

PERFORMANCE IMPROVEMENT OF AMMONIA PRODUCTION FROM HYDROGEN THROUGH EXERGY ANALYSIS

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ABSTRACT

Ammonia is a very interesting product, whose traditional uses - refrigeration, emissions control and fertilizers production, are being further extended by the energy and ecological transition. Ammonia is very interesting as a fuel for mobility, mainly naval and possibly airborne transport, and can play a substantial role in chemical storage, especially if compared with direct Hydrogen storage, because of easier management of distributed appliances. The Haber-Bosch process of Ammonia production from Hydrogen, supposed of green origin, was thoroughly revised, and matched to the actual productivity of a large-scale electrolyzer. This included internal regeneration of heat, and the possibility of producing electricity to compensate for the consumption of the compressors needed for operation. The necessary equipment was preliminary sized, and good opportunities were found for matching to a steam cycle, an ORC and an absorption unit (needed at the end of the process to achieve a final temperature of 10°C, which is necessary for the production of liquid NH₃). The new configuration allows the plant to reach an exergy efficiency of 92,7%, by recovering almost 4MWe trough the steam and OCR power cycles.

1 INTRODUCTION

Ammonia has been in use in the industry for a long time. It plays a major role in agriculture as a fertilizer and is also widely used for refrigeration (it is a natural refrigerant) and as a reactant for emissions control in combustion systems (from automotive to stationary power generation). Further development of the use of Ammonia is foreseen in the energy and ecological transition (Negro et al., 2023). Specifically, Ammonia is raising interest for chemical storage of energy as an alternative to compressed or liquefied Hydrogen (Zhao et al., 2022). Moreover, Ammonia will play an essential role in propulsion systems, certainly for ships (Aakko-Sansa et al., 2023) and possibly for aircraft (Webber and Job, 2021; Tiwari et al., 2024). Ammonia promises to be an important product in the forthcoming years, through its versatility and a tradition of being used in the industry of cold production and utilization. The use of Ammonia is particularly attractive coupled to renewable energies (Ong et al., 2024): Green Ammonia is closely linked to the production and use of Hydrogen. In fact, Hydrogen can be converted with good efficiency in Ammonia through the Haber-Bosch Process (Ojelade et al., 2023; Spatolisano and Pellegrini, 2023), and the process can be inverted to produce Hydrogen when needed thereby facilitating transport, storage and final use for fuel cells or other local uses (Kojima et. al., 2022; Mukelabai et al., 2021). As for the green origin, Hydrogen can be produced by several green technologies, among which electrolysis driven from Photovoltaics or other Renewables; landfill gas (Gonzalez-Arias et al., 2024), and Hydrogen Sulfide (Ghayam et al., 201). This together with the possibility of several industrial uses for both products (Hydrogen and Ammonia) confirms the relevant interest in this technology. The purpose of this study is to introduce process integration through internal regeneration of heat and coupling to production of power, thereby improving the performance through the reduction of heat and power required for the process of chemical synthesis of Ammonia.

2 REFERENCE CASE

As a reference case, the reactor chain proposed by Ishaq and Dincer (2020) was selected. This corresponds to a typical Haber-Bosch process and was selected because the thermodynamic conditions for all streams were fully documented allowing replication of results. The molar flow rates can be found in a table in the cited reference. A critical analysis of the system evidenced that reaching the conditions necessary to produce liquid Ammonia ($T < 10^{\circ}\text{C}$) was not possible by cooling using heat transfer to the environment. Consequently, it was decided to add a final cooling stage. The flow sheet of the process is synthesized in Figure 1:

