Coupling Solid Oxide Electrolyser (SOE) and ammonia production plant

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Abstract

Ammonia is one of the most produced chemicals worldwide and currently is synthesized using nitrogen separated from air and hydrogen from natural gas reforming with consequent high consumption of fossil fuel and high emission of CO_2. A renewable path for ammonia production is desirable considering also the potential development of ammonia as energy carrier. This study reports design and analysis of an innovative system for the production of green ammonia using electricity from renewable energy sources. This concept couples Solid Oxide Electrolysis (SOE), for the production of hydrogen, with an improved Haber Bosch Reactor (HBR), for ammonia synthesis. An air separator is also introduced to supply pure nitrogen. SOE operates with extremely high efficiency recovering high temperature heat from the Haber Bosch reactor. Aspen was used to developed a model to study the performance of the plant. Both the SOE and the HBR operate at 650°C. Ammonia production with zero emission of CO_2 can be obtained with a reduction of 40% of power input compared to equivalent plant.

Keywords: Sustainable Ammonia synthesis, Energy storage, Sold Oxide Electrolyser

1 Introduction

Ammonia production plays a significant role in the world emission of CO_2. Ammonia is an intermediate chemical for the final production of all fertilizers based on urea that represents 78% of European fertilizers [1]. In addition, ammonia was presented recently as a potential fuel and as an eligible energy vector [2]. Such opportunity comes from ammonia high density in terms of energy content. Volumetric and gravimetric energy density of ammonia at room temperature and 10 bar are 22.5 MJ/kg and 13.6 GJ/m^3 respectively, higher than other candidates such as hydrogen and methanol and not far from fuels from fossil sources such as gasoline, diesel and compressed natural gas. The utilization of ammonia as a fuel was reported with interesting results in all traditional power units [3]. Ammonia combustion develops heat that can be used both in internal and external combustion engine [XX]. In addition, the use of ammonia as a fuel is also demonstrated in fuel cells with consequent advantages in terms of low emissions and high efficiency. Ammonia is a carbon free fuel, no CO_2 is emitted when burnt, and in fuel cell applications the risk of NO_x production is reduced because no direct mix between oxygen and ammonia occurs. A sustainable use of ammonia both as chemical and as fuel requires a renewable production of NH_3 [4,5,XXX]. Ammonia is usually produced in the Haber Bosch (HB) loop reactor from pure hydrogen and nitrogen that are fed and recirculated in the reactor, operating at high pressure and high temperature. Hydrogen is usually produced from fossil sources, such as natural gas, in an autothermal steam methane reformer or from a steam methane reformer and while nitrogen is separated from air. Both hydrogen and nitrogen should be supplied using renewable energy as a primary source: such as biomass, wind or solar [6,7]. In particular, from water

electrolysis and air separation powered by renewable electricity it is possible to produce the so called green ammonia without any CO2 emission[8].

This kind of plant can also be used in electric grids with a large penetration of intermittent renewable energy sources to store energy into a fuel that allows the physical and temporal separation, of energy supply and demand. The green ammonia plant allows to store directly the renewable electricity into a chemical with high energy density and easy to stock and to transport. This concept was recently presented and studied in literature [9]. Some recent publications have shown that carbon free ammonia can be obtained within a range of consumption of 10-12 kWh/kg NH_3 [9-11].

Recent development of Solid Oxide Fuel Cells (SOFCs) brought novel interest on high temperature Solid Oxide Electrolysers (SOEs), based on the same materials and design [12]. SOEs operate with high power density and efficiency than traditional electrolysers, especially if fed with high temperature waste heat, because the electrochemical conversion of water at high temperatures opens the opportunity to store both heat and electricity in the produced hydrogen [13]. Such opportunity is currently under study in industrial processes where waste heat recovery at high temperature is available. For example, the coupling is possible with nuclear power plants where heat is usually a by-product [14], or with solar collectors in solar thermal power plants, where renewable heat comes from the sun [13]. In this scenario, the coupling of SOE and HB process is extremely interesting. NH_3 synthesis is an exothermic chemical reaction at high temperature and pressure, thus in the energy balance of the plant, a large amount of heat is available. The integration between the HB process and the SOE potentially allows to transfer the heat produced by the HB reactor to the SOE to increase its performance. Moreover, the feasibility of ammonia production from renewable energy via electrolysis of water is of fundamental importance to produce sustainable fuels and chemicals.

This study proposes an improvement to green ammonia production plants introducing for the first time a SOE for H_2 production in a HB process. An electrochemical model and a thermodynamic simulation of a system layout, in which a SOE and an NH_3 plant are integrated and operated at high pressure and temperature, have been developed to evaluate the potential of the proposed concept with respect to other green solutions and to a reference benchmark case, based on the use of a fossil fuel. The effect on the global efficiency and on avoided CO_2 emissions is evaluated. This work can enhance the development of green ammonia and can offer, at the same time, an interesting application of SOE. In the following paragraphs the theory and modelling of SOE and HB process are presented, the design of the model is described and, finally, main results are analysed and commented.

