Comparison of Process Options for Sustainable Ammonia Production

Ammonia is one of the most produced chemicals in the world, with a production of about 150 million metric tons a year. It is critical for improved yields in modern agriculture as well as a chemical feedstock to various other processes. Today, Steam Methane Reforming (SMR), which uses fossil based natural gas as its feedstock, is the most widely used method for ammonia production. In this process, the natural gas is used to produce hydrogen, which is then reacted with nitrogen from the air to form ammonia. This technology generates a significant amount of greenhouse gases (GHGs), which has led to proposals for new processes that lower the carbon intensity of ammonia production while still maintaining process efficiency.

One approach for reducing GHGs from the conventional SMR process is either sequestration of vented CO_2, carbon capture from process flue gas, or a combination of the two. These methods have sometimes been dubbed “Blue Ammonia”. Another approach, sometimes called “Green Ammonia”, utilizes water electrolysis as its source of hydrogen. The use of water electrolysis allows water and renewable sources of electricity, such as wind and solar, to supplant natural gas as the feedstock for the required hydrogen production. Two categories of electrolysis units include alkaline water electrolysis (AWE) and polymer electrolyte membrane electrolysis (PEM). While the SMR process can use air as its source of nitrogen, the AWE and PEM based technologies require pure nitrogen to be available. A third category of electrolysis, solid oxide electrolysis (SOE), can also generate pure hydrogen from renewable electricity, but unlike AWE and PEM, does not require pure nitrogen. SOE also provides additional avenues of heat integration between hydrogen production and ammonia synthesis that is lacking from the other electrolysis technologies.

A comparison is made between the various newer technologies to a conventional SMR system using a steady-state simulator. This comparison includes the configuration and requirements of each system, as well as each system’s carbon intensity and power requirements per ton of ammonia produced.

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INTRODUCTION

Ammonia is produced via Haber-Bosh synthesis from hydrogen and nitrogen. Nitrogen is usually obtained from the air, or in rare cases, it could be found in natural gas wells. The hydrogen can be obtained from hydrocarbons or via electrolysis from water. In North America, most of the hydrogen is produced from natural, with 95% of capacity. In the EU, 86% of capacity is based on natural gas and 8% on naphtha. (1) Methane has the highest ratio between hydrogen and carbon atoms and therefore produces of the least CO_2 from all the candidate fossil fuels. Hydrogen can also be obtained from electrolysis of water and then be used for ammonia production. Various alternative process steps involving membranes, air separation, or replacing the secondary reformer with an auto-thermal reformer are frequently mentioned. (2)

In this paper, we show and compare the results from simulating nine alternative ammonia production processes. All simulations were performed using Bryan Research & Engineering, LLC's ProMax® 6.0 process simulation software. For each case, key flow rates that impact operating costs are tabulated for each major process step. As time and location vary, the prices for these process flows may differ greatly. But these flow rates that affect operating costs will always be available here to serve as a reference. Frequently, people are being asked to select a cleaner ammonia production process and these results should be helpful in performing such evaluations.

List of Alternative Ammonia Production Cases

All studied processes vary in how the hydrogen and nitrogen are obtained but they all use the same Haber-Bosch three-bed ammonia synthesis scheme. All options have their synthesis loop purge gas scrubbed with water and then ammonia stripped from the water. This recovered ammonia is mixed with the main ammonia to form the final ammonia product.

The abbreviated names for the ammonia production processes are:

1. SMR: conventional ammonia production using primary and secondary reformer and having no CO_2 capture and sequestration
2. ATR: primary reformer with autothermal reformer and having no CO_2 capture and sequestration
3. SMR – syngas CCUS: conventional ammonia production but capturing and sequestering just the syngas-derived CO_2
4. ATR – syngas CCUS: ATR ammonia production but capturing and sequestering just the syngas-derived CO_2
5. SMR – full CCUS: conventional ammonia production but capturing and sequestering syngas and flue gas-derived CO_2
6. ATR – full CCUS: ATR ammonia production but capturing and sequestering syngas and flue gas-derived CO_2
7. PEM Green NH_3: PEM electrolysis for H2 production and Cryogenic Air Separation to produce N_2
8. AWE Green NH_3: Alkaline Water Electrolysis for H2 production and Cryogenic Air Separation to produce N_2
9. SOE Green NH_3: Solid Oxide Electrolysis to produce H_2 plus excess H_2 to combust O_2 in N_2 fortified air (by membrane)

METHODOLOGY

Simulation Assumptions

For all simulations, some basic equipment and environmental assumptions will be made across the board. These are:

- Ammonia production rate basis – 1000 tonne/d
- Max. outlet temperature of compressors – 140 °C
- Process outlet temperature for air cooled exchangers – 49 °C
- Pressure drops of columns –1 bar per 9 trays
- Pressure drops of heat exchangers – 0.3 bar
- Polytrophic efficiencies of compressors – 75%
- Efficiency of pumps – 65%

Natural Gas used for both SMR feed to produce syngas and furnace feed to provide heat are composed of:

	Mol%
Nitrogen	0.09
Carbon Dioxide	1.5
Methane	95.4
Ethane	2.5
Propane	0.5
Water	0.01

Fuel Gases of other compositions would probably be used for heating the reformer, but natural gas was used in this study to maintain consistency.

Conventional SMR and ATR Model Specifications

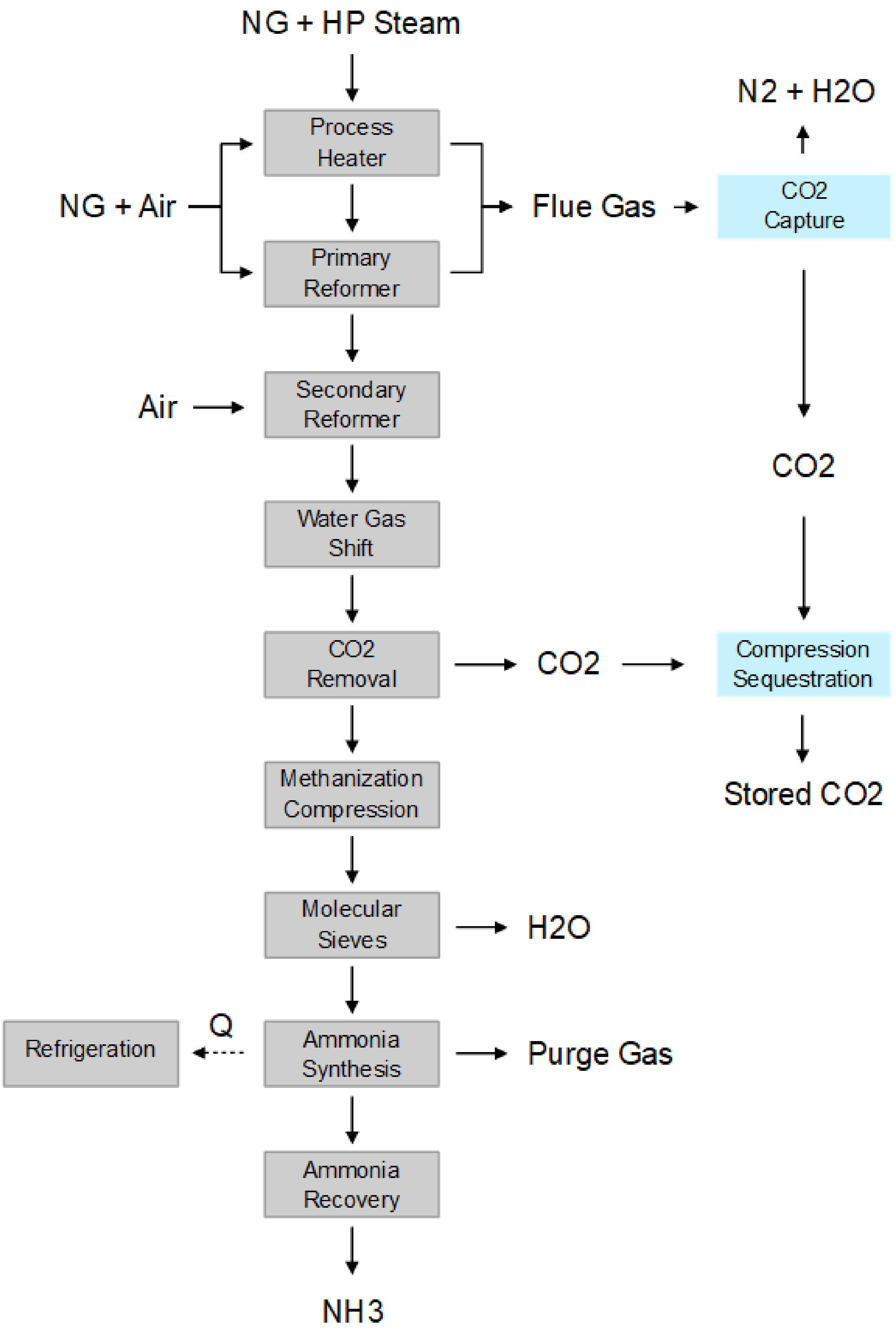
There are many possible process options for ammonia production. They can differ in the production of synthetic gas, the water gas shift reactors, the method for CO_2 removal, oxygenate removal or methanation, and the configuration of the ammonia reactors. In this study, we decided to focus on two conventional processes that mainly differ in the preparation of the synthetic gas. Both studied processes use autothermal and steam methane reformers.

