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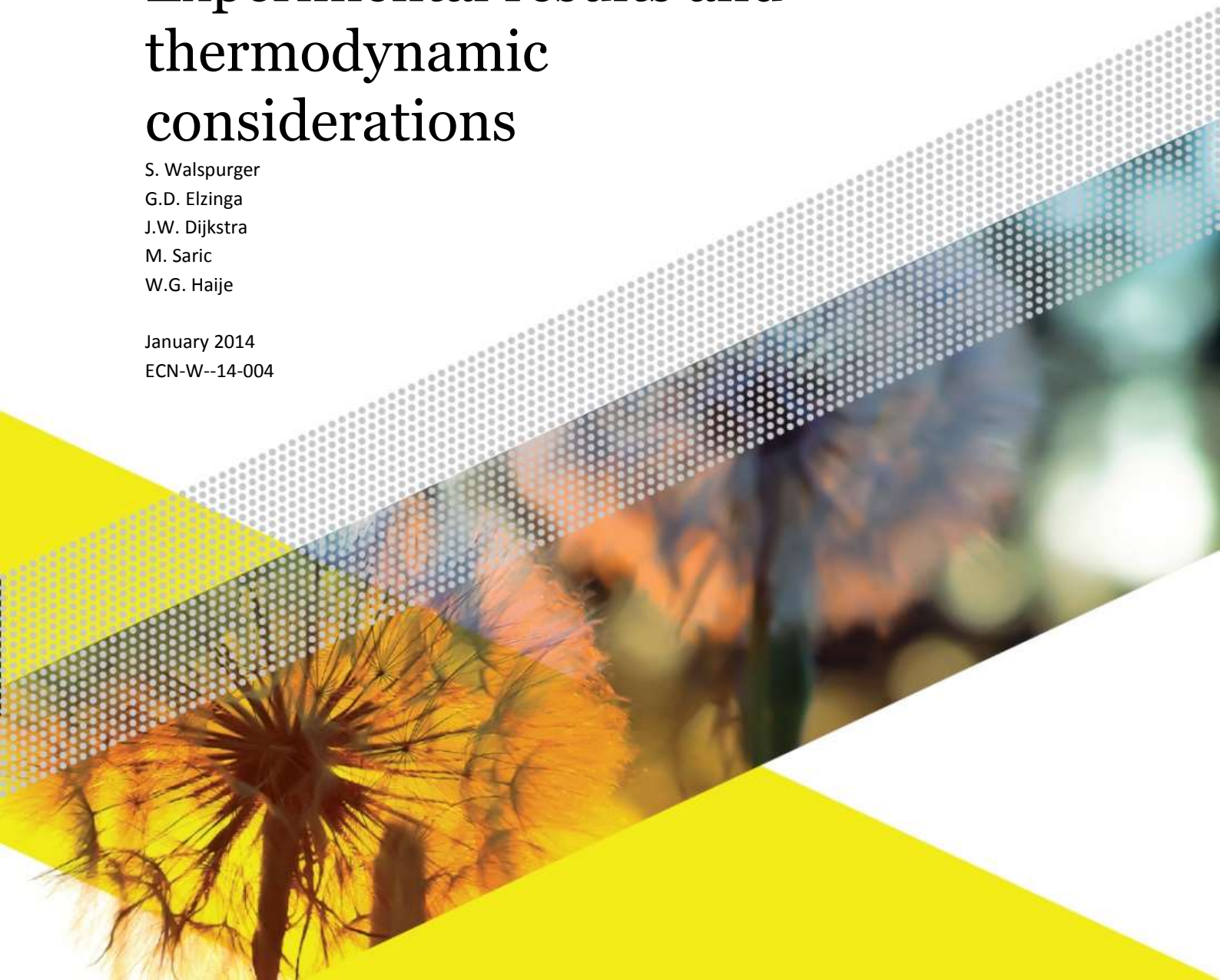

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Sorption enhanced methanation for substitute natural gas production: Experimental results and thermodynamic considerations

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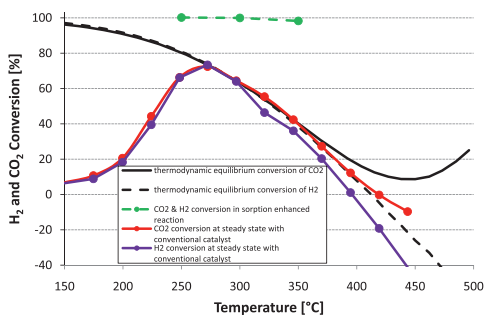
HIGHLIGHTS

- High grade SNG production at methanation pressure below 10 bar.
- Sorption enhanced methanation process saves up to 40% compression duty.
- Commercial Nickel based catalyst and zeolite 4A yield 100% CH_4 between 250 and 350 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

The Sabatier process may become a ubiquitous process for the production of renewable substitute natural gas from biomass or from any CO_2 source coupled with renewable hydrogen. While a conventional Sabatier process typically requires cascade reactors and high operational pressure, i.e. 40–60 bars at least, to yield an SNG product matching the specification for injection in the natural gas infrastructure, the sorption enhanced Sabatier reaction has the potential of producing high grade methane product at operational pressures below 10 bar. The energy duty for compression work may then decrease from 10% to 6% of the total process energy balance, in the case where reactants are supplied at atmospheric pressure. The sorption enhanced methanation was demonstrated at atmospheric pressure with commercial Nickel based catalyst and zeolite 4A adsorbent between 250 and 350 °C reaching close to 100% conversion.
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1. Introduction