2 Theoretical background and model development

2.1 Considerations for coupling and SOE electrochemical model

Ammonia synthesis is an exothermal process based on the following chemical reaction:

$$\frac{3}{2}H_2 + \frac{1}{2}N_2 \leftrightarrow NH_3 \qquad \text{(i)}$$

The distinctive features of this equilibrium reaction is that the contrasting effects of pressure and temperature limit its thermodynamics and kinetics, according to the following equations [15]:

$$K_{NH_3} = K_\varphi \cdot K_p = \left(\frac{\varphi_{NH_3}}{\varphi_{N_2}^{1/2} \cdot \varphi_{H_2}^{3/2}}\right) \cdot \left(\frac{n_{NH_3}}{n_{N_2}^{1/2} \cdot n_{H_2}^{3/2}} \cdot \frac{n_{tot}}{P_{tot}}\right) \qquad \text{(ii)}$$

$$r_{NH_3} = r_{dir} - r_{ind} = k_1 \cdot P_{N_2} \cdot \left(\frac{P_{H_2}^3}{P_{NH_3}^2}\right)^{\alpha} - k_2 \cdot \left(\frac{P_{NH_3}^2}{P_{H_2}^3}\right)^{\beta} \quad \alpha + \beta = 1; \;\; \alpha, \beta > 0 \qquad \text{(iii)}$$

The first is the chemical equilibrium constant in which non ideal fugacity coefficients are accounted in the term K_φ. The term K_p account for the reactor operating conditions. The second is the so-called Temkin-Phyzev rate equation for ammonia reaction kinetics. According to these two equations, an efficient and high conversion of reactants in ammonia is favoured by:

- High pressure and temperature of the reactor.
- Stoichiometric H_2/N_2 ratio in the reactor feeding stream.
- Absence of inerts or diluting species.

Ammonia synthesis is thus realized mainly with the plant design developed by Haber and Bosch (HB). The design regards the number and the relative position of many functional units around the synthesis reactor, in order to obtain an overall recycling loop. The fundamental units required to realize an HB plant are:

- A gas clean-up unit, to purify the raw syngas coming from upstream processes if any.
- A compression unit, to compress purified syngas to the HB reactor pressure.
- Heat exchanger and flash drum units for heat recovery and condensation of ammonia.
- Auxiliary streams for purging inert gasses out from loop and for recirculation of unconverted gasses.

The HB design is shown in Figure XX.

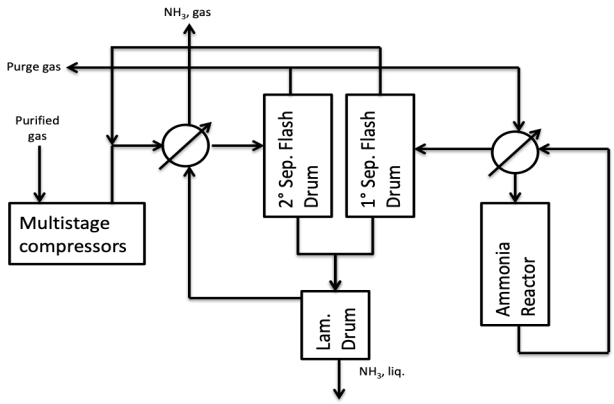

Figure 1 HB process layout for production of NH_3

The first two points determine the conversion per pass in the HB, according to thermodynamics and kinetics of equations (ii) and (iii). The last two points mainly contribute to the global conversion and productivity of the plant. Nevertheless, considering the presence of high and low temperature units, heat recovery issues arises and they both influence the energy efficiency and the production of pure ammonia [16]. The HB process considered in this work is based on a modern layout, to optimize the above mentioned parameters by coupling it with a SOE. SOE conceptual scheme is depicted in Figure 2.

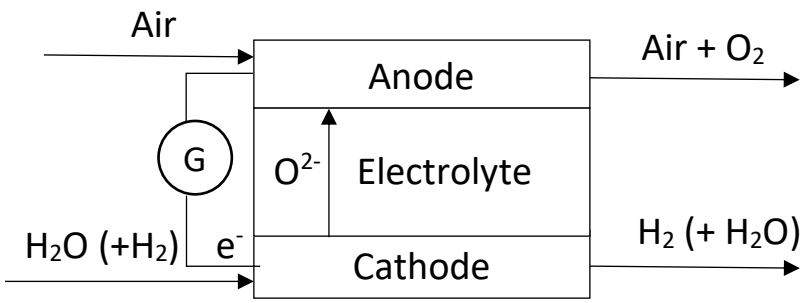

Figure 2 SOE conceptual scheme

Anodic and cathodic reactions are:

Anode $$O^{2-} \rightarrow 2e^{-} + \frac{1}{2}O_2$$ (iv)

Cathode $$H_2O + 2e^{-} \rightarrow H_2 + O^{2-}$$ (iv)

The overall electrolysis reaction is the following:

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2$$ (iv)

The reaction is endothermic and the inlet energy, equal to ΔH, has to be supplied externally. In the electrochemical devices, like fuel cells, such energy is supplied as electrical (ΔG) and thermal energy ($T\Delta S$). Thermal energy is usually generated inside the cell, recovering heat from internal polarization losses. With the increase of temperature, total energy requirement (ΔH) increases but the amount of electrical energy is smaller. The results is a higher efficiency of the high temperature electrolyser than low temperature ones. If part of the heat necessary is supplied by an external source, it is possible to achieve efficiency higher than one, obtaining the conversion of thermal energy into chemicals.

Thermodynamic values at 650°C are reported in Table 1. Note that values are normalized for one mole of H_2 produced (electrolysis) or reacting (ammonia synthesis).

	Temperature [°C]	Pressure [bar]	ΔH [kJ/mol H_2]	$T\Delta S$ [kJ/mol H_2]	ΔG [kJ/mol H_2]
Water electrolysis	650	1	-247.03	-49.57	197.46
Ammonia synthesis	550	250	35.76	37.75	-1.99

Table 1 Thermodynamic values of involved reactions

Ammonia synthesis can supply up to 73% (36.24 kJ/mol H_2) of the heat required, in terms of entropy, of the electrolysis reaction (49.57 kJ/mol H_2. In order to couple thermodynamic and electrochemical calculations for integration with the HB process, a zero dimension model for the SOE was developed as follows.

