Proceedings of ASME Turbo Expo 2022
Turbomachinery Technical Conference and Exposition
GT2022
June 13-17, 2022, Rotterdam, The Netherlands

GT2022-81838

DRAFT: THERMODYNAMIC ASSESSMENT OF THE CONVERSION OF A TYPICAL CCGT POWER PLANT TO A FULLY E-FUEL FIRED UNIT

Jérôme Rigaud
University of Mons (UMONS)
Energy Engineering
Place du Parc 20
7000 Mons, Belgium

Ward De Paepe
University of Mons (UMONS)
Thermal Engineering
and Combustion Unit
Place du Parc 20
7000 Mons, Belgium

Hannes Laget
Engie Laborelec
Green Thermal Generation
and Energy Storage
Rodestraat 125
1630 Linkebeek, Belgium

ABSTRACT

With increasing needs for flexibility in the electricity grid, combined with longer periods of low electricity prices due to an oversupply of renewable electricity, alternative solutions which include the production of carbon-free fuel, in combination with the use of combined cycle power plants are identified as possible solution. These so-called Power-to-Gas-to-Power solutions (P2G2P), with hydrogen and ammonia as fuel, require further research to determine their feasibility. Within this scope, the European collaborative project FLEXnCONFU aims at providing an answer. The specific project idea is to recover excess grid power to produce hydrogen through proton exchange membrane (PEM) water electrolysis. Then, this hydrogen could be directly stored, or it could feed an ammonia synthesis process. Finally, the decarbonised fuels (ammonia and/or hydrogen) are burned in the gas turbine to produce electricity with no greenhouse gases (GHG) emission. Moreover, with the current climate concern, the need for research in the P2G2P domain must be a priority. The aim of this paper is thus to evaluate the impacts of P2G2P systems integration in a power plant. The different concepts have been applied to an existing ENGIE plant, based in Belgium, with the idea of installing all the technologies (electrolysers, compressors and storage, as well as ammonia fabrication units) on the power plant site. Simulations have shown that a considerable production time is needed to operate the plant several hours using these e-fuels. Moreover, hydrogen storage requires an extremely huge footprint hence it looks more reasonable to operate ammonia synthesis to store large quantity of decarbonised fuel given the site space constraints. Additionally, Aspen plus models have been realised to evaluate the global efficiency of the P2G2P systems as well as the specific cooling requirements of the added technologies. The global efficiency for the P2H2P (with hydrogen) system is 32%. For the P2A2P (with pure ammonia) and P2A2H2P (part of the produced ammonia is cracked to recover hydrogen and entering the combustion chamber of the CCGT with a blend of 70% NH_3 and 30% H_2) systems, this global efficiency is reduced respectively to 24% and 19%. From these results, it is thus apparent that there remain still several challenges that need to be overcome to make P2G2P an efficient way to decarbonise electricity production. These main challenges are: Increase the efficiency of the transformation processes to limit the power losses; Enhance hydrogen storage technologies to limit the footprint or develop an efficient hydrogen distribution; Reduce the cost of P2G technologies and especially of PEM electrolyzers; Progress on decarbonised fuels combustion and concretely limit NO_x emission for the NH_3 firing configuration.

NOMENCLATURE

CCGT Combined Cycle Gas Turbine
ASU Air Separation Unit
GHG Greenhouse Gases
GT Gas Turbine
HR Heat Rate

LHV Lower Heating Value
NG Natural Gas
P2A Power-to-Ammonia
P2G Power-to-Gas
P2H Power-to-Hydrogen
P2G2P Power-to-Gas-to-Power
PEM Proton Exchange Membrane
RES Renewable Energy Source

INTRODUCTION

To attain a carbon neutral society, renewable energy sources (RES) must be integrated into the electricity grid in a flexible way. However, RES are unpredictable, intermittent, and variable energy sources that must be coupled with other assets such as batteries or thermal power plants to ensure the reliability of the supply. Existing thermal power plants can play an important role by changing fuels from natural gas to e-fuels, which is the subject of the FLEXnCONFU project [1] (**FLEX**ibilize combined cycle power plant through Power-to-X solutions using non-**CON**ventional **FU**els), that has been granted by the EU's Horizon 2020 research and innovation programme to perform research on this flexibility challenge. The project gathers more than 20 universities, technology suppliers and end users around the adaptation of combined cycle gas turbines plants to flexible e-fuel operation.

With the emergence of RES, fossil fuel power plants will no longer operate as a base-load electric power provider, but their role will shift to providing flexible and varying power to compensate for the lack of RES and while doing so, balancing production and demand, ensuring security of supply and grid balancing. This shift in role of thermal power plants is challenging, given that strong fluctuations reduce the plant efficiency (and so increase the quantity of fuel burned for the same amount of electricity produced), increase the pollutant emissions, and reduce the operating lifetime of the plants' components. The FLEXnCONFU idea is to reduce these fluctuations in the operation by producing non-conventional decarbonised fuels (hydrogen and/or ammonia) using innovative power-to-gas (P2G) solutions. The interest of the P2G solutions, in comparison with other energy storage solutions, lies in the potential long storage time. Indeed the molecules could be stored for months, while batteries can only store for hours/days [2]. Afterwards, the decarbonised fuel can be burned in the power plant to produce energy leading to a reduction of Greenhouse Gases (GHG) emissions (in comparison with the use of conventional fuels).

The main goal of the project is thus to demonstrate, in a real combined cycle plant, the feasibility and the economic viability of the power-to-gas-to-power (P2G2P) solution to provide a more flexible power system. To achieve this main goal, the FLEXnCONFU consortium has set specific technical objectives:

1. Demonstration of the full P2H2P chain at EDP's Ribatejo power plant (Figure 1a). The target is to operate 1000 hours.
2. Experiencing the combustion of non-conventional fuels (hydrogen and ammonia) and design of a micro gas turbine combustion chamber to burn up to 100% of decarbonised fuels at Cardiff University.
3. Development of a power-to-ammonia (P2A) solution connected to a T100 micro gas turbine installed within a smart grid (Figure 1b) at Savona lab of the University of Genova. The objective is to obtain a P2A system working at relatively low temperature and pressure ($T<300^{\circ}C$ and $p<35$ bars).
4. Technical, economic, and safety feasibility studies and environmental sustainability demonstration of the concept for brown-field and green-field development in different countries in Europe.

