

## Study of the Efficiency of a HT Power-to-Gas Process

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Power-to-Gas processes are investigated since they offer solutions for renewable energy storing and transportation. In the present study, an original Power-to-Substitute Natural Gas (SNG) process combining high-temperature steam electrolysis and CO<sub>2</sub> methanation is designed and simulated. A specific modelling approach of the electrolysis based on experimental measurements is used, and a methanation modelling involving a kinetic law is also introduced. Both of these modelling are then integrated into the whole process simulation as well as a unit for residual CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O gas cleaning. Having set all the process units, simulation is performed for a reference case where the electrolyser and the methanation reactors are designed. This case allows to produce 2.7 Nm<sup>3</sup><sub>SNG</sub>/h/m<sup>2</sup><sub>SOEC</sub> with an electrical-to-HHV fuel efficiency equalling 74.5 %, whereas current low-electrolysis processes show an HHV efficiency near 60 %. The produced SNG meets the specifications required for network injection. A sensitivity analysis has been made around the working point conditions of the electrolyser and the methanation units. From this study, we observed that no parameter set allows to have higher values of both process efficiency and SNG production than in the reference case.

### 1. Introduction

In the current global development of sustainable energy resources, a new storage need for electricity produced from renewable sources is rising. Wind and solar plant production periods are dependant from weather conditions and fluctuate daily, monthly and seasonally. Thus, to increase the share of renewables in the energy mix, storage solutions must be implemented in order to insure to satisfy the demand and to valorise each kW renewably produced.

The solution proposed here offers to store and transport energy through the gas network instead of the electrical network. Several solutions for energy storage exist and address mainly the issue of short period storage. However, innovative research projects are interested in the Power-to-Gas concept (Gahleitner, 2013), this solution aiming at converting electricity into H<sub>2</sub> or CH<sub>4</sub>. Then, it becomes possible to inject this final gas into the natural gas network already existing, allowing to store and deliver natural gas and its substitute. Demonstrative facilities currently in work involve low-temperature electrolysis and aim at producing hydrogen or methane. A unique project of a demonstration plant led by Sunfire plans to use High-Temperature Steam Electrolysis (HTSE) to produce hydrogen (Gahleitner, 2013).

The renewable power storage process simulated here is an original Power-to-SNG architecture due to the synergy of HTSE and the Sabatier reaction. HTSE produces H<sub>2</sub> which is used to hydrogenate CO<sub>2</sub> to form CH<sub>4</sub>, main component of natural gas. CO<sub>2</sub> hydrogenation is highly exothermal and the heat released is used to generate steam feeding the electrolyser. As storage into the gas network is foreseen, a cleaning step to meet the gas network composition and calorific value requirements is considered.

The frame of the Power-to-SNG process is firstly defined. Then, the process is detailed, with a focus on each main unit: electrolysis, methane production and purification. To perform process simulations, a modelling for HTSE based on experimental observations is implemented. Simulations are performed and the influence on the process efficiency and SNG production is observed. Previous investigation on the influence of the process perimeter has been led (De Saint Jean et al., 2013). The present work focuses on the influence of the process working point variations.

## 2. Power-to-SNG process : aims, description and modelling

### 2.1 Aims

This power-to-SNG process aims at storing renewable electrical energy by injection of SNG into the natural gas network. To do so, SNG is expected to meet some requirements on composition, on High Heating Value HHV and on Wobbe index  $W$ , as specified in Table 1. The injection pressure depends on the network chosen: distribution network is at 0.4 MPa and transportation network is at 1.6 MPa or at 8.0 MPa.