In a SOE, reaction (iv) is an electrochemical reaction which occurs in the electrolyser. The results are the two reactions here below:

$$H_2O + 2e^- \rightarrow H_2 + O^{2.-} \quad \text{cathode} \tag{v}$$

$$\frac{1}{2}O_2 + 2e^{\cdot -} \rightarrow O^{2.-} \quad \text{anode} \tag{vi}$$

Electrical inputs supplies the electron flows involved in the reactions. In electrolyzers, voltage is a function of current density and can be described with a very simple linear law as follows:

$$V = OCV + ASR(T) * J \tag{vii}$$

Were OCV is the Open Circuit Voltage, ASR is Area Specific Resistance and J is current density. Both OCV and ASR are function of temperature. This simplified approach is supported by experimental results that show how the polarization curve is highly linear at high temperature [ref]. In additions authors already demonstrated how ASR does not change between SOFC and SOE operation [17]. This assumption will be used in defining values of ASR. In the following equation (iv) SOE electrical power density is described as follows:

$$P_e = V * J = OCVJ + ASR * J^2 \tag{viii}$$

Energy output of the SOE is the energy of produced hydrogen. Such energy is the chemical energy of the fuel usually quantified in the LHV. For this study such energy was considered the enthalpy of the reaction (i) equivalent to the LHV of the fuel. Differently from LHV, the calculation was performed at the operative temperature. Specific chemical energy (in terms of energy flow per unit area) converted in the SOE is defined as follows:

$$\Delta H = dh(T) * H_{2mol} \tag{ix}$$

Where H_{2mol} is the specific molar flow (mol/m^2) of hydrogen and dh(T) is the enthalpy of the reaction (i). Hydrogen specific flow and current density are connected to the electrochemical parameters by the equation:

$$H_{2mol} = \frac{J}{2 * F} \tag{x}$$

Where F is the Faraday constant. Differently from fuel cells, the reaction in electrolysers is endothermal and the heat generated from process irreversibilities, such as current losses, are in equilibrium with reaction requirements. The energy balance is completed by the contribution of heat transfer with the external (Q). The latter takes into account the SOFC heat losses into the environment and the heat inlet from the environment that may come from a high temperature heat source, as in this application. External heat (Q) is calculated, for the present study, as a function of hydrogen energy production by the following equation

$$Q = k * \Delta H \tag{xi}$$

The energy equilibrium of the SOE is defined by the following equation:

$$P_e = \Delta H + Q = \Delta H(1 + k) \tag{xii}$$

Differently from fuel cells, were produced heat has to be subtracted by the air flow, in SOE the external heat contribution plays an importantrole not only on the operative temperature but also in the performances. Considering the stack at constant temperature, equation (viii) directly relates current density and temperature

to the external heat, in this case factor k. Thus, temperature definition and k allow to calculate the current density. Considering the previous equations J can be calculated as:

$$J = \frac{1}{ASR}\left(\frac{dh(T) * (1+k)}{2 * F} - OCV\right) \quad \text{(xiii)}$$

Efficiency is calculated as the ration between energy output (ΔH) and energy input (P_e) by the following equation:

$$\eta = \frac{\Delta H}{P_e} = \frac{1}{1+k} \quad \text{(iiv)}$$

Note that the efficiency is only a function of external heat contribution (k). In the specific case of k=0 the SOE operates in adiabatic conditions (no heat exchange with the environment) with a 100% theoretical efficiency. This operational condition is called thermoneutral. All equations were implemented in a zero-dimensional model developed using Excel and FluidProp© as database for thermodynamic parameters. The OCV value was calculated using the well-known Nernst equation considering as cathodic inlet a steam flow with 10% hydrogen (necessary for the integrity of the electrode) and as anodic flow air. ASR values are derived from a SOFC commercial product [17] due to the aforementioned equivalence with SOE ones.

2.2 Description of developed case studies

In order to assess the profitability of coupling SOE and HB process for the production of green ammonia, Process Flow Diagrams (PFDs) were realized in the AspenPlus environment to compare different scenarios. In particular, three case studies were developed: a reference case, named NG-REF-HB, with conventional NH_3 production from natural gas, a low temperature electrolysis case, named EL-PSA-HB, with H_2 and N_2 produced from commercial electrolyser and Pressure Swing Adsorption (PSA) respectively, and finally the case of SOE and HB with heat recovery from the HBR in which the low temperature electrolysis is replaced by the high temperature one. An advanced HB flowsheet has been drawn using AspenPlus Suite, according to the scheme of Figure 3 below, and is always the same for each case.

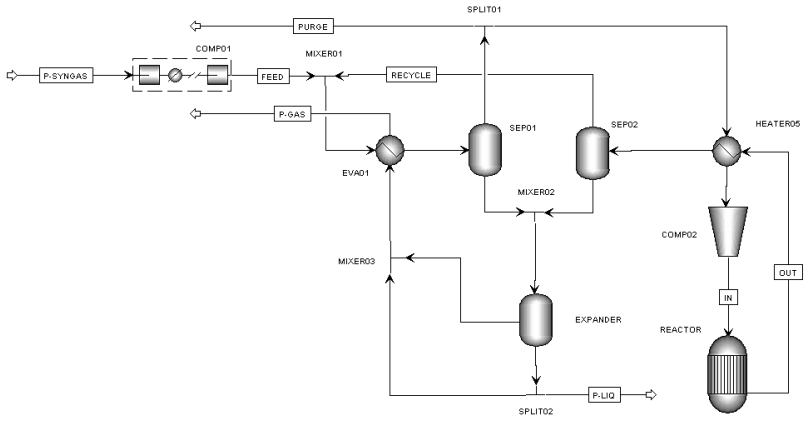

Figure 3 Flowsheet of the HB loop developed in AspenPlus

The description of the parameters used in AspenPlus is as follows. The "MCompr" block type was used with the rigorous ASME method for efficiency, heat and power consumption calculation of the multistage compressor unit COMPO01. Intercooling temperature after each stage and the final discharge pressure were specified for this block. EVA01 is modelled with a "HeatX" block type and the cold stream outlet temperature is fixed in order to exchange as much heat as possible. The specifications for the remaining blocks are summarized in Table 2.

