

Process modelling of an innovative Power to LNG demonstration plant

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Abstract

The continuous increase of electricity production from renewable energy sources (RES) introduces the intrinsic fluctuating characteristic of RES in the electric power grid, causing non-trivial grid management issues (e.g. grid congestion). In this work, an innovative power to liquefied methane concept was developed and process simulations for a 200 kW_{el} demonstration plant were carried out. The proposed concept is based on water electrolysis to produce hydrogen, CO₂ capture from air using solid adsorption materials, catalytic CO₂ methanation, gas separation and a single mixed refrigerant (SMR) liquefaction process.

The gas separation unit produces an exhaust stream, rich in hydrogen and carbon dioxide but also in methane, that is recycled to the methanation unit inlet. A thermodynamic analysis excluded the possibility of carbon deposition formation in the methanation reactor due to methane recirculation. The gas separation system was designed using a combination of temperature swing adsorption techniques (stream dehumidification) and membrane separation (CO₂ separation). After a screening of different polyimide type membranes, a two-stage layout was selected and dimensioned. Subsequently the liquefaction unit was developed optimizing the SMR composition and pressures to minimize the total work required. Hence, the minimum work required for the liquefaction resulted being 0,57 kWh_{el}/kg_{LNG}.

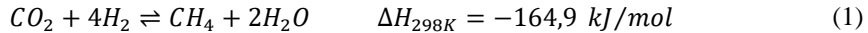
Finally, the thermal integration was performed to minimize the external heat requirement. The heat produced by the electrolyser and methanation unit is greater than the thermal energy requirement by the CO₂ capturing unit during desorption. A process efficiency up to 52,6% (electric to chemical) resulted from the study.

Introduction

As the increase in the adoption of renewable energy sources (RES) for electricity production grows also the electric grid management gets more and more complicated. This is caused by the fluctuating and intermittent production characteristic that RES have making balancing the electric grid a challenging issue. There are a few technologies that can tackle with this issue: flywheels, supercapacitors, batteries, compressed air storage, pumped hydroelectric storage, power-to-gas (PtG) and power-to-liquid.

The PtG technology received in the past years a lot of attention since it appears to

be a promising solution in converting excess renewable electricity in a gaseous energy carrier. In PtG water is converted into hydrogen using electricity in a water electrolysis process. Since hydrogen does not have a transportation and distribution infrastructure it is further converted into methane by means of the Sabatier reaction (1). The CO₂ required to perform this reaction can be obtained from biogas upgrading plants or even captured from air.



The produced methane has the same proprieties as natural gas and can then be injected in the natural gas grid and the product gas is called substitute or synthetic natural gas. In case grid injection is not feasible the produced gas can be liquefied obtaining liquefied natural gas (LNG). LNG has received a lot of interest in the past years as new applications have been studied (i.e. heavy trucks and light-duty freight/passengers vehicles [1] and marine transportation [2]).

In this work we focus on the process simulation of a novel demo plant that uses CO₂ captured from air and produces liquefied gas equivalent to LNG.

Process description and simulation model overview

Renewable electricity is used to produce hydrogen through water electrolyzer for which different technologies are available: alkaline electrolysis cells (AEC), proton exchange membrane electrolysis cells (PEMEC) and solid oxide electrolysis cells (SOEC). For this simulation an alkaline electrolyzer was used since it is the most mature and low capital cost technology even though it has a slightly lower efficiency with respect to PEMEC. The AEC unit used in the demo has a power consumption of 4,9 kWh_{el}/Nm³_{H₂} (including all the utilities) and this translates to a module efficiency of 71,7% HHV basis (60,7% LHV basis). The demo plant's electrolyzer module can be fed with up to 200 kW of electricity allowing for the evaluation of hydrogen flowrate and heat production.

CO₂ capture from air is a challenging process since the mean concentration is 400 ppm. Carbon dioxide is captured by moving air through an adsorption material that traps the CO₂ inside. When the material is saturated the desorption phase is performed using heat and afterwards the cycle is restarted. The sorption material is generally functionalised with amine groups for a better selectivity towards carbon dioxide. The specific energy requirements for a CO₂ capture unit were taken from the datasheet of a commercially available collector and these are as follows: 300 kW_{el}/ton_{CO₂} and 2000 kWh_{th}/ton_{CO₂}. The obtained carbon dioxide is then mixed with the hydrogen coming from the electrolyzer.

The CO₂ and H₂ blend stream is mixed with the recycle stream and the CO₂ and H₂ ratio is maintained at reaction stoichiometric ratio of 4. This stream is fed to the methanation reactor where the highly exothermic methanation reaction occurs. Different reactor configurations were considered: series of adiabatic reactors with intercooling, an adiabatic and an isothermal with intercooling and two isothermal reactors with intercooling. However, none of these solutions would manage to

reach the required purity to the liquefaction unit and a purification unit will be needed. Hence, a refrigerated reactor that still can guarantee CO_2 conversions $\geq 95\%$ was used in the simulation.

