purity of 5.0. However, the additional costs of the membrane and compressor need to be considered. The question is whether these cost reductions outweigh the additional costs of the membrane and compressor.
per kg, the electricity costs per kg to operate the systems, the CAPEX costs per kg and the OPEX costs per kg. The result of the above calculation shows that the specific hydrogen costs for the hybrid enhanced hydrogen generation system are only 9% higher than for the state-of-the-art hydrogen generation system.

Potential Impact:
The project topic is within the field of “Hydrogen Production & Distribution” with a goal to develop separation and purification processes suitable for producing hydrogen at a purity to match the applications of interest (i.e. Transport, Stationary and Early Markets requirements) and with lower purification cost focusing on small-scale hydrogen production systems. The envisaged cost decrease stems from the enhancement of hydrogen recovery in the hybrid membrane-PSA unit. The improved hydrogen recovery of a hybrid system has been demonstrated in the project, but the membrane performance does not still meet the performance targets to fully exploit the potential of the hybrid system. Since incorporation of the membrane module in the hydrogen purification PSA unit does lead to an increase in the CAPEX cost of the system, the production cost of the membrane has to be kept low and should be a minor fraction of the total CAPEX cost. For example, if the membrane unit corresponds to 10% of the total CAPEX cost, it should lead to enhancement of hydrogen recovery by more than 10% to be considered attractive.

The project impact is mainly on the following application areas:

- Hydrogen production: The development of an improved H2 purification system is expected to improve the economics of H2 production at all scales. H2 production from hydrocarbons (mainly natural gas, but also diesel and biofuels) can be considered as an intermediate step before moving into production from renewable sources via electrolysis. By improving the economics of H2 production it will also assist in developing the necessary procedures and infrastructure for H2 storage and distribution.
- Stationary & portable applications. Such applications range between 5kW and 100 kW which are within the production range of the project target. Stationary applications are important for the early market opportunities they provide, since they are not dependent on a hydrogen infrastructure.

An improved hybrid membrane-PSA CO2/H2 separation process can also provide a way to produce a sequestration-ready CO2 stream, thus reducing the amount of CO2 released in the atmosphere in the H2 production. This will be one additional step towards reducing greenhouse gas emissions.

The use of fuel cell powered cars can be one of the solutions to reduce the energy dependence of the transport sector on fossil fuels and subsequent CO2 emissions. The most common view on hydrogen infrastructure implementation refers to small refueling stations. When refilling demand increases, the size and number of tank stations will increase as well. During this period of roll-out the amount of hydrogen per tank station will be too much to be trucked-in and the energy losses and CO2 emissions to distribute hydrogen by truck will become too high due to the difficult transport logistics. A cost effective on-site hydrogen generator is important element of the needed hydrogen infrastructure for fuel-cell cars. On-site hydrogen generator systems can be also used in various other markets in the field of small-scale hydrogen supply for industrial use where cylinders or tube-trailers of hydrogen are used currently. The costs of the hydrogen produced by on-site reforming are lower due to fuel and energy savings. Near term markets include metal fabrication, glass manufacturing, hydrogenation of fats and generator cooling of power plants.

Membrane development for separation of hydrogen from reformate streams at ambient conditions remains the subject of many R&D activities. The introduction of the membrane technology into a PSA application offers several advantages compared to the conventional PSA processes. Improved efficiency and lower CAPEX cost lead to a reduction in the overall production cost of hydrogen. The membrane technology also reduces the energy demand of the process, which can further contribute to a reduction in CO2 emissions.
the bottleneck for successful application of the hybrid membrane-PSA separation system. The improved performance of the hybrid system was indicated even with the employment of a commercial membrane with far less than optimal characteristics. It is understandable, therefore, that the full potential of the hybrid system can be obtained with the use of the appropriate membrane, which for the time being is not available. Pursuing further the hybrid system should rely on R&D activities related to membrane material development and scale up. The PSA part of the hybrid system can be considered as relatively mature and an extensive experience on its control and operation has been acquired during the course of the project.

List of Websites:
http://hy2seps2.iceht.forth.gr/

**Last update:** 12 August 2015
**Record number:** 169285