Specification	HBR	SEP01	SEP02	EXPANDER
Temperature (°C)	550	0	20	-
Pressure (bar)	250	250	250	1
Heat Duty (kW)	-	-	-	0

Table 2 Block specifications for the HB loop

The rigorous "RGibbs" reactor block is used to model the HBR with the Aspen built-in PENG-ROB method for physical and chemical equilibrium calculations. The vapour-liquid equilibrium flash drum model "Flash2" is the block used for SEP01, SEP02 and EXPANDER. The splitting ratio, i.e. the amount of purge gas, of the block SPLIT01 is used as convergence variable for the PFD. In order to increase the ammonia recovery from HBR product stream, the tail gas from EXPANDER and a part of the liquid ammonia produced are used to push the cooling of the feeding stream in EVA01. The cold stream coming out from this block, i.e. P-GAS, is gaseous NH_3 with some traces of inerts which can be still considered as useful product of the plant. The HB loop thus described produces ammonia both in liquid and gaseous forms.

The complete PFD of the reference case, NG-REF-HB is shown in Figure 4.

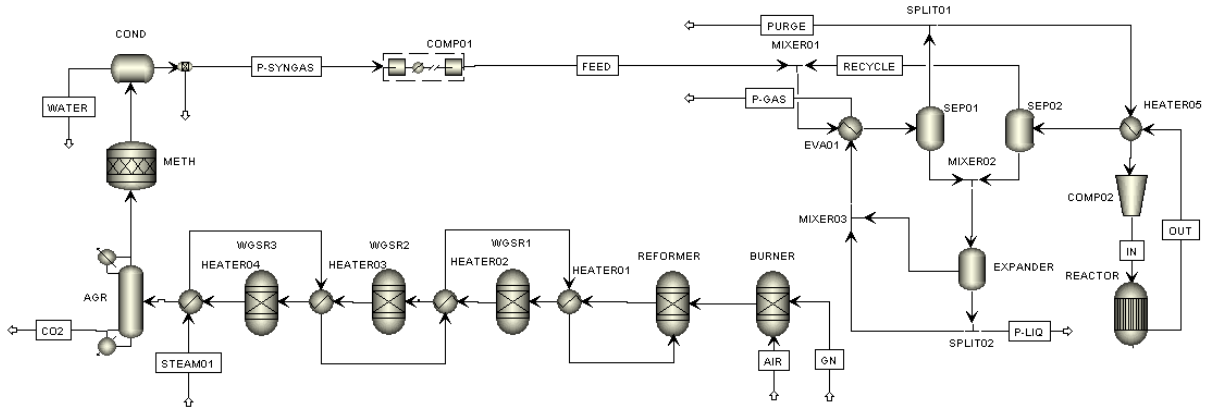

Figure 4 Flowsheet diagram of the reference case NG-REF-HB

Natural gas and air, at room temperature, are fed to an adiabatic combustor (BURNER), and a partial gasification process occurs with H_2 and CO formed together with CO_2. The N_2 necessary for NH_3 synthesis is fed in with the AIR stream. In the block REFORMER, a pre-heated steam stream is added to the burnt gas. The Steam-to-Carbon ratio (S/C) is fixed at 2 so that the Steam Methane Reforming (SMR) reaction can take place. Afterwards, three reactors are used (WGSR1, WGSR2, WGSR3) to complete the Water Gas Shift reaction (WGS). The reactions involved in these blocks are the following:

$$CH_4 + H_2O = CO + 3H_2 \quad \text{(xv)}$$

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2 \quad \text{(xvi)}$$

$$CO + H_2O = CO_2 + H_2 \quad \text{(xvii)}$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad \text{(xviii)}$$

The reactor block used to model all these units is “RGibbs” and the built-in NRTL Aspen property method was used for calculations. The Acid Gas Removal unit (AGR), the Methanator unit (METH) and the Condenser (COND) are devoted to the physical and chemical separation and removal of CO_2, CO and H_2O after the WGS section. A “Sep” block with standard specifications concerning temperature (≈50-80°C) and separation efficiency (>90%) is used for the AGR block [18]. An adiabatic “RStoic” reactor block is used by METH to convert residual CO_2 and COND is a “Flash2” block type, operated at 15°C to allow and complete gas/liquid separation. Table 3 summarizes the specifications of those last three blocks.

Specification	AGR	METH	COND
Temperature (°C)	50	-	15
Pressure (bar)	1	1	1
Heat Duty (kW)	-	0	-

Table 3 Block specifications for clean-up section

The second case is named EL-PSA-HB and its schematic flow diagram is shown in Figure 5.