Table 1: Gas specifications on French natural gas network

		H quality	L quality
HHV	kWh/Nm <sup>3</sup>	10.7 - 12.8	9.5 - 10.5
$W = \text{HHV}/\rho$	kWh/Nm <sup>3</sup>	13.4 - 15.7	11.8 - 13.0
Composition	% <sub>vol</sub>	CO < 2, CO <sub>2</sub> < 3, H <sub>2</sub> < 6	
	mg/Nm <sup>3</sup>	H <sub>2</sub> O < 55	

The first step of the process consists in producing renewable hydrogen from water and electrical energy in a high-temperature electrolyser. Then, this hydrogen is used with additional CO<sub>2</sub> to feed the methanation reactors. CO<sub>2</sub> is assumed to come from industrial capture processes. The gas exiting the methanation unit contains CH<sub>4</sub> but also a large amount of water and unreacted H<sub>2</sub> and CO<sub>2</sub>. So, it is purified into the last unit to satisfy the requirements. Considering that SNG must be pressurised at, at least, 0.4 MPa to be injected into the network, the process is expected to work at a high enough pressure to finally achieve 0.4 MPa. The process is simulated with the software Prosim Plus<sup>TM</sup>, which proposes libraries of thermodynamic modelling and engineering process elementary module.

### 2.2 High-temperature steam electrolysis unit

The main function of this unit is to split steam into H<sub>2</sub> and O<sub>2</sub> according to reaction R1 by the application of an electrical voltage at around 923 K – 1,123 K in a Solid Oxide Electrolysis Cell SOEC.



The HTSE unit consists of a water pump, a steam generator and heaters to generate pressurised steam. An electrical heater is required to complete the gas heating (+50 K) before entering the electrolyser. To keep a reducing atmosphere on the hydrogen electrode, a gas recirculation is implemented until reaching  $x_{\text{H}_2} = 10\%$  at the electrode inlet. The last step in the electrolyser unit consists in cooling down the hydrogen-rich gas for thermal integration and removing unreacted steam by condensation until having 0.5 mol% of H<sub>2</sub>O in the gas.

Due to the recent interest for SOEC, no module of this compound is implemented in the simulation software Prosim Plus<sup>TM</sup>. As a consequence, a specific modelling, based on experimental measurements at cell level is implemented. As a major hypothesis, the electrolyser is assumed to run isothermally and adiabatically at the thermal-neutral voltage  $U_{\text{tn}}$ . The approach developed here is based on energy and mass balances, and to describe electrochemical phenomena, an experimental data-based law is implemented. The electrolyser working point is characterised by  $T_{\text{SOEC}}$ ,  $P_{\text{SOEC}}$ , the cathodic flow-rate  $n_{\text{cath}}$  and  $U_{\text{tn}}$ . Modelling parameters are the electrolyser active area  $S$ , the equivalent electrical resistance  $R_{\text{eq}}$  and the hydraulic resistance  $R$ .

The modelling determines the current density  $j$  on each cell, the fraction  $SC$ , defined in Eq(1), of the incoming steam converted into H<sub>2</sub> and the consumed electrical energy. In Eq(1)  $n_{\text{H}_2\text{R}}$  is the molar flow rate of H<sub>2</sub> produced by the electrolyser and  $x_{\text{H}_2\text{O},\text{in}}$  is the molar fraction of steam in the cathodic inlet stream.

$$SC = \dot{n}_{\text{H}_2\text{R}} / x_{\text{H}_2\text{O},\text{in}} \dot{n}_{\text{cath}} \quad (1)$$

It also affects resulting molar flow rates, compositions and pressure to the leaving streams, as depicted in Figure 1. Considering the autothermal reactor (see Figure 1), the molar balance is established, according to the chemical reaction R1, and the energy balance leads to Eq(2),  $\mathcal{F}$  being the Faraday constant.

$$2\mathcal{F} \dot{n}_{\text{H}_2\text{R}} = |j| S \quad (2)$$

Equations used so far do not take into account the electrochemical phenomenon which is characterised by the current density  $j$  at  $U_{\text{tn}}$ , for a fixed value of  $n_{\text{cath}}$ .