Nowadays the economical and societal development relies heavily on fossil fuels in both developed and developing countries. A major drawback of this development pattern is the accumulation of an enormous quantity (400 ppm) of the greenhouse gas CO_2 in the atmosphere that has a significant role in climate change. Furthermore the amount of affordable fossil fuels is finite and conventional oil and gas resources are rapidly being depleted. However with the increasing penetration of solar and wind technologies for electricity generation, the production of renewable fuels becomes an attractive option to recycle CO_2 while decreasing the global CO_2 emissions and becomes an economically viable alternative to ever more costly unconventional fossil fuels [1–3]. Methanol, Hydrogen, Methane, Formic Acid, Ammonia may all fulfil the criteria of renewable fuel. While methanol has many advantages concerning transport and storage as a liquid fuel and the possibility of direct conversion to base chemicals via the methanol to olefin route [4], hydrogen which is the carbon neutral fuel *par excellence* cannot be conveniently and cheaply transported and stored for further use. Methane is an outstanding renewable fuel, being a hydrogen-rich energy carrier with a relatively high energy density compared to hydrogen. Remarkably, renewable methane

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generated by biomass fermentation, also called biogas or biomethane, has been introduced in many countries as a primary energy resource for the generation of heat and power or for direct injection in gas grids for the distribution of energy to industrial or private end users. Furthermore the use of renewable methane benefits from a relatively large public acceptance and benefits from the transmission, distribution and storage infrastructure that has been continuously improved for the use of natural gas for many decades [5]. Of particular interest, natural gas storage is currently used for the seasonal and strategic storage of primary energy and has sufficient discharge time and capacity to provide a reliable secured renewable fuel supply. With the soaring production of gas from tight gas and shale gas reservoirs, and the development of liquified natural gas (LNG) large facilities, the globalized gas transport infrastructure will be undoubtedly a key platform in the transition towards the use of a fully sustainable energy mix [6].

The conversion of renewable power to renewable methane enables connecting the existing power grid and natural gas grid thereby allowing for adjusted storage of significant amounts of power and providing CO_2-neutral fuels using the natural gas grid and associated infrastructure as a storage facility [7]. For instance using the excess renewable electricity available from the large capacity renewable technologies for H_2 production via the electrolysis of water and subsequent reduction of captured CO_2 in a methanation or Sabatier process offers a method of converting the excess electricity into renewable methane.

In this perspective, the catalytic conversion of CO_2 and H_2 to methane that has been discovered in the early 20th century by Sabatier and Senderens [8], is of great interest. The formation of methane is a very exothermic process favoured at low temperature and high pressure by the following thermodynamic equilibrium:

$$CO_2 + 4H_2 \Longleftrightarrow CH_4 + 2H_2O \quad \Delta H_{298} = -165\,\text{kJ/mol}$$

Commercial catalytic materials usually operate preferably between 250 and 450 °C, up to 600 °C for the most robust generation, and were developed for the substitute natural gas (SNG) synthesis from heavy feedstock, coal or biomass [9]. The conventional process uses a cascade of adiabatic reactors with intermediate cooling steps and recycles [10] to reach sufficiently high methane purity in the SNG product in order to allow for injection in the natural gas grid that has tight compositional specifications. In the methanation process, it is important to recover and use the heat released by the methanation reaction smartly since it represents about 20% of the energy provided to the system.

In this work, the sorption enhanced methanation reaction concept based on the Le Chatelier principle and already applied in other thermodynamic equilibrium based reactions [11–16] is studied both to improve the use of excess heat provided by the methanation reaction and to reach high SNG grade, possibly at lower operational pressure. Accordingly, the steam generated by the methanation reaction is removed from the gas phase in the catalytic bed by adding a sorbent material to the catalyst or more conveniently by designing a catalyst with adsorbent functionality [17]. This dehydration of the SNG product is thus carried out simultaneously with the methanation reaction in a regenerative process that uses heat to desorb the water from the sorbent material. The strategy for the regeneration of the sorbent may be designed based on the materials properties (steam capacity, adsorption energy) and consists of temperature swing and/or pressure swing with or without purge gas, in circulating bed or fixed bed reactors.

In the first part of this contribution the detailed discussion of the analysis of the thermodynamics shows to what extent higher methane quality may be reached by implementing the sorption enhanced process, as well as the limits of the process. In the second part of this paper experimental work provides a proof of concept of the sorption enhanced methanation process that may be used as a ubiquitous SNG upgrading process for the production of renewable methane and SNG from biomass. While the thorough study of the process design remains out of the scope of the present article, the plausible regenerative conditions are discussed in the last section.

2. Materials and methods

The thermodynamic modelling of the methanation process by conversion of H_2 and CO_2 was developed in the flow-sheeting tool ASPEN Plus to identify the feed characteristics and the target performance of the methanation reactor(s). A basis of design study gave the starting points of modelling and the battery limit conditions. The CO_2 stream considered for the simulation had a purity of 100% and was available at 1.6 bar and 40 °C, which are typically the specifications found in CO_2 captured in industrial process using amine absorption, that is further used in food industry for example. The hydrogen produced by an electrolysis process had a purity of 100% and was delivered at 1 bar and 40 °C to the methanation system. The lay-out of the methanation section is depicted in Fig. 1. It consisted of three methanation reactors (R1, R2, R3) with a recycle from the second to the first reactor. Intermediate cooling with water knock-out was considered for removing the heat generated by the exothermic reaction. The amount of recycle was determined by an iterative process aimed at limiting the temperature rise below the recommended maximum operating temperature by the catalyst vendors in the first methanation reactor. The recycle ratio remained between 0.7 and 0.8, and are comparable values to the ones described for the Lurgi and Haldor Topsoe's TREMP (Topsoe's Recycle Methanation Process) processes [9,18]. In the feed lines as well as in the product line a compressor was present to achieve the desired pressure (not depicted). The objective was to obtain directly downstream the methanation section SNG of sufficient quality for feeding in the Groningen gas grid with the following specifications: $CO_2 < 3\%$, $H_2 < 0.5\%$, $CO < 0.5\%$, $H_2O < 90$ ppm (Dew point at −10 °C), SNG pressure of 60 bar.

