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Thermodynamic analysis of a Na-O-H thermochemical cycle coupled to a Gas Turbine Modular Helium Reactor (GT-MHR)

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Abstract. Hydrogen (H₂) is considered a clean fuel because its combustion releases heat, water and near-zero carbon emissions. This substance can be produced through many routes, including thermochemical cycles in which water molecules are split into oxygen and hydrogen through specific chemical reactions supported by an appropriate heat source at specific temperature conditions. There are a wide variety of thermochemical cycles under development, many of them require temperatures higher than 1000°C while others, like the cycles U-Eu-Br, Mg-Cl and Cu-Cl can operate below 550°C. The reduction in the temperature levels of a thermochemical process allows the use of various energy options, facilitating H₂ production. So, the main aim of the paper is to analyze hydrogen production according to the Na-O-H thermochemical process whose required heat is supplied by a Gas Turbine Modular Helium Reactor (GT-MHR), a nuclear power plant (NPP) with low cost and low carbon emissions. The Na-O-H is a fresh chemical process that can operate at temperatures close to 400°C. The system will be studied in the software Engineering Equation Solver (EES) according to the first and second laws of thermodynamics. The results indicate that such system can produce around 3.654 kg/s of H₂ considering a mass flow rate of 500 kg/s of helium coolant at 850°C coming from GT-MHR.

1. Introduction

Hydrogen (H₂) is expected to be one of the energy carriers in a sustainable future [1] due to the following reasons: its combustion mainly releases heat, water and near-zero carbon emissions [2]; its usage in fuel cells has high electricity conversion without any pollutant [3]; calorific value or energy content higher than any fossil fuel [4]. In this way, hydrogen could be used to sustain the growing energy consumption around the world mainly caused by the expansion in population, urbanization and industrialization [5].

Hydrogen can be produced through many routes [2,6-10], even from fossil fuels and their derivatives in steam reforming, coal gasification and partial oxidation processes [7]. Such routes are responsible for around 99 % of all hydrogen consumed in industries [4]. Besides that, fossil fuels are non-renewable and finite natural resources, and they probably will exhaust in some future moment. This context contributes to the development of alternative technologies of hydrogen production from other resources instead fossil ones [4] such as thermochemical water splitting cycles.



A thermochemical water splitting cycle indirectly cracks water molecules into oxygen and hydrogen through cyclic chemical reactions supported by a heat source. This process happens with the need of very low or even none electricity [11]. Moreover, all the chemical substances present in such cycles are able to be cyclic reused with no loss of material, except water which is the material responsible for providing hydrogen [11] and can be obtained from many sources like desalination processes or industrial water treatment. In addition, some of the existing thermochemical cycles can provide economic advantages, making them potential candidates to provide hydrogen in large scale [3].

There are a wide variety of thermochemical cycles under development, many of them require heat sources at temperatures higher than 1000°C [12-14] while others, like the cycles U-Eu-Br (uranium-europium-bromium) [15,16], Mg-Cl (magnesium-chlorine) [17,18] and Cu-Cl (copper-chlorine) [19,20], demand temperature limits around 300°C, 450°C and 550°C, respectively. The reduction in the temperature requirements of a thermochemical cycle allows the use of a variety of heat sources, facilitating H₂ production.

About the magnesium-chlorine cycle, Ozcan and Dincer [17] proposed a new four-step for this cycle. This new configuration allows the cycle to operate at temperatures between 450-500°C against 530°C of the conventional three-step. Additionally, this new four-step has better thermodynamic efficiency than the three-step [17]. Still, Ozcan and Dincer [18] analyzed this new four-step Mg-Cl cycle and concluded that it have exergy and energy efficiency of 52% and 43.7%, respectively.

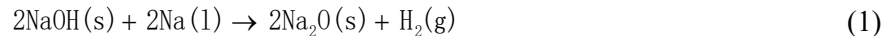
In relation to the copper-chlorine cycle, its highest operating temperature is around 550°C; Ouagued *et al* [19] carried out a research to estimate the potential of Algeria to produce hydrogen using a Cu-Cl thermochemical cycle coupled to a solar parabolic trough collector. According to the final results, the authors conclude that such system is able to produce approximately 84 tons of hydrogen/year with energy efficiency close to 48%. Additionally, Wu *et al* [20] compared different configurations of the Cu-Cl cycle. They are 3-step, 4-step and 5-step. These configurations have the same function that is to produce hydrogen but each one of them is based on different numbers of chemical reactions represented by the numbers of steps in each one. Among the final results obtained by Wu *et al* [20], the 4-step cycle is a potential candidate to be used as a commercial system because it demands less components or devices and low energy consumption when compared to other Cu-Cl configurations in addition to its relatively high energy efficiency around 40% or above depending on operational condition.

Finally, about the U-Eu-Br cycle Petri *et al* [15] carried out a literature review about three different thermochemical processes whose maximum operational temperature is below 550°C; Cu-Cl, Mg-Cl and U-Eu-Br. According to the authors, the Cu-Cl operates at 530°C; the Mg-Cl operates close to 500°C while the U-Eu-Br cycle can operate at around 300°C; this is the lowest level of temperature for thermochemical cycle that only demands heat and none electricity[15].

In this line of reason, Miyaoka *et al* [21] proposed three chemical reactions capable to produce hydrogen with relatively low temperature levels, the Na-O-H cycle. This new cycle is composed by the elements: sodium (Na), oxygen (O) and hydrogen (H). Such cycle are able to operate at highest temperature near to 400-500°C or even below, what facilitates hydrogen production and allows the use of different energy systems [21] like Gas Turbine Modular Helium Reactor (GT-MHR), a nuclear technology. Starting from Miyaoka *et al* [21] conclusions and results, Marques *et al* [22] proposed a hydrogen production plant based on the Na-O-H process using a Sodium Cooled Fast Reactor (SFR) as the heat source. According to the results obtained by Marques *et al* [22], they are produced around 1.321 kg/s of hydrogen when using 915 kg/s of steam at 510°C and 17 MPa coming from the SFR nuclear power plant.