The first configuration uses the heat generated from burning flue gas in a furnace to provide reforming reaction heat and for preheating the feed. The second reformer is autothermal, it uses a specific amount of air to achieve a stochiometric ratio of 1:3 between nitrogen and hydrogen after the water gas shift and methanation reactors, this ratio is required for the optimal ammonia production rate. The second configuration uses the autothermal reactor (ATR) as the main reformer. In ATR, natural gas is partially burned (partial oxidation - POX) to generate the heat for the steam methane reforming. Since the outlet stream of the autothermal reactor reaches about 1000 °C it is used to heat the second reformer (reforming exchanger), that is fed with steam and methane. This concept has been proven by Kellog.(1) This process option has better heat integration; however, the main disadvantage of this configuration is the necessity of pure oxygen for partial oxidation. The air does not contain enough oxygen to power the endothermic steam methane reforming reaction while also achieving the stochiometric ratio between nitrogen and hydrogen for ammonia synthesis. An air separation unit must be used to enhance the air with oxygen.

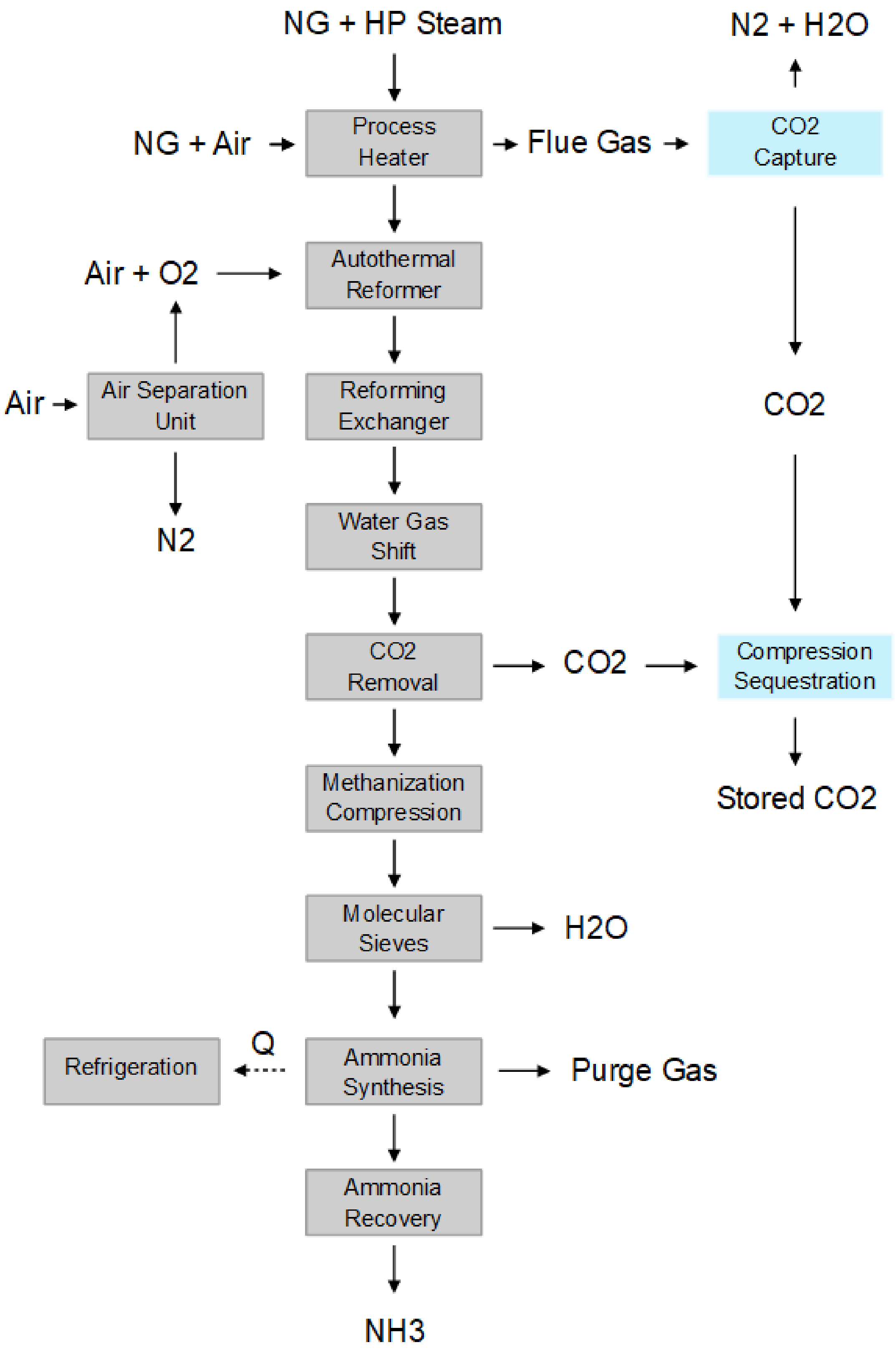
Downstream from SMR towards ammonia synthesis, there aren't any significant process differences between the two studied conventional process options. The reaction mixture is fed to the waste heat boiler, where it generates high-pressure steam (HP Steam) necessary for the steam methane reforming. After cooling, the remaining carbon monoxide reacts with water in a cascade of two water-gas-shift reactors. The first reactor operates at a higher temperature and its goal is to minimize the concentration of carbon monoxide on the outlet of the second reactor. The outlet mixture is then fed to the CO_2 removal unit, where most of the CO_2 is absorbed in the mixture of MDEA, piperazine, and water. After the regeneration of the amine solvent, the CO_2 is released at nearly atmospheric pressure, making this stream the main source of the CO_2 from the whole ammonia production process.