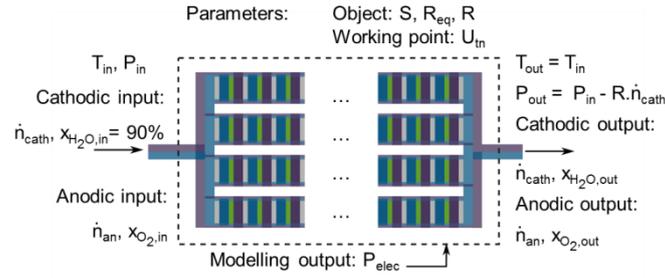


Figure 1: Reference volume and boundary conditions of the autothermal electrolyser

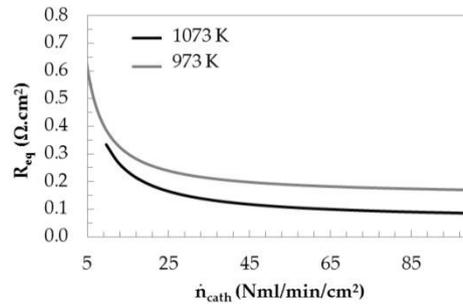


Figure 2: Regressions between  $R_{eq}$  and  $n_{cath}$  obtained at  $T = 1,073$  K and  $973$  K,  $P = 0.1$  MPa,  $H_2/H_2O = 10/90$ ,  $U_{op} = U_{in}$ , on the commercial electrode supported cell. Pure oxygen sweep on the anode side

The unknown parameter  $j$  is determined thanks to an empirical relation. Experimental data are generated and analysed for this purpose. A commercial cell is tested to determine the relation between  $n_{cath}$  and the parameter  $R_{eq}$ , defined in Eq(3),  $U_{Nernst}$  being the reversible cell voltage. Regressions Eq(4) are obtained, depending on  $T$ .  $U$  are in V,  $n_{cath}$  in NmL/min/cm<sup>2</sup> and  $R_{eq}$  in Ω.cm<sup>2</sup>.

$$R_{eq} = (U_{Nernst} - U_{op})/j \quad (3)$$

$$R_{eq} = 24,561.8 (U_{op} - U_{Nernst})(1 + 45.150 / \dot{n}_{cath}) / (2\mathcal{F} x_{H_2O,in}) \quad 1,073 \text{ K} \quad (4a)$$

$$R_{eq} = 68,522.9 (U_{op} - U_{Nernst})(1 + 15.739 / \dot{n}_{cath}) / (2\mathcal{F} x_{H_2O,in}) \quad 973 \text{ K} \quad (4b)$$

For the heat-exchangers required in this unit, modules from Prosim Plus<sup>TM</sup> software are used with the following assumptions. For liquid water, one heat exchanger is used to heat it up to the boiling temperature, then it is vaporised into the steam generator and for steam super-heating, a cascade of heat exchangers is used, see figure 3. A pressure loss of 0.02 MPa per exchanger is implemented and if maximal temperature is less than 873 K, the temperature gap between the inlet and the outlet of one exchanger is set to 150 K, and this gap is reduced to 100 K for maximal temperature greater than 873 K. The electrical heater, having an assumed electrical efficiency of 0.9, is added just before entering the electrolyser to increase temperature by 50 K. Finally, a second heat-exchanger cascade, with the same hypotheses as earlier, is used to cool-down the cathodic stream. SOECs require direct current electrical supply, so an AC/DC inverter is considered with an assumed efficiency of 0.92.

### 2.3 Methane production unit

Methane is produced from  $H_2$  and  $CO_2$  by Sabatier reaction R2. This is a catalytic and highly exothermic reaction. When operating conditions are soundly chosen, reaction R2 can be considered as the unique possible chemical reaction between  $H_2$  and  $CO_2$  (Gao et al. 2011).



Due to the reaction exothermicity, a thermal management strategy is required to avoid very high temperature in catalyst bed which would lead to catalyst deactivation. In a first approach, a classical adiabatic architecture developed in the past for syngas methanation is adapted (Heyne et al., 2010): 4 adiabatic reactors are associated in series, alternating with cooling steps.