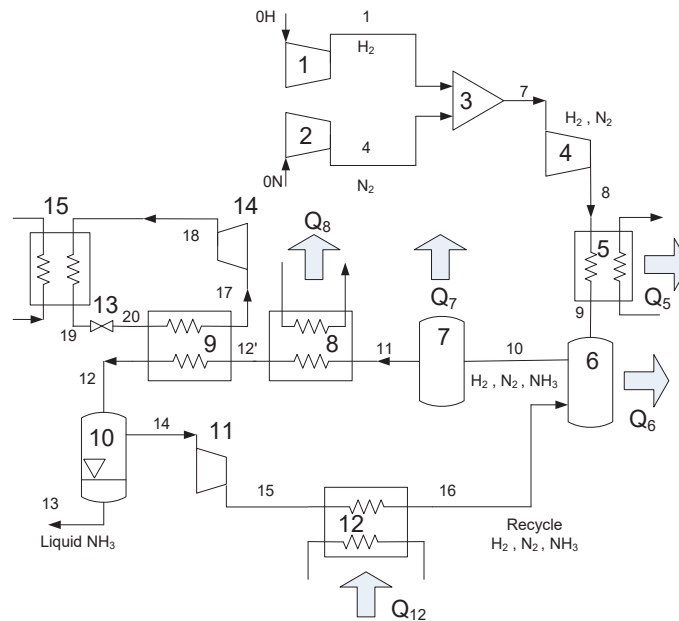


Figure 1: Flow sheet of the process with identification of components and streams

The streams of Hydrogen (S0H) and Nitrogen (S0N) are compressed and mixed; after cooling in HE5 (Q₅) they are directed at Reactor R6 (isothermal, requiring external cooling Q₆). This reactor also has the inlet flow of the recycle gas stream (for this reason it is kept separate from Reactor R7 which follows). The exit stream S10 from reactor R6 contains H₂, N₂ and NH₃, and is directed to Reactor R7 (again, assumed isothermal with removal of heat Q₇) which improves the NH₃ content of the gas stream. An external heater HE8 removes heat Q₈ (in the present scheme, dissipated to the environment), and is followed by a refrigeration step (driven by a compression refrigeration unit) which cools the stream S12 down to the 10°C necessary for producing liquid ammonia, exiting as a product from the bottom of separator 10. The gas stream S14 (recycle stream containing H₂, N₂ and a reduced amount of NH₃) is heated in the Heat exchanger HE12 providing the heat rate Q₁₂ and is then recycled at reactor R6. The system described by Ishaq and Dincer (2020) is of very small size – not corresponding to a possible real case. Consequently, it was decided to rescale it to an input Hydrogen flow rate corresponding to the productivity of a large (100 MWe) commercial alkaline Hydrogen electrolyzer¹. This unit is rated for 19400 Nm³/h of Hydrogen; the data assumed for the model are summarized in Table 1. A stream of Nitrogen is also needed in stoichiometric quantity compared to the ammonia formation reaction:



¹ <https://nelhydrogen.com/wp-content/uploads/2024/01/Electrolysers-Brochure-Rev-D-1.pdf>

Table 1: Data assumed for the reference case

p_{0H}	200	kPa	Δp_{loop}	100	kPa
T_{0H}	25	°C	T_9	350	°C
\dot{V}_{0H}	19400	Nm ³ /h	T_{10}	370	°C
p_{0N}	500	kPa	T_{12}	10	°C
T_{0N}	30	°C	$\eta_{is;comp}$	72	%
\dot{V}_{0N}	6508	Nm ³ /h	$e_{ch;N2}$	720	kJ/kmol
p_1, p_4	700	kPa	$e_{ch;H2}$	236100	kJ/kmol
p_7	5000	kPa	$e_{ch;NH3}$	337900	kJ/kmol

3 DESCRIPTION OF THE MODEL

3.1 Mass and energy

Throughout the system, a variable mixture of H₂, N₂ and NH₃ is flowing. The applicability of perfect gas assumption for the mixture was checked through the evaluation of the local compressibility factor Z : as the system is only moderately pressurized (50 bar) $0,9 < Z < 1$ for all chemical species involved. While assuming perfect gas behavior for the mixture, it was decided to use real fluid properties for Ammonia at points S12, S14 and S15. All thermodynamic data were aligned to JANAF reference conditions. The pure fluid properties were evaluated through calls to EES property libraries (gas or real fluid). A check was performed for local mixture compositions in critical points with UNISIM Design (using SRK third-order EOS for the mixture components) and showed agreement within 3% for all points under the conditions encountered in the process.

The enthalpy of the mixture is given by the sum of the enthalpies of the components:

$$m_M * h_M = m_{H2} * h_{H2} + m_{N2} * h_{N2} + m_{NH3} * h_{NH3} \quad (2)$$

The enthalpies of the components are obtained from the conditions of temperature and pressure.

The entropy of the mixture is given by the sum of the entropies of the components:

$$m_M * s_M = m_{H2} * s_{H2} + m_{N2} * s_{N2} + m_{NH3} * s_{NH3} \quad (3)$$

The entropies of the components are obtained from the temperature and pressure conditions.