Despite its low temperature requirements, the system proposed by Miyaoka *et al* [21] is still under development. So, in order to contribute to the development of such cycle, in a similar way like Marques *et al* [22] did, the main aim of the paper is to analyze a hydrogen production unit using the Na-O-H process whose required heat is supplied by a Gas Turbine Modular Helium Reactor (GT-MHR). In this way it will be possible to estimate the amount of hydrogen produced in such

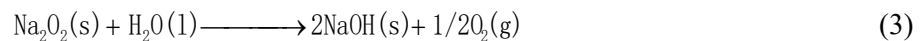
The first chemical process takes place when liquid sodium (Na) and solid sodium hydroxide (NaOH) react to each other, equation (1), producing gaseous hydrogen (H₂) and solid sodium oxide (Na₂O). This process is represented by points 1 to 5 in figure 1. Na and NaOH could be mixed together, without reacting (point 3), before they go to reactor 1 [22]. Miyaoka *et al* [21] performed such reaction at 300 and 350°C under argon atmosphere at 0.1 MPa. According to experimental data from Xu *et al* [26], such reaction also can be performed close to 275 °C. Equation (1) is endothermic and the heat required maintaining it in reactor 1 is supplied by helium coolant coming from the NPP (points 16 and 17).



The second chemical transformation, equation (2), happens when sodium oxide decomposes into sodium peroxide (Na₂O₂) and sodium gas (Na), points 6, 7 and 9, through heat transfer in reactor 2 which energy is supplied by helium coolant coming from the GT-MHR through points 15 and 16. Miyaoka *et al.* [21] performed this reaction at 400 and 500 °C in an evacuated atmosphere. Sodium gas will be condensed into liquid by releasing heat to a cooling system [22]. Then, liquid sodium will be pumped and mixed (points 2, 3 and 8) with the solid hydroxide formed in equation (3), allowing again the chemical reaction (1) [22].



The last chemical process, equation (3), occurs when heated liquid water (H₂O) reacts with sodium peroxide to produce oxygen (O₂) and sodium hydroxide (points 10 to 14). Water will be heated using heat from the coolant after it leaves reactor 1. The oxygen produced can be stored and sold while the sodium hydroxide (NaOH) will be mixed with liquid sodium to react again in reactor 1 as previously described [22]. Equation (1) was carried out by Miyaoka *et al* [21] at 100°C and 0.1 MPa in an argon atmosphere.



Like any thermochemical cycle, water is consumed to produce hydrogen while the other chemicals are recycled without any loss. Each milling process is responsible for reducing the size of inputs in order to facilitate chemical reactions [22]. Additionally, together with milling operations, it can exist treatment processes to remove some kind of impurities like humidity or adjust the composition of the chemicals involved in the processes [22].

In relation to the GT-MHR, helium coolant at low temperature (point 27) removes heat from reactor core. After leaving it, helium coolant, now at high temperature (28), is separated into two streams, one to the hydrogen unit through point 15, and another to gas turbine (21) to produce electricity. After leaving turbine (point 22), the coolant flows inside recuperator, a heat exchanger whose function is to preheat the coolant before it reaches reactor core. In the next step, helium releases heat in pre-cooler (points 23 and 24.a) to sea water (points 29 and 30). Finally, helium is compressed in two stages with intermediate cooling (points 24.a to 24.b; 31 and 32), heated in recuperator (points 25.b and 26) and mixed with helium leaving the hydrogen unit through point 18 to return to reactor core (point 27) in order to begin the thermodynamic process again.

2.2. Thermodynamic principles for control volumes operating at steady state conditions

The physical statements used to develop the paper are mass conservation, the first law of thermodynamics and second law of thermodynamics for control volumes applied for the system and its devices described in figure 1. All these principles can be found in many references like thermodynamic books [27, 28] and they are widely used to evaluate many engineering devices such as turbines, pumps and heat exchanges.

2.2.1. Mass conservation. The thermodynamic principle of mass conservation determines the amount

of mass that flows through equipment. Such statement, considering steady state situations, is mathematically represented by equation (4).

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \quad (4)$$

2.2.2. Energy conservation and the first law of thermodynamics. Energy conservation based on the first law of thermodynamics determines energy exchange in different engineering devices during their operations. The first law applied for control volumes in steady state condition, neglecting changes in potential and kinetic energies, is determined by equation (5). h is the thermodynamic property enthalpy leaving (out) or entering (in) the component under analysis.

$$\dot{Q} - \dot{W} = \sum \dot{m}_{out} h_{out} - \sum \dot{m}_{in} h_{in} \quad (5)$$

In addition, changes in specific enthalpy are calculated according to equation (6). C is the property specific heat.

$$h_i - h_{i-1} = C\Delta T \quad (6)$$

2.2.3. Entropy generation and the second principle of thermodynamics. The second principle of thermodynamics determines if a certain phenomenon, transformation or process are able to occur considering its entropy generation. Entropy generation for control volumes is determined considering following balance.

$$\dot{S}_G = \sum \dot{m}_{out} s_{out} - \sum \dot{m}_{in} s_{in} - \sum \frac{\dot{Q}}{T} \quad (7)$$

The property entropy (s) and its variation are calculated according to equation (8).

$$s_i - s_{i-1} = C \ln \frac{T_i}{T_{i-1}} \quad (8)$$

Both specific entropy (s) and enthalpy (h) also represent enthalpy of formation (ΔH_f^0) and entropy of formation (S^0) in situation involving chemical transformations

2.3. Mathematical model and considerations

The physical principles described in section 2.2 are now applied to evaluate the system defined in figure 1. All equations presented here will be implemented in the Engineering Equation Solver (EES) software [29] available at Universidade Federal de Minas Gerais (UFMG) with the following considerations [22]:

- All devices operate according to steady state conditions.
- Every chemical processes occur according to stoichiometric proportions, with a yield of 100%, at certain thermodynamic conditions defined in section 2.4.
- Heat and pressure losses inside and between components are neglected due to the lack of proper information to calculate such variables. In this way, they will be considered too small to impact on system overall performance.
- Input power related to Na and water pumps are neglected due to the same reasons described in the last item.
- The chemical processes in reactor chamber 1 and reactor chamber 2 occur at vacuum condition.
- Milling and mixer processes are evaluated only considering mass balances.
- He coolant returns to NPP from hydrogen plant through point 18 with the same temperature condition as point 26, resulting in a temperature value for point 27 equal to points 18 and 26.
- Constant specific heat at standard conditions (25°C, 1atm).