Reactor inlet temperature is set at 573 K, as a trade-off between the low temperature thermodynamically required and a high enough temperature for catalyst activation. Methanation step is usually led between 553 and 823 K, 0.7 MPa and 1.8 MPa, with  $H_2 / CO_2 = 4$  to maximize  $CH_4$  production. Lunde and Kester (1974) were interested in  $CO_2$  methanation kinetics with a ruthenium-based catalyst. They obtained the kinetic law expressed in Eq(5) where  $r_{CH_4}$  is in  $mol/s/m^3_{cat}$ ,  $T$  in K and  $P$  in MPa.

$$r_{CH_4} = 2691.67 \cdot 10^3 \cdot e^{(-64121/RT)} \left( P_{CO_2} P_{H_2}^4 - P_{CH_4} P_{H_2}^2 / K_{eq}(T) \right) \quad (5)$$

In Prosim Plus<sup>TM</sup>, chemical reactors are modelled with a pseudo-homogeneous and one-dimensional equation system. All the reactors used in our process simulation are specified with this kinetic law.

## 2.4 Purification unit

The purification unit has 3 functions:  $CO_2$  capture by amine scrubbing,  $H_2$  separation by filtration and  $H_2O$  removing by condensation. To remove  $CO_2$ , chemical absorption into an aqueous solution containing 30 wt% in mono-ethanol amine (Amann et al., 2009) is used. Existing modules of an absorption column and a stripper for amine regeneration are used.  $CO_2$  recovered from the regeneration step is recycled towards the methanation unit inlet. Concerning  $H_2$  separation, the gas is sent through an 80 % recovering membrane, which isolates hydrogen present in the SNG. This hydrogen is then compressed and sent to the methanation unit inlet for recycling. The last step of purification consists in removing water by condensation.  $CH_4$ -rich stream is cooled-down until reaching the satisfying water content, water is separated and the gas is heated-up to 293 K. Here again, heat-exchanger cascade is designed as previously.

## 3. Power-to-SNG process simulations

### 3.1 General hypotheses

The present simulations aim at determining the efficiency  $\eta_{elec, HHV}$  and the quantity of SNG  $Q_{SNG}$  produced by a process integrating an electrolyser of a 25- $m^2$  active surface area. The methanation reactors are designed from the reference case to convert up to 98 % of the incoming reactants. They are kept identical in all simulation cases.

A pinch analysis module is integrated into the simulation to determine the minimal hot and cold utilities required by the process. Then, the electrical power consumption to produce these utilities is determined. For the hot utility, a 0.9 efficient electrical-heater is used and for the cool utility, two different-temperature refrigeration units are proposed, 217 K and 270 K, showing an electrical-to-thermal efficiency of 1.4 and 1.73.

### 3.2 Reference case

The reference case is simulated with parameter values indicated in Table 2. Process is depicted in Figure 3. To simplify the view, each cascade of heat exchangers is represented by one exchanger. Mixed lines show an electrical consumption. The process efficiency is calculated with Eq(6) with  $Q_{SNG}$  the molar flow-rate of SNG produced and  $P_{elec, HTSE}$ ,  $P_{elec, heat}$ ,  $P_{elec, cold}$  and  $P_{elec, mech}$  the associated electrical energy consumption for each item.

Table 2: Parameters for reference case simulation and sensitivity analysis. \*SC corresponding value at  $U_{in}$

		Reference case	Sensitivity analysis
Recycl. R1	%	75	40, 50
$H_2 / CO_2$		4	3.8, 4.2
$T_{meth,i}$	K	573	553
$T_{SOEC}$	K	1073	973
$P_{SOEC}$	MPa	0.87	1.0, 1.7
$n_{cath}$	NmL/min/cm <sup>2</sup>	25.9	61.6, 39.8, 18,8
SC*	%	75	45, 60, 85

$$\eta_{elec, HHV} = \dot{Q}_{SNG} \cdot HHV_{SNG} / (P_{elec, HTSE} + P_{elec, heat} + P_{elec, cold} + P_{elec, mech}) \quad (6)$$