Heat and work are calculated with energy balances:

$$Q = m * (h_o - h_i) \quad (4)$$

$$W = m * (h_o - h_i) \quad (5)$$

Conservation of mass is applied and verified for all streams. Molar calculations are performed at each point to follow the composition of the mixture along its evolution.

3.2 Exergy

Exergy is calculated for each stream separating physical and chemical contributions.

The physical exergy of the mixture is given by the sum of the physical exergies of the components:

$$m_M * e_{ph_M} = m_{H2} * e_{ph_{H2}} + m_{N2} * e_{ph_{N2}} + m_{NH3} * e_{ph_{NH3}} \quad (6)$$

The physical exergy of every component is calculated from enthalpy and entropy referring to standard conditions:

$$e_{ph} = h - h_0 - T_0 * (s - s_0) \quad (7)$$

Where s_0 and h_0 are the enthalpy and entropy for the considered specie calculated at standard ambient conditions of 25 °C and 101 kPa; $T_0 = 298,15$ K.

The chemical exergy of the mixture is given by the sum of the chemical exergies of the components (Table 1):

$$m_{MM} * e_{ch_M} = m_{MM_{H2}} * e_{ch_{H2}} + m_{MM_{N2}} * e_{ch_{N2}} + m_{MM_{NH3}} * e_{ch_{NH3}} \quad (8)$$

The total exergy of the mixture is the sum of the physical and chemical exergies:

$$E_M = m_M * e_{ph_M} + m_{MM_M} * e_{ch_M} \quad (9)$$

3.3 Detailed Treatment of heat transfer - Production of liquid NH₃

All reactors are treated as isothermal, following the approach by Ishaq and Dincer (2020). This means that they must be cooled: the reactor cooling heat duty was calculated from the stream steady-state energy balance.

All the heat exchangers were modeled in detail with a counter-current discretization (50 segments) to trace the temperature profiles of the hot and cold streams. In each segment the heat exchanged Q_j is converted into a $dh_{c,j} = Q_j/m_{c,j}$ for the cold stream and $dh_{h,j} = Q_j/m_{h,j}$ for the hot stream. New j-segment enthalpy values are calculated subtracting $dh_{h,j}$ to the (j-1) value of enthalpy of the hot stream and adding $dh_{c,j}$ to that of the cold stream. The values of enthalpy are used to calculate the temperature of the two streams. The local energy balance (heat transferred over segment j) stands as follows:

$$Q_j = m_{h,j} * (h_{h,j-1} - h_{h,j}) \quad (10)$$

$$Q_j = m_{c,j} * (h_{c,j} - h_{c,j-1}) \quad (11)$$

A special case is the NH₃ condensing heat exchanger HE9, which produces the final product liquid stream of Ammonia. As heat transfer (cooling) proceeds along the heat exchanger hot stream side, progressive condensation of Ammonia takes place (as well as the cooling of nitrogen and hydrogen in the gas mixture). This reduces the Ammonia fraction in the gaseous state and subtracts the enthalpy of condensation to the hot stream (depending on the amount of ammonia condensed in the specific j segment). As the hot stream is subject to condensation of NH₃, the procedure to trace the temperature profile is modified imposing the drop in temperature in each segment instead of the heat exchanged, up to the final temperature of 10 °C. The partial pressure, i.e. saturation pressure, of ammonia at the temperature T_j in each segment is calculated and the amount of NH₃ remaining in the vapor phase is determined and, by difference, the amount condensed ($\Delta m_{NH_3,j}^{liq}$). Also, the partial pressure of hydrogen and nitrogen are recalculated. Q_j is found using the following equation for the hot stream, corresponding to the procedure "Condensation of mixed vapors" described in Kern (2019):

$$Q_j = m_{M,j}^{vap} (h_{M,j-1}^{vap} - h_{M,j}^{vap}) + m_{NH_3,j-1}^{liq} (h_{NH_3,j-1}^{liq} - h_{NH_3,j}^{liq}) + \Delta m_{NH_3,j}^{liq} (h_{NH_3,j-1}^{vap} - h_{NH_3,j}^{liq}) \quad (12)$$

The cold stream is treated as in equation 11.

As an example of the results, Figure 2 shows the calculated temperature profile in the heat exchanger HE9: the starting point of condensation is evidenced.