- Sodium hydroxide, liquid sodium and hot water have the same temperature required in reactor 3. Such value should be higher than 100°C to avoid the solidification of liquid sodium because such substance is required in its liquid form in reactor 1 or equation (1).
- All the chemicals are recycled without any loss, except water that is consumed during the process.

EES was chosen as the tool to develop the paper specially due to its relatively simplicity to implement mathematical equations and because this software has a wide library of thermodynamic properties.

2.3.1. Mass and energy balance equations. Based on stoichiometric from equations (1)-(3) and the specific molecular weight for every chemical posteriorly presented in section 2.4, it is noted that the relation between hydrogen mass flow rate and the mass flow rate of the other substances in the Na-O-H cycle is given by equations (9) to (14).

$$\dot{m}_{\text{NaOH}} = 40\dot{m}_{\text{H}_2} \quad (9)$$

$$\dot{m}_{\text{Na}} = 23\dot{m}_{\text{H}_2} \quad (10)$$

$$\dot{m}_{\text{Na}_2\text{O}} = 62\dot{m}_{\text{H}_2} \quad (11)$$

$$\dot{m}_{\text{Na}_2\text{O}_2} = 39\dot{m}_{\text{H}_2} \quad (12)$$

$$\dot{m}_{\text{H}_2\text{O}} = 9\dot{m}_{\text{H}_2} \quad (13)$$

$$\dot{m}_{\text{O}_2} = 8\dot{m}_{\text{H}_2} \quad (14)$$

In table 1 can be seen the mass and energy balances for each device in the analyzed system after applying equations (4) and (5).

Table 1. Mass and energy balances for some devices in the hydrogen unit and GT-MHR.

Component	Mass balance	Energy balance
Nuclear Reactor	$\dot{m}_{27} = \dot{m}_{28} = \dot{m}_{18} + \dot{m}_{26}$ $\dot{m}_{28} = \dot{m}_{15} + \dot{m}_{21}$	$\dot{Q}_{\text{NuclearReactor}} = \dot{m}_{28}h_{28} - \dot{m}_{27}h_{27}$
Turbine	$\dot{m}_{21} = \dot{m}_{22}$	$\dot{W}_{\text{Turbine}} = \dot{m}_{22}h_{22} - \dot{m}_{21}h_{21}$
Recuperator	$\dot{m}_{22} = \dot{m}_{23}$ $\dot{m}_{25.b} = \dot{m}_{26}$	$\dot{Q}_{\text{Recuperator}} = \dot{m}_{22}h_{22} - \dot{m}_{23}h_{23}$
Precooler	$\dot{m}_{23} = \dot{m}_{24.a}$ $\dot{m}_{29} = \dot{m}_{30}$	$\dot{Q}_{\text{Precooler}} = \dot{m}_{23}h_{23} - \dot{m}_{24.a}h_{24.a}$
Compressor 1	$\dot{m}_{24.a} = \dot{m}_{24.b}$	$\dot{W}_{\text{compressor}_1} = \dot{m}_{24.b}h_{24.b} - \dot{m}_{24.a}h_{24.a}$
Intercooler	$\dot{m}_{25.a} = \dot{m}_{24.b}$ $\dot{m}_{31} = \dot{m}_{32}$	$\dot{Q}_{\text{Intercooler}} = \dot{m}_{25.a}h_{25.a} - \dot{m}_{24.b}h_{24.b}$
Compressor 2	$\dot{m}_{25.b} = \dot{m}_{25.a}$	$\dot{W}_{\text{compressor}_2} = \dot{m}_{25.b}h_{25.b} - \dot{m}_{25.a}h_{25.a}$

Reactor 1	$\dot{m}_3 = \dot{m}_4 + \dot{m}_5$	$\dot{Q}_{\text{Reactor},1} = \dot{m}_4 h_4 + \dot{m}_5 h_5 - \dot{m}_3 h_3$
	$\dot{m}_{16} = \dot{m}_{17}$	$\dot{Q}_{\text{Reactor},1} = \dot{m}_{16} h_{16} - \dot{m}_{17} h_{17}$
Reactor 2	$\dot{m}_6 = \dot{m}_7 + \dot{m}_9$	$\dot{Q}_{\text{Reactor},2} = \dot{m}_7 h_7 + \dot{m}_9 h_9 - \dot{m}_6 h_6$
	$\dot{m}_{15} = \dot{m}_{16}$	$\dot{Q}_{\text{Reactor},2} = \dot{m}_{15} h_{15} - \dot{m}_{16} h_{16}$
Reactor 3	$\dot{m}_{10} + \dot{m}_{13} = \dot{m}_{11} + \dot{m}_{14}$	$\dot{Q}_{\text{Reactor},3} = (\dot{m}_{11} h_{11} + \dot{m}_{14} h_{14}) -$ $-(\dot{m}_{13} h_{13} + \dot{m}_{10} h_{10})$
Na condenser	$\dot{m}_7 = \dot{m}_8$	$\dot{Q}_{\text{Na,Condenser}} = \dot{m}_{20} h_{20} - \dot{m}_{19} h_{19}$ $\dot{Q}_{\text{Na,Condenser}} = \dot{m}_7 h_7 - \dot{m}_8 h_8$
Water heater	$\dot{m}_{12} = \dot{m}_{13}$	$\dot{Q}_{\text{Waterheater}} = \dot{m}_{17} h_{17} - \dot{m}_{18} h_{18}$
	$\dot{m}_{17} = \dot{m}_{18}$	$\dot{Q}_{\text{Waterheater}} = \dot{m}_{13} h_{13} - \dot{m}_{12} h_{12}$

Additionally, y in equation (15) corresponds to the amount or percentage of helium coolant coming from the NPP that is directed to the Na-O-H plant. Y varies from 0 to 1. So, the mass of H_2 produced depends on the mass flow rate of He coolant coming from the GT-MHR directed to the hydrogen plant.

$$\dot{m}_{15} = y * \dot{m}_{28} \quad (15)$$

The net power produced by system in addition to its thermal efficiency is calculated according to the following equations.

$$\dot{W}_{\text{Net}} = \dot{W}_{\text{Turbine}} - \dot{W}_{\text{compressor}} \quad (16)$$

$$\eta_{\text{thermal}} = \frac{\dot{W}_{\text{Net}}}{\dot{Q}_{\text{NuclearReactor}}} \quad (17)$$

2.3.2. Entropy balance equations. In table 2 are described the entropy generation for some devices in the system after applying equation (7).