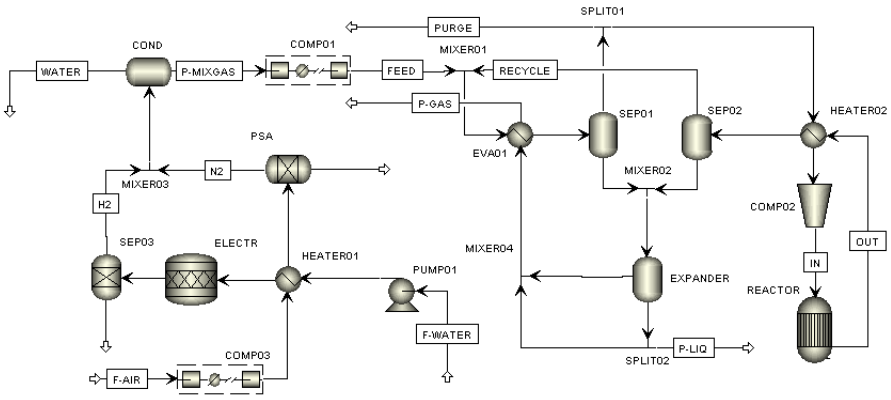

Figure 5 Flowsheet diagram of the low temperature electrolysis case EL-PSA-HB

The HB loop is the same as above, while the upstream architecture for low temperature electrolysis and PSA is simpler: water is compressed in a hydraulic pump (PUMP01) and heated in a counter current heat exchanger (HEATER01) to the electrolyser (ELECTR) operating conditions, namely 80°C and 30 bar. The built-in “Pump” block has been used to model PUMP01, HEATER01 is a “HeatX” block type and ELECTR is an “RGibbs” reactor block. The electrochemical calculations for ELECTR block are based on commercial alkaline electrolyzers data from literature [19]. The PSA standard process was modelled in Aspen Plus by means of a compressor (COMP03) and a separator (PSA) in series at 30 bar, room temperature and overall N_2 purity of 99.9% [20]. The property method used in this section was the NRTL built-in Aspen model.

Finally, the last case is the SOE-PSA-HB process illustrated in the PFD of Figure 6.

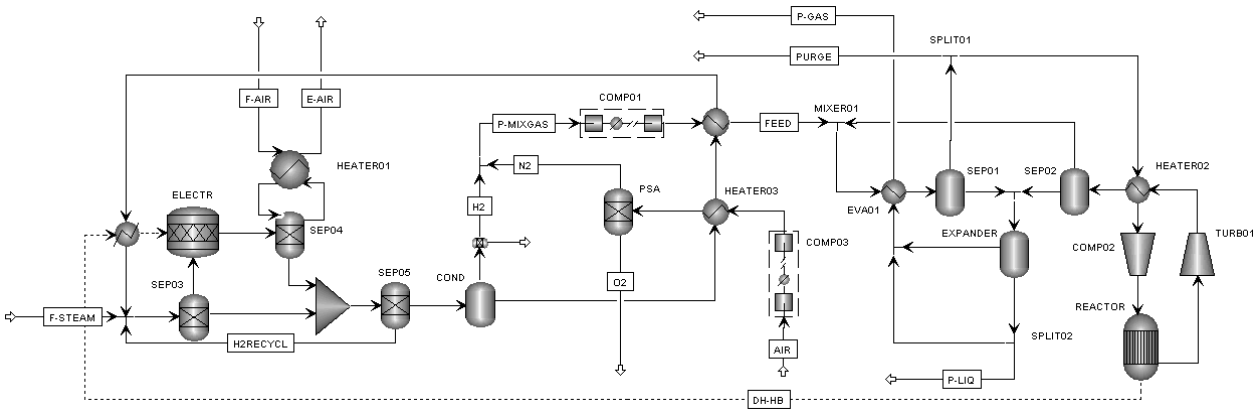

Figure 6 Flowsheet diagram of the high temperature electrolysis case SOE-PSA-HB

In this case only, the ammonia reactor was forced to operate at 650°C and 550 bar. In order to have comparable results with the previous cases, the different pressure level is controlled only in the HB REACTOR block by using a pair of compressor/turbine before and after the block (COMP02, TURB01). Selected temperature and pressure are the highest that can be accepted for HB process and, at the same time, this temperature is the lowest possible to consider in a SOE at the present stage of development. The upstream section, representing the SOE unit, was adapted from a previous work [21] and slightly modified by just the addition of a condenser (COND) to separate produced hydrogen (H2) from residual water, and a pre-heater at anode side (HEATER01), for preheating of the sweeping air (F-AIR) by heat recovery from oxygen enriched air (E-AIR) coming from anode outlet. The water separated from the COND block is used for cooling the feeding air of PSA block (AIR), and the feeding stream (FEED) before the HB loop. Afterward, separated water is recycled to SOE as steam. Finally, the tear stream DH-HB represents the chemical heat available from the REACTOR block, due to ammonia reaction according equation (i), that is used in SOE. Similarly to the EL-PSA-HB case, an external subroutine was used for electrochemical calculations, based on the model described in section 2.1, in order to consider the thermal contribution of HB coupling to the SOE energy balance. The only inputs to the subroutine are the operational temperature, already set at 650°C, and the heat supplied to the SOE (DH-HB) per unit of hydrogen produced, to calculate k used in equation (xi).

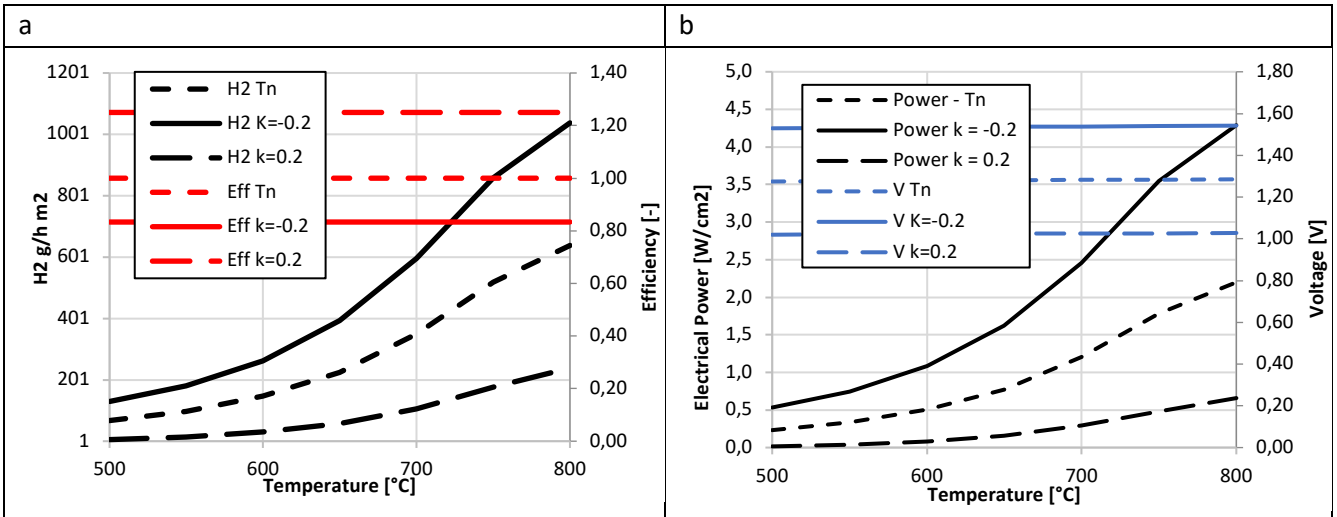

Figure 7 Effect of temperature and k on hydrogen production rate and efficiency (a) and on electrical power and voltage (b)