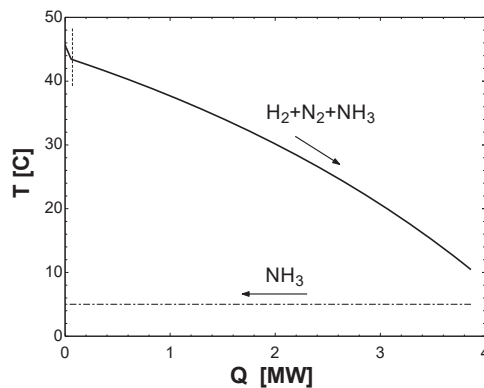


Figure 2: Temperature profile in the condensing heat exchanger HE9

3.4 Exergy destructions and losses

Table 2 collects synthetically the equations applied for the calculation of exergy destructions and losses, following the approach from Bejan et al., 1989. Heat exergy was used for the exergy loss for reactors 5 and 6.

The direct exergy efficiency is given by:

$$\eta_{ex;dir} = \frac{E_{product}}{E_{fuel}} \tag{13}$$

While the indirect exergy efficiency can be calculated considering all destructions and losses in all the system components.

$$\eta_{ex;ind} = 1 - \frac{\sum_i ExD_i + \sum_i ExL_i}{E_{fuel}} \tag{14}$$

Table 2: Reference case - equations for exergy destructions and losses

Id	Component	Ex. Destruction + Loss	Exergy destruction	Exergy loss
1	<i>H₂ Compr.</i>		$ExD_1 = E_{0H} - E_1 + W_1$	
2	<i>N₂ Compr.</i>		$ExD_2 = E_{0N} - E_4 + W_2$	
3	<i>Mixer</i>		$ExD_3 = E_1 + E_4 - E_7$	
4	<i>Compressor</i>		$ExD_4 = E_7 - E_8 + W_4$	
5	<i>Cooler</i>			$ExL_5 = E_8 - E_9$
6	<i>Reactor 1</i>	$ExDL_6 = E_9 + E_{16} - E_{10}$	$ExD_6 = ExDL_6 - ExL_6$	$ExL_6 = (1 - \frac{T_0}{T_{10}}) * Q_6$
7	<i>Reactor 2</i>	$ExDL_7 = E_{10} - E_{11}$	$ExD_7 = ExDL_7 - ExL_7$	$ExL_7 = (1 - \frac{T_0}{T_{11}}) * Q_7$
8	<i>NH₃ Condenser 1</i>			$ExL_8 = E_{11} - E_{12}$
9	<i>Evaporator (NH₃ Condenser 2)</i>		$ExD_9 = E_{20} - E_{17} + E_{12} - E_{12}$	
10	<i>Separator</i>		$ExD_{10} = E_{12} - E_{13} - E_{14}$	
11	<i>Recycle Compr.</i>		$ExD_{11} = E_{14} - E_{15} + W_{11}$	
12	<i>Ext. Heater</i>		$ExD_{12} = E_{15} - E_{16} + Ex_{in,12}$	
13	<i>Exp. Valve</i>		$ExD_{13} = E_{19} - E_{20}$	
14	<i>CC Compr.</i>		$ExD_{14} = E_{17} - E_{18} + W_{14}$	
15	<i>CC Cond.</i>			$ExL_{15} = E_{18} - E_{19}$

4 RESULTS (REFERENCE CASE)

The results of the stream calculations are resumed in Table 3. Table 4 collects the heat rates and power transfers. Table 5 collects the results of exergy destructions and losses for the reference case. Figure 3 shows a graphical representation of the exergy balance. The total exergy of the outgoing flow of liquid Ammonia is $E_{product} = 55360 \text{ kW}$. The exergy efficiency of the plant is $\eta_{ex} = 79,7 \%$.

The exergy destruction in the heater of the recycle line (*Ext. Heater*) is significant. This is because, since the reference case (Ishaq and Dincer, 2020) lacks details on the heat supply, we have assumed a worst-case scenario where the recirculating fluid is heated by combustion, using the chemical exergy of an external fuel. While this is not realistic, it highlights the importance of proper thermal management in such processes. For comparison, considering a perfect heat transfer in that component ($ExD_{12} = 0$), the exergy efficiency of the plant will increase to $\eta_{ex} = 83,89 \%$.

