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Current and future role of Haber-Bosch ammonia in a carbon-free energy landscape

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Supporting Information

S.1 Calculations for Figure 4

The energy loss during electrolysis was calculated assuming 60% efficiency for alkaline electrolysers and PEM electrolysers, 75% efficiency for a future PEM electrolyser, and 80% for SO electrolyser.

The energy for N2 production was assumed to be 0.33 GJ t_{NH3}^{-1} using PSA. [1]

The energy loss from compression was calculated using the total compression energy from a typical 1995 process (6.6 GJ t_{NH3}^{-1}) and assuming 95% efficiency electric turbines compared to 45% efficient steam turbine. In the case of high pressure electrolysis, the compression energy loss was calculated assuming 5 stages of compression, or which 4 are eliminated for hydrogen when using high pressure electrolysis.

The heat loss is equal to the heat of reaction: 2.7 GJ t_{NH3}^{-1}.

Table S1: Comparison of the energy requirements, efficiency and energy losses of conventional methane-fed Haber Bosch processes and electrically-powered alternatives.

	Year	**Technology**	**Energy input GJ/t$_{NH3}$**	**Energy Losses GJ/t$_{NH3}$**	**Overall efficiency %**	**Energy losses**							Ref
						H_2 production			N_2 production GJ/t$_{NH3}$	NH_3 production		Others GJ/t$_{NH3}$	
						SMR GJ/t$_{NH3}$	WGSR GJ/t$_{NH3}$	Steam turbine compressors GJ/t$_{NH3}$		Purge / Other GJ/t$_{NH3}$	Steam turbine compressors GJ/t$_{NH3}$		
Conventional methane -fed Haber Bosch processes	1970s	Model of a typical 1970s design with 2.5 GJ/t steam export.	36.4	17.7	51.2	1.37	5.69[f]	1.81	-	1.81	2.88	4.15[d]	[2]
	1980s	ICI pre-'AMV concept'.	35.0	15.3	56.3	8.4	1.4	2.1	-	1.4	1.3	0.70	[3]
	1990s	Low Energy Process	29.3	10.9	63.5	1.0	1.3	2.2[a]	-	1.72	4.4[a]	0.33	[4]
	2010s	Low energy process with 1.55 GJ/t steam export	30.3	11.7	61.4			6.6 (inc. NH_3)[g]	-		-	5.1	[5]
	2010s	EC BAT Definition Example	28.0	9.4[e]	66.4	0.7	-	2.2	-	-	2.1	4.4[c]	[6]

						Energy losses					
								NH_3 production			
	Year	**Technology**	**Energy input GJ/t_{NH3}**	**Energy Losses GJ/t_{NH3}**	**Overall efficiency %**	H_2 production by Electrolysis of Water	N_2 production GJ/t_{NH3}	Purge / Other GJ/t_{NH3}	Steam turbine compressors GJ/t_{NH3}	Other GJ/t_{NH3}	Ref
Electrically – powered future Haber Bosch	1970s	Alkaline electrolysis (80°C, 1 atm)	39.7	14.5	63.5	11.7	0.2	n/a	2.6	n/a	[7]
	2010s	Model Alkaline electrolysis (1 atm)	45.6	20.5	55	16.7	0.33	n/a	3.1	0.33	
	2010s	Model PEM electrolysis (1 atm)	39.7	14.6	63	10.8	0.33	n/a	3.1	0.33	
	2010s	Model PEM electrolysis (30 atm)	38.4	13.3	65	10.8	0.33	n/a	1.8	0.33	

[a] Steam turbine losses for the H_2 production and NH_3 production are split 32.7% to 67.3 % respectively based on compressor duties presented by Dybkjaer (1995) for a highly efficient process.

[b] Steam export.

[c] Unrecovered process heat excluding flue gas losses which are included under the SMR losses.

[d] This will include losses to ambient.

[e] This data applies the typical energy balance presented in the EC BAT document with the quoted minimum energy input.

[f] Heat loss to environment. This data applies to a three column tri-ethanolamine CO_2 scrubbing system which is significantly more energy intensive compared to modern methods such as the Selexol process.[g] Energy loss data is reported for the overall methane to ammonia process and is not broken down further.

S.2 Calculations for Figure 5

All calculations were done using 100 kg hr^{-1} as the ammonia production rate.