The methanation outlet stream is made of water, methane, hydrogen and carbon dioxide. In order to be able to liquefy methane, the stream has to have a CO_2 concentration below 50 ppm and a water concentration below 1 ppm to avoid freezing in the condenser. Hence, a gas separation unit is required: steam condensation by cooling the stream, temperature swing adsorption (TSA) to remove the water vapor residue, membrane gas separation unit to lower hydrogen and carbon dioxide in the stream and finally a polishing TSA to lower CO_2 and H_2O content to the required concentration. The membrane gas separation unit was simulated using a shortcut method for a hollow fiber module in countercurrent [3] while the TSA modules were commercially available units.

At this point the stream is fed to the liquefaction unit and the hydrogen rich boil-off stream is recycled to the process. The liquefaction technology chosen is the single mixed refrigerant (SMR) solution. The composition of the refrigerant and pressure were optimized using the genetic algorithm [4] to minimize the energy demand keeping the constraint of the minimum temperature approach between cold and hot streams equal to 3°C .

Finally, a thermodynamic analysis was performed to investigate if recycling methane to the reactor inlet could cause the formation of carbon deposition.

In Figure 1 the block flow diagram of the process is reported with preliminary mass and energy balance.

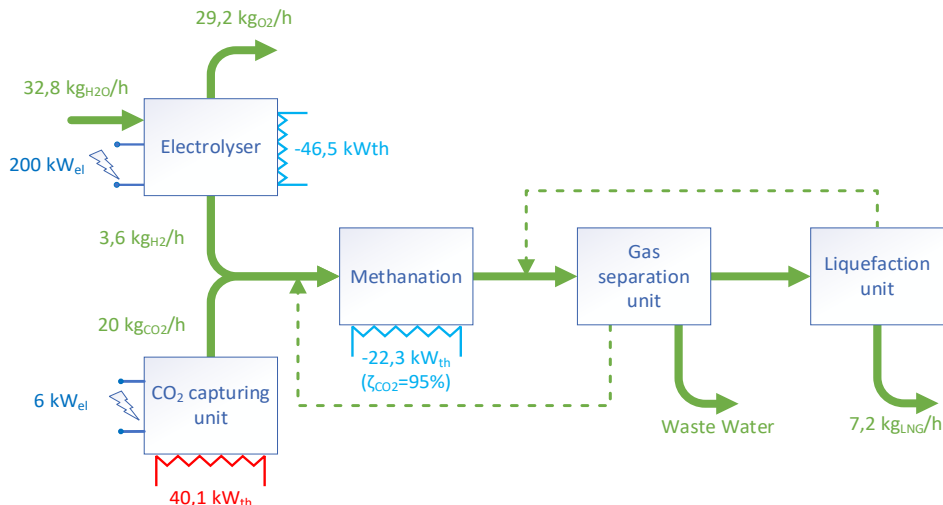


Figure 1. Block flow diagram with preliminary mass and energy balance

Results and discussion

The target for the demo plant in terms of electricity to the electrolyser was set equal to 200 kW, resulting in a total hydrogen production of 3,6 kg_{H2}/h (41,3

$\text{Nm}^3_{\text{H}_2}/\text{h}$). The CO_2 inlet flow was calculated by keeping the stoichiometric ratio ($\text{H}_2/\text{CO}_2=4$), including also the non-stoichiometric recycle stream. A CO_2 flow rate of $20 \text{ kg}_{\text{CO}_2}/\text{h}$ ($10,3 \text{ Nm}^3_{\text{CO}_2}/\text{h}$) resulted from the simulation. The carbon dioxide capturing unit energy requirements are $6,0 \text{ kW}$ of electricity and $40,1 \text{ kW}$ of heat. After mixing the H_2 , CO_2 and recycle the resulting stream is heated to $280 \text{ }^\circ\text{C}$; the calculated duty of the heat exchanger is $5,3 \text{ kW}$. Since the reactor is cooled the $21,9 \text{ kW}$ of heat produced by the methanation reaction are removed. About 60% of the methanation outlet stream is made of water vapor, the majority of which (97,8%) is separated in a water-cooled condenser that cools the stream to 40°C resulting in a duty of the condenser of $14,8 \text{ kW}$. The stream is then sent to the drying module to complete the operation. The dried stream is then compressed to 13 bar,a and sent to a membrane gas separation system. The most used membrane type in CO_2 gas separation is the glassy polymer category thanks to their selectivity, excellent thin film forming, good mechanical properties and higher permeability to low molecular weight species [5]. After the screening of numerous membranes, we concluded that a single module is not able to perform the wanted separation with reasonable cut ratio. Therefore, a two-stage membrane separation unit was implemented with the permeate of the first stage (rich in H_2 and CO_2) recycled to the methanation unit and the permeate of the second stage (rich in methane) recycled to the first stage inlet. The optimized configuration was obtained with two modules using the membrane in Table 1 with 20 m^2 of active area each.