The conversion in the methanation reactors were modelled using the Gibbs minimisation. The methanation reactors' operational temperature ranges were defined based on two different types of commercial catalysts used for methanation. The maximum temperature of all 3 reactors is 650 °C, inlet temperatures of methanation reactor R1, R2 and R3 were 300, 250 and 220 °C respectively. Because of the pressure difference between the feed and the final product on specification, the operating pressure of

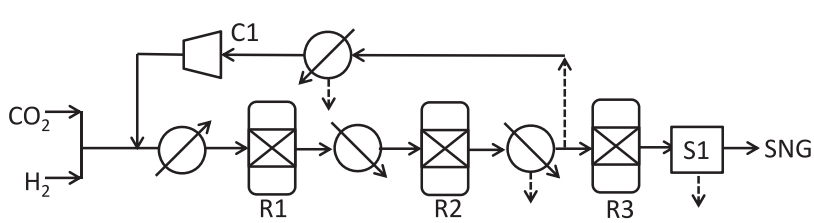

Fig. 1. Methanation process configuration with 3 reactors (R1, R2, R3) in series with recycle, intercoolers with water knock-out and drying S1.

the process has been considered as a variable in a sensitivity study up to the grid pressure of 60 bar. In the methanation process a lot of water must be removed to match the SNG specifications for grid injection. Some water may be also removed by the intermediate cooling/water knock-out stages between the methanation reactors. A compressor was used in the recycle loop and was simulated with an isentropic efficiency of 0.85. A cooling step to 150 °C was added upstream the compressor for operation within the required temperature range. Any water that was condensed at this temperature was removed by knock-out. The final water removal S1 was first simulated as a separate glycol dehydration unit downstream the methanation for the conventional methanation case modelling.

Most of the conversion takes place in the first section of the methanation process resulting in a temperature rise in the first and second methanation reactors that approaches the limits that the catalyst may withstand. It is thus reasonable to implement a sorption enhanced process in place of the third reactor, that is used mostly to enhance the conversion such that tight product specifications may be matched. Therefore for a simple modelling of the influence of in situ water removal, the reactor R3 was considered either as a conventional reactor or as a sorption enhanced reactor. In the case of conventional reactor, R3 was modelled by a single Gibbs minimisation reactor. In contrast, when considering the sorption-enhanced methanation process case, the dehydration reaction step was combined with the reaction in which water was removed simultaneously with the reaction. The outlet of the third reactor in sorption enhanced case was assumed to be at chemical equilibrium, given that a pre-specified amount of water was taken up by the sorbent. Therefore a 3-step construct model was used to simulate the reactor R3. First a stoichiometric reactor with quantitative conversion of H_2 to H_2O was implemented, followed by removal of a pre-specified amount of H_2O, and finally a Gibbs minimisation reactor was implemented to calculate the equilibrium composition corresponding to the remaining water. The pre-defined amount of H_2O removed by the sorbent was set to 99.5% of the water as present in the feed and produced by full conversion of all H_2 in the feed.

A proprietary nickel based catalyst kindly supplied by CRI/Criterion Catalyst Company, Ltd. was used for the experimental study. Note that this catalyst was not specifically designed for CO_2 hydrogenation. Prior to the experiments, the catalyst was pre-treated with 10% H_2 in N_2 (total flow 100 ml/min) from 25 to 250 °C during 2 h. In the conventional methanation reaction, the catalyst bed was homogeneously diluted with alpha alumina AKP-15 (supplied by Sumitomo Chemicals) mimicking the dilution conditions of the sorption enhanced experiment (i.e. diluted by sorbent).

Both catalyst and alpha alumina (mass ratio 1:2.7) were introduced as pellets with 212–425 μm diameter, to avoid excessive pressure drop and meet the conditions for plug flow regime. The experiments were performed on a fully automated test-rig designed for catalyst and sorption research purposes. The controlling system consisted of a pool of calibrated Bronkhorst mass flow controllers, including a liquid flow controller and a CEM unit for humidification of the gas stream together with two 3-way solenoid valves that were used either to direct the feed gas over the reactor or to by-pass it. Wizcon software was used to control all flows, temperatures and valve positions while programming was made to perform successive cyclic experiments. A quartz electrically heated oven was used in which a quartz reactor (ID: 10 mm) was placed. Several type-K thermocouples with Eurotherm controllers were positioned in close proximity to the sorbent/catalyst bed to control and monitor the temperature of the bed. The reaction products were analysed online using two complementary detection methods: CO_2 and water were analysed by IR Infrared detector (Midac FTIR I1803) while CO_2, H_2, CH_4 and N_2 concentrations were measured by gas chromatography on a Hewlett Packard M200H double channel micro-GC (Poraplot Q and molecular sieves 5A stationary phases). Before injection into the gas chromatograph, the stream was dried by a Permapure MD-series gas dryer system. For the catalytic activity test, the total feed was 150 ml/min flow, consisting of 2.5% CO_2, 9.9% H_2, 81.7% CH_4 and 5.9% N_2.