The expected impact of the FLEXnCONFU project is the demonstration of power-to-gas-to-power solutions that will increase the flexibility of combined cycle gas turbines (CCGTs) on the marker. Moreover, the project aims at contributing to the reduction of GHG emissions and to the development of the future power grid. The expected technical impacts are:

1. Reduction of minimum load by -10%
2. Increase of power plant efficiency by 5%
3. Increase of yearly operating hours by 5 to 10%
4. Reduction of yearly start-up numbers by -10%
5. Reduction of natural gas (NG) consumption by -10 to -20%

The aspects of the project discussed in this article are the evaluation of the impacts of the on-site P2G systems integration and installation in an existing CCGT power plant. Especially, this work consists of:

1. The characteristics of the P2G systems: production rate, installation and storage footprint, and energy consumption
2. The integration of decarbonised fuels in the cycle: impacts on the efficiency, the emissions, the composition, and the mass flow rates of the flue gases
3. The indirect effects linked with the installation of P2G systems: increase of the cooling requirements

P2G SYSTEM CHARACTERIZATION

Power-to-Hydrogen

Figure 2 shows the power-to-hydrogen system investigated as part of the FLEXnCONFU project. Hydrogen is generated from water in the electrolyzer when surplus electricity is available. Then the hydrogen is compressed to be stored and when the price of electricity will be high (high demand) H_2 could be mixed with NG upstream the GT to be burned, without any GHG emission, in the combustion chamber. The excess grid power is not only used to perform the electrolysis but also to compress H_2.

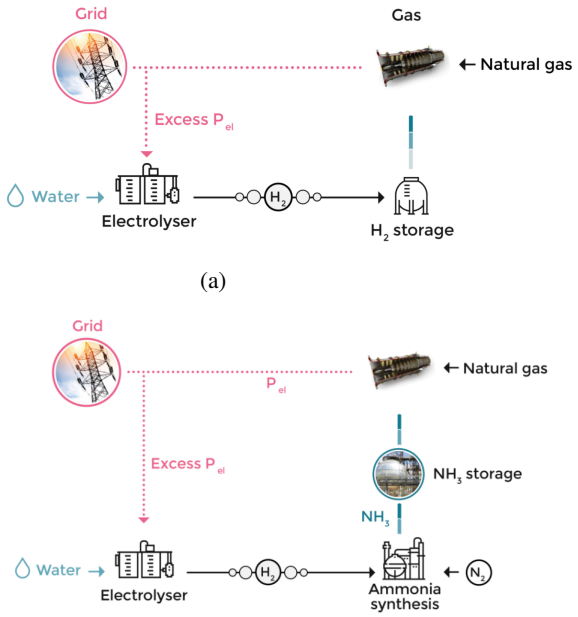

FIGURE 1: Power-to-hydrogen-to-power concept (a), where excess grid power is used to produce hydrogen from water thanks to the electrolyzer and Power-to-ammonia-to-power concept (b), where produced hydrogen is used in an ammonia synthesis process [3]

The selected electrolyzer for this project is the HyLYZER 4000 from HYDROGENICS ($P_{nom} = 20$ MW). This PEM electrolyzer has a power consumption of 4.3 kWh/Nm^3 of H_2 produced and a footprint of 20×25 m. The power consumption relative to the compression of hydrogen (considered to behave as a perfect gas) is computed by the assumption of a polytropic multi-staged compression with intermediate cooling.

As the main objective of the P2G systems is to replace NG by decarbonised fuels, it is interesting to evaluate the possibility to operate a power plant fully hydrogen fired. To this end, it is possible to compute the needed hydrogen mass flow rate by taking the assumption of a constant thermal power supply. Then, by imposing the operating time and the storage pressure, the total hydrogen volume can be determined. And finally, the production time is deduced from the excess grid power.

For the Engie power plant of Saint-Ghislain, the considered plant in this study which is capable of producing 350 MW_e of useful electrical power while consuming 62000 Nm^3/h of NG, 76 electrolyzer production hours, using 100 MW_e excess grid power, are needed to produce enough hydrogen to operate the cycle at nominal load during 8 hours. The associated required footprint for the electrolyzer and the storage are calculated as respectively 2847 m^2 and 23682 m^2 (or 270 pressure tanks storing

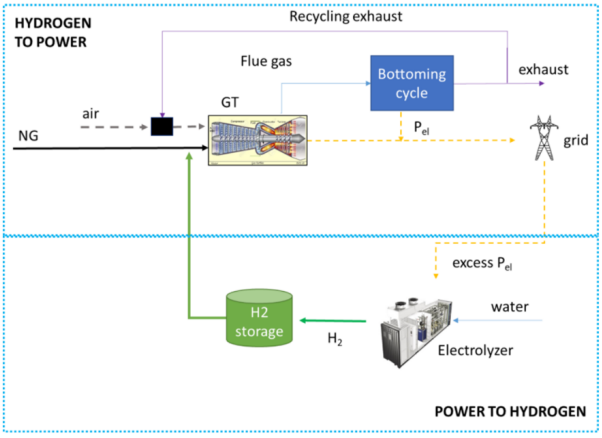

FIGURE 2: Power to hydrogen to power system: the integration of hydrogen in the combustion chamber allows to reduce the GHG emissions [4].

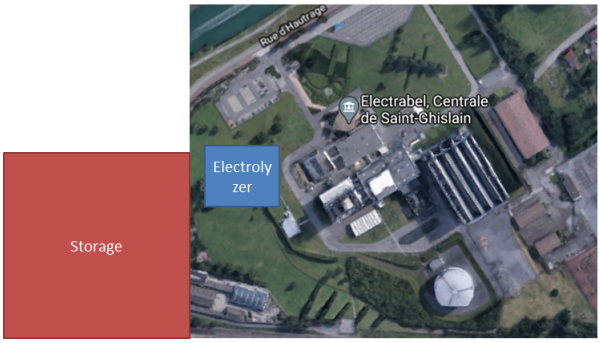

FIGURE 3: The satellite view of the site showing both global power plant footprint as well as the necessary footprint for the P2H system to operate 8 hours fully H_2 fired, clearly highlights that this storage footprint it too big for integration

hydrogen at 200 bar). To give a visual impression of this computed footprint, a satellite view of the entire site including the global power plant footprint as well as the necessary footprint for the P2H system to operate 8 hours fully H_2 fired with , is presented in Figure 3. It is clear that the necessary storage footprint is too big to be integrated in the existing Saint-Ghislain site.