General equation for compression energy (1) assuming polytropic compression.

$$W = m\frac{1}{\eta_{turb}}\frac{n}{n-1} * ZRT * \left(\left(\frac{P}{P_0}\right)^{\frac{n-1}{n}} - 1\right)$$

$$\frac{n-1}{n} = \frac{\frac{1}{\eta}(k-1)}{k}$$

m is molar flow rate. k is ratio of heat capacities. η is polytropic efficiency (taken to be 0.75 for centrifugal compressor), and η_{turb} is turbine efficiency (taken to be 0.75 for steam turbine and 0.95 for electric turbine).

Capital cost correlation were done using the following equation. [8]

$$Capital = C_{fixed} + C_{ref}\left(\frac{X}{X_{ref}}\right)^{a}$$

Table S.2: Capital cost correlation factors. [8]

Unit	C fixed	C ref	X ref	a
Compressor	7400	7690000	1000 KW	0.9
Heat Exchanger	28600	208000	100 m^2	0.71
Reactor	66800	268000	20 m^3	0.52

S.2.1 High Pressure Methane Driven Process

It is assumed the highest possible compression factor for a centrifugal compressor is 3 due to temperature limitations. Therefore, compression up to 150 bar is divided into 5 steps with interstage cooling. This results in an energy consumption of approximately 5.3 GJ t_{NH3}^{-1} (0.7 GJ t_{NH3}^{-1} smaller than literature) and a capital cost of $1.66 million.

The amount of moles recycled is determined assuming the reactor gets to 90 % of equilibrium (40.4 bar at 150 bar total and 400 °C).

$$Rec\ moles = Moles\ produced * \frac{P_{non-condensed}}{P_{condensed}} = \frac{3.27\frac{mol}{s}}{2} * \frac{150 - 40.4}{40.4} = 4.43$$

Recycle compression was calculated to be 2.3 KW based on a loop pressure drop of 10 bar.

The energy consumption for refrigeration compressor was taken from literature to be 0.5 GJ/ton, which corresponds to a power of 13.89 KW and a capital of $171k.

The capital costs of the heat exchangers includes cooling the reactor effluent in addition to interstage cooling for the first 4 compression stages. The heat capacity of the fluid was assumed to be 30 J mol^{-1} K^{-1} (ammonia will be higher at high temperatures). The temperature gradient for heat exchange was assumed to be 15 °C. The heat transfer coefficient was assumed to be 0.03 KW m^{-2} K^{-1} for a gas. The change in temperature was assumed to be 380 °C for the reactor effluent (addition 50 °C needed for condensation not included). The temperature change for interstage cooling was assumed to bring the temperature back to the initial 300K.

The size of the reactor was calculated using the Sehested rate equation and discretizing the reactor [9]. It was assumed the inlet ammonia pressure was the condensation vapour pressure (1.9 bar) and the outlet pressure was 90 % of the reaction equilibrium pressure at 150 bar total and 400 °C (43.5 bar ammonia).

S.2.2 High Pressure Electric Driven

The calculations closely mirrored those for the methane driven process, with the first 4 stages including only the nitrogen gas (because of high pressure electrolysis – which in practice could output 80 bar hydrogen) and an efficiency of 0.95 rather than 0.45. This results in a compression energy of 0.89 GJ t_{NH3}^{-1} and a capital cost of $475k.

The amount of moles recycled were exactly the same, but the compressor power decreased to 1.08 KW due to increased efficiency. The refrigeration compressor decreases to 10.96 KW and $140k.

The heat exchanger capital was calculated in the same manner, with the first two interstages requiring much less cooling due to only nitrogen in the stream. Capital costs drop to $676k.

The size of the reactor was identical to the previous case.

This process losses an additional 2.7 GJ t_{NH3}^{-1} of heat from the reactor.

S.2.3 Medium Pressure with Condensation

Feed gas compression occurred in three stages rather than five. None of the stages included hydrogen due to high pressure electrolysis.

The moles recycled were calculated based on 90 % of the equilibrium pressure (1.26 bar) and the vapor pressure at -33 °C (1 bar).

$$Moles\ recycled = \frac{3.27\frac{moles}{s}}{2} * \frac{20 - 0.26}{0.26} = 124\frac{moles}{s}$$

Assuming 1.5 bar loop pressure drop, this results in the compressor power of 34 KW (1.24 GJ t_{NH3}^{-1}) and a cost of $377k.