For the adsorption tests zeolite 4A (Merck) was tested in cyclic adsorption/desorption. Zeolite materials are indeed capable of taking very low partial pressure of steam with substantial uptake capacity at temperature of 200 °C and higher [13,19,20]. The adsorption experiments were carried out at 200, 250 and 300 °C with a feed composition of 3.9% H_2O, 33.3% CH_4 and 62.8% N_2 with a flow of 150 ml/min. The sorbent was regenerated with a flow of dry nitrogen at 350, 400 or 450 °C respectively, during 1 h. About 1 g of sieved material was used in these experiments.

Finally the sorption enhanced methanation reaction was tested at 250, 300 and 350 °C with various regeneration temperature. The sample consisted of a mix of the Ni-based catalyst and zeolite 4A of sieve fraction with a particle diameter of 212–425 μm. It contained 5 times more zeolite than catalyst in mass.

The same inlet flow rate (identical dry feed composition) was used for the sorption enhanced methanation experiments as well as for the conventional methanation experiments. Also, the same amount of catalyst was used. The amount of sorbent needed was chosen considering the time of sorption needed (at least 5 min) considering full conversion. The regeneration was carried out at increased temperature with a flow of 150 ml/min containing 90% nitrogen and 10% hydrogen until full desorption.

3. Results

The current gas transport infrastructure is not designed for accommodating large amount of hydrogen next to methane and the other components of natural gas such as CO_2, N_2 and low amounts of higher hydrocarbons. In The Netherlands for instance, the natural gas grid specifications currently allow only for very low hydrogen content (up to 0.5%), which makes the methanation or Sabatier process a ubiquitous process to be used in biomass gasification producer gas upgrade to SNG or any process based on the CO_2 methanation with renewable hydrogen. However, the thermodynamics of the exothermic Sabatier reaction favour the complete conversion of hydrogen to methane at high operating pressure and low process temperature only. Fig. 2 discloses the theoretical hydrogen concentration in the dry product stream at the outlet of the methanation section, upstream the final water removal, as a function of the operational pressure, when the 3-reactor process

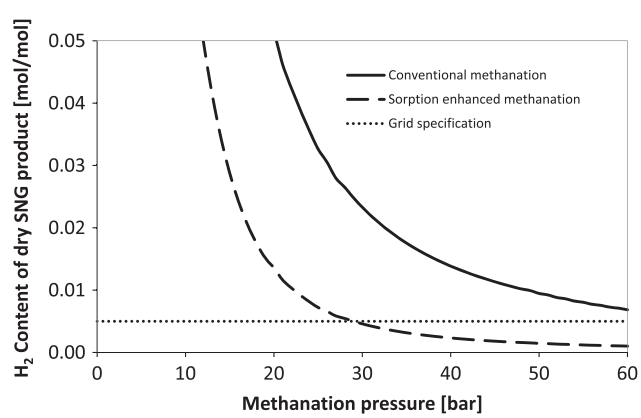

Fig. 2. H_2 level in SNG produced for the conventional methanation case (3-reactor configuration) and for the sorption enhanced methanation case (sorption enhanced process in place of the 3rd reactor). The horizontal dotted line represents the maximum amount of H_2 allowed in the Dutch gas grid.

described in Fig. 1 is considered. Obviously, within the recommended operational limits of the methanation catalyst, below the pressure of the natural gas grid of 60 bar, the current gas grid H_2 specification cannot be met with conventional adiabatic reactors.

For operational pressure ⩽60 bar, either additional reactors or additional cleaning steps must be envisaged to match the grid specifications. In contrast, the simulation of an integrated methanation reactor with water removal in place of the 3rd conventional reactor shows that the H_2 level in the SNG produced would be significantly lower and that the grid specifications for hydrogen are met at much lower operational pressure. The advantage of a sorption enhanced methanation process for the production of grid quality SNG would thus be best expressed in the lower operational pressure range, as shown by the dashed line in Fig. 2. Furthermore, additional simulations (not presented) indicate that even lower operating pressure is possible when considering more effective removal of water in the sorption enhanced reactor, when a sorbent material capable of taking up reversibly low partial pressure of water is used.

Fig. 2 also shows that for a given maximum H_2 amount, the methanation section can be operated at a much lower pressure when using sorption enhanced methanation in reactor R3 in comparison with conventional methanation.

There is indeed a potential energy saving in the compression work to be supplied to the system when in place of compressing hydrogen and CO_2 to high methanation operating pressure, the SNG product is compressed to the natural gas grid specification instead. This can be illustrated by a simple analytical analysis. The minimum compression energy duty with 3 three-stage compressor with intercooling were calculated using Eq. (1), that is a valid for an ideal compressible adiabatic flow (ideal gas is assumed) [21], with an isentropic efficiency of 0.85:

$$W = \frac{1}{\eta_{\text{isentropic}}} \frac{kRT}{k-1} \left[\left(\frac{p_2}{p_1}\right)^{\frac{(k-1)}{k}} + \left(\frac{p_3}{p_2}\right)^{\frac{(k-1)}{k}} + \left(\frac{p_4}{p_3}\right)^{\frac{(k-1)}{k}} - 3 \right] \quad (1)$$