After the CO_2 removal unit, the residues of carbon oxides react with hydrogen in the methanation reactor, forming methane and water. This step is necessary to prevent the catalyst for ammonia synthesis from poisoning. (3) Most water remaining in the sweet gas after the methanation will be removed during the compression and the remaining part of the water is removed via molecular sieves. The last step of this process is ammonia synthesis, which generates low-pressure steam that is used upstream of this process.

Following are two conventional process schemes (grey boxes) followed by detail description of model set ups. Blue boxes are possible process adjustments leading to carbon dioxide emission reduction, the impact is commented in Results.



Scheme 1 SMR: Conventional ammonia production using primary and secondary reformer with CCUS



Scheme 2 ATR: Conventional ammonia production using autothermal reformer and reforming exchanger with CCUS

SMR and Water Gas Shift Specifications

- Steam-to-Carbon ratio – 3
- Carbon Monoxide (CO) in first (high temperature) Water Gas Shift Reactor – 3 mol%
- CO in second (low temperature) Water Gas Shift Reactor – 0.1 mol%

ATR (SM + POX) and Water Gas Shift Specifications

- Steam-to-Carbon ratio – 1, recommendation 0.6 – 1.5
- Oxygen to Carbon ratio – 0.88, recommendation 0.6 – 1.0
- Reforming Exchanger – steam to carbon ratio 2.5
- Carbon Monoxide (CO) in first (high temperature) Water Gas Shift Reactor – 3 mol%
- Low Temperature Shift Outlet Temperature – same as SMR Case at 192 °C since 0.1% CO could not be achieved

CO_2 Removal from Syngas Specifications

- Absorber modeled using ProMax “Heat and Mass Transfer” Model Type and “TSWEET Absorber/Stripper” Column Type
- Absorber has 23 sieve trays with top 2 being for water wash all specified to 70% Flooding
- Tray Spacing – 0.61 m
- System Factor – 0.8
- Weir Height – 7.62 cm
- 2 Pass Trays for Water Wash and 4 Pass Trays for Amine Contact
- Solvent Recipe – 45 wt.% MDEA / 5 wt.% Piperazine
- Water Wash – 0.5 m^3/h
- Solvent Rate – Adjusted to achieve 10 ppm CO_2 in Syngas
- Solvent Temperature to Absorber – 51.7 °C
- Rich Flash – 4.5 barg
- Solvent to Regenerator – 90.6 °C
- Regenerator Column – 10 ideal stages with solvent feeding 2nd stage from top, Ideal Stage “Model Type”, and “TSWEET Stripper” Column Type
- Regenerator Pressure – 0.37 barg
- Condenser Outlet Temperature – 49 °C
- Lean Loading – 0.02 mol CO_2 / mol (MDEA + Piperazine)

Methanation and Effluent Compression Specifications

- Methanation Reactor Inlet – 260 °C
- Compression – to 150 barg following general assumptions for compressors and air coolers

For the cases where CO_2 is Sequestered and/or the Flue Gas CO_2 is Captured, the following specifications were made:

CO_2 Removal from Flue Gas Specifications

- Inlet Flue Gas is cooled by a water quench to 50 °C
- Absorber modeled using ProMax “Heat and Mass Transfer” Model Type and “TSWEET Absorber/Stripper” Column Type
- Absorber has 30 m of IMTP #50 metal packing specified to 70% Flooding
- System Factor – 0.8
- Solvent Recipe – 30 wt.% MEA
- Solvent Rate – Adjusted to achieve 98% Recovery of CO2 from Flue Gas
- Solvent Temperature to Absorber – 55 °C
- Solvent to Regenerator – 114 °C
- Regenerator Column – 10 ideal stages with solvent feeding 2nd stage from top, Ideal Stage “Model Type”, and “TSWEET Stripper” Column Type
- Regenerator Pressure – 1.38 barg
- Condenser Outlet Temperature – 49 °C
- Lean Loading – 0.2 mol CO_2 / mol MEA

Haber Bosch Ammonia Synthesis Model Specifications

Although the nine processes under study have different paths to producing a suitable feedstock for the ammonia synthesis loop, all of them feed into the same ammonia synthesis model. The described loop can be found in Ullman's Encyclopedia of Industrial Chemistry. (1) In these ammonia synthesis models there are three beds each having these specifications:

- Dimensions so that there is 25 to 35% nitrogen conversion per pass
- Ammonia Synthesis Reaction Stoichiometry:

Component	Equilibrium	Forward Reaction	Reverse Reaction
Hydrogen	-3	1.5	-1.5
Nitrogen	-1	1	0
Ammonia	2	-1	1

- Forward Reaction Rate Equation:

$$r_{N2}\ (\text{kmol/m3*h}) = 17900\ e^{(-10474.5\ /\ T(K))}$$

- Reverse Reaction Rate Equation:

$$r_{N2}\ (\text{kmol/m3*h}) = 2.57\text{x}1016\ e^{(-23869.7\ /\ T(K))}$$

- Synthesis Loop Pressure – 150 barg
- Reactor Bed Outlet Temperature – 488 °C
- Synthesis Loop Purge Split Fraction – minimum 0.2% or enough to maintain inerts below 15 mol%
- Oxygenates in Synthesis Loop (H_2O, NO, CO_2, CO, etc) - < 5 ppm
- Ammonia Recovery Scrubber – Air Cooled Water contacting purge gas in a 7 ideal stage absorber
- Ammonia Recovery Stripper – Condenser Outlet Temperature is 60 °C and the reboiler is set to a 0.25 Boilup Ratio (Reboiler Vapor / Reboiler Feed)
- Refrigeration for Chiller – Propane chiller with two-stage compressor and economizer. 1st Stage Discharge Pressure is 5.19 barg and 2nd Stage is 17.6 barg.

Acid Gas Injection (AGI) Specifications

CO_2 Acid Gases are to be compressed according to the general compression rules to a pressure of 100 barg with water removed at each interstage separator.

Air Separation Plant Specifications

In the ATR process, there needs to be an Air Separation Unit for so that pure oxygen can be injected into the feed air. The Air Separation Process for the ATR and for the PEM and AWE Electrolysis options is based on the ProMax 6.0 "Air Separation Plant" Example File located in the Midstream/Gas Processing group. The simulation produces 99% O_2 at 0.71 barg and 27 °C. The Nitrogen product used in the electrolyzer-based processes is also at 99% purity 0.48 barg and 34 °C.