Power-to-Ammonia

P2H computations have shown that H_2 storage is far from optimal. An alternative is to store it under liquid form bounded to nitrogen. Figure 4 shows the power-to-ammonia system. Hydrogen generated by electrolysis reacts with nitrogen that comes from an air separation unit (ASU) to form ammonia. Then am-

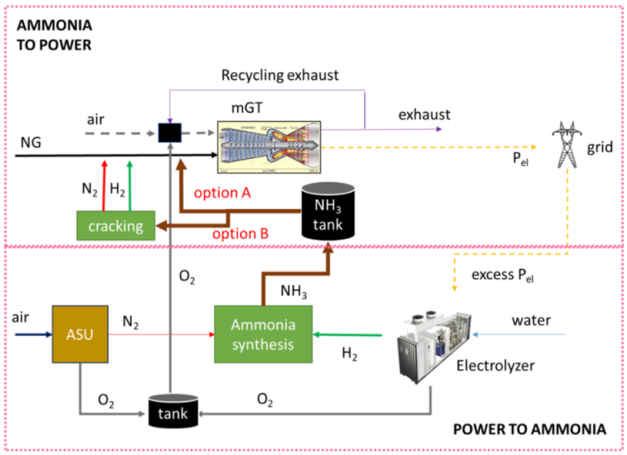

FIGURE 4: Power-to-ammonia system: Hydrogen generated by electrolysis reacts with nitrogen that comes from an air separation unit (ASU) to form ammonia. Then ammonia is stored to be later integrated in the CCGT cycle. [4]

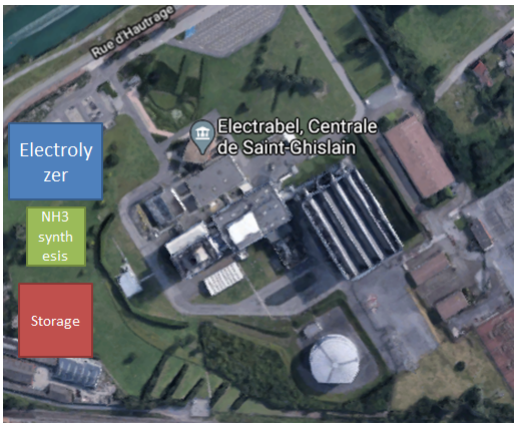

FIGURE 5: The satellite view of the site showing both global power plant footprint as well as the necessary footprint for the P2A system to operate 8 hours fully NH_3 fired, clearly highlights that it is possible to integrate the system in Saint-Ghislain site.

monia is stored to be later integrated in the CCGT cycle. The advantage of ammonia in comparison to hydrogen is that it can be stored easily in its liquid phase and so it implies a considerable reduction of the necessary storage footprint. Another advantage compared to hydrogen storage is the compatibility with classical cast iron and carbon steel storage tanks. However, the ammonia synthesis process (namely the Haber-Bosch process) requires additional power after the electrolysis, jeopardising the overall efficiency, and so the optimal choice between P2H and P2A is not obvious. The stored ammonia can be used directly in the CCGT (option A on Figure 4) or cracked to reform hydrogen (option B on Figure 4). The advantage of option B is that the presence of ammonia in the combustion chamber is avoided. Indeed, an efficient ammonia combustion is difficult to attain due to the low combustion speed, and the important NO_x emissions induced [5].

Similar to the P2H system, it is interesting to evaluate the theoretical possibility to operate a power plant fully ammonia fired. Similar to the P2H system, first, by taking the assumption of a constant thermal power supply, it is possible to compute the needed ammonia mass flow rate to run the cycle. Then, by imposing the operating time and the storage pressure, the total ammonia volume can be determined. Finally, the production time is deduced from the excess grid power used for NH_3 production. To operate during 8 hours fully NH_3 fired, a production time of 88 hours using a 100 MW_e electrolyzer is needed, while the footprints of this electrolyzer, storage, and finally the ammonia plant are assessed at 2907 m^2, 2346 m^2, and 1453 m^2 respectively. In comparison to fully hydrogen fired operating during 8 hours, the production time is a little higher (+16%) due to the lower P2G conversion efficiency but the global footprint has been considerably reduced (-75%) mainly thanks to the reduction of the storage footprint (-90%). Unlike the P2H system, Figure 5 shows that it is possible to integrate in the existing Saint-Ghislain site the necessary P2A system to operate fully NH_3 fired during 8 hours.

IMPACT OF E-FUELS ON CCGT CYCLE

Aspen Plus models of the CCGT and of the P2G systems have been developed to evaluate the impacts of P2G systems integration in a power plant on its global performance. These models have allowed to evaluate the impact of the introduction of decarbonised fuels in the cycle and the operating conditions of P2G systems, including energy consumption, decarbonised fuels produced mass flow rates, and required water feed.

CCGT modelling

The gas turbine model is composed of a multi stage air compressor, a combustion chamber by-passed by 8% of the air and a turbine. The used input data for the Aspen model, taken from the actual Engie Saint-Ghislain GE 9FA gas turbine, are given in Table 1. The steam turbine has been modelled as a black box in a way to fit with the actual data of the Engie Saint-Ghislain power plant and by considering a stack temperature of 85°C.

The gas turbine of the CCGT is modelled in Aspen using 3 block: a compressor, combustion chamber and turbine block. The Aspen compressor block allows to integrate staged compression, including intercooling by introducing the number of stages, the compression ratio and the outlet temperature of the compressor (to account for the intercooling). These parameters have been taken directly from the real compressor of the Saint-Ghislain En-

TABLE 1: CCGT Aspen model input data

Parameter	Value	Unit
Air mass flow rate	628.7	kg/s
Compression ratio	18	
Compressor outlet temperature	365	°C
Natural gas mass flow rate	14.1	kg/s
Combustion chamber outlet temperature	1260	°C
Turbine inlet temperature	1197	°C
Turbine outlet temperature	586	°C
Gas turbine power	240	MW