where

$$p_2 = \left(p_1^2 p_4\right)^{1/3} \text{ and } p_3 = \left(p_4^2 p_1\right)^{1/3}.$$

k is the heat capacity ratio (C_p/C_v) of single gas, T is the intercooling temperature corresponding to the inlet temperature of the compressor (assumed to be 323 K), p_1 and p_4 are the initial and final pressure value while p_2 and p_3 are the optimal inter-stage pressures for ideal gas, assuming that no pressure drop occurs in the intercooler. The mixture of CO_2 and H_2 available at 1 bar is first compressed to the methanation operational pressure and the SNG is further compressed from the methanation operational pressure to the final grid specification pressure (60 bar). The sum of the compression energy is plotted in Fig. 3 as a function of the operating pressure. Remarkably the advantages of operating the methanation at relatively low pressure may contribute to compression energy saving up to 61% at 5 bar and even more when the methanation is carried out at lower pressure. In absolute values, the compression energy duty may represents up to 10% of the energy content of the SNG product when the worst case scenario, i.e. compression of the mixture of CO_2 and H_2 from 1 bar to 60 bar, is considered. In addition, compression energy is supplied by electrical power that may be generated by re-electrification of SNG, which would lead to an actual thermal energy consumption of about 20% of the SNG product, in the worst case. By operating the methanation section below 10 bar, the compression energy duty may thus be limited to less than 6%, which adds a decisive argument in favour of the sorption enhanced methanation next to the combination of catalytic reaction and dehydration and the heat integration with the whole conversion chain. While H_2 may be obtained by electrolysis under pressure with a good efficiency in practice, and CO_2 may be supplied at moderate pressure directly from scrubbing systems (like amine absorption), the savings of compression costs still appear to be significant when the operational conditions are between 5 and 20 bar compared to operations at 60 bar.

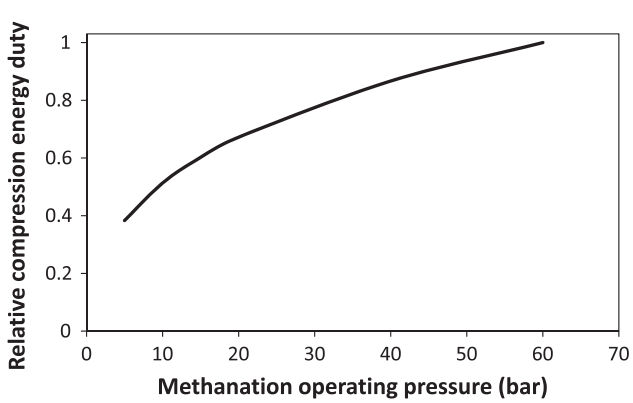

Fig. 3. Relative compression energy duty as a function of the operating pressure considering that H_2 and CO_2 at the inlet of the process are available at 1 bar and methane (SNG) must be compressed to 60 bar for injection in the grid.

In the sorption enhanced methanation, the sorption performance of any water sorbent is affected by the temperature rise resulting from the methanation reaction. Furthermore adsorption is an exothermic process that is favoured at low temperature and high pressure, which implies that sorbent materials for sorption enhanced methanation must have a very high affinity for water to obtain sufficient enhancement effect, even at low water partial pressure. In addition the material must be capable of taking up water in a range of relatively high temperatures corresponding to the catalytic process conditions (for instance between 200 and 400 °C) and release it in a later regeneration step by increasing the temperature or by decreasing the water pressure. In this respect, the simulation model showed that the temperature rise in the first and second methanation reactor is quite high and lies in the 500–600 °C and 450–550 °C ranges respectively, depending on the recycle configuration and the type of catalyst considered. It appears therefore that the most reasonable option – that does not rely on intricate and costly isothermal reactor design – is to implement a sorption enhanced step in place of the third reactor. The temperature rise in the third reactor is indeed quite limited in most cases since the amount of reactant to be converted is well below the amounts converted in the 1st and 2nd reactors. For instance considering two reactors in series with a recycle loop, operating at an operational pressure of 25 bar, the inlet composition of the sorption enhanced reactor that would be placed downstream the second reactor after a water condenser, would be about 2.5% CO_2, 10% H_2, 82.5% CH_4 and 5.0% H_2O. The corresponding conversion to be achieved in the sorption enhanced reactor would thus allow for a limited temperature rise. The heat released by the methanation reaction may be calculated by considering the thermodynamic equilibrium data. For example when considering an inlet reactor temperature of 200 °C, the adiabatic temperature rise would be 123 °C, with a maximum temperature of 323 °C. Down to operating pressures of 10 bar, the temperature rise in the third reactor is limited to 400 °C, while below 10 bar too much of CO_2 and H_2 remain in the gas phase that must be converted in the third reactor, leading to excessive temperature rise to consider a sorption enhanced process. For these reasons, a mixture of 2.5% CO_2, 10% H_2, 82.5% CH_4 and 5.0% H_2O was considered for an experimental proof of concept of the sorption enhanced methanation reaction with a proprietary Nickel based catalyst supplied by CRI and a zeolite sorbent. For the proof of principle it was decided to operate at atmospheric pressure since these conditions offer sufficient

differential between equilibrium conversion and full conversion, such that the sorption enhanced effect may be unambiguously demonstrated.