3 Results and discussion

Figure XX reports the variation of hydrogen production rate and efficiency (a) and of electrical power input and voltage (b) as a function of temperature for three values of k: k=0 (thermoneutral), k=0.2 (heat into the SOE) and k=-0.2 (heat losses). Figure 7 (a) shows a trade-off between efficiency and hydrogen production: with higher values of k smaller efficiency can be obtained. As expected from equation (xiv), efficiency is not affected by temperature variation while hydrogen production increases with temperature due to the decrease of internal resistances (ASR). Regarding Figure 7 (b), Electrical Power density increases with temperature and is higher when k in smaller (heat losses). Cell voltage remains constant at current density variation while increases when k decreases. Thermoneutral voltage obtained is approximately 1.29 V in agreement with the literature [12].
Considering the coupling of ammonia synthesis with SOE, it is possible to calculate the k factor, considering the heat flow from the ammonia reactor calculated from the Aspen model. At operational temperature of 650°C all other SOE parameters are calculated and reported in Table 4.

Parameter	Units	Value
k	-	0.14
Temperature	°C	650
ASR	$\Omega \cdot cm^2$	0.57
OCV	V	0.94
H_2	$g/h \cdot m^2$	108.18
J	A/cm^2	0.29
Voltage	V	1.10
Power density	W/cm^2	0.37
η	-	1.16

Table 4 SOE parameter when integrated with NH_3 synthesis

The following Table 5 shows the major comparative parameters for the three scenarios. They refer only to the HB loop subsection of the flowsheet.

	$(H_2/N_2)_{FEED}$ (mol/mol)	$(H_2/N_2)_{IN}$ (mol/mol)	Rec. Ratio (mol/mol)	Purge Ratio (mol/mol)	η_{glob} (%)	η_{react} (%)
NG-REF-HB	3.07	3.17	3.33	0.44	61.12	18.25
EL-PSA-HB	3.01	3.02	4.29	0.08	92.33	21.06
SOE-PSA-HB	3.00	3.03	4.30	0.06	93.40	19.53

Table 5 HB loop performances for the three different case studies

Comparing the values, remarkable differences are visible between the reference case, i.e. NG-REF-HB, and the remaining two, while the results obtained for the two cases with the use of electrolyzers seem to be very similar. The first two plants, the first fed with Natural Gas and the second based on a low temperature standard electrolyzer, can be operated at middle HB reactor conditions (250 atm and 550°C). SOE necessarily requires

heavy HB reactor conditions (550 atm and 650°C) for coupling, as discussed in section 2.1. Contrarily to what could be expected, the conversion per pass and the global efficiency is very different for NG-REF-HB and EL-PSA-HB, even if temperature and pressure of the HB reactor is the same. This is due to the high content of inert in the reference case, i.e. CH_4, that dilute the reactant steam and affect negatively the K_p term as envisaged from equation (ii). Moreover, the dilution of the products by the presence of CH_4 affects the physical separation of ammonia because it reduces the partial pressure of NH_3 in SEP01 and SEP02 blocks. This is the cause of the low η_{glob} and the deviation of the H_2/N_2 ratio inside the HB loop. As a consequence, the resulting purge ratio, i.e. the purge gas stream, should be higher in order to avoid the accumulation of inerts in the loop. On the contrary, the two cases with electrolyzers have very similar HB loop performances due to the complete absence of inerts. This a distinguishing feature of ammonia production when electrolysis and air separation are used to provide the H_2/N_2 mixture. In particular, the purge ratio is very small, so that more reactant can be recycled to the reactor instead of being purged with inerts. As a consequence, the recycle ratio, the NH_3 produced and the global efficiency increase.

In Table 6 are reported the overall energy consumptions and the equivalent Green House Gas (GHG) emissions of the three cases. They are normalized on the total quantity of ammonia produced. As reference, positive values are intended as energy provided to the system, while negative values represent energy that should be subtracted from the system.

	Spec. Chemical consumption (kWh/kg_{NH3})	Spec. Electric consumption (kWh_{el}/kg_{NH3})	Spec. Total consumption (kWh/kg_{NH3})	Spec. Heat consumption (kWh_{th}/kg_{NH3})	LHV of purge gas (MJ/kg)	GHG emissions (kg_{CO2}/kg_{NH3})
NG-REF-HB	12.81	1.77	14.59	-1.20	26.76	2.05
EL-PSA-HB	0	14.25	14.25	-1.63	21.35	0
SOE-PSA-HB	0	8.30	8.30	-1.14	21.43	0