Table 3: Reference case - stream calculations

Id	m [kg/s]	T [°C]	P [kPa]	h [kJ/kg]	s [kJ/ kgK]	E [kW]	e [kJ/kg]
0N	2,26	30	500	5,189	6,379	378,2	167,35
0H	0,4844	25	200	0	61,96	57587	118883,2
1	0,4844	203,4	700	2574	63,56	58603	120980,6
4	2,26	72,53	700	49,34	6,416	453,5	200,7
7	2,745	170,4	700	494,8	17,08	58582	21341,4
8	2,745	623,5	5000	2070	17,61	62473	22758,8
9	2,745	350	5000	1111	16,33	60884	22180
10	7,374	370	5000	48,82	14,94	158792	21534,
11	7,374	370	5000	-373,5	14,25	157083	21302,
12'	7,374	45	5000	-1368	12,1	154490	20950,
12	7,374	10	5000	-1894	10,33	154496	20951
13	2,745	10	5000	-3995	5,867	55361	20168
14	4,629	10	4900	-647,4	13	99111	21411
15	4,629	12,3	5000	-640,5	13	99134	21416
16	4,629	350	5000	445,7	15,52	100689	21752

Table 4: Reference case - heat and power transfers

Id	Heat Component	Heat [kW]	Id	Work Component	Power [kW]
5	Cooler	-2633	1	H ₂ compressor	1247
6	Reactor 1	-4752	2	N ₂ compressor	99,8
7	Reactor 2	-3115	4	Mixture H ₂ - N ₂ Compressor	4324
8	NH ₃ Condenser 1	-7331	11	Recycle Compressor	32
12	Ext. Heater	5028	14	CC Compressor	766,2
9	Evaporator (internal)	(-3878)			
15	CC Cond. (to ambient)	-4644			
Overall Heat, kW		-17447	Overall work, kW		6469,01

Table 5: Reference case - exergy destructions and losses

Id	Component	ExDL [kW]	ExD [kW]	ExL [kW]	ExD _{rel} [%]	ExL _{rel} [%]
1	H ₂ Compr.	230,7	230,7		0,33	
2	N ₂ Compr.	24,5	24,5		0,04	
3	Mixer	474,3	474,3		0,68	
4	Compressor	433,4	433,4		0,62	
5	Cooler	1590		1590		2,29
6	Reactor 1	2781	232	2549	0,33	3,67
7	Reactor 2	1709	37,6	1671	0,05	2,4
8	NH ₃ Condenser 1	2593		2593		3,73
10	Separator	24,3	24,3		0,04	
11	Recycle Compr.	9,4	9,4		0,01	
12	Ext. Heater	3472,5	3472,5		5	
9	Evaporator (NH ₃ Condenser 2)	272	272		0,4	
14	CC Compressor	173,3	173,3		0,25	
15	CC Condenser	280,8		280,8		0,4
13	CC Valve	33,4	33,4		0,05	

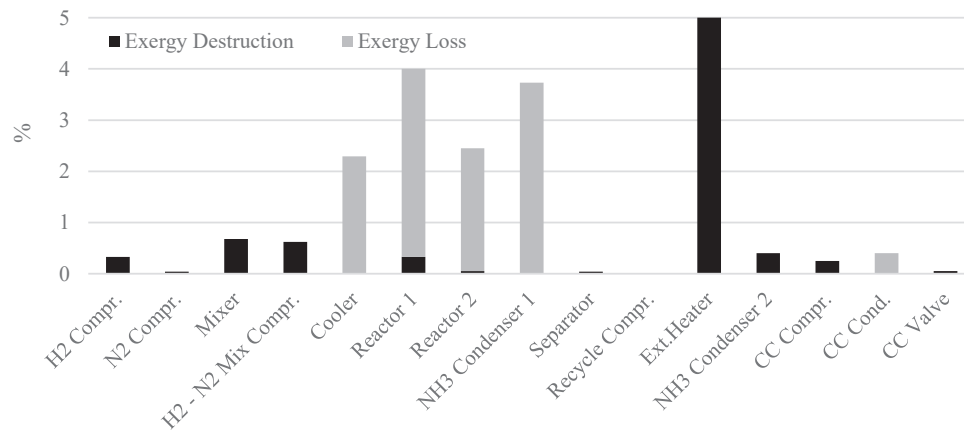


Figure 3: Reference case - relative exergy destruction and losses

5 PROCESS IMPROVEMENT

5.1 Promoting internal regeneration and heat recovery

The process described in Ishaq and Dincer – here resized, and modified for improvement and practical operation - offers opportunities for internal regeneration and heat recovery, as is evident from the overall heat balance (- 17,5 MWt, from Table 4). The improvement is directed to production of power, as the process is power-intensive because of the consumption of work for compressors drive (6,5 MWe on the whole). The idea is to try to reduce both the power consumption and the heat duty. The revised process schematic is shown in Figure 4.