The reference case produces 67.5 Nm<sup>3</sup>/h of SNG with  $\eta_{elec, HHV} = 74.5$  %. The SNG contains 1.59 % of  $CO_2$ , 1.60 % of  $H_2$  and 42.52 mg/Nm<sup>3</sup> of  $H_2O$ . Its HHV achieving 10.75 kWh/Nm<sup>3</sup> and its Wobbe index equalling 14.35 kWh/Nm<sup>3</sup>, it is in the H-quality range. The total associated electrical consumption is

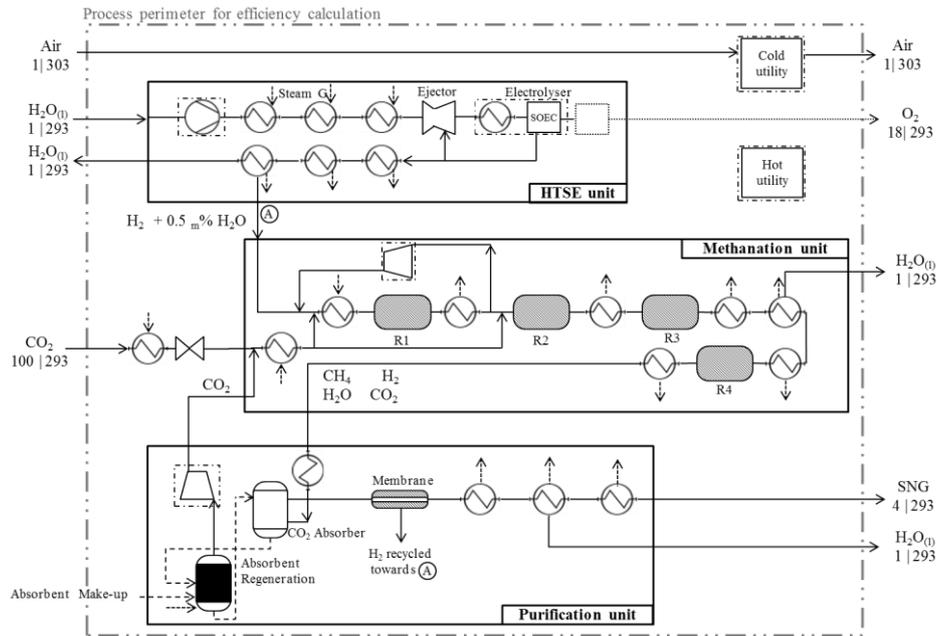


Figure 3: High-temperature Power-to-SNG process. Physical data are reported as  $P$  (MPa) |  $T$  (K). Arrows: heat supply/remove, mixed lines: electrical consumption

974 kW<sub>AC</sub>, shared at 90 % for electrolysis. Efficiency of low-temperature alkaline process is around 62 % based on the HHV, for a system converting electrical energy into SNG, (Zuberbühler and Specht, 2012). Here, the beneficial effect of high-temperature electrolysis is observed.

### 3.3 Sensitivity analysis

Having designed the Power-to-SNG process for the reference case, a sensitivity analysis (see Table 2) is led. Effects of the methanation and the HTSE working point variations are analysed and Figure 4 summarizes the most significant effects. From this point of view, firstly has been observed that there is no parameter which would maximize both process efficiency and SNG production.