Table 6 Energy performances for the three different case studies

The first evident results is that for the case EL-PSA-HB and SOE-PSA-HB the specific chemical consumption is zero: these systems are fed only by air and water so that there is no energy cost. On the contrary, the NG-REF-HB uses a fuel, i.e. CH_4, as feedstock. As expected, only the first case has a net environmental impact in terms of GHG emissions due to the CO_2 release during the reforming and clean-up operations of the fuel. This is mainly concentrated in the AGR block because it is one of the units devoted to the removal of oxygenated species from the syngas for NH_3 synthesis. The remaining two cases have no net emissions because their feedstock is "carbon-free". The contribution to emissions, due to the carbon contained in the purge gas of the NG-REF-HB, is not considered because, as shown in the table, the LHV of this stream is of interest in order to be used as a secondary fuel or as a chemical feedstock. Moreover, keeping in mind the previous purge ratios and global efficiencies, it could be concluded that the quantity of purge gas produced is considerable in the first system but negligible in the last two. Finally, a significant difference on the total and heat consumptions occur for all cases. In particular, even though the HB loop performances are quite the same, the cases with electrolyzer have very different consumptions. Comparing the reference case and the standard electrolyzer case, it is worth to observe that the total consumption is not so different, so that there is a little benefit in preferring the electrolysis pathway, power-intensive but low impacting, rather than the traditional one, based on fossil fuel and less electricity-consuming with the perspective to produce a valuable tail gas. However, the results show that in the case of coupling SOE,

PSA and HB, the total energy consumption can be potentially lower than all other solutions proposed. To better understand this, in Figure 9 the detailed consumption of heat is specified for the main ancillaries of the three developed scenarios. For the reference case, which has many ancillaries if compared to the other cases, there is a considerable endothermic term, due to the heat required by the reformer block, and a high exothermic contribution from the compression units, due to the interrefrigerations.

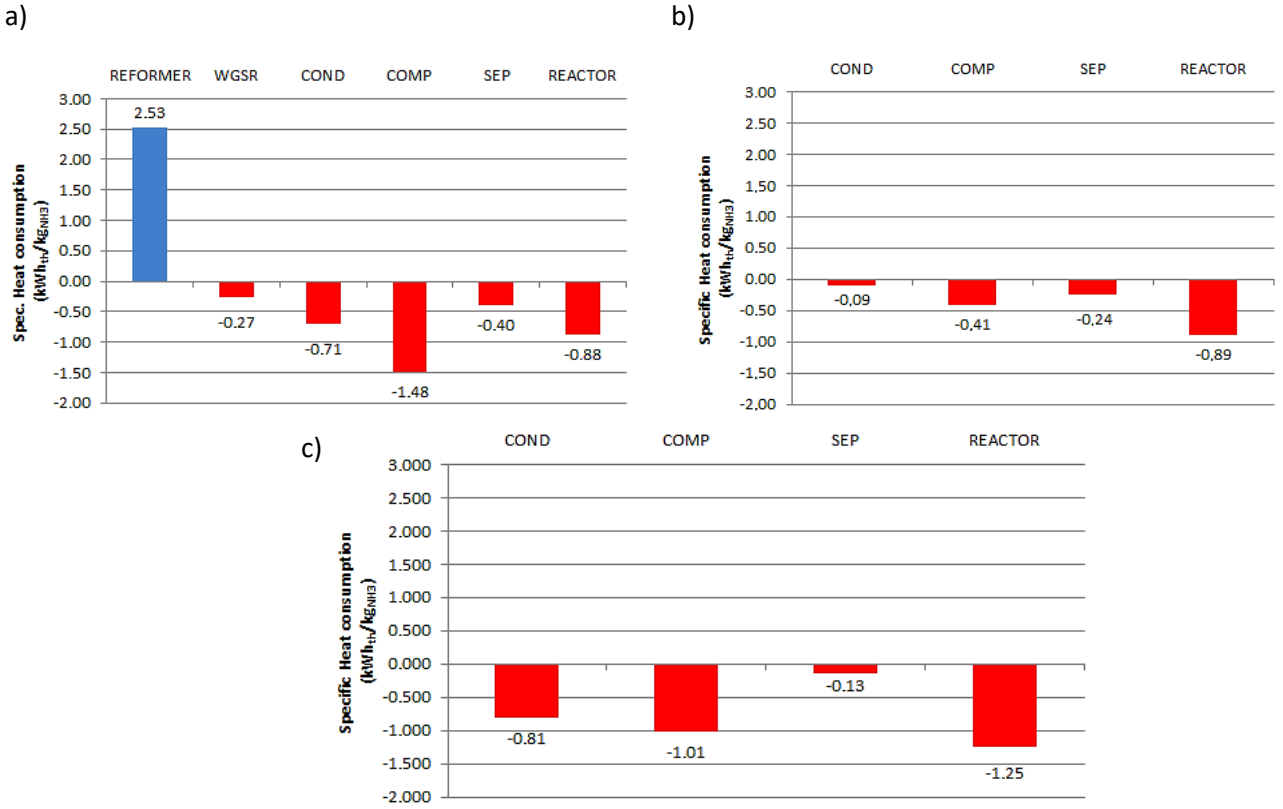

Figure 8 Specific heat consumption of ancillaries:

a) NG-REF-HB; b) EL-PSA-HB; c) SOE-PSA-HB.

The other two cases have smaller contributions, due to the simpler layout with no fuel thermal treatments or gas clean-up units. Comparing Figure 9a and 9b, the heat available from HB reactor is the same because the operating conditions are the same but, due to the presence of a high amount of inerts, the heat that should be removed from hot streams is higher. The presence of species other than H_2, N_2 and NH_3 in the HB loop is a strong limit for productivity but also energy efficiency of traditional HB plant because, if compared to the contribution of an electrolysis-based plant, they cause lower conversions and high waste heat. From this point of view, the SOE-PSA-HB offers more flexibility and opportunity for a convenient recovery of waste heat. In Figure 9c not all the contributions reported are really lost because, the heat from COND and REACTOR are used to achieve the thermal equilibrium of the SOE block because this acts as a “heat sink” for the system. In detail the heat from REACTOR is entirely used to feed SOE and is an input for the design of the electrolyzer. An additional advantage of this configuration is that no cooling of ammonia reactor is required reducing the environmental impact in terms of plant heat waste. One of the actual issue for SOE is that it requires a large amount of heat, or a high current density, from external sources to sustain the high temperature electrolysis process. If SOE and HB loop can be operated at similar temperatures, their coupling offer the opportunity to recover the large amount of

heat available from HB reactor to achieve a stable thermal equilibrium in the SOE, without increasing the current density, i.e. the electricity consumption, as explained in the model above. The single contributions of COND and REACTOR in the SOE-PSA-HB case are reported for completeness and to show how they become of interest if compared to that of the mild HB reactor conditions.