At first the activity of the proprietary Nickel based catalyst supplied by CRI was tested with alpha alumina used as a diluting medium. The selected inlet gas composition was 2.4% CO_2, 9.4% H_2, 77.8% CH_4, 4.7% H_2O and 5.6% N_2, nitrogen being the internal standard used for calculating the mass balance. Fig. 4 discloses both H_2 and CO_2 conversion level as a function of the catalytic bed temperature. With this catalyst, at a gas hourly space velocity of about 2500 h^{-1}, the equilibrium conversion was reached between 260 and 275 °C. Consistent with the thermodynamic equilibrium, the catalytic conversion at 272 °C was about 73 ± 1% for both H_2 and CO_2. The corresponding methane purity may thus reach not more than 96.1% (on dry basis) and more importantly the hydrogen content of the product may not be lower than 3.1% (on dry basis), which is still largely above the tight grid specifications mentioned earlier. Besides, the catalytic test revealed that at higher operating temperature, the consumption of methane is favoured as a result of the low operating pressures mostly and in agreement with the thermodynamics of the Sabatier reaction (see Fig. 2 and related discussion), as indicated by the negative conversion values observed above 400 °C. Hence for relatively low conversion ranges that correspond to adiabatic temperature rise of up to 200 °C and for operation at low pressures, sorption enhanced methanation has the potential of circumventing the conversion barriers encountered in conventional methanation reactors, when high methane purity and low hydrogen content are targeted.

Zeolite 4A was selected for regenerative water sorption experiments at temperature between 200 and 300 °C, at atmospheric pressure, with a nitrogen flow containing 3.9% water for the adsorption feed (Table 1). The sorbent was regenerated at temperature between 350 and 450 °C, using a dry nitrogen flow at atmospheric pressure, for observing the effect of the regeneration temperature. Furthermore the influence of CO_2 on adsorption capacity of water was tested in complementary experiments. Unsurprisingly, Table 1 shows that the water sorption capacity of zeolite 4A decreased significantly when adsorption temperature increased from 200 to 300 °C. This confirms the earlier statement that any sorption enhanced methanation process must be considered in a system where a rather moderate temperature rise may find place. In contrast the effect of the regeneration temperature had not a large effect on the uptake capacity of the sorbent. Regeneration time and absence of water in the purge gas may have a more pronounced effect although this was not further tested in this work. Remarkably the presence of small amount of CO_2 in the feed had a significant impact on the performances of the sorbent, decreasing the water sorption capacity by about 15–20%, whereas the capacity for CO_2 was limited to very low levels. This

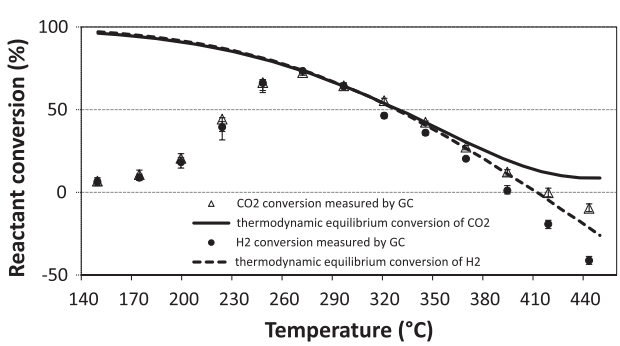

Fig. 4. CO_2 and H_2 conversion as a function of temperature on the proprietary Ni-based CRI methanation catalyst. Inlet composition: 2.4% CO_2, 9.4% H_2, 77.8% CH_4, 4.7% H_2O and 5.6% N_2, atmospheric pressure, total flow: 150 ml/min, material mass: 3.6 g (mass ratio alpha alumina:catalyst = 5:1).

competitive adsorption between CO_2 and H_2O may very well be triggered by the presence of alkali cations acting as charge compensating cations, present as a consequence of incomplete ion exchange during the preparation of NH_4^+ zeolite that is the precursor of the H^+-form zeolite tested in this experiment. The alkali cations are known to enhance indeed the CO_2 uptake properties of zeolite by increasing their basicity [22–26]. However one may not exclude other mechanisms. Based on the water uptake performances of the zeolite 4A and on the catalytic activity of the Nickel based catalyst, the experimental conditions for the demonstration of the sorption enhanced reaction were defined.

The proprietary Nickel-based catalyst and the zeolite 4A were mixed and pelletized together in a 1:5 mass ratio and were contacted with a gaseous stream comparable to a dry effluent exiting the 2nd reactor of a methanation process. Prior to contacting the mixed catalyst and sorbent material, a pretreatment consisting of drying with a dry mixture of 10% H_2 in N_2 at 400 °C for 2 h was applied. The reactor was then cooled down to the operating temperature and by-passed with the selected composition to ensure a good mixing of the components. Once the temperature and feeding conditions were stable, the reactor was opened and the material was exposed to the selected methanation composition. Fig. 5 discloses the transient response corresponding to the sorption enhanced methanation. Right after the start of the experiment, the methane concentration reaches 93.5 ± 2.0% which corresponds indeed to the concentration calculated on dry basis at full conversion of H_2 and CO_2. The mass balance was verified with the N_2 internal standard and was reconciled within the accuracy limit of the detection system. Although the analysis of concentrations between 80% and 95% remains challenging, the methodology selected herein allowed for a relatively good accuracy as shown by the error bars in Fig. 5. Before the breakthrough of water, a slip of CO_2 preceded both breakthroughs of CO_2 and H_2. Water breakthrough was only detected about 2 min later in the experiment carried out at 250 °C but one may not preclude the presence of low amount of water slip that may indeed precede the main water breakthrough. Low water slip may indeed hinder the sorption enhancement effect. However the shape of the breakthrough curve of water indicates that uptake kinetics are rather slow. This maybe due to slow mass transfer between the catalytic sites and the adsorbing sites resulting into CO_2 and H_2 breakthrough before water breakthrough. Besides, when water breakthrough occurred, both hydrogen and CO_2 reached a concentration equivalent to the concentration expected with the catalytic activity exhibited by the catalyst (Fig. 4). The sorption enhanced experiment was reproduced 10 times with a constant breakthrough time that denoted a good regenerability of the sorbent, while the sorbent uptake capacity was not ostensibly affected by the regeneration conditions. Further studies of the resistance of the catalytic material to various regeneration conditions are ongoing. Moreover it is shown that conversion is close to 100%. In this work, the operating temperature was then increased to 300 and 350 °C in order to assess the performances of the materials under conditions that may be encountered in an adiabatic reactor with relatively high temperature rise.