The relevant changes with respect to the reference case are the following:

- A regenerative Heat Exchanger RHE12 was added to remove the external heating load by preheating of the recycle stream to Reactor R6.
- A steam cycle section is added, recovering heat from two Gas Coolers (HE5, superheater; and HE8, first part of the economizer). The final part of the economizer and the evaporator are placed inside Reactor R6.
- HE8 recovers heat from the exit stream of reactor R7; in order to obtain a good match of the heat capacities, the exit flow rate (stream S11) is split in two separate streams: the first one (stream S27) is directed to the RHE12, the second preheats the water (first part of the steam cycle economizer) in HE8.
- An oil (Therminol VP1) heat transfer circuit is used to cool the reactors R6 and R7 for the remaining heat not used for the steam cycle, reaching a temperature of 360 °C.
- The oil circuit feeds an ORC cycle that uses Toluene as the working fluid (this represents a good fluid match for this temperature level). A schematic of the connection of the oil circuit to the ORC and Absorption cycle is provided in Figure 5. The oil is cooled down from a temperature of 360 °C to 303,1 °C and provides a total Q_{ORC} heat of 1,3 MWt to the economizer and evaporator of the ORC cycle.
- After the ORC cycle, the oil provides heat to the generator of an absorption refrigeration unit that is proposed to achieve the final cooling and condensation of the NH_3 liquid stream. A triple-effect water/LiBr unit was chosen. The oil enters the generator at a temperature of 303,1 °C and releases Q_{abs} heat of about 2 MWt to the cooling cycle. The oil then returns to the reactors at a temperature of 210°C. The coupling to a high-temperature heat source and the triple-effect arrangement allow to reach a $\text{COP} = 1,84$, so that the cooling capacity for condensation of Ammonia is the required value of about 3,6 MWt.

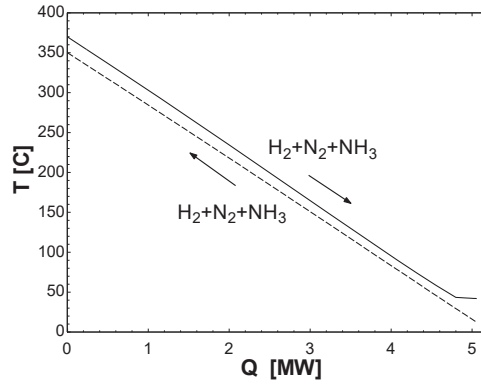


Figure 6: Q-T profile of the regenerative Heat Exchanger RHE12.

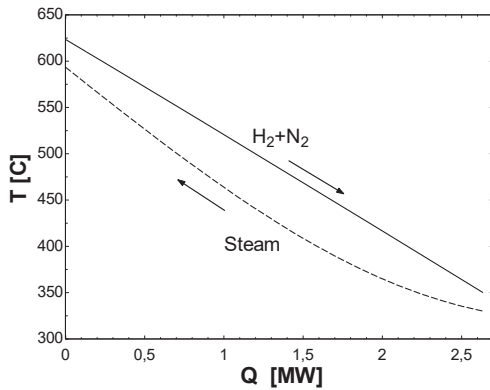


Figure 7: Q-T profile of the steam superheater, HE5.

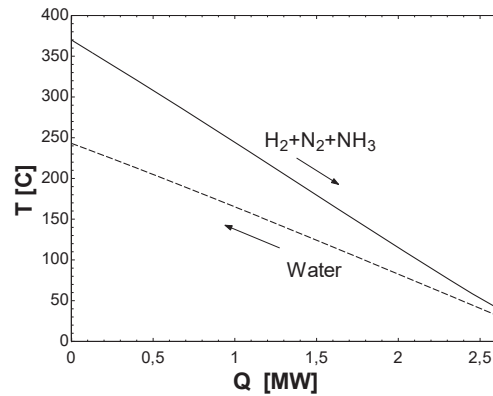


Figure 8: Q-T profile of the first part of the economizer, HE8.