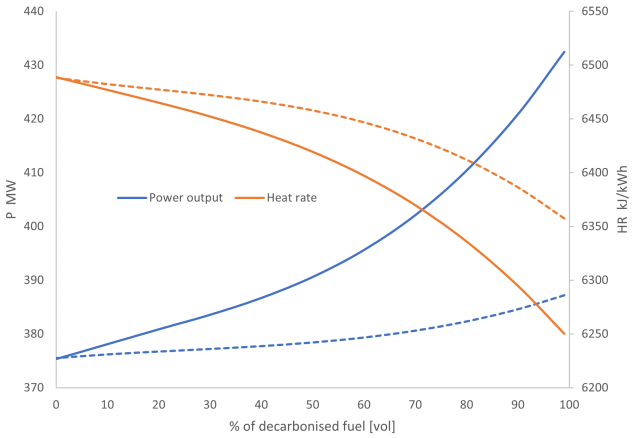

FIGURE 6: CCGT operating curves as a function of the percentage of decarbonised fuel (hydrogen in dotted-lines or ammonia in solid-lines) in the fuel: shifting to e-fuels results in larger power output and increased efficiency

gie power plant. In a similar way, the expansion is modelled by a classical Aspen turbine block using isentropic efficiency and discharge pressure, again, values for both were taken from the available data from the Saint-Ghislain power plant. Finally, for the combustion chamber, a *RStoic* reactor was selected. With this kind of reactor, the combustion reactions must be manually introduced including the conversion ratio. In this study, this conversion ratio was taken equal to 100% (assuming complete combustion). This approach has been validated by replacing the reactor block by a *RGibbs* reactor block, which minimises the Gibbs free energy. Both methods resulted in exactly the same outcome with a total combustion of the fuel. Concerning the property method, Peng-Robinson has been selected based on the proposition of the Aspen methods assistant as well as on studies found in literature, i.e., Liu and al. who have modelled a CCGT in Aspen for simulating the operation of a triple-pressure reheat cycle [6] and Yee et al., who presented an overview and comparative analysis of gas turbine models for system stability studies [7]. Finally, the heat recovery steam generator is modelled as a heat exchanger with a given value of outlet temperature that allows to access the thermal power entering the steam turbine cycle.

These Aspen simulations result in an overall performance of the cycle of 375 MW_e electrical power output for an efficiency of 55% (corresponding to a Heat Rate (HR) of 6487.75 kJ/kWh) at nominal operating conditions using NG as fuel. These results correspond to the available data of the power plant. Moreover, the model can be adapted to operate with a mixture of decarbonised fuel (hydrogen or ammonia) and NG. In this case, the fuel flow rate is chosen to keep the temperature at the outlet of the combustion chamber constant. We can observe in Figure 6 that increasing the proportion of decarbonised fuel in the mixture increases the power output and decreases the heat rate (increases the efficiency). These effects are more important in the case of ammonia integration. Considering the specific impact of increasing the fraction of decarbonised fuel on the global performance, it is important to note that in both cases (ammonia and hydrogen) the power increase occurs mainly in the gas turbine while the increase in power output of the steam cycle is rather negligible (less than 1% increase for hydrogen). On the one hand, hydrogen has a higher mass LHV than natural gas. Consequently less fuel is needed to operate fully hydrogen fired than when operated fully NG fired. Hence, for the same amount of air compressed, the flue gas mass flow rate entering the turbine is smaller, given the lower fuel mass flow rate. It is thus expected that the power output of the gas turbine would be smaller as well. However, the altering flue gases composition has a positive impact on the heat capacity and compensates the decrease of mass flow rate (lager water fractions leads to increased heat capacity). On the other hand, ammonia has a lower mass LHV than natural gas. Consequently the higher the ammonia percentage in the fuel is, the more the fuel mass flow rate must increase to keep the turbine inlet temperature constant. Hence, for a constant amount of compressed air, the flue gas mass flow rate entering the turbine will increase. In addition, as it was the case for the hydrogen, the flue gases composition when using ammonia as fuel has a positive impact on the heat capacity. The combination of these two positive impacts (mass flow rate entering the turbine and heat capacity increases) explains why the gas turbine performance is improved. However, operating fully ammonia fired is technically difficult due to combustion issues. Within the FLEXnCONFU, to tackle this problem, operating at a mixture of 70% ammonia and 30% hydrogen is studied

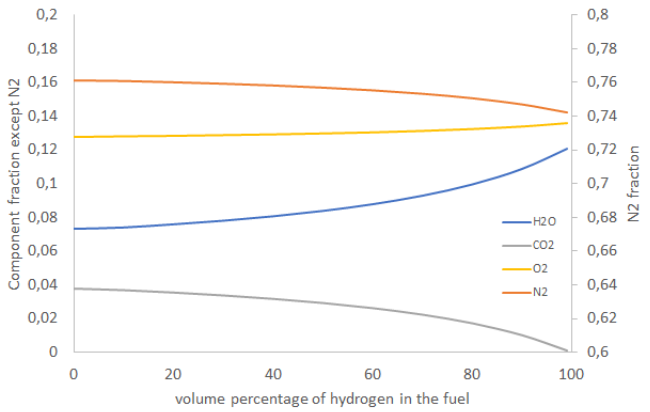

FIGURE 7: Flue gases composition as a function of the hydrogen percentage in the fuel : as expected, by increasing the fraction of e-fuel, the CO2 emissions are reduced drastically

The main goal of using decarbonised fuel was to reduce the CO_2 emissions. Figure 7 presents the evolution of the flue gases composition as a function of the amount of hydrogen introduced (same results are observed for ammonia introduction). We can observe that the main effect of decarbonised fuel introduction is indeed a reduction of the CO_2 emissions. This CO_2 is replaced by H_2O in the flue gases (and water and N_2 in the case of nitrogen combustion). Additionally, Figure 7 clearly highlights that the CO_2 reduction becomes only interesting at high decarbonised fuel percentage in the mixture (around 70%).

PEM electrolyzer modelling

PEM electrolyzer is the central component of the P2G system. A PEM electrolyzer uses electrical energy to produce oxygen and proton from water in the anode side. The produced protons that pass through the membrane to the cathode side are reduced by electrons from the external circuit producing hydrogen. The water decomposition starts when the voltage of the electrical DC power source connected to the electrodes is higher than the thermodynamic reversible potential [8]. The potential difference between the anode and cathode electrodes under reversible conditions is called the reversible cell potential E^0_{rev}. The reversible cell potential E^0_{rev} corresponds to the minimal electrical work needed to split water. However, the water splitting reaction generates entropy and hence the voltage required to trigger the reaction is higher than the reversible cell potential and is called thermoneutral voltage at standard state (E^0_{th}). Once the current passes through the cell, irreversible losses occur that make the actual required voltage for splitting water higher than the thermoneutral voltage at standard state. These losses can be divided in two types: the Faradaic losses (activation losses) and the non-Faradaic losses (mainly ohmic losses). Activation losses find their origin in electro-mechanical reaction activation: the thermodynamic equilibrium is shifted and this results in a reduction of the reaction velocity. During operation, the predominant losses are due to the cell resistance. The total ohmic losses are computed applying Ohm's law.