Table 1. Membrane permeability

	Permeability (barrer ^a)			Ideal selectivity	
	H_2	CO_2	CH_4	H_2/CH_4	CO_2/CH_4
<i>TBDAI-6FDA-PI</i> [6]	253	155	3,3	76,7	46,9

$$^a 1 \text{ barrer} = 1 \times 10^{-10} \text{ cm}^3_{\text{STD}} \text{ cm s}^{-1} \text{ cm}^{-2} \text{ cm}_{\text{Hg}}^{-1}$$

At this point, the SMR liquefaction process was simulated and optimized. The pressure of the lamination was set to 3,4 bar and the optimized composition and pressure are reported in Table 2.

Table 2: Refrigerant composition, pressures and performance

Refrigerant composition (%.mol)							Pressure	Refrigerant flow	Required work
N_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	Iso-pentane	bar	$\frac{\text{kg}_{\text{REF}}}{\text{kg}_{\text{LNG}}}$	$\frac{\text{kWh}}{\text{kg}_{\text{LNG}}}$
12,0	42,1	-	17,9	13,7	-	14,3	32,6	7,9	0,57

Next the thermodynamic analysis on the reactive system excluded the possibility of carbon deposition in the ranges of temperature and pressure of the methanation unit ($280\text{-}500 \text{ }^\circ\text{C}$ and $4\text{-}10 \text{ bar}$).

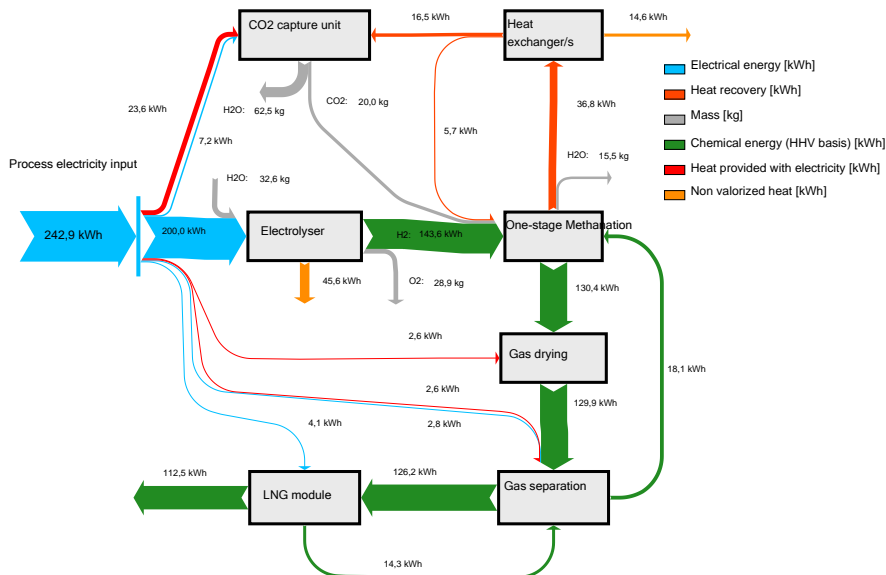


Figure 2. Energy and mass balance Sankey diagram for the optimized system

Finally, the heat integration analysis was performed. The electrolyser heat is not useful since it is generated at a low temperature of (75-80 °C) hence no heat recovery is feasible for the plant needs. Since the methanation reaction is highly exothermic part of the produced heat is supplied to the feed stream, to meet the required temperature at the reactor inlet of 280 °C, while the remaining part is sent to the CO₂ capturing unit. In Figure 2 the Sankey diagram for the energy and mass balance is reported for stationary operation at nominal capacity. By using this system integration layout ~41% of the heat required by the CO₂ capturing unit is coming from excess heat produced by the methanation reactor.

Conclusions

A concept to produce synthetic LNG using hydrogen generated from excess renewable electricity and carbon dioxide captured from air was analysed in this study. Process simulations of the concept were performed including optimisation of single units and whole plant by including thermal integration. The simulation model accounted for the efficiency of commercially available technologies (i.e. electrolysis and CO₂ capture).

A thermodynamic analysis focused on the methanation reactor excluded the carbon formation in the range of possible operating. Subsequently, a membrane gas separation system was developed: screening of different membranes and choosing the appropriate module layout. A two-stage membrane system resulted adequate for the stream purification. Besides this, choosing the appropriate separation system would give the possibility for the produced gas to be injected into the

natural gas grid or undergo liquefaction allowing for a flexible operation. Afterwards, the optimization of the SMR liquefaction system confirmed that the tested refrigerant compositions can be used. Among the several considered mixtures, the ethylene-propane refrigerant gave the lowest energy consumption of 0,57 kWh/kg_{LNG}.

Finally, after heat recovery an overall plant efficiency of 46,3% electrical to chemical conversion was calculated for the demo plant. However, the use of an electrolysis system operating at slightly higher temperature would allow to recover the produced heat and use it in the carbon dioxide capturing unit and the two TSA modules. This would allow to reach an electrical to chemical efficiency of 52,6%.

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