The direct consequence of this fact can be immediately realized if the single electric consumptions are compared as shown in Figure 10:

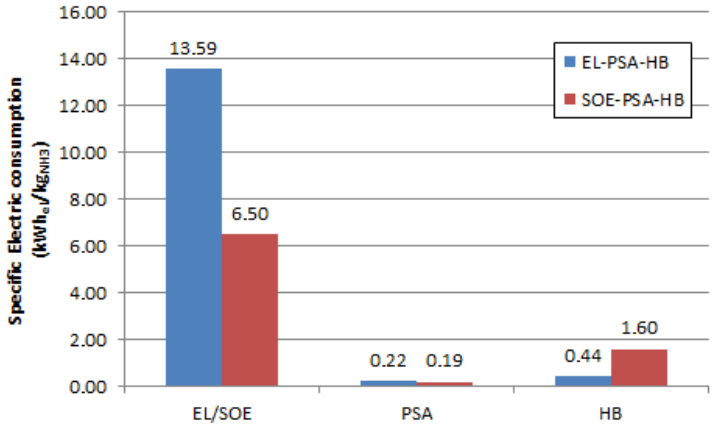

Figure 9 Comparison of the electric consumption for EL-PSA-HB and SOE-PSA-HB cases

The first two columns clearly indicates the advantage of the high temperature electrolysis over the low temperature one, if additional heat is provided from another source. The consumptions related to the PSA subsection are the same for both cases, as expected, while the electric consumptions related to the compression units of the HB loop are very different, essentially due to the high pressure imposed at the REACTOR block of the SOE-PSA-HB. It is worth noting that for the reference case the electric consumption is represented only by the compression units in the HB loop, and that its value is 1.77 kWh/kg$_{NH3}$, the highest among the three scenarios, because a large part of this energy is used to compress inerts which dilutes the syngas stream.

The coupling of SOE and HB deeply affects the energy balance of the plant when the electrolysis is used in place of the reforming of a fossil fuel. Moreover, the type of electrolysis process modifies the distribution of energy consumption within the plant itself. The situation is briefly explained in Figure 11.

a) b)

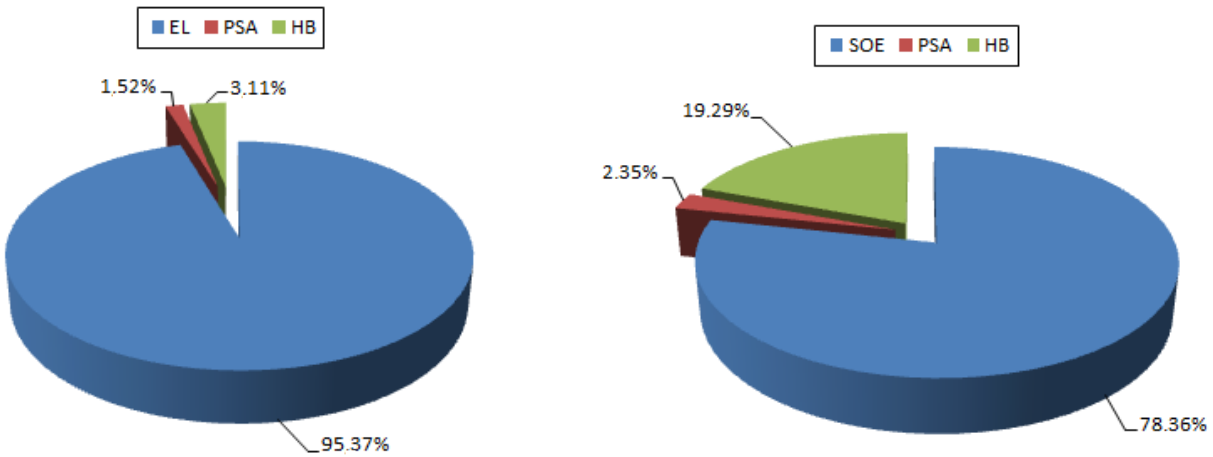

Figure 10 Distribution of the specific electric consumption:

a) EL-PSA-HB; b) SOE-PSA-HB.

When a low temperature electrolysis is used to produce the syngas for the HB loop, the electric consumption related to the electrolyzer operation is >95% of the total, i.e. the overall energy balance is in practice restricted to the electrolyzer, so that there is no flexibility and the whole plant is dependent from the electrolysis subsection. On the other hand, when a SOE is implemented, its impact on the overall energy balance is lower, as shown in Figure 11: the share for the electrolysis subsection decreases from 95.37% to 78.36%.

4 Conclusions

A novel system for the production of green ammonia was designed and analysed. The introduction of high temperature electrolyzer, such as SOE, permits to increase efficiency and system integration. The high efficiency of SOE permits electrical input reduction of the electrolyzer unit and to recover heat produced in the Haber Bosh reactor. The electricity consumption is decreased down to 14,25 kWh/Kg NH_3 and zero emission of CO_2 is obtained. In the field of chemical production the new system permits the production of zero emission ammonia and increase the flexibility of the plan compared to traditional electrolyzer. Considering also the use of ammonia as a fuel and the energy storage application, an high efficiency and high flexible concept is developed. Renewable electrical energy can be stored into a liquid vector that can be transported and directly used both for power and transport application.

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