The link between the electrical quantities and the amount of hydrogen produced is established by the application of Faraday's laws. Faraday's laws are represented by the following equation:

$$m = \frac{Q}{F}\frac{M}{z} \tag{1}$$

with m the mass of hydrogen produced, Q the total electrical load, F the Faraday constant, M the molar mass and z the valence. In the typical case of a DC power supply, we have that $Q = It$. Then Faraday's law can be re-expressed to give the number of moles of hydrogen produced:

$$n = \frac{It}{F}\frac{1}{z}. \tag{2}$$

The core activity of the electrolyzer system is the conversion of electrical energy into hydrogen. For this reason, electrochemical models are the most important part of the electrolyzer modeling, establishing the link between the electrical power (input) and hydrogen flow (output). To determine the electrical quantities of the electrolyzer, models from literature are used [9,10,11,12,13,14,15,16,17]. The most common representation of the electrolyzer performance is the polarization curve. The polarization curve represents the relation between the current density and voltage. Nafeh [9] modeled the electrolyzer voltage (V) using the following expression:

$$V = E_{cell} + V_{Act,c} + V_{Act,a} + IR_i, \tag{3}$$

where E_{cell} is the open circuit voltage, $V_{Act,c}$ and $V_{Act,a}$ are the cathode and anode activation over-potentials and R_i the equivalent resistance of the cell caused by the non-infinite conductivity of the cell. The open circuit voltage is determined typically by the Nernst equation. This equation has already been verified by several researchers (Han et al., 2016 [10]; Yigit and Selamet, 2016 [11]; Ruuskanen et al., 2017 [12]; Moradi Nafchi et al., 2019 [13]; Toghyani et al.,2019 [14]):

$$E_{cell} = E^0_{rev} + \frac{RT}{2F}\left[\ln\left(\frac{p_{H_2}p^{1/2}_{O_2}}{p_{H_20}}\right)\right], \tag{4}$$

where p is the partial pressure, T the temperature, F the Faraday constant and E^0_{rev} is the reversible cell potential at standard

temperature and pressure. The most common expression used by many authors to determine the activation over-potentials (Marangio et al., 2009 [15]; Agbli et al., 2011; Awasthi et al., 2011 [16]; Kim et al., 2013 [17]; Abdin et al., 2015 [18]; Yigit and Selamet [11], 2016; Ruuskanen et al., 2017 [12]; Sartory et al., 2017 [19]; Moradi Nafchi et al., 2019 [13]) is based in the Butler-Volmer equation:

$$V_{Act} = \frac{RT_a}{\alpha_a F}\text{arcsinh}\left(\frac{I}{2I_{0,a}}\right) + \frac{RT_c}{\alpha_c F}\text{arcsinh}\left(\frac{I}{2I_{0,c}}\right), \quad (5)$$

where $I_{0,a}(I_{0,a})$ is the exchange current density at the anode(cathode) and $\alpha_a(\alpha_c)$ is the charge transfer coefficients at anode(cathode). Finally the electrical models of the equations 4 and 5 allow to rewrite the relation 3 as a complex expression $V = f(I)$. This complex equation could be approached by the expression (demonstrated by Atlam [20] and adapted to fit with the electrolyzer used as part of the FLEXnCONFU project):

$$V = 1.4760 - 1.4760e^{\frac{-5}{0.02}I} + 0.8436I. \quad (6)$$

Lastly, combining Equation 6 and the Faraday law allows to obtain an indirect relation between the power supply to the cell and the hydrogen production rate. Using Equation 6 and knowing that the power supply is equal to the voltage multiplied by the current allows to obtain the value of the current. This value is then injected in Equation 2 to compute the hydrogen flow rate. The computed hydrogen flow rates at ambient conditions are presented in Figure 8. The model is close (maximal uncertainty of 0.4 ml/min) to the measurements (HYDROGENICS data [21]) and can thus be considered validated.

P2H modelling

Power-to-hydrogen system has also been simulated using Aspen. The system is composed of the electrolyzer that has been modelled using the methodology presented in the previous section and of a volumetric compressor with $\eta_{iso} = 0.785$ to 200 bar to store hydrogen at high pressure. In Aspen, the compression is classically modelled by a compressor block and, in absence of a real electrolyzer block, the electrolysis is approached by a combination of available blocks (reactor, pump and separator). The selected property method is Peng-Robinson since it is the method recommended by the Aspen user guide [22] for gas processing. To validate the model, the results obtained with Aspen have been compared with the PEM electrolyzer provided by Proton onsite to the department of energy of Politecnico di Milano [23], with the MYRTE platform located on Corsica [24], within the CUTE project [25] and with the results given by EDP as part of the FLEXnCONFU project.

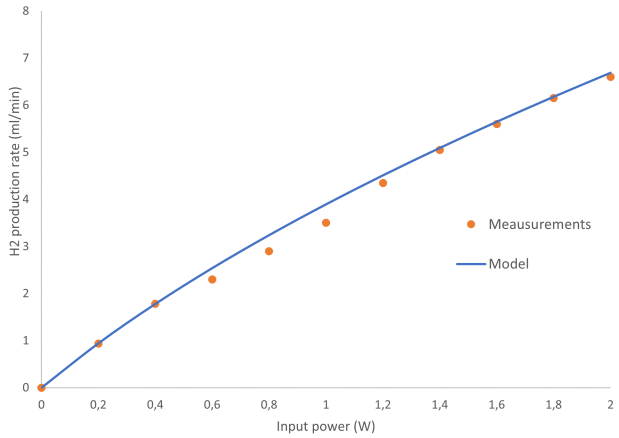

FIGURE 8: The simulated hydrogen production rate as function of the input power matches well with the experimental results.

The design variable of the system is the power supply from the grid that is used to perform the electrolysis and to compress hydrogen. For an excess grid power of 100 MW_e, the Aspen model gives the following results:

1. Hydrogen production: 1767 kg/h
2. Necessary water feed: 19730 kg/h
3. Oxygen co-produced: 14800 kg/h
4. Power distribution: electrolyzer 96.4% and compressor 3.6%

P2A modelling

The power-to-ammonia system is composed of a typical Haber-Bosch process alimented with hydrogen by the electrolyzer and in nitrogen by an air separator unit (ASU). An ASU is a liquefier that allows to separate oxygen and nitrogen from air using the Joule-Thomson effect (throughout expansion in an adiabatic valve, we have an isenthalpic process with variation of temperature and pressure). In the Haber-Bosch process, as represented in Figure 9, the hydrogen and nitrogen mixture is taken at specific conditions to enter the reactor (500°C and 200 bars). Then the products are condensed and liquid ammonia is extracted. The vapour fraction is recovered and recirculated to avoid reactant losses.