Table 2 shows the breakthrough times for H_2 and H_2O at various sorption enhanced reaction temperatures, while regeneration conditions were kept at 450 °C, in between the cyclic experiments. The water breakthrough time indicated that the water sorption capacity decreased when temperature increased. The corresponding breakthrough water capacities were 1.52 mmol/g, 1.31 mmol/g and 1.07 mmol/g at 250, 300 and 350 °C respectively, when considering the total amount of water formed during the complete conversion of H_2 and CO_2 in addition to the amount of water produced during the period where incomplete methanation was observed, after CO_2 and H_2 breakthrough. These values are to be related to the sorption capacities measured by water sorption

Table 1
H_2O and CO_2 adsorption capacities of zeolite 4A calculated from breakthrough experiments at various temperatures, at a total pressure of 1 bar (N_2 balance).

Adsorption temperature (°C)	Regeneration temperature (°C)	Pressure of H_2O (bar)	Pressure of CO_2 (bar)	H_2O breakthrough capacity (mmol/g)	CO_2 breakthrough capacity (mmol/g)
200	350	0.039		1.89	–
200	400	0.039		2.00	–
200	450	0.039		1.87	–
250	350	0.039		1.43	–
250	400	0.039		1.44	–
250	450	0.039		1.48	–
300	350	0.039		1.14	–
300	400	0.039		1.22	–
300	450	0.039		1.16	–
200	400	0.039	0.025	1.69	0.083
250	400	0.039	0.025	1.23	0.066
300	400	0.039	0.025	0.98	0.060

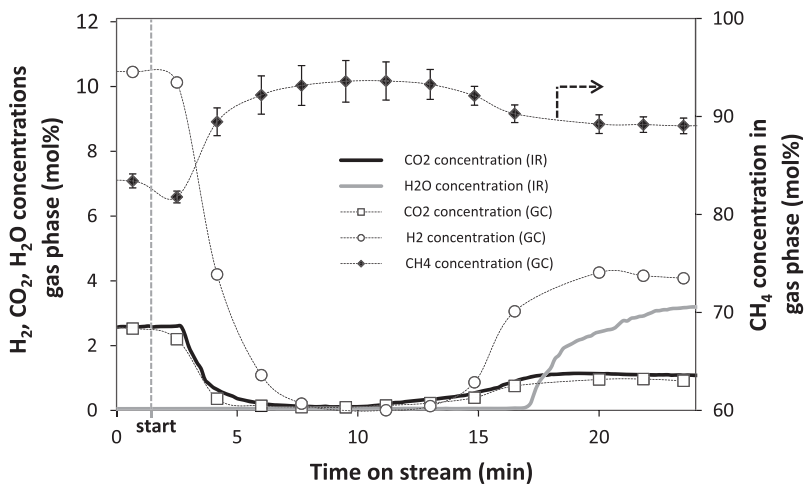

Fig. 5. Sorption enhanced methanation illustrated by the 5th breakthrough curve of a cyclic series of regenerative experiments. Adsorption conditions: 250 °C, atmospheric pressure, inlet composition: 2.5% CO_2, 9.9% H_2, 81.6% CH_4, 6.0% N_2, total flow: 150 ml/min, total material mass: 3.6 g (zeolite 4A:catalyst = 5:1). Before the experiment, the materials were regenerated with a mixture of H_2:N_2 at a ratio of 1:9 at 450 °C and then cooled down to 250 °C. The reactor contains mostly N_2 and is by-passed before the reaction with the inlet mixture. The transient observed when the experiment is started are due to the gas phase present in the tubing included in the by-pass loop, situated downstream the reactor and upstream the detector.

Table 2
Breakthrough time as a function of the operating temperature in the sorption enhanced methanation.

Sorption enhanced methanation operating temperature (°C)	H_2O breakthrough duration (min)	H_2 breakthrough duration (min)
250	16.3	12.0
300	14.0	10.5
350	11.3	8.8

and CO_2 water sorption experiments, summarized in Table 1. The slightly higher values observed in the sorption enhanced methanation experiments may be due to the combination of slightly higher water partial pressure (0.05 bar at total conversion) and some water capacity of the catalytic material that counted for 1/6 of the total amount of bed material in these experiments. Remarkably the breakthrough time remained quite long, even at temperature up to 350 °C which opens promising perspectives for this technology since neither the sorbent material nor the catalyst material were specifically developed for the present application.