Green Ammonia Model Specifications

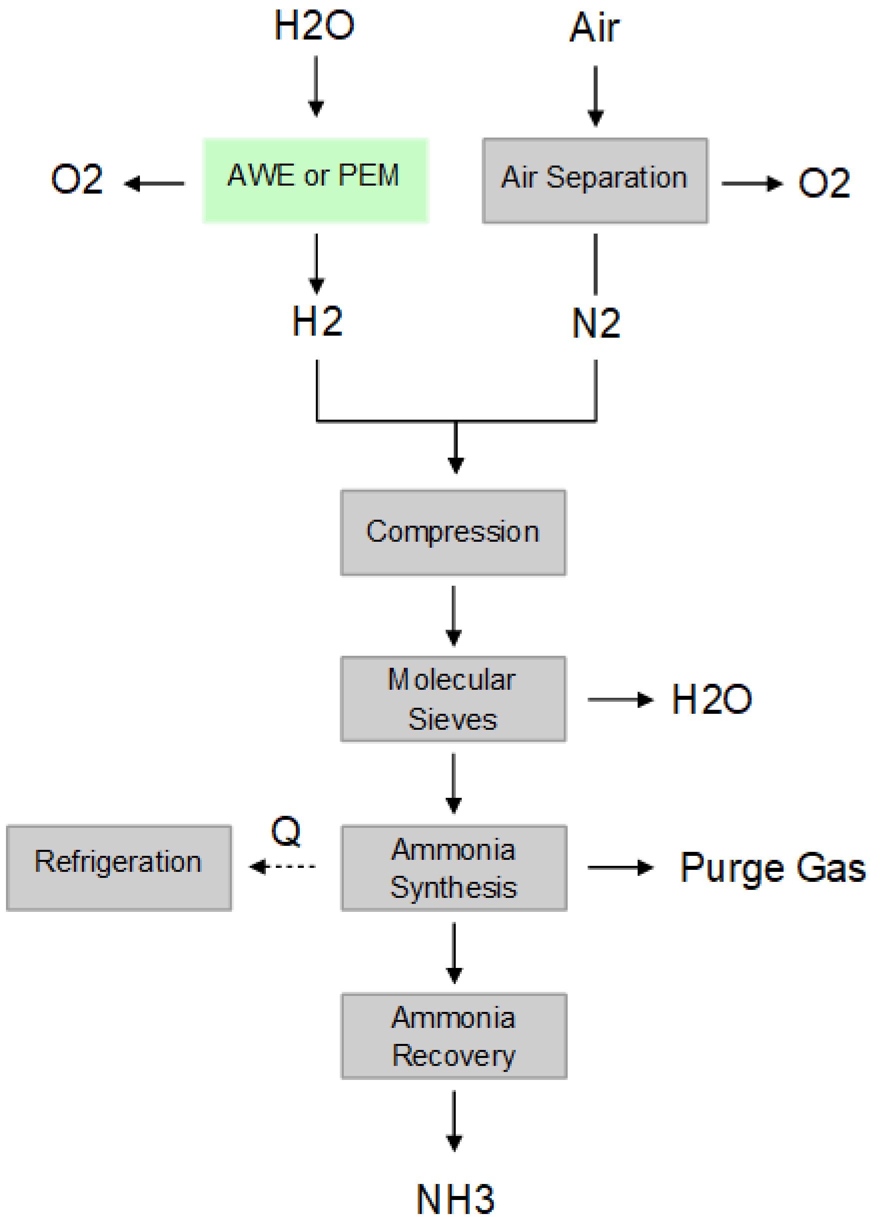
The Electrolyzer sections of the models that produce hydrogen from electricity are based on these ProMax 6.0 Example Files located in the Sustainability / Hydrogen Processes group:

- Green Ammonia with PEM
- Alkaline Water Electrolysis
- Solid Oxide Electrolysis

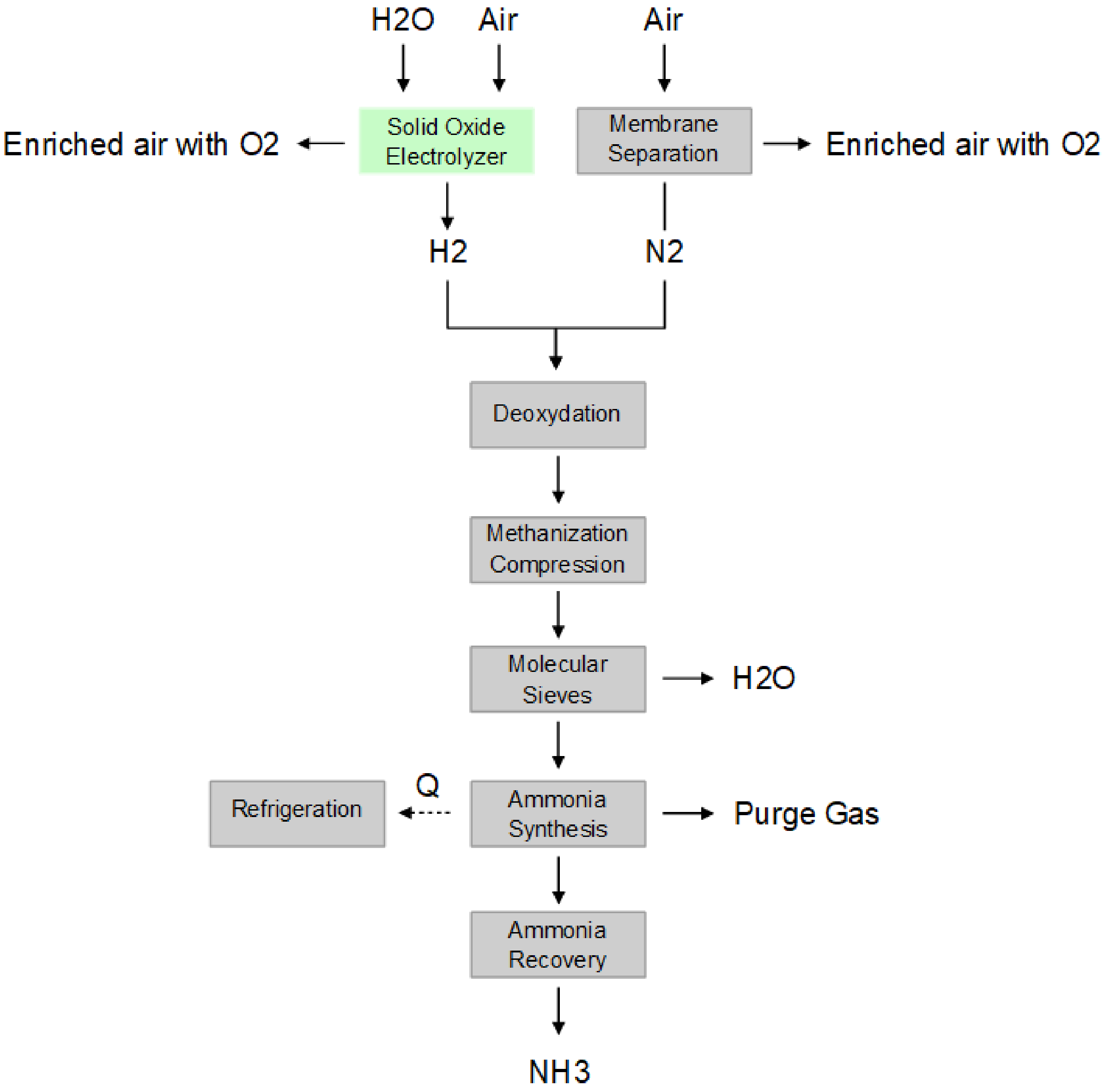
The main characteristic performance properties for electrolyzers are their Current Density (A/cm^2) and Total Voltage (V) at the operating point. In ProMax, the thermodynamic calculations calculate the Thermoneutral portion of the Voltage leaving the Overpotential portion of Total Voltage to be specified by the user. Also of importance are the crossover rates of components across the membrane which are not caused by the desired electrolysis process. For instance, hydrogen is intended to evolve on the cathode side of the membrane but there is a small amount of hydrogen crossover back to the anode side where the oxygen product forms. In PEM electrolysis, there is also some drag of water from the anode to the cathode as hydrogen forms on the cathode side. This is represented by the Electro-Osmotic Drag Coefficient which is only relevant to the PEM Electrolyzer. The values of these properties and more that are used for each electrolyzer model are listed here:

	AWE	SOE	PEM
Current Density (A/cm^2)	1.5	4	0.413
Inlet Temperature (°C)	70°C	720°C	80°C
H_2 Pressure (barg)			
O_2 Pressure (barg)			
H_2O Conversion (% per pass)	9.2	0.11	50
Cell Total Voltage (V)	1.719	2.143	1.285
Cell Overpotential Voltage (V)	.25	-.02	.67
Crossover H_2 (% of H_2 produced)	0.5	2	0.5
Crossover O_2 (% of H_2 produced)	0.5	2	0
Electro-Osmotic Drag Coefficient (mol H_2O / mol H_2)	0	0	0.7
Cell Area (m^2)	2.6	15.6	5.22
Cells per Stack	27	100	100
Stacks	698	10	10

Following are two process schemes, using all three types of electrolyzers for production of green ammonia, all other process steps were described in previous process options.



Scheme 3 Green Ammonia Production with AWE or PEM



Scheme 4 Green Ammonia Production with Solid Oxide Electrolyzer

RESULTS

For each case that was run, the ammonia production was verified to be 1000 tonne/d. Then the following properties which impact operating costs were gathered from each flowsheet of each model case:

- Natural gas – used for process feed in the SMR and ATR cases
- NG Preheating – Natural gas (but probably fuel gas in practice) required for heating the reformer
- CO_2 – uncaptured CO_2 or potential combustion CO_2 contained uncaptured outlet streams
- O_2 – O_2 produced by Air Separation units that might have some value in nearby facilities
- Fuel Gas Heat – Heating value from combustion of outlet streams less process heat required
- Electricity Consumption – Electricity required by equipment and electrolyzers less power generated by turbines
- HP Steam – 33.5 barg steam produced or consumed
- LP Steam – 3.5 barg steam produced or consumed

Conventional Ammonia Production

Tables 1 and 2 show key material and energy flow rates for the main processing steps in the conventional SMR and ATR cases. Corresponding to these are the gray boxes in Schemes 1 and 2 showing schematics of the main process steps. Schemes from the ProMax model flowsheets are too numerous to be included in this work. Positive values represent net production by the process step for that heat or energy category. Negative values indicate net consumption.

Table 1 Conventional SMR

Flowsheet	**Natural Gas** t/d	**NG Preheating** t/d	**CO_2** t/d	**O_2** t/d	**Fuel Gas Heat** GJ/h	**Electricity consumption** MW DC	**HP Steam** t/d	**LP Steam** t/d
Steam Methane Reforming	-469	-180	465	0	-358	-6.6	-1522	525
Water Gas Shift	0	0	0	0	0	0.0	1612	797
Syngas CO_2 Removal	0	0	1226	0	1	-1.1	0	-2160
Methanation/Compression	0	0	0	0	0	-11.0	0	0
Ammonia Synthesis	0	0	14	0	57	-1.0	779	299
Ammonia Recovery	0	0	0	0	15	-0.3	0	-139
Refrigeration	0	0	0	0	0	-16.6	0	0
Total SMR	**-469**	**-180**	**1704**	**0**	**-285**	**-36.5**	**869**	**-677**

Table 2 Conventional ATR

	Natural Gas t/d	**NG Preheating** t/d	**CO_2** t/d	**O_2** t/d	**Fuel Gas Heat** GJ/h	**Electricity consumption** MW DC	**HP Steam** t/d	**LP Steam** t/d
Air Separation	0	0	0	0	0	-4.1	0	0
SM + AT Reforming	-589	-56	152	0	-117	-7.3	0	173
Water Gas Shift	0	0	0	0	0	0.0	1067	384
Syngas CO_2 Removal	0	0	1466	0	2	-1.1	0	-2555
Methanation/Compression	0	0	0	0	0	-12.0	0	0
Ammonia Synthesis	0	0	83	0	167	-0.7	761	412
Ammonia Recovery	0	0	0	0	28	-0.3	0	-154
Refrigeration	0	0	0	0	0	-14.6	0	0
Total ATR	**-589**	**-56**	**1701**	**0**	**79**	**-40.2**	**1828**	**-1740**

Carbon Capture Modifications & Strategies

Conventional ammonia production has two main sources of carbon dioxide. The first source is the flue gas, produced during the preheating of the feed and heat consumed for the reaction for the option using steam methane reforming without POX. The second source is the CO_2 released from the regenerator of the CO2 removal unit.

The production of CO_2 relates to the consumption of natural gas (NG) for each option. The first configuration uses 469 t/d of natural gas (NG) for steam methane reforming and 180 t/d of NG is used to generate heat for the reforming and preheating of the feed. The second configuration uses a higher amount of NG for the feed due to the autothermal reformer, 589 t/d. The flow of NG for preheating is lower compared to the previous process option, 56 t/d. If we sum up the NG consumption for both SMR options, we'll find out that it is almost identical. For the SMR the consumption is 649 t/d of NG and for the SMR using autothermal reformer consumes 645 t/d of NG. Therefore, we must focus on the details between these two SMR processes, mainly on the electricity consumption and CO_2 capture strategy.

Electricity consumption

Since autothermal reformer requires enhanced air with oxygen, the air separation unit must be implemented. The electric energy consumption of the AS unit is about 10 % of the whole ammonia process. Therefore, the SMR option has about 10% lower electric energy consumption. The increase in energy consumption can be also find in every CCUS strategy due to power requirements for the compression of CO_2.

CCUS strategies

If no CO_2 is stored, the CO_2 intensity of both processes is about 1.7 t of CO_2 per 1 t of NH_3. If we compress and store only the CO_2 that has already been captured during the CO_2 removal step in the process, we'll get to lower CO_2 intensities. The option with Steam Methane Reformer has the capacity to store 72 % of the total CO_2 generated by the process. Changing the CO_2 intensity to 0.48 t of CO_2 per 1 t of NH_3. The increase in the power consumption is 5.4 MW due to compression, which relates to a 15% energy consumption increase. The ATR option has the capacity to store 86 % of the total CO_2 generated by the process. Changing the CO_2 intensity to 0.24 t of CO_2 per 1 t of NH_3. However, it will increase the overall energy consumption by 6.5 MW, which corresponds to 16 % of the whole ammonia process consumption. This step is the easiest for decarbonizing this process because it requires only a new compression station and piping.

The numerical description offers the tables 3 and 4.