This Haber-Bosch process is well known and several studies are available presenting the modeling of ammonia synthesis. The Aspen model developed for the study presented in this paper is based on the work of Florez-Orrego [26]. In particular, following selection for the input parameters has been made: Peng-Robinson as property method, a compressor discharge pressure of 270 bars, a *RStoic* reactor at a temperature of 500°C and a pressure loss of 2 bars, a condensation at 0°C and a flash separa-

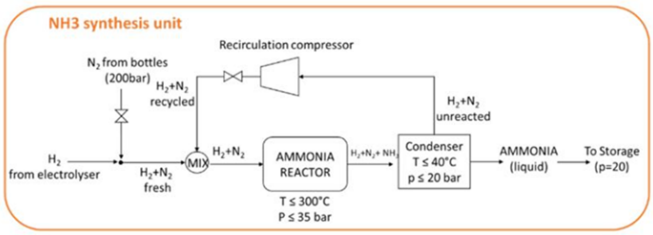

FIGURE 9: Schematic representation of the Haber Bosch process [4]

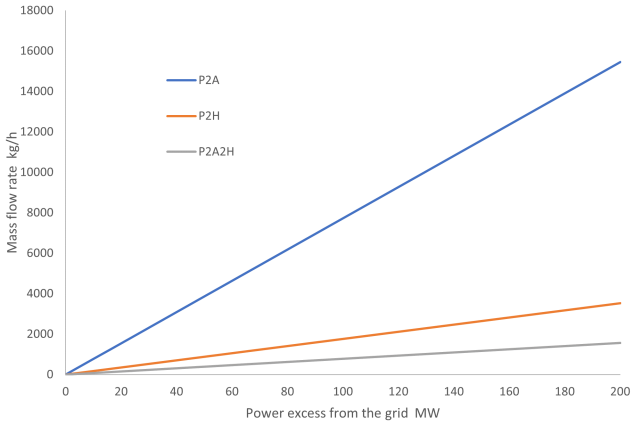

FIGURE 10: P2G: decarbonised fuel mass flow rate production as a function of the excess grid power, showing that ammonia synthesis to deal with storage issues has a clear energy cost.

tor to separate liquid and gas phases. In a similar way as for the P2H system, the results obtained with Aspen have been validated with the results obtained by the university of Genova as part of the FLEXnCONFU project but also with the commercial Power-to-Ammonia system of Proton Ventures [27] and the data issued from a ISPT (Institute for sustainable process technology) report on the feasibility of P2A.

The design variable of the P2A2P system is the power supply from the grid that is used for the electrolyzer, the air separation unit and the compressors of the Haber-Bosch process. For a power-to-ammonia system based on a 100 MW electrolyzer, the Aspen model gives the following results:

1. Ammonia production: 8680 kg/h
2. Oxygen co-produced: 16300 kg/h
3. Thermal power to evacuate: 29MW
4. Power distribution: electrolyzer 89%, compressors 4% and ASU 7%

P2A2H modelling

As previously discussed, storage of hydrogen in ammonia form is a way to limit the necessary storage footprint and allows to take advantage of the ammonia storage technology maturity. Then hydrogen could be recovered from ammonia through ammonia decomposition to enhance the flame speed and to limit NO_x emissions during combustion. Classically, ammonia decomposition occurs in a membrane reactor where the chemical reaction and the selective separation of one of the products (hydrogen in our case) occur simultaneously.

In the Aspen model that simulates ammonia decomposition to recover hydrogen, the stored ammonia (that indirectly comes from Haber-Bosch process) is heated up to 410°C and then enters the membrane reactor where hydrogen is recovered. The temperature has been chosen to attain a conversion rate of 20% to correspond with the configuration where the fuel is a mixture composed of 70% ammonia and 30% hydrogen. Higher conversion rate could be attained by increasing this selected temperature.

The characteristics of decarbonised fuel production as a function of the excess grid power is compared for the three investigated systems (P2H, P2A and P2A2H) in Figure 10. Obviously, we can observe than P2A2H system appears less interesting than P2H system but it allows to deal with the storage issues.

Global efficiency

Generally, the P2G system can be considered as a conversion from electrical excess grid power to chemical potential power. Then the decarbonised fuel is burned in the combustion chamber of the combined cycle gas turbine to be reconverted into electrical power. It is thus interesting to determine the amount of excess grid power that is finally recovered in electrical power. The developed Aspen models allow to determine this. Indeed by imposing an excess grid power of 100 MW, the P2G models (P2A, P2H or P2A2H) give the produced mass flow rate of decarbonised fuel as well as its composition (and so its Lower Heating Value (LHV)). Once the potential chemical power determined, we can directly compute the electrical output power through cycle efficiency (that is function of the fuel composition).

Figure 11 presents respectively the Sankey diagram for P2H, P2A and P2A2H (Mix 70% ammonia/30% hydrogen fired) systems. From these Sankey diagrams, it is clear that the P2H system is the pathway that allows to recover the largest amount of the input power (31.73%). However, operating with pure hydrogen leads to storage issues, as highlighted before. Hence, concerning P2A and P2A2H systems, Aspen simulations show that operating fully ammonia fired allows to recover a larger amount of the initial energy input (24.2%) than operating with a mix 70% ammonia/30% hydrogen fired (18.94%). However, it is important to keep in mind that burning ammonia is much more difficult due to NO_x. The difficulty is to find a trade off between combustion stability, emissions, storage footprint, and finally the global

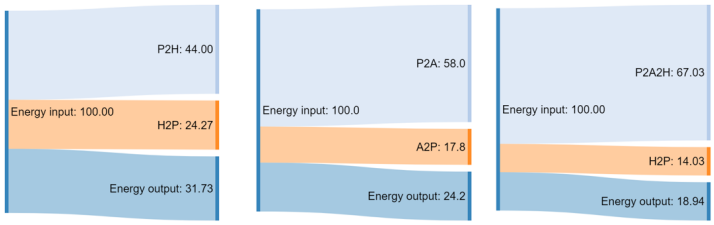

FIGURE 11: Sankey diagram for 100 MW of energy output. From left to right: P2H, P2A and P2A2H

roundtrip efficiency.

Oxygen co-produced management

For all the investigated P2G technologies, we can observe that a non-negligible amount of oxygen is produced. However, different studies (in example a report from INERIS on electrolyzers [28]) have shown that oxygen valorization is very difficult to accomplish. The industrial actors that could potentially be interested by this oxygen excess are hospitals, injection in water to limit biological issue next a barrage, welding and underwater activities. An ethic way to avoid the waste of the oxygen co-produced would be to reject this oxygen into the natural water reserve (typically a river) that operates as cold source for the steam condensation in the steam turbine cycle. Indeed, it would have a positive effect on the environment including fishes health that is severely damaged by heat rejections in summer. Oxygen valorization by its classical distribution system is tough because oxygen is classically transported in liquefied form by trucks. Without an oxygen liquefier unit next to the electrolyzer, the valorization is only possible via local direct usage.