Table 2. Entropy balance for some equipments in the hydrogen unit and GT-MHR.

Component	Entropy balance
Nuclear Reactor	$\dot{S}_{\text{G,NuclearReactor}} = \dot{m}_{28} s_{28} - \dot{m}_{27} s_{27}$
Turbine	$\dot{S}_{\text{G,Turbine}} = \dot{m}_{22} s_{22} - \dot{m}_{21} s_{21}$
Recuperator	$\dot{S}_{\text{G,Recuperator}} = \dot{m}_{23} s_{23} + \dot{m}_{26} s_{26} - \dot{m}_{22} s_{22} - \dot{m}_{25} s_{25}$
Precooler	$\dot{S}_{\text{G,Precooler}} = \dot{m}_{24.a} s_{24.a} + \dot{m}_{30} s_{30} - \dot{m}_{23} s_{23} - \dot{m}_{29} s_{29}$
Compressor 1	$\dot{S}_{\text{G,Compressor}_1} = \dot{m}_{24.b} s_{24.b} - \dot{m}_{24.a} s_{24.a}$
Intercooler	$\dot{S}_{\text{G,Intercooler}} = \dot{m}_{25.a} s_{25.a} + \dot{m}_{32} s_{32} - \dot{m}_{24.b} s_{24.b} - \dot{m}_{31} s_{31}$
Compressor 2	$\dot{S}_{\text{G,Compressor}_2} = \dot{m}_{25.b} s_{25.b} - \dot{m}_{25.a} s_{25.a}$
Reactor 1	$\dot{S}_{\text{G,Reactor},1} = \dot{S}_{\text{Products}} - \dot{S}_{\text{Reactants}} = \dot{m}_4 s_4 + \dot{m}_5 s_5 - \dot{m}_3 s_3$
Reactor 2	$\dot{S}_{\text{G,Reactor},2} = \dot{S}_{\text{Products}} - \dot{S}_{\text{Reactants}} = \dot{m}_7 s_7 + \dot{m}_9 s_9 - \dot{m}_6 s_6$

$$\begin{aligned} \text{Reactor 3} \quad \dot{S}_{G,\text{Reactor},3} &= \dot{S}_{\text{Products}} - \dot{S}_{\text{Reactants}} = \dot{m}_{11}s_{11} + \dot{m}_{14}s_{14} - \dot{m}_{10}s_{10} - \dot{m}_{13}s_{13} \\ \text{Water heater} \quad \dot{S}_{G,\text{Waterheater}} &= \dot{m}_{13}h_{13} + \dot{m}_{18}h_{18} - \dot{m}_{12}h_{12} - \dot{m}_{17}h_{17} \end{aligned}$$

Na condenser only will be evaluated according to the first law of thermodynamics because the source data related to it, provided in the next section, is not enough to provide a trustworthy analysis of the second law.

2.4. Input source data

The input source data needed to evaluate the system presented in figure 1 are described below in tables 3 and 4. Enthalpy and entropy of formation, specific heat (25°C; 1 atm) plus the molecular weight for every chemical were found in the references [30,31]. Enthalpy and entropy of formation for each chemical compound for a situation out of the standard condition are determined by equations (6) and (8) respectively, together with constant specific heat at 25°C.

Table 3. Thermodynamic properties at standard condition [30,31].

Chemical	Molecular weight [g/mol]	Enthalpy of formation $\Delta H_f^0(25^\circ\text{C})$ [kJ/mol]	Entropy of formation $S^0(25^\circ\text{C})$ [Jmol ⁻¹ K ⁻¹]	Specific Heat C (25°C) [Jmol ⁻¹ K ⁻¹]
NaOH	39.97	-425.9	64.46	59.45
Na(g)	22.98	107.5	153.7	20.8
Na(l)	22.98	2.41	57.86	59.53
Na ₂ O(s)	61.95	-414.2	75.1	69.1
H ₂ (g)	2.00	0	130.7	28.88
Na ₂ O ₂ (s)	77.94	-510.9	95	89.2
H ₂ O(l)	17.99	-285.8	70	75.3
O ₂ (g)	31.98	0	205.2	29.4

Each chemical process in the hydrogen plant, equations (1)-(3), only occur at certain thermodynamic conditions of temperature and pressure defined according to experimental results from [21,26]. Equation (1) occurs at 280°C plus evacuated atmosphere; equation (2) occurs at 400°C plus evacuated atmosphere; equation (3) occurs at a minimum temperature of 100°C or above under atmosphere condition [22].

Table 4. Thermodynamic properties of helium and water in a GT-MHR (adapted from [23,24]).

State n° [i]	Fluid [-]	Pressure P [kPa]	Temperature T [°C]	Enthalpy ^a h [kJ/kg]	Entropy ^a s [kJkg ⁻¹ K ⁻¹]
21	Helium	7930	850	5861	25.81
22	Helium	2630	475.4	3901	26
23	Helium	2580	158.1	2253	23.17
24.a	Helium	2580	30	1588	21.34
24.b	Helium	4423	112.5	2022	21.47
25.a	Helium	4423	30	1594	20.22
25.b	Helium	8110	112.5	2034	20.22
26	Helium	8030	440.1	3734	23.43
27	Helium	8030	440.1	3734	23.43
28	Helium	7930	850	5861	25.81
29 ^a	Sea water	200	25	104.8	0.367
30 ^a	Sea water	200	30	125.7	0.4365
31 ^a	Sea water	200	25	104.8	0.367
32 ^a	Sea water	200	30	125.7	0.4365

^a provided by the authors.