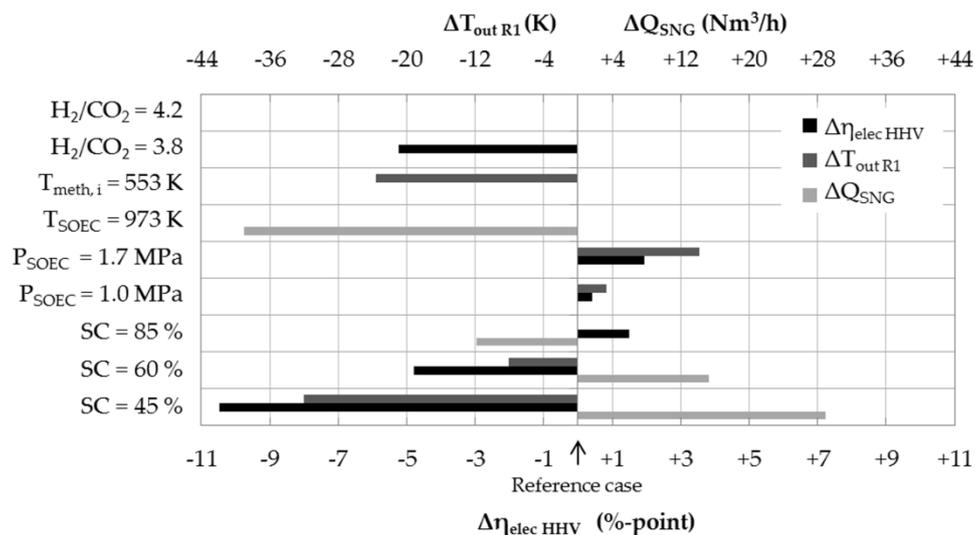


Figure 4: Significant effects of parameter variations on several values describing the efficiency and the SNG production

Considering the process efficiency, having a steam conversion rate in the electrolyser of 45 % or 60 % instead of 75 % involves an efficiency decrease of 10.5 points and 4.8 points. Increasing SC to 85 % leads to a gain of 1.5 point. It is not advantageous to decrease SC for the process efficiency.

Increasing the pressure implies a better conversion at the methanation stage notified by a higher value of  $T_{out R1}$ , leading to a higher process efficiency. In this case, gas HHV is 10.95 kWh/Nm<sup>3</sup> at  $P_{SOEC} = 1.7$  MPa which is higher than HHV obtained in the reference case (10.75 kWh/Nm<sup>3</sup>).

Working with a default in hydrogen supply ( $H_2/CO_2 = 3.8$  case) is not favourable for  $\eta_{elec HHV}$  which decreases down to 69.2 %. The volume of gas to purify is more important than for the reference case, leading to an overconsumption of the cold utility for water removing.

The process designed in the reference case produces 67.5 Nm<sup>3</sup>/h. This amount is strongly increased when SC is lower.  $Q_{SNG}$  is 43 % higher for SC = 45 % and 23 % higher for SC = 60 %, whereas it decreases by 17 % for SC = 85 %. If the electrolyser works at 973 K instead of 1,073 K,  $Q_{SNG}$  decreases by 58 %, due to the effective performance loss of the electrolyser: for the same active area, the hydrogen production is deeply lower at 973 K than at 1,073 K.

Parameters linked to the methanation step working point are not influencing the volume of SNG produced in the studied range.

Concerning the variation of the maximal temperature achieved inside the methanation reactors  $T_{out R1}$ , it is observed that the lower SC is, the more important  $H_2$  production is, in absolute. In this case, methanation reactors are too small to convert all reactants and then  $T_{out R1}$  is lower. In the case where the inlet temperature of reactor is reduced by 20 K, then  $T_{out R1}$  also decreases by around 20 K, due to a kinetic effect.

#### 4. Conclusions

Simulations of a Power-to-SNG process have been done, involving preliminary work on HTSE and methanation modelling. For the hydrogen production by high-temperature steam electrolysis, a specific modelling, based on experimental data, has been developed. After having implemented these elementary modelling, the overall process is designed, including reactant pressure and temperature setting, electrochemical and chemical transformations and SNG purification.

Process shows a high performance since  $\eta_{elec HHV}$  is 74.5 % for the reference case simulation, producing 67.5 Nm<sup>3</sup>/h of SNG for an electrolyser with an active area of 25 m<sup>2</sup>. A sensitivity analysis has been led and shows that modifying internal parameters involves variations onto the process efficiency and the volume of SNG produced. No working point allows to have higher values of both SNG production and process efficiency. It has been shown that it is preferable to work at SC higher than 45 % during the electrolysis step; otherwise the efficiency would be similar to this of low-temperature process, near 60 %. Still in efficiency consideration, it is also recommended to avoid a default in hydrogen supply during the methanation step.

This work being a part of a larger investigation on technical and economic feasibility of high-temperature Power-to-Gas processes, future work interesting in SOEC degradation will be done in order to characterize investment and operating costs of such processes.

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