HEAT MANAGEMENT

The different processes involved in the P2G systems have heat or cooling requirements. The aim of this section is to integrate these requirements in a global scheme allowing to discuss the feasibility of heat recovery within the system. To this end, we will consider the most complete P2G system, namely the power-to-ammonia-to-hydrogen-to-power system. In this system, the excess grid power is used to generate hydrogen in a PEM electrolyzer while nitrogen is provided by an air separation unit. Then, hydrogen and nitrogen enter into the Haber-Bosch process where ammonia is generated, which can then be stored. Finally, we aim at operating the CCGT with decarbonised fuel, hence ammonia is heated to be partially decomposed in hydrogen and the power plant is fired using a mix 70% ammonia/30% hydrogen as fuel. For this system (based on a 100 MW_e PEM electrolyzer), the different cooling and heat requirements, directly deduced from the Aspen models, are:

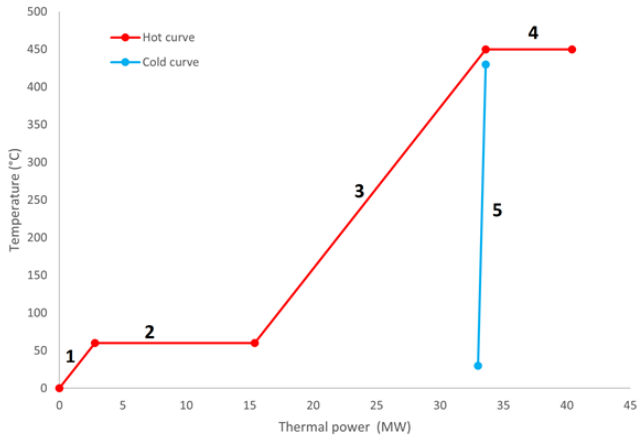

FIGURE 12: Pinch analysis method: graphic view. 1. Haber-Bosch condensation 2. Electrolyzer cooling 3. Haber-Bosch condensation 4. Haber-Bosch reactor cooling 5. Ammonia decomposition. It appears that most of the heat rejected by 1,2,3 and 4 can not be valued by 5

1. Cooling the PEM electrolyzer: 12.6 MW_{th} at 60°C
2. Haber-Bosch process: cooling the reactor: 6.8 MW_{th} at 450°C
3. Haber-Bosch: condensation: 21 MW_{th} from 450°C to 0°C
4. Necessary heat to decompose ammonia: 600 kW_{th} from 30°C to 430°C

The pinch analysis method [29], that consists in composing a hot curve that regroups all the cooling requirements and a cold curve that regroups all the heat requirements and placing them in a graph with the temperature on the Y-axis and the thermal power exchanged on the X-axis, has been used to discuss the feasibility of heat recuperation. Considering a 20°C pinch, we see in Figure 12 that it is indeed possible to recover heat to operate the ammonia decomposition. However we can observe that there remains a large amount of heat to be evacuated (39.8 MW_{th}).

To reduce these requirements and to value the available thermal power, it is possible to add an additional heat user (the heat rejections will for example operate as hot source for an ORC cycle). Two heat users are added in Figure 13 (dotted-lines). The constant temperature of the heat users have been chosen to correspond with the hot sources of a Rankine cycle. The temperature of the high temperature heat user (on the right part of the graph) is imposed by the pinch assumed equal to 20°C. However, an optimization between the heat recuperation efficiency and the Rankine cycle efficiency has to be realized to determine the temperature of the second heat user (on the left part of the graph). We immediately notice that these additions allow to reduce the external cooling requirements.

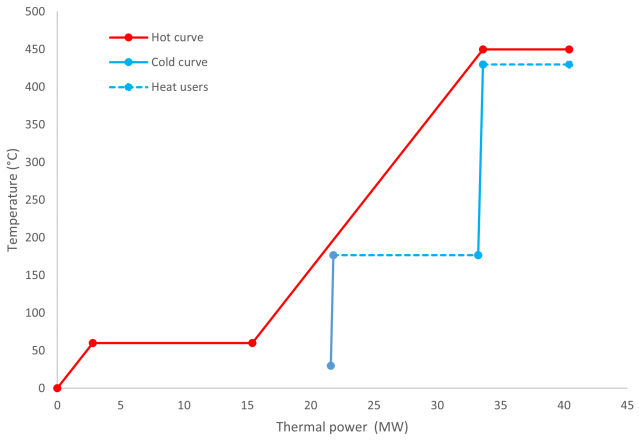

FIGURE 13: Pinch analysis method: addition of two heat users (dotted lines)

Conclusion

In this paper, innovative P2G solutions to level CCGT loads by producing decarbonised fuels, that could be burned in the same power plant reducing GHG emissions, have been explored. As a reminder, the article aims to focus on three points :

1. The characteristics of the P2G systems: production rate, installation and storage footprint, and energy consumption.
2. The integration of decarbonised fuels in the cycle: impacts on the efficiency, the emissions, the composition, and the mass flow rates of the flue gases.
3. The indirect effects linked with the installation of P2G systems: increase of the cooling requirements.

First, the P2H system has been investigated. However, results indicated that the necessary storage surface relative to the amount of hydrogen needed to run the CCGT fully H_2 fired during several hours is huge and make the system installation very difficult. Thanks to its capacity to be stored in liquid state, a solution to reduce the necessary storage surface is to operate P2A. The main drawback relative to ammonia is the difficulties associated to its combustion (e.g., NO_x emissions). If one wants to operate fully decarbonised fuels fired, it is mandatory to crack at least a part of the ammonia to recover hydrogen and burn a blend of ammonia and hydrogen. Moreover, in addition of necessary storage surface considerations, P2G systems present important production times too. As illustration, a P2H system that operates during 8 hours with an excess grid power of 100 MW produces a certain amount of hydrogen that would allow to run the CCGT fully H_2 fired only for 50 minutes. The production time and the necessary storage surface could be limited by reducing the percentage of decarbonised fuel in the fuel blend. However, the CO_2 reduction in the flue gases becomes interesting only at high decarbonised fuel percentage in the blend.