Table 3 SMR with syngas CO_2 AGI

Flowsheet	**Natural Gas**	**NG Preheating**	**CO_2**	**O_2**	**Fuel Gas Heat**	**Electricity consumption**	**HP Steam**	**LP Steam**
	t/d	t/d	t/d	t/d	GJ/h	MW DC	t/d	t/d
Steam Methane Reforming	-469	-180	465	0	-358	-6.6	-1522	525
Water Gas Shift	0	0	0	0	0	0.0	1612	797
Syngas CO_2 Removal	0	0	0	0	1	-1.1	0	-2160
Methanation/Compression	0	0	0	0	0	-11.0	0	0
Ammonia Synthesis	0	0	14	0	57	-1.0	779	299
Ammonia Recovery	0	0	0	0	15	-0.3	0	-139
Refrigeration	0	0	0	0	0	-16.6	0	0
Acid Gas Injection	0	0	0	0	0	-5.4	0	0
Total SMR – Syngas CO_2 AGI	**-469**	**-180**	**478**	**0**	**-285**	**-41.9**	**869**	**-677**

Table 4 ATR with syngas CO_2 AGI

Flowsheet	Natural Gas	NG Preheating	CO_2	O_2	Fuel Gas Heat	Electricity consumption	HP Steam	LP Steam
	t/d	t/d	t/d	t/d	GJ/h	MW DC	t/d	t/d
Air Separation	0	`	0	0	0	-4.1	0	0
SM + AT Reforming	-589	-56	152	0	-117	-7.3	0	173
Water Gas Shift	0	0	0	0	0	0.0	1067	384
Syngas CO_2 Removal	0	0	0	0	2	-1.1	0	-2555
Methanation/Compression	0	0	0	0	0	-12.0	0	0
Ammonia Synthesis	0	0	83	0	167	-0.7	761	412
Ammonia Recovery	0	0	0	0	28	-0.3	0	-154
Refrigeration	0	0	0	0	0	-14.6	0	0
Acid Gas Injection	0	0	0	0	0	-6.5	0	0
Total ATR – Syngas CO_2 AGI	**-589**	**-56**	**235**	**0**	**79**	**-46.6**	**1828**	**-1740**

To fully decarbonize these conventional processes, reducing the carbon intensity to the limits it processes requires a new CO_2 capture unit (“CO_2 capture” in the top blue rectangle on the schemes 1 and 2). As we can see in the tables the steam consumption increases due to the reboiler of the new amine unit and the electric energy increases due to the higher flow of captured CO_2.

The option with SMR with full CCUS can store 98.7 % of CO_2 that has been generated. The CO_2 intensity drops to 0.02 t of CO_2 per 1 t of NH_3. However, the power consumption increases by about 7.5 MW, which is 20.5 % compared to a conventional process that is equipped with any CCUS. The remaining CO_2 emissions come from the purge gas in the ammonia synthesis. If we would like to achieve a net zero for this process, we could use the purge gas for preheating.

The option with ATR with full CCUS stores is 95 %. The CO_2 intensity drops to 0.09 of CO_2 per 1 t of NH_3. The consumption of energy increases by 7.1 MW, which is 17.8 % compared to conventional processes that are not using any CCUS. If we would like to improve this process and achieve net zero, we could increase the steam / HC ratio to achieve higher yields of CO_2 at the WGS reaction and to decrease the flowrate of purge gas. It might also be used for preheating the feed for ATR.

The numerical description offers the tables 5 and 6.

Table 5 SMR – Full CCS

Flowsheet	**Natural Gas** t/d	**NG Preheating** t/d	**CO_2** t/d	**O_2** t/d	**Fuel Gas Heat** GJ/h	**Electricity consumption** MW DC	**HP Steam** t/d	**LP Steam** t/d
Steam Methane Reforming	-469	-180	0	0	-358	-6.6	-1522	525
Water Gas Shift	0	0	0	0	0	0.0	1612	797
Syngas CO_2 Removal	0	0	0	0	1	-1.1	0	-2160
Methanation/Compression	0	0	0	0	0	-11.0	0	0
Ammonia Synthesis	0	0	14	0	57	-1.0	779	299
Ammonia Recovery	0	0	0	0	15	-0.3	0	-139
Refrigeration	0	0	0	0	0	-16.6	0	0
Acid Gas Injection	0	0	0	0	0	-7.4	0	0
Flue Gas CO_2 Removal	0	0	9	0	0	-0.1	0	-977
Total SMR – Full CCS	**-469**	**-180**	**22**	**0**	**-285**	**-44.0**	**869**	**-1653**

Table 6 ATR – Full CCS

Flowsheet	**Natural Gas** t/d	**NG Preheating** t/d	**CO_2** t/d	**O_2** t/d	**Fuel Gas Heat** GJ/h	**Electricity consumption** MW DC	**HP Steam** t/d	**LP Steam** t/d
Air Separation	0	0	0	0	0	-4.1	0	0
SM + AT Reforming	-589	-56	0	0	-117	-7.3	0	173
Water Gas Shift	0	0	0	0	0	0.0	1067	384
Syngas CO_2 Removal	0	0	0	0	2	-1.1	0	-2555
Methanation/Compression	0	0	0	0	0	-12.0	0	0
Ammonia Synthesis	0	0	83	0	167	-0.7	761	412
Ammonia Recovery	0	0	0	0	28	-0.3	0	-154
Refrigeration	0	0	0	0	0	-14.6	0	0
Acid Gas Injection	0	0	0	0	0	-7.1	0	0
Flue Gas CO_2 Removal	0	0	2	0	0	0.0	0	-306
Total ATR – Full CCS	**-589**	**-56**	**85**	**0**	**79**	**-47.3**	**1828**	**-2046**

Electric energy CO_2 footprint

Electric energy might be also a source of CO_2. If renewable electric energy is supplied from wind, solar, or nuclear to power the ammonia plant, we can assume that the CO_2 footprint behind electricity is zero. However, if we would use the natural gas turbine as a producer of electric energy, we can expect about 852 t/d of CO_2 to be produced per 100 MW, from 310 t/d of NG. If we would use the NG turbine to power all the above-mentioned processes, it would increase the CO_2 intensity for all cases. ATR options increase up to 0.5 t of CO_2 per 1 t of NH_3 and SMR options up to 0.4 t of CO_2 per 1 t of NH_3. There is an option to capture, and store produced CO_2 from the gas turbine however that would require a new CO_2 removal unit and it would decrease the output of electric energy from the gas turbine by 15%. (4)

Green Ammonia Production

Production of ammonia via electrolysis has been investigated with alkaline water, polymer exchange membrane and solid oxide electrolyzer. All electrolyzer options require significant amounts of electrical energy. The source of this energy determines the CO_2 intensity of the produced ammonia. If 100% of the electric energy for the electrolysis is supplied from natural gas turbine, the CO_2 intensity for process using PEM electrolyzer is 4.1 t of CO_2 per 1 t of NH_3. (4) If we would use coal or diesel, the CO_2 intensity would be even higher. The CO_2 intensity comparable to the conventional processes without CCS can be achieved with electrolysis that uses half energy from NG and half from renewable sources. If renewable electric energy is used for the whole process, the carbon footprint of the process is zero and so is the consumption of natural gas. The process will also generate high pressure and low-pressure stream that has no usage in this process so it can be connected to the other process that could use it. During the green ammonia production via AWE and PEM electrolysis huge amounts of pure oxygen are produced, 1.7 t per 1 t of NH_3. The oxygen comes from two main sources, air separation unit and electrolysis. The oxygen should not be seen as a waste, that is vented to the atmosphere but rather used in pharmaceutical industry, as an oxidation agent for rocket fuel, in water treatment for wet oxidation, to enhance the air in sulfur recovery units, it could be used in steel production for convertors or in autothermal reformers. The combination with autothermal reformers has been theoretically investigated in this study.