4. Discussion

The thermodynamic analysis of the Sabatier process clearly showed that the conventional catalytic process necessitates multiple cascade reactors and high operational pressure to match sufficient SNG quality to allow for injection in the natural gas grid at current gas quality standards. However a number of processes for SNG production such as bio-methanation by anaerobic digestion and thermo-chemical biomass gasification may be operated at limited pressure, below 10 bars, for technical reasons. Moreover the possibility of using these processes for the production of renewable SNG by adding hydrogen generated by water electrolysis using renewable electricity calls for the development of effective and reliable methanation process that may produce grid quality SNG, while limiting the energy cost of compression of large amount of reactants. Therefore the sorption enhanced methanation process that allows for production of high grade SNG at relatively low pressure is a promising technology that allows for compression energy saving of up to 40% when methanation is operated at 10 bar instead of 60 bar, while the gaseous reactants are available at a pressure of 1 bar. When both H_2 and CO_2 are obtained at higher pressure, the savings of compression energy obtained by the use of sorption enhanced obviously become less dramatic, but still remain significant when both gases are supplied at <20 bar. For instance in the methanation of biomass gasification feed streams, in which CO_2 may be converted to SNG when H_2 is available from an electrolysis process, it is anticipated that the gasification product stream will be supplied at pressure <10 bar, when more efficient indirect gasification technology is used [27].

The experimental proof of principle reported herein showed that commercial materials are capable of operating in cyclic sorption enhanced conditions at the temperature range that are anticipated in the process. While breakthrough experiments exhibited already rather good capacity and catalytic activity, dedicated materials for this applications may further improve the performances of the process. For instance the development of novel efficient catalysts for Sabatier reaction [17,28,29] that are specifically developed for CO_2 conversion and a mixture of CO/CO_2 may contribute to reaching higher process performances. Similarly the specific design of dedicated sorbent material for water sorption at relevant temperature, or alternatively the staging of sorption enhanced reactors with different sorbent may greatly enhance the performances of the process by optimizing the regeneration conditions. Furthermore the experimental results also pointed clearly at the importance of improving the mass transfer rate between the catalytic sites and the adsorbent sites. This may be achieved by conceiving novel bi-functional materials such as was advocated by Borgschulte et al. [17] in their recent contribution. By tailoring both the catalytic function and the affinity for steam of the zeolitic material, by fine tuning of the microporous topology and the chemical composition of the zeolitic framework that have direct influence on the steam uptake capacity [19,20], the process performances may be indeed optimized by the rational design of bi functional materials. Besides, the current results do not give a direct indication of the energy requirement of the process. Also the local temperature in the bed rise is of some concern since large local temperature rise will affect the capacity in part of the bed during the adsorption. Recently Parlikkad et al. have showed that methanation catalyst operate very efficiently in the top part of conventional bed operated at steady state causing a very sharp temperature rise on minute bed length [30]. Because the mass transfer zone associated with the steam sorption moves gradually in the adsorptive catalytic bed during the sorption enhanced methanation, the temperature rise related to highly efficient methanation catalyst may lead to dramatic effects on the transient performances of both sorbent and catalyst thereby affecting their breakthrough profiles and cyclic capacity. In contrast, it clearly appears that during desorption a higher temperature helps at removing the absorbed water. The proof of concept demonstrated in this report is indeed based on a temperature swing adsorption cycle that uses a purge gas. A proper choice of the regeneration pressure, temperature and the amount of purge gas will be therefore key parameters for optimizing the energy requirement of the process. Moreover the sorbent material selection will critically affect the operational costs since the energy requirement for the regeneration is directly related to the adsorption energy of steam on the selected material. In this respect, the optimization of the energy consumption of the process depends on the conception of a dedicated material that allows for the lowest temperature swing possible. Accordingly, the possibility to develop materials with sufficiently high capacity when used in pressure swing adsorption cycle, possibly with a purge gas, may open broader perspectives for steam enhanced reaction processes. Providing more quantitative data on the potential energy savings induced by the use of dedicated materials in the steam enhanced sorption methanation will require a more detailed experimental and modelling effort also involving possible integration with other parts of the methanation process. The experimental results on water sorption on zeolite 4A are encouraging and showed that the regeneration temperature may not necessarily by much higher than the operating conditions but that the availability of a dry purge gas may be critical to keep the energy requirement low. For instance the purge gas could be the H_2 produced by the electrolyser at the condition it is dried beforehand. The use of CO_2 as purge gas could be an alternative at the condition that the stability of the catalyst is not affected. Besides, when considering natural gas fields with high CO_2 content that could be converted to SNG with renewable hydrogen, there may be some inert such as nitrogen or helium available for purge gas. At this point in-depth calculations for the identification of the most appropriate regeneration method appear to be relevant only when specific case are considered. The parallel development of materials and process design is thus of utmost importance for the demonstration of the performances of this process at larger scale in identified relevant cases.

5. Conclusion

The sorption enhanced methanation reaction process showed unique performances for high grade SNG production at low methanation pressure using commercial materials. Operating the methanation process at low pressure has been shown to enable significant energy savings for the production of SNG from a number of important processes in the production of biofuels and renewable fuels. The process showed 100% conversion of H_2 to SNG, allowing for matching the specifications for injection in natural gas grid that are not designed for hydrogen transport and storage. While process energetic performance optimization may obviously benefit from the heat integration with the exothermic methanation reaction, the parallel development of dedicated bifunctional adsorbent/catalyst materials and smart process configuration is key for the translation of these advantages in a cost effective SNG upgrading method, applicable in number of processes related to renewable methane and "green gas" production.

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