5.2 Results for the improved process

Table 7 collects the operating parameters of the added components, which were determined following a parametric investigation which examined in detail the sensitivity of performance. The final choice of these design parameters results from a compromise between overall performance (efficiency) and technological constraints. Table 8 shows synthetically the resulting heat and work transfers. The exergy destruction and losses also include the internal terms within the absorption cycle, with an exergy destruction of 263,52 kW (sum of the destructions of all components except the generator and the evaporator, for which the values are synthesized in Table 9), and an exergy loss of 165,64 kW.

The whole process does not require external heat supply: the exergy inputs are represented by the power drive of the compressors, which is compensated by over 4 MWe generated by the steam and ORC turbines. E_{fuel} is the total exergy of inflows (power and reactants) minus the power produced by the plant's recovery cycles:

$$E_{fuel} = W_1 + W_2 + W_4 + W_{11} + W_{15} + W_{20} + W_{abs,p} + E_{0H} + E_{0N} - W_{18} - W_{16} = 59688 \text{ kW} \quad (15)$$

$E_{product}$ is the total exergy of the outgoing flow of liquid Ammonia:

$$E_{product} = E_{14} = 55360 \text{ kW} \quad (16)$$

The exergy efficiency of the improved plant can be calculated in the direct and indirect way and results to be an appealing $\eta_{ex} = 92,7\%$.

Table 7: Main parameters of Steam cycle, Organic Rankine Cycle, Oil Circuit and Absorption cycle

Steam cycle			ORC cycle		Oil circuit		Absorption cycle				
$T_{in,HE8}$	33,7	°C	$T_{in,eco}$	84,32	°C	$T_{in,R6}$	210	°C	T_{gen}	200	°C
$T_{in,R6}$	243	°C	T_{eva}	300	°C	$T_{in,R7}$	216,5	°C	T_{eva}	5	°C
T_{eva}	330	°C	T_{cond}	30	°C	$T_{in,ORC}$	360	°C	p_{high}	336,83	kPa
T_{sh}	595,5	°C	p_{orc}	3286	kPa	$T_{in,abs}$	303,1	°C	p_{inter}	46,72	kPa
p_{hrsg}	12858	kPa	ϵ_{rhe}	80	%				p_{low}	4,25	kPa
p_{cond}	5	kPa							$p_{eva,abs}$	0,87	kPa
									ϵ_{hex}	70	%

Table 8: Heat and work transfers of the Steam cycle, Organic Rankine Cycle, and Absorption cycle

Steam cycle			ORC cycle		Absorption cycle			
W_{turb}	-3592	kW	W_{turb}	-440,5	kW	$W_{abs, pump}$	1,4	kW
W_{pump}	43,46	kW	W_{pump}	10,21	kW	Q_{eva}	3574	kW
$Q_{eco,HE8}$	2582	kW	Q_{orc}	1299	kW	Q_{gen}	1994,1	kW
$Q_{eco,R6}$	1354	kW						
Q_{eva}	3269	kW						
Q_{sh}	2635	kW						

Table 9: Improved case - Exergy destructions and losses

Id	Component	ExD [kW]	ExL [kW]	ExD _{rel} [%]	ExL _{rel} [%]
1	H ₂ Compr.	230,7		0,39	
2	N ₂ Compr.	24,5		0,04	
3	Mixer	474,3		0,8	
4	Compressor	433,4		0,73	
5	Cooler - SH	71,0		0,12	
6	Reactor 1- ECO + EVA + oil	443,1		0,74	
7	Reactor 2 - oil	251,1		0,42	
8	NH ₃ Cond. 1 - ECO	229,9		0,39	
13	NH ₃ Cond. 2 (to ambient)		3,6		0,01
9	Evaporator (NH ₃ Condenser 3)	238		0,4	
10	Separator	24,3		0,04	
11	Recycle Compressor	9,4		0,02	
12	RHE	138,3		0,23	
14	Condenser - steam cycle		161,9		0,27
15	Pump - steam cycle	6,34		0,01	
16	Turbine - steam cycle	768,3		1,29	
17	ECO + EVA - ORC	157,7		0,26	
18	Turbine - ORC	37,9		0,06	
19	RHE - ORC	13,2		0,02	
21	Cond. - ORC		15,8		0,03
20	Pump - ORC	2,5		0,004	
22	Generator - abs cycle	165,4		0,28	