The energy consumption for refrigeration was calculated from the literature value for a conventional process condensing at -33 °C (0.8 GJ t_{NH3}^{-1}) and multiplying it by the ratio of recycled moles from the conventional case to the low pressure case (28) to get a energy consumption of 22.4 GJ t_{NH3}^{-1}. This corresponds to 622KW compressor costing $5.02 million.

The heat exchangers for the interstage cooling are identical to those of the previous case, but the reactor effluent heat exchanger is much larger. It exchanges 1452 KW and cost 2.94 million. (not including the heat exchanger to go from atmospheric to -33 °C).

The size of the reactor was calculated using the same method as previous and using the new vapour pressure of ammonia during condensation and reaction equilibrium pressure.

This process also losses 2.7 GJ t_{NH3}^{-1} of heat in the reaction.

S.2.4 Medium Pressure with Absorption

The feed gas compression is identical to the previous case.

The recycle moles, while not as large as the previous, are still large.

$$Moles\ recycled = \frac{3.27\frac{moles}{s}}{2} * \frac{20 - 1.26}{1.26} = 24.3\frac{moles}{s}$$

This assumes the absorbent is able to remove all of the ammonia. Using a 1 bar pressure drop approximated from literature, this results in a 4.4 kW compressor costing $66k.

Refrigeration compressor is no longer needed.

The reactor effluent heat exchanger now only has to cool the gas 200 °C rather than 380 °C (plus refrig), so the heat exchange is 203 KW with a cost of $682k.

Additional energy consumption comes from that required for regenerating the absorbent, as taken from literature to be 9.15 GJ t_{NH3}^{-1} for a temperature change of 300 °C[10]. However, this energy requirement could partially be accommodated by 2.7 GJ t_{NH3}^{-1} of waste heat from the reactor, so the total heat loss is 6.45 GJ t_{NH3}^{-1}. In the case of high pressure synthesis (150 bar) with an absorbent, it is assumed that the temperature only needs to increase by 200˚C because it will also be accompanied by a pressure swing, and therefore the energy loss is 3.4 GJ t_{NH3}^{-1}.

Regeneration of the absorbent with a heater does not add to the capital cost.

The size of reactor size was calculated as previously, but assuming all of the ammonia is removed by absorption.

S.2.5 Atmospheric Pressure with Absorption

It is assumed that no feed compression is necessary due to the high pressure electrolysis.

It is assumed that the outlet of the reactor is 1.5 bar with an equilibrium pressure of 0.009 bar.

$$Moles\ recycled = \frac{3.27\frac{moles}{s}}{2} * \frac{1.5 - 0.0081}{0.0081} = 301\frac{moles}{s}$$

Assuming 1.5 bar pressure drop (probably low due to the extremely high recycle), the recycle compressor is 835kW (30.1 GJ t_{NH3}^{-1}) for a cost of $6.5 million.

The heat exchanger has a load of 1825 kW due to the large recycle and a cost of $3.5 million.

The heat losses are those required to regenerate the absorbent by 200 °C as previously (3.4 GJ t_{NH3}^{-1}).

The size of the reactor was calculated as previous, assuming 90 % of the equilibrium ammonia pressure (0.009 bar) and assuming the absorbent can remove ammonia down to 0.001 bar. Since a more active Ru catalyst would be used in this case rather than the iron catalyst which is the basis for the Sehested equation, it was arbitrarily assumed that the reactor would be 10X small than in the iron case.

S.2.6 In-situ absorption with high temperature regeneration or ammonia compression

It is assumed that there is a single compression stage for nitrogen up to approximately 3 bar.

There is no recycle heat exchanger or compressor.

In the case of high temperature regeneration, it is assumed that the absorbent temperature needs to be increased by 100 °C to reach an equilibrium pressure high enough to condense ammonia with cooling water using a 40.5 kW heat exchanger costs $220k. Furthermore, since the heat of reactor cannot be used for this temperature increase, an additional 2.7 GJ t_{NH3}^{-1} is lost.

In the case of ammonia compression, the absorbent is regenerated at atmospheric pressure with a 25 °C temperature change. The ammonia is then compressed in 3 stages to 11.5 bar to condense with water. These compressions consume 0.61 GJ t_{NH3}^{-1} total and cost $240k.

The size of the reactor (with absorbent) was calculated assuming a constant rate with a total pressure of 3 bar, ammonia pressure of 0.001 bar and a temperature of 400 °C. This size of reactor was then increased 3-fold to account for the absorbent. This cost was double to account for the batch operation of the reactor.

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