Table 7 PEM – Green Ammonia

Flowsheet	**Natural Gas**	**CO_2**	**O_2**	**Fuel Gas Heat**	**Electricity consumption**	**HP Steam**	**LP Steam**
	t/d	t/d	t/d	GJ/h	MW DC	t/d	t/d
PEM Electrolysis	0	0	1442	0	-431.4	0	0
Air Separation	0	0	249	0	-4.0	0	0
N_2 Compress	0	0	0	0	-4.9	0	0
Ammonia Synthesis	0	0	0	6	-8.4	814	658
NH_3 Recovery	0	0	0	0	0.2	0	-124
Refrigeration	0	0	0	0	-9.9	0	0
Total PEM Green NH_3	**0**	**0**	**1692**	**6**	**-458.5**	**814**	**534**

Table 8 AWE – Green Ammonia

Flowsheet	**Natural Gas** t/d	**CO_2** t/d	**O_2** t/d	**Fuel Gas Heat** GJ/h	**Electricity consumption** MW DC	**HP Steam** t/d	**LP Steam** t/d
Alkaline Water Electrolysis	0	0	1445	0	-348.5	0	0
Air Separation	0	0	260	0	-4.0	0	0
N_2 Compression	0	0	0	0	-5.0	0	0
Ammonia Synthesis	0	0	0	5	-10.0	806	662
NH_3 Recovery	0	0	0	0	-0.2	0	-130
Refrigeration	0	0	0	0	-9.9	0	0
Total AWE	**0**	**0**	**1704**	**5**	**-377.5**	**806**	**532**

Solid Oxide Electrolysis

In the Solid Oxide Electrolysis case, there is no steam generation and a small amount of steam consumption in the NH_3 Recovery step. There is no need for an air separation unit because at high electrolyzer outlet temperatures, excess hydrogen will react with oxygen in the air feed to form water. In this case, ambient air is passed through a cellulose acetate air separation membrane to reduce the oxygen content from 21 to 10 mol%. By this step, less excess hydrogen is required to combust the oxygen. The solid oxide electrolyzer is the most energy efficient of the electrolyzers because it operates at high temperature. However, since more hydrogen must be produced to consume the oxygen, its electricity requirement is not that much less than the AWE case. Solid Oxide Electrolysis also needs a high temperature heat source to preheat all the feeds to electrolyzer temperature and to maintain operation at a 749°C. Also of note is that the crossover hydrogen and oxygen portions combust with their bulk counterpart molecule which heats the electrolyzer. Crossover hydrogen and oxygen were set to 2% to gain enough heat to sustain the electrolyzer. If this is higher than crossover capabilities, then this is a lost opportunity that causes excess hydrogen production. Further heat integration to reduce crossover needs merit further study. Nonetheless, the SOE process is interesting for applications where steam has very low value.

Table 9 SOE – Green Ammonia

Flowsheet	**Natural Gas** t/d	**CO_2** t/d	**O_2** t/d	**Fuel Gas Heat** GJ/h	**Electricity consumption** MW DC	**HP Steam** t/d	**LP Steam** t/d
Solid Oxide Module	0	0	2954	0	-295.8	0	0
Solid Oxide External	0	0	0	0	-6.6	0	0
Membrane Separation	0	0	275	0	-4.4	0	0
CO_2 Removal	0	0	0	0	0.0	0	-3
Ammonia Synthesis	0	0	0	26	-24.8	0	0
NH_3 Recovery	0	0	0	0	-0.2	0	-150
Refrigeration	0	0	0	0	-10.3	0	0
Total SOE Green NH_3	**0**	**0**	**3228***	**26**	**-342.3**	**0**	**-153**

*O_2 from SOE Green Ammonia tied in the mixture of 36.5 mol% O_2 and 63.5 % N_2.

Table 10 Complete results

Process option	Natural Gas t/d	CO_2 t/d	O_2 t/d	Fuel Gas Heat GJ/h	Electricity consumption MW DC	HP Steam t/d	LP Steam t/d	Carbon Intensity t CO_2 per t of NH_3
SMR	-649	1704	0	-285	-36.5	869	-677	1.70
SMR - syngas CCUS	-649	478	0	-285	-41.9	869	-677	0.48
SMR - full CCUS	-649	22	0	-285	-44.0	869	-1653	0.02
ATR	-645	1701	0	79	-40.2	1828	-1740	1.70
ATR - syngas CCUS	-645	235	0	79	-46.6	1828	-1740	0.24
ATR - full CCS	-645	85	0	79	-47.3	1828	-2046	0.09
PEM Green NH_3	0	0	1692	6	-458.5	814	534	0
AWE Green NH_3	0	0	1704	5	-377.1	806	532	0
SOE Green NH_3	0	0	3228*	26	-342.3	0	-153	0

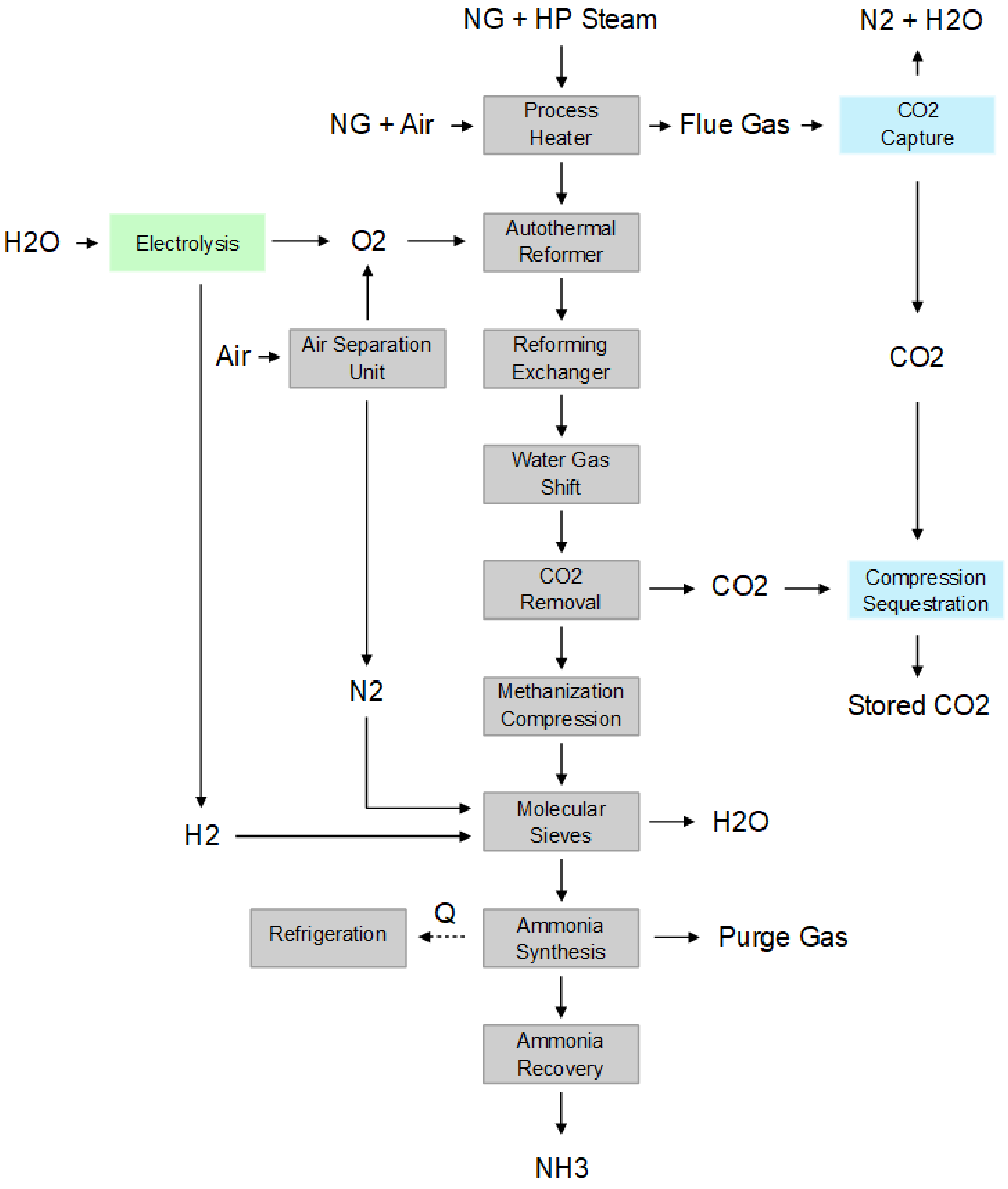
Electrolysis Implementation in Conventional Process