Table 4 presents the thermodynamic properties of every point in the GT-MHR. The values of temperature and pressure for helium coolant were obtained from [23,24] while the values of h and s in every point were obtained in EES software after providing the values of temperature and pressure. In the case of sea water used to cool helium in pre-cooler and inter-cooler (points 29, 30, 31 and 32) was considered a temperature difference of 5°C between sea water inlet and outlet. Additionally, in the hydrogen unit, sea water (points 19 and 20) was also used to condense sodium gas in Na condenser (points 19 and 20). The total mass flow rate of helium coolant coming from the NPP was considered as 500 kg/s . The thermodynamic properties related to the points 24 and 25 (compressors) are just approximations because the compression process is performed according to many compression steps with intermediate cooling and maybe loss of heat and pressure. In this way, compressors only will be evaluated according to the first law of thermodynamics. The nuclear reactor has a maximum thermal output of 1063 MW .

3. Results

3.1. Thermodynamic states for each point of the system

In table 5 are presented the final results related to thermodynamic properties for each point in the hydrogen plant. Such results converge when helium leaves chemical reactor 1 at approximately 450°C and reactor 2 close to 465°C in order to reach a temperature of 440.9°C after it leaves water heater and return to nuclear reactor whose required inlet temperature is close to 440°C . Consequently, this situation impacts on the final temperature of chemical reaction (3) and points 1 to 4, 8, 9, 13 and 14, whose temperature are equal to 192.7°C . Such points have the same temperature values in order to avoid a heat transfer process, during the mixing of streams 1 and 2 to produce stream 3 as in figure 1. This temperature value (192.7°C) prevents the solidification of liquid sodium after its condensation and before it goes to reactor 1 where sodium is required in liquid phase.

Table 5. Final results of thermodynamic properties in the hydrogen unit.

State n° [i]	Chemical [-]	Temperature T_i [$^{\circ}\text{C}$]	Pressure P_i [kPa]	$\Delta H_f^0(T)$ or h [kJ/kg]	$S^0(T)$ or s [kJkg $^{-1}$ K $^{-1}$]
1	NaOH(s)	192.7	101.35	-10407	1.613
2	Na (l)	192.7	101.35	539.3	3.674
3	NaOH (s)	192.7	101.35	-10407	1.613
3	Na (l)	192.7	101.35	539.3	3.674
4	H ₂ (g)	280	0	3682	74.28
5	Na ₂ O(s)	280	0	-6402	1.902
6	Na ₂ O(s)	280	0	-6402	1.902
7	Na(g)	400	0	5017	7.426
8	Na(l)	192.7	101.35	539.3	3.674
9	Na ₂ O ₂ (s)	400	0	-6126	2.151
10	Na ₂ O ₂ (s)	400	0	-6126	2.151
11	O ₂ (g)	192.7	101.35	154.2	6.417
12 ^a	H ₂ O(l)	25	-	104.8	0.367
13 ^a	H ₂ O(l)	192.7	-	819.7	2.262
14	NaOH(s)	192.7	101.35	-10407	1.613
15	He(g)	850	7930	5861	25.81
16	He(g)	465	7930	3863	23.63
17	He(g)	450	7930	3785	23.53
18	He(g)	440.9	7930	3738	23.46

^a values obtained considering liquid water at T with $x = 0$.

3.2. Mass flow rate of chemicals in the hydrogen plant

In table 6 are presented the stoichiometric values for each chemical in the Na-O-H system considering equations (9)-(14) as a function of y . As can be seen in table 6, when $y = 1$, 3.654 kg/s of H₂ are

produced with 226.5 kg/s of Na₂O when 84.03 kg/s of Na(l) react with 146.1 kg/s of solid NaOH in reactor chamber 1. Still, in reactor 2, 226.5 kg/s of Na₂O decompose into 84.03 kg/s of sodium gas and 142.5 kg/s of Na₂O₂. In reactor 3, 142.5 kg/s of solid Na₂O₂ react with 32.88 kg/s of H₂O to produce 29.23 kg/s of O₂ and 146.1 kg/s of solid sodium hydroxide (NaOH).

Table 6. Stoichiometric mass flow rate of chemicals in the hydrogen plant in function of y .

y	\dot{m}_{15} [kg/s]	\dot{m}_{H_2} [kg/s]	\dot{m}_{Na} [kg/s]	\dot{m}_{NaOH} [kg/s]	\dot{m}_{Na_2O} [kg/s]	$\dot{m}_{Na_2O_2}$ [kg/s]	\dot{m}_{H_2O} [kg/s]	\dot{m}_{O_2} [kg/s]
0.109 (10.9 %)	54.5	0.3983	9.16	15.93	24.69	15.53	3.584	3.186
0.208 (20.8 %)	104	0.76	17.48	30.4	47.12	29.64	6.84	6.08
0.307 (30.7 %)	153.5	1.122	25.8	44.87	69.54	43.75	10.1	8.973
0.406 (40.6 %)	203	1.483	34.12	59.34	91.97	57.85	13.35	11.87
0.505 (50.5 %)	252.5	1.845	42.44	73.8	114.4	71.96	16.61	14.76
0.604 (60.4 %)	302	2.207	50.76	88.27	136.8	86.07	19.86	17.65
0.703 (70.3 %)	351.5	2.569	59.08	102.7	159.2	100.2	23.12	20.55
0.802 (80.2 %)	401	2.93	67.4	117.2	181.7	114.3	26.37	23.44
0.901 (90.2 %)	450.5	3.292	75.72	131.7	204.1	128.4	29.63	26.34
1 (100 %)	500	3.654	84.03	146.1	226.5	142.5	32.88	29.23

3.3. H₂ production, energy efficiency, turbine and compressors power as function of y

In table 7 can be seen the amount of hydrogen produced in addition to the electrical power generated in turbine, the work consumed by compressors and the thermal efficiency of the system as a function of the mass flow rate of helium coolant in the NPP (\dot{m}_{21}) and in the hydrogen production unit (\dot{m}_{15}). Analyzing the results presented in table 7, it concludes that when 10% of the total mass of helium ($y = 0.1$) is directed to the Na-O-H unit are produced around 0.3983 kg/s of H₂, generated 873.2 MW in turbine and are consumed 193.1 MW by compressor 1 and 196.2 MW by compressor 2 in the nuclear plant. In this case, the system has thermal efficiency close to 0.4547. Similarly, when 100 % of helium coolant is directed to the hydrogen plant ($y = 1$) are produced 3.654 kg/s of H₂ without electricity generation in the GT-MHR system, thermal efficiency is 0, because all He is used to produced hydrogen in the Na-O-H plant instead electricity in the NPP.