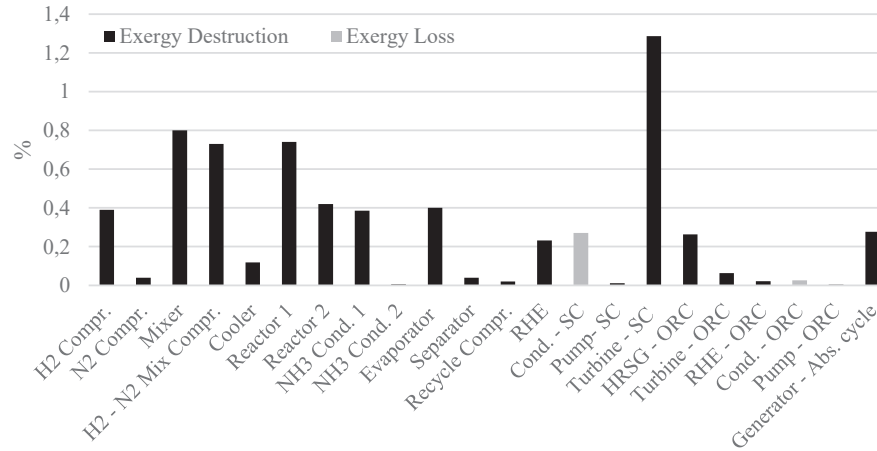


Figure 9: Relative Exergy destructions and losses – improved process

6 CONCLUSIONS

The process for Ammonia production from Hydrogen and Nitrogen was thoroughly revised, rescaled and validated, introducing necessary provisions as the final cooling stage. The present analysis assumes that Hydrogen (possibly of green origin) and Nitrogen are provided externally, and focuses on the conversion process, which is appealing for energy storage, production of ammonia to be used as a synfuel, or other applications such as production of fertilizers or use as reducing reactant in many industrial processes. A detailed exergy analysis was set up, and the opportunities for process improvement were identified (reducing the external interactions in terms of heat and power). The main results are the following:

- It is possible to convert Hydrogen in Ammonia with a very good exergy efficiency – 79,7% in the base case and 92,7% in the improved configuration after process integration.
- In the base case, the exergy balance showed a high relevance of exergy losses (recovery of reactor cooling was not considered) for a total of 12,5 %; considerable exergy destruction was taking place at the level of external heat supply (about 5 %).
- Process integration included: #1 internal regenerative heat recovery #2 recovery of reactor cooling through a steam cycle #3 introduction of an oil heat transfer circuit providing heat to an ORC (with RHE) and to an absorption cycle #4 provision of cold for the final step of NH₃ condensation through an absorption cycle (heat provided from the oil heat recovery circuit).
- Conditions for process integration were determined with care through matching of the heat capacities (introducing a split where necessary) and considering technological constraints.
- The result is that external provision of heat (5 MWt) is completely canceled; moreover, power is recovered from the steam and ORC turbines, so that the overall compressor power is reduced from 6469 kWe (base case) to 5760 kWe (improved case).
- The exergy efficiency after improvement reaches the very high value of 92,7%; another key performance indicator is the exergy needed to produce 1 kg of Ammonia, which is lowered from 25305 kJ/kg_{NH₃} to 21744 kJ/kg_{NH₃}.

NOMENCLATURE

p	pressure	(kPa)	E	exergy	(kW)
T	temperature	(°C)	e	specific exergy	(kJ/kg)
m	mass flowrate	(kg/s)	Q	heat	(kW)
m _{MM}	molar flowrate	(kmol/s)	W	work	(kW)
T	temperature	(°C)	ε	effectiveness (Heat exchanger)	
h	specific enthalpy	(kJ/kg)	η	efficiency	(%)
s	specific entropy	(kJ/kg*K)	ExD	exergy destruction	(kW)

ExL	exergy loss	(kW)	ExDL	sum of ExL and ExD	(kW)
Subscripts			dir	direct	
abs	absorber		fuel	fuel	
c	cold		ind	indirect	
comp	compressor		M	mixture	
ch	chemical		o	outlet	
h	hot		p	pump	
i	inlet		ph	physical	
is	isentropic		product	product (NH ₃)	
ex	exergy		rel	relative	
R	reactor				

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