The Aspen plus model of the CCGT realised as part of this work has shown that the decarbonised fuels introduction implies an increase of the power output and of the cycle efficiency especially in the case of ammonia integration. Finally, the multiplication of transformation processes increases the losses and reduces the overall efficiency of the global P2G2P system. Furthermore, the P2G systems models have shown that the installation of P2G systems implies large cooling requirements. The heat excess could potentially be recovered to operate ammonia decomposition and to run Rankine cycles that will produce additional electrical power. However, as a time delay must be introduced between heat rejections and heat recoveries, heat storage technologies must be investigated.

Future Work

The main conclusion of this work is that it remains lot of challenges to make P2G an efficient way to decarbonise electricity production. The main challenges are:

1. Increase the efficiency of the transformation processes to limit the power losses;
2. Enhance hydrogen storage technologies to limit the footprint or develop an efficient hydrogen distribution grid to avoid the needed storage capacity;
3. Reduce the cost of P2G technologies and especially of PEM electrolyzers
4. Progress on decarbonised fuels combustion and concretely limit NO_x emission for the NH_3 firing configuration

REFERENCES

[1] FLEXnCONFU, 2020. “Flexibilize combined cycle power plant through power-to-x solutions using non-conventional fuels”. *European Commission*.

[2] PASCAL KOSCHWITZ, TECHNICAL UNIVERSITY OF DARMSTADT, E. S., and TECHNOLOGIES, G., 2020. “Power to ammonia to power (p2a2p)”. *ETN WEBINAR FLEXIBLE POWER GENERATION*, November.

[3] FLEXnCONFU, 2020. “https://flexnconfu.eu/”. *European Union’s Horizon 2020 research*.

[4] Paula Ramos, D. B., 2020. “Preliminary results and next steps”. *FLEXnCONFU project WP1 technical meeting*, September.

[5] Wai Siong; Chai Yulei; Bao Pengfei; Jin Guang Tang, L. Z., 2021. “A review on ammonia ammonia/hydrogen and ammonia/methane fuels”. *Renewable and Sustainable Energy Reviews*.

[6] Zuming Liu, I. K., 2018. “Simulation of a combined cycle gas turbine power plant in aspen hysis”. *Energy Procedia*.

[7] Soon Kiat; Yee Jovica; V. Milanovic; F. Michael, H., 2008.

"Overview and comparative analysis of gas turbine models for system stability studies". *IEE transactions on power System*.

[8] Pinto, D. F. A., 2020. "A review on pem electrolyzer modelling: guidelines for beginners". *Journal of cleaner production*.

[9] Nafeh, 2011. "Hydrogen production from a pv/pem electrolyzer system using a neural-network-based mppt algorithm". *Int. J. Numer. Model. Electron.Network. Dev. Field.*

[10] Han B.; Mo J.; Kang Z., Z. F., 2016. "Effects of membrane electrode assembly properties on two-phase transport and performance in proton exchange membrane electrolyzer cells". *Electrochim. Acta.*

[11] Selamet, Y. T., 2016. "Mathematical modeling and dynamic simulink simulation of high-pressure pem electrolyzer system.". *Int. J. Hydrogen Energy*.

[12] Ruuskanen V.; Koponen J.; Huoman K.; Kosonen A.; Niemela M., A. J., 2017. "Pem water electrolyzer model for a power-hardware-in-loop simulator.". *Int. J. Hydrogen Energy*.

[13] Moradi Nafchi F.; Afshari E.; Baniasadi E., J. N., 2019. "A parametric study of polymer membrane electrolyser performance, energy and exergy analyses.". *Int. J. Hydrogen Energy*.

[14] Toghyani S.; Fakhradini S.; Afshari E.; Baniasadi E.; Abdollahzadeh Jamalabadi M.Y., S. S., 2019. "Optimization of operating parameters of a polymer exchange membrane electrolyzer". *Int. J. Hydrogen Energy*.

[15] Marangio F.; Santarelli M., C. M., 2009. "Theoretical model and experimental analysis of a high pressure pem water electrolyser for hydrogen production". *Int. J. Hydrogen Energy*.

[16] Agbli K.S.; Pera M.C;. Hissel D.; Rallieres O.; Turpin C., D., 2011. "Multi-physics simulation of a pem electrolyser: energetic macroscopic representation approach.". *Int. J. Hydrogen Energy*.

[17] Kim H.; Park M., L., 2013. "One-dimensional dynamic modeling of a highpressure water electrolysis system for hydrogen production". *Int. J. Hydrogen Energy*.

[18] Gray, A. Z. W. C., 2015. "Modelling and simulation of a proton exchange membrane (pem) electrolyser cell.". *Int. J. Hydrogen Energy*.

[19] Sartory M.; Wallnofer-Ogris E.; Salman P.; Fellinger T.; Justl M.; Trattner A., K. M., 2017. "Theoretical and experimental analysis of an asymmetric high pressure pem water electrolyser up to 155 bar". *Int. J. Hydrogen Energy*.

[20] O, A., 2009. "An experimental and modelling study of a photovoltaic/proton-exchange membrane electrolyzer system". *Int. J. Hydrogen Energy*.

[21] HYDROGENICS, 2018. "Renewable hydrogen solutions". *Brochure*.

[22] INC, A. T., 2000. "Aspen plus user guide version 10.2". *Design Simulation and optimization systems*.

[23] Paolo Colbertaldo; Sonia Laura Gomez Alaez, S. C., 2017. "Zero dimensional dynamic modeling of pem electrolyzers". *Energy Procedia*.

[24] Manuel Espinosa-Lopez; Christophe Darras; Philippe Poggi; Raynal Glises; Philippe Baucour; Andre Rakotondrainibe; Serge Besse, P. S.-C., 2017. "Modelling and experimental validation of a 46 kw pem high pressure water electrolyzer". *Renewable energy*.

[25] K. Stolzenburg; V. Tsatsami, H. G., 2017. "Lessons learned from infrastructure operation in the cute project". *International Journal of Hydrogen Energy*.

[26] de Oliveira Junior, D. F.-O. S., 2016. "Modeling and optimization of an industrial ammonia synthesis unit : an exergy approach". *Elsevier Energy*.

[27] Ventures, P., 2020. "Company presentation". *Slidepack*.

[28] WEINBERGER, V. D. D. S. P. B., 2016. "Etude comparative des reglementations guides et normes concernant les electrolyseurs et le stockage d'hydrogene". *INERIS*.

[29] Dumont, P. E., 2020. "Thermodynamique avancée intégration thermique des besoins en chaleur et en froid". *Faculté polytechnique de Mons*.