Table 7. Hydrogen production, turbine and compressor power as a function of y .

y	\dot{m}_{28} [kg/s]	\dot{m}_{21} [kg/s]	\dot{m}_{15} [kg/s]	\dot{m}_{H_2} [kg/s]	$\dot{W}_{Turbine}$ [MW]	$\dot{W}_{Compressor1}$ [MW]	$\dot{W}_{Compressor2}$ [MW]	η
0.01 (1%)	500	495	5	0.03654	970.2	215	218	0.5052
0.109 (10.9 %)	500	445.5	54.5	0.3983	873.2	193.5	196.2	0.4547
0.208 (20.8 %)	500	396	104	0.76	776.2	172	174.4	0.4042
0.307 (30.7 %)	500	346.5	153.5	1.122	679.2	150.5	152.6	0.3536
0.406 (40.6 %)	500	297	203	1.483	582.1	129	130.8	0.3031
0.505 (50.5 %)	500	247.5	252.5	1.845	485.1	107.5	109	0.2526
0.604 (60.4 %)	500	198	302	2.207	388.1	86.02	87.19	0.2021
0.703 (70.3 %)	500	148.5	351.5	2.569	291.1	64.51	65.4	0.1516
0.802 (80.2 %)	500	99	401	2.93	194	43.01	43.6	0.101
0.901 (90.2 %)	500	49.5	450.5	3.292	97.02	21.5	21.8	0.0505
1 (100 %)	500	0	500	3.654	0	0	0	0

Additionally, figures 2 and 3 provide a graphical visualization about the information given in table 7. As can be seen in these figures, when y varies from 0 to 1, the amount of hydrogen produced in the system improves from 0 to 3.654 (figure 2) while system thermal efficiency decreases from 0.5052 to 0 (figure 3). Again, it happens because all the mass flow rate of helium is used to produce hydrogen

instead electricity in the power plant. This value of thermal efficiency, around 0.5, is the expected value for a GT-MHR system as can be seen in the references [23-25].

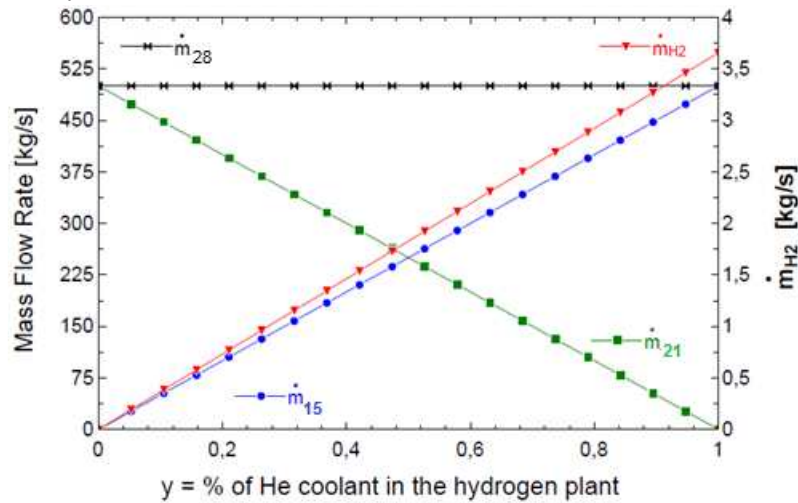


Figure 2. H₂ production as a function of y.

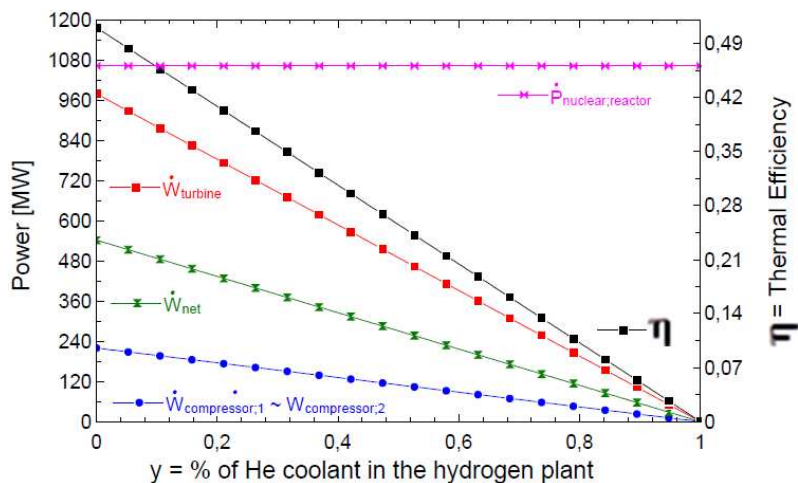


Figure 3. Energy efficiency of NPP as a function of y.

3.4. Energy and entropy analysis for chemical reactors in the hydrogen unit

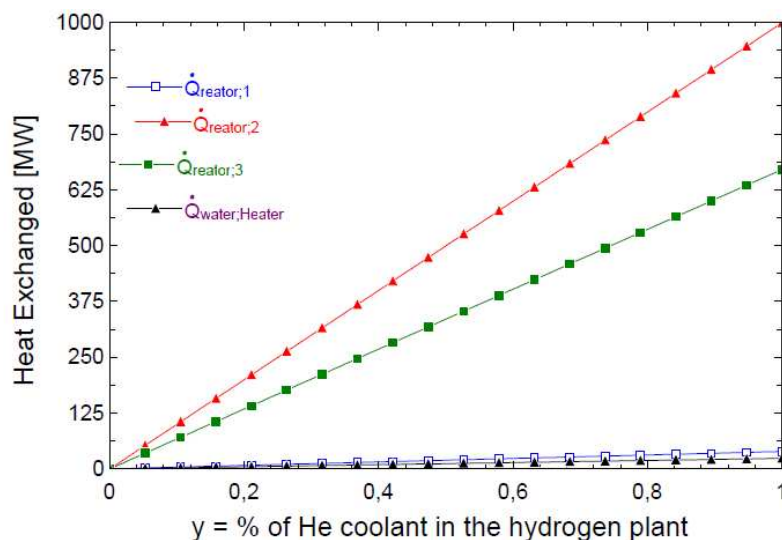
Table 8 presents thermal energy and entropy generation related to chemical reactor 1, chemical reactor 2 and chemical reactor 3 according to the amount of helium coolant in the hydrogen plant (y). According to the results, when $y = 0.1$, reactor chamber 1, reactor chamber 2 and reactor chamber 3 exchanged respectively 4.242 MW, 108.9 MW and 73.08 MW with a respective entropy generation of 0.02779 MW/K, 0.05447 MW/K and 0.003225 MW/K. On the other hand, when all helium from nuclear reactor is directed to the hydrogen unit ($y = 1$), reactor 1, reactor 2 and reactor 3 exchanged respectively 38.91 MW, 998.9 MW and 670.5 MW with a respective entropy generation of 0.2549 MW/K, 0.4997 MW/K and 0.02959 MW/K.