There are two possible improvements, for the processes using the ATR for hydrogen generation, that could reduce waste and consumption of hydrocarbons. The ATR requires enhanced air with oxygen. The oxygen usually comes from the Air Separation unit and the most amount of nitrogen is due to its quantity usually vented to the atmosphere.

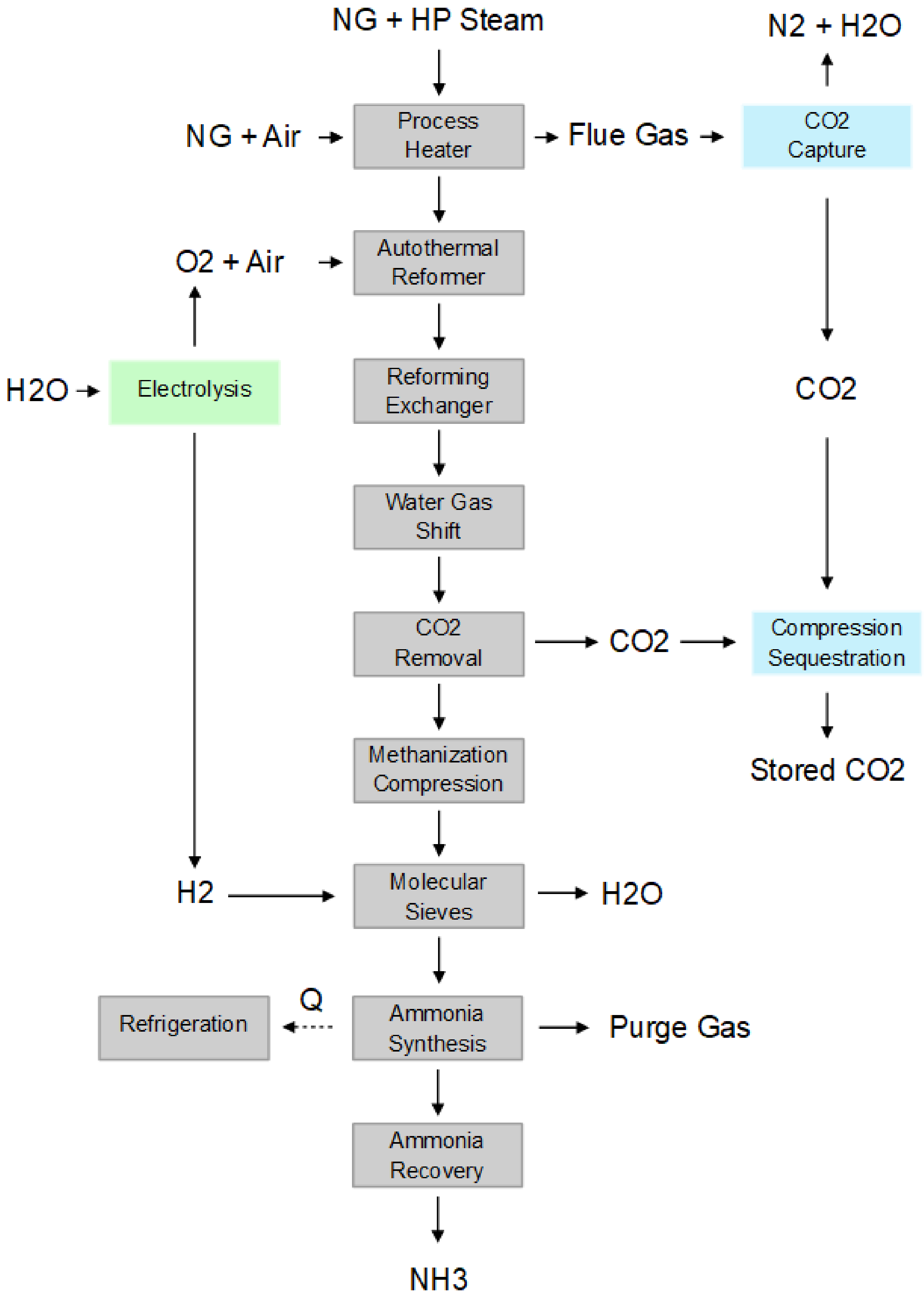
In the first option, the Air Separation unit is replaced with the AWE or PEM, where produced green hydrogen is compressed together with N_2 and H_2 from the conventional process and used for ammonia synthesis. In this option, the oxygen from electrolysis can fully subsidize the air separation unit. If SOE is used instead of AWE or PEM, enhanced air generated from SOE can be used as a feed to the autothermal reactor.

The second option is mixing the pure oxygen from the electrolysis and air separation unit, using it as an oxidizing agent for the autothermal reformer. This option requires a burner that would be able to maintain the higher temperatures during its operation, however since there is no nitrogen from the air, the whole equipment could be smaller, compared to all other mentioned options using the autothermal reformer. The nitrogen from the air separation unit together with hydrogen from electrolysis and hydrogen from the CO_2 removal unit will be compressed together and fed to molecular sieves followed by ammonia synthesis.

Implementing electrolysis in the ATR ammonia production process option have a great influence on the overall process, reducing the consumption of natural gas and vented nitrogen, due to adding hydrogen from electrolysis and sufficiently using the produced enhanced air or oxygen from the electrolysis, which otherwise would need to find usage in a different process or would be vented to the atmosphere.



Scheme 5 ATR full CCS with AWE or PEM



Scheme 6 ATR full CCS with AWE, PEM, or SOE

CONCLUSION

This study focuses on possible process enhancements with the target to reduce the CO_2 footprint of ammonia production. Several process options have been investigated with different modifications and the following are the conclusions for each option. The easiest option to reduce the current CO_2 emissions from ammonia production is the compression and sequestration of CO_2 from syngas. The full CCS requires the above new carbon capture unit. Due to compression electric energy consumption of the plant rises. The other options for ammonia production are using electrolysis and air separation units. The process with AWE and PEM produces significant amounts of high- and low-pressure steam and pure oxygen, however, it requires 900 - 1000 % electric energy of conventional processes running on natural gas. The SOE consumes the HP and LP steam and therefore it doesn’t necessary to be connected to other processes, however, the amount of enhanced air, produced by SOE is significant and could find usage for example for ATR. The last two options are using electrolysis with ATR, to reduce natural gas consumption and CO_2 emissions. This is one of the examples of how to use oxygen from electrolysis. Oxygen is many times overseeded product of electrolysis, and it should not be vented to the atmosphere but rather compressed and purified for various applications. Ammonia production has great potential to become a net zero process, due to the suitability of CCUS and synergy with electrolysis.

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