Table 8. Heat exchanged and entropy generated for chemical reactors in the hydrogen plant.

y	$\dot{Q}_{\text{Reactor},1}$ [MW]	$\dot{Q}_{\text{Reactor},2}$ [MW]	$\dot{Q}_{\text{Reactor},3}$ [MW]	$\dot{S}_{G,\text{Reactor},1}$ [MW/K]	$\dot{S}_{G,\text{Reactor},2}$ [MW/K]	$\dot{S}_{G,\text{Reactor},3}$ [MW/K]
0.01 (1%)	0.3891	9.989	6.705	0.002549	0.004997	0.0002959
0.109 (10.9 %)	4.242	108.9	73.08	0.02779	0.05447	0.003225
0.208 (20.8 %)	8.094	207.8	139.5	0.05303	0.1039	0.006154
0.307 (30.7 %)	11.95	306.7	205.8	0.07827	0.1534	0.009084
0.406 (40.6 %)	15.8	405.5	272.2	0.1035	0.2029	0.01201
0.505 (50.5 %)	19.65	504.4	338.6	0.1287	0.2524	0.01494
0.604 (60.4 %)	23.5	603.3	405	0.154	0.3018	0.01787
0.703 (70.3 %)	27.36	702.2	471.3	0.1792	0.3513	0.0208
0.802 (80.2 %)	31.21	801.1	537.7	0.2045	0.4008	0.02373
0.901 (90.2 %)	35.06	900	604.1	0.2297	0.4503	0.02666
1 (100 %)	38.91	998.9	670.5	0.2549	0.4997	0.02959

Complementing the results presented in table 8, for the specific case when $y = 0.2$, turbine produces 784 MW of electricity and produces 0.07337 MW/K of entropy; recuperator and precooling exchange respectively 659 MW and 263.7 MW while Na condenser releases 75.26 MW. The values of entropy generation higher than 0 for the components analyzed above indicated that the processes related to them are able to occur. Still, the amount of heat exchanged and entropy generated in reactor 2 are higher than those for reactor 1 and 3. Such results are in agreement with the research carried out by Miyaoka *et al* [21]. This condition is an indicative that the proposed model, considering its limitations, is in accordance with the practical experiment performed by Miyaoka *et al* [21].

The values presented in table 8 are graphically represented in figures 4 and 5 which also cover the behavior associated with heat exchanged and entropy generation for water heater in the hydrogen plant. Based on these two figures, when y varies from 0 to 1, the amount of energy exchanged in reactor chamber 1, reactor chamber 2, reactor chamber 3 and water heater increase respectively from 0 to 38.91 MW, 998.9 MW, 670.5 MW and 23.51 MW while their entropy generation increase respectively from 0 to 0.2549 MW/K, 0.4997 MW/K, 0.04234 MW/K and 0.02959 MW/K.

**Figure 4.** Thermal energy for chemical reactors in the hydrogen plant in function of y .

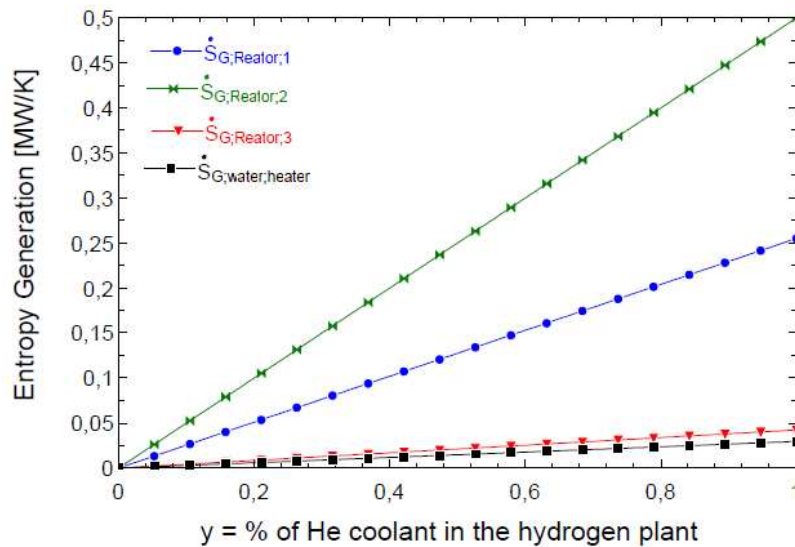


Figure 5. Entropy generation for chemical reactors in the hydrogen plant in function of y .

4. Final conclusions

In the work was proposed a theoretical hydrogen production plant based on the Na-O-H cycle proposed by Miyaoka *et al* [21]. Such system are able to operate at temperatures about 400-500°C. When such process is coupled to a Gas Turbine Modular Helium Reactor it can produce a maximum of 3.654 kg/s of hydrogen when heat is supplied by 500 kg/s of helium coolant at 850°C. This is a maximized theoretical value because some considerations were made to model the system like constant specific heat and neglecting heat loss in its devices. The Na-O-H system still is at an early stage of development with few papers but it could change in future due to its relatively low temperature requirements, what facilitates hydrogen production. In future papers, authors will perform an economic study, a practical experiment in a pilot plant and analyze the Na-O-H system considering other energy sources.

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References

- [1] Liberatore R, Lanchi M, Giaconia A and Tarquini P 2012 Energy and economic assessment of an industrial plant for the hydrogen production by water-splitting through the sulfur-iodine thermochemical cycle powered by concentrated solar energy *Int. J. Hydrog. Energy* **37(12)** 9550-65
- [2] Acar C and Dincer I 2014 Comparative assessment of hydrogen production methods from renewable and non-renewable sources *Int. J. Hydrog. Energy* **39(1)** 1-12
- [3] Ouagued M, Khellaf A and Loukarfi L 2017 Performance analyses of Cu-Cl hydrogen production integrated solar parabolic trough collector system under Algerian climate *Int. J. Hydrog. Energy* **43(6)** 3451-65
- [4] Sayyaadi H and Boroujeni M S 2017 Conceptual design, process integration, and optimization of a solar CuCl thermochemical hydrogen production plant *Int. J. Hydrog. Energy* **42(5)** 2771-89
- [5] Balta M T, Dincer I and Hepbasli A 2014 Performance assessment of solar-driven integrated Mg-Cl cycle for hydrogen production *Int. J. Hydrog. Energy* **39(35)** 20652-61

- [6] Ozbilen A, Dincer I and Rosen M A 2013 Comparative environmental impact and efficiency assessment of selected hydrogen production methods *EIA Review* **42** 1-9
- [7] Balat M 2008 Potential importance of hydrogen as a future solution to environmental and transportation problems *Int. J. Hydrog. Energy* **33(15)** 4013-29
- [8] Joshi A S, Dincer I and Reddy B V 2010 Exergetic assessment of solar hydrogen production methods *Int. J. Hydrog. Energy* **35(10)** 4901-08
- [9] Dufour J, Serrano D P, Gálvez J L, González A, Soria E and Fierro J L 2012 Life cycle assessment of alternatives for hydrogen production from renewable and fossil sources *Int. J. Hydrog. Energy* **37(2)** 1173-83
- [10] Dincer I and Acar, C 2015 Review and evaluation of hydrogen production methods for better sustainability *Int. J. Hydrog. Energy* **40(34)** 11094-111
- [11] Dincer I 2012 Green methods for hydrogen production *Int. J. Hydrog. Energy* **37(2)** 1954-71
- [12] Yalcin S 1989 A review of nuclear hydrogen production *Int. J. Hydrog. Energy* **14(8)** 551-61
- [13] Abanades S, Charvin P, Flamant G and Neveu P 2006 Screening of water-splitting thermochemical cycles potentially attractive for hydrogen production by concentrated solar energy *Energy* **31(14)** 2805-22
- [14] Yan X L and Hino R (Eds.) 2011 CRC Press *Nuclear Hydrogen Production Handbook* (Florida: Boca Raton)
- [15] Petri M C, Yildiz B and Klickman A E 2006 US work on technical and economic aspects of electrolytic, thermochemical, and hybrid processes for hydrogen production at temperatures below 550°C *Int. J. Nucl. Hydrogen Prod. Appl.* **1(1)** 79-91
- [16] Petri M C, Klickman A E and Hori M 2007 Hydrogen production options for water-cooled nuclear power plants *Int. Conf. on Non-Electric Applications of Nuclear Power* (Oarai)
- [17] Ozcan H and Dincer I 2016 Modeling of a new four-step magnesium–chlorine cycle with dry HCl capture for more efficient hydrogen production *Int. J. Hydrog. Energy* **41(19)** 7792-801
- [18] Ozcan H and Dincer I 2016 Comparative performance assessment of three configurations of magnesium–chlorine cycle *Int. J. Hydrog. Energy* **41(2)** 845-56
- [19] Ouagued M, Khellaf A and Loukarfi L 2018 Performance analyses of Cu–Cl hydrogen production integrated solar parabolic trough collector system under Algerian climate *Int. J. Hydrog. Energy* **43** 3451-65
- [20] Wu W, Chen H Y and Hwang J J 2017 Energy analysis of a class of copper–chlorine (Cu–Cl) thermochemical cycles *Int. J. Hydrog. Energy* **42(25)** 15990-6002
- [21] Miyaoka H, Ichikawa T, Nakamura N and Kojima Y 2012 Low-temperature water-splitting by sodium redox reaction *Int. J. Hydrog. Energy* **37(23)** 17709-14
- [22] Marques J G O, Costa A L and Pereira C 2018 Na-O-H thermochemical water splitting cycle: A new approach in hydrogen production based on sodium cooled fast reactor *Int. J. Hydrog. Energy* **43(16)** 7738-53
- [23] Mohammadkhani F, Shokati N, Mahmoudi S M S, Yari M and Rosen M A 2014 Exergoeconomic assessment and parametric study of a Gas Turbine-Modular Helium Reactor combined with two Organic Rankine Cycles *Energy* **65** 533-43
- [24] Zare V and Mahmoudi S M S 2015 A thermodynamic comparison between organic Rankine and Kalina cycles for waste heat recovery from the Gas Turbine-Modular Helium Reactor *Energy* **79** 398-406
- [25] Şahin H M, Erol Ö and Acir A 2012 Utilization of thorium in a gas turbine–modular helium reactor *Energy Convers. Manag.* **63** 25-30
- [26] Xu Q, Wang R, Kiyobayashi T, Kuriyama N and Kobayashi T 2006 Reaction of hydrogen with sodium oxide: a reversible hydrogenation/dehydrogenation system *J. Power Sources* **155(2)** 167-71
- [27] Moran M J, Shapiro H N, Boettner D D and Bailey M B 2010 John Wiley & Sons *Fundamentals of Engineering Thermodynamics* (New Jersey: Hoboken)
- [28] Klein S and Nellis G 2012 *Thermodynamics* (New York: Cambridge)

- [29] Klein S A 1992 *EES: Engineering Equation Solver for the Microsoft Windows Operating System EES Manual Commercial and Professional Versions F-Chart software* (Wisconsin: Madison)
- [30] Lide D R 2004 CRC PRESS *Handbook of Chemistry and Physics* (Florida: Boca Raton)
- [31] NIST Chemistry webbook; NIST standard reference database No. 69. Available on